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Thermodynamic Analysis of a Conceptual Fixed-Bed Solar Thermochemical Cavity Receiver–Reactor Array for Water Splitting Via Ceria Redox Cycling

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We propose a novel solar thermochemical receiver–reactor array concept for hydrogen production via ceria redox cycling. The receiver–reactor array can improve the solar-to-fuel efficiency by realizing the heat recuperation, reduction, and oxidation processes synchronously. A linear matrix model and a lumped parameter model are developed to predict thermal performance of the new solar thermochemical system. The system thermal performance is characterized by heat recovery effectiveness of solid-phase and solar-to-fuel efficiency. Investigated parameters include reduction temperature, oxygen partial pressure, number of receiver–reactors, concentration ratio, and gas-phase heat recovery effectiveness. For baseline conditions, the solid-phase heat recovery effectiveness and the solar-to-fuel efficiency are found to be 81% and 27%, respectively. For perfect gas-phase heat recovery and a solar concentration ratio of 5,000, the solar-to-fuel efficiency exceeds 40%.

Keywords: solar thermochemistry, water splitting, non-stoichiometry, cerium oxide, heat recovery

INTRODUCTION

Solar fuels offer great promise to a sustainable future and can be produced via several pathways such as photo-, electro-, and thermochemical processes, as well as their various combinations (Steinfeld, 2005). Compared to the other processes, the solar thermochemical approach utilizes the entire solar spectrum, allowing for higher theoretical solar-to-fuel efficiency (Steinfeld, 2005; Siegel et al., 2013; Muhich et al., 2016; Bader and Lipiński, 2017). In particular, the two-step non-stoichiometric based redox cycles have been an attractive research area over the past decade (Chueh and Haile, 2010; Furler et al., 2012a; Marxer et al., 2017; Steinfeld, 2019; Qian et al., 2021). Synthesis gas (syngas, a mixture of H₂ and CO) can be produced in two steps. In the first, endothermic step, a metal oxide is non-stoichiometrically reduced, driven by concentrated solar irradiation. In the second, exothermic

Abbreviations: 0D, zero dimensional; CPC, compound parabolic concentrator; CRR, cavity receiver–reactor; DNI, direct normal irradiance; HTF, heat transfer fluid; HXer, heat-exchanger; LMM, linear matrix model; LPM, lumped parameter method; RPC, reticulated porous ceria; TR, tower reflector.
step, the reduced metal oxide is oxidized with the H₂O and/or CO₂ and H₂ and/or CO are produced, respectively.

A key figure of merit to assess the commercial viability of the solar thermochemical pathway for fuel production is the solar-to-fuel efficiency (defined in Eq. 26). A threshold efficiency value of 20% has been suggested to compete with low-risk approaches such as electrolysis (Siegel et al., 2013). Although solar thermochemical water splitting has a high theoretical solar-to-fuel conversion efficiency of 75% (Steinfeld, 2005), to date the experimental record of this technology is only 5.25% for splitting of CO₂ into CO and O₂ (Marxer et al., 2017). Improvement of the solar-to-fuel efficiency critically relies on the development of both superior redox materials and novel reactor designs (Lapp et al., 2012; Miller et al., 2014; Hathaway et al., 2016; Muhich et al., 2018; Li et al., 2021). A wide variety of non-stoichiometric redox materials have been investigated, including pure and doped ceria, as well as perovskites (Chueh et al., 2010; Hao et al., 2014; Qian et al., 2021). Among these candidates, undoped ceria offers a great promise for efficient fuel production due to its fast kinetics, robust cyclability, and high selectivity, and is thus selected as the model material in this study (Abanades et al., 2010; Chueh et al., 2010; Furler et al., 2012b; Marxer et al., 2017).

Many reactor designs were proposed and tested with the ultimate goal of improving the solar-to-fuel efficiency (Chueh et al., 2010; Diver et al., 2010; Lapp et al., 2013; Dähler et al., 2018; Wang et al., 2020; Wang et al., 2021). They can be categorized into designs with solid and/or gas heat recuperation (Ermanoski et al., 2013; Lapp and Lipiński, 2014; Hathaway et al., 2016) and designs without heat recuperation (Welte et al., 2016; Marxer et al., 2017). The majority of the reactor systems demonstrated so far are based on the fixed-bed type due to the design simplicity and convenient operation (Chueh et al., 2010; Furler et al., 2012b; Hathaway et al., 2016; Marxer et al., 2017; Haeusler et al., 2020; Sun-to-liquid, 2020). However, a key challenge associated with designing an efficient fixed-bed reactor system is to recover the solid sensible heat under temperature-swing cycling due to the immobility of the redox material. This is particularly relevant when using undoped ceria because its efficiency is critically limited by the energy penalty to heat the solid phase (Hathaway et al., 2016; Muhich et al., 2018; Li et al., 2021). A multi-chamber fixed-bed reactor concept was developed by Yuan et al. that allows for solid heat recuperation by using liquid metal as the heat transfer fluid. This concept promises a thermal-to-chemical efficiency of 20% and a heat recovery effectiveness of 80%, but at the expense of complicated design and operation (Yuan et al., 2015). A more generic design concept incorporating counterflow solid heat exchange was proposed by Falter et al., though the design poses technical challenges to practical operation of moving the high-temperature redox materials (Falter et al., 2015). Besides, a new receiver–reactor system with integrated thermocline heat recovery was proposed but lacks theoretical or experimental investigations (Steinfeld et al., 2019). To our best knowledge, realizing efficient solid-phase heat recovery in the fixed-bed reactor system with a simple design and operating strategy is absent in the literature.

In our previous work, we proposed a modified solar beam-down system for realizing solid-phase heat recovery for the fixed-bed reactor configuration, where the analysis of the optical system was presented in detail (Li et al., 2020b). In the present work, we introduce the design of the array of receiver–reactors, coupled to the beam-down system, together with the operating strategy for realizing solid-phase heat recovery. The main merits of this work are: (i) the heat recovery is realized without the need of moving redox materials; (ii) the heat of the solid phase is recovered by the direct gas–solid heat exchange in series; and (iii) hydrogen is produced continuously. The model receiver–reactor system comprising recuperation, reduction, and oxidation zones is introduced in “Problem Statement” section. Model assumptions, as well as mathematical models, are described in sections “Methodology and Assumptions” and “Mathematical Model”. Section “Results and Discussion” presents the assessment of the heat recovery effectiveness from the solid phase and the sensitivity analysis of the total solar-to-fuel efficiency depending on key parameters, including reduction temperature, relative oxygen partial pressure, receiver–reactor numbers, concentration ratio, and gas-phase heat recovery effectiveness.

PROBLEM STATEMENT

Thermochemical water splitting (WS) process based on two-step ceria redox cycles is considered in this study:

\[
\begin{align*}
\text{solar, endothermic step:} & \quad \frac{1}{\Delta \delta} \text{CeO}_2 - \delta_{\text{ox}} \rightarrow \frac{1}{\Delta \delta} \text{CeO}_2 - \delta_{\text{red}} + \frac{1}{2} \text{O}_2 \\
\text{non-solar, exothermic step:} & \quad \frac{1}{\Delta \delta} \text{CeO}_2 - \delta_{\text{red}} + \text{H}_2\text{O} \rightarrow \frac{1}{\Delta \delta} \text{CeO}_2 - \delta_{\text{ox}} + \text{H}_2
\end{align*}
\]

where \( \Delta \delta = \delta_{\text{red}} - \delta_{\text{ox}} \) is the change in non-stoichiometry.

Figure 1 depicts the schematic of the proposed beam-down thermochemical system featuring a heliostat field, a tower, a rotating hyperboloidal tower reflector (TR), and a stationary cavity receiver–reactor (CRR) array coupled with compound parabolic concentrators (CPCs) (Li et al., 2020b). The rotating TR directs the concentrated solar irradiation alternately to each CRR through the aperture of the CPCs. Since the focus of this paper is on the reactor system, the radiative input from the optical system is modeled here in a simplified manner assuming step-wise irradiation.

Figure 2 shows an example of an 8-CRR array that is arranged in a circular layout and fixed on a pedestal (not shown). The system is divided into three zones: reduction (red), oxidation (blue), recuperation (including pre-heating and pre-cooling subzones, yellow) zones. The same amount of the monolithic reticulated porous ceria (RPC) is contained in each CRR.² The reduction reaction is realized in the CRR

²RPC and Al₂O₃-made containers have been successfully demonstrated in a series of solar thermochemical water/CO₂ splitting systems. Assessment of potential materials issues is beyond the scope of this study.
irradiated by the concentrated sunlight (red). The oxidation reaction is realized in the CRR on the opposite side (blue). All other CRRs (yellow) are separated by the central axis into two groups, and heat is exchanged between the two groups. To reduce the emission loss, the aperture of the receiver–reactor is opened only when being irradiated by the concentrated sunlight, and is kept closed otherwise. The CRRs are connected to the neighboring ones and to the gas-phase heat exchangers via pipes. Therefore, the inert gas and water flow through each receiver–reactor to sweep the RPC alternately.

As the rotating TR directs the concentrated sunlight to the stationary CRR array in a clockwise manner, the CRR array can be viewed as “rotating” counter-clockwise relative to the position of concentrated solar irradiation. The operating procedure for one cycle duration $\tau$ is shown in Figure 3. States 1 and 2 represent the beginning of the $n$th cycle, and the time instant after “rotating” the CRR array counter-clockwise in one phase, respectively. The transition from State 1 to 2 is assumed instantaneous and thus both states are treated to occur at the same time instant $(n-1)\tau$. States 3 and 4 represent the initial and final states of the thermochemical process of the $n$th cycle, respectively. For ensuring the synchronization of reduction, oxidation, and recuperation processes, the duration of States 3 and 4, $\tau$, is determined by the duration of the reduction step, and the other two processes are proceeding simultaneously for the same duration $\tau$ by adjusting the flow rates of water and sweep gas. After a complete cycle, the system returns to State 1.

**Reduction Zone**

As shown in Figure 3, we assume that the CRR array rotates counter-clockwise by one phase during a change from State 1 to State 2. Therefore, the CRR in $(N+1)$ position of the recuperation zone moves into the reduction zone, where it will be irradiated by concentrated solar irradiation. Then, pure $N_2$ is used to sweep RPC of the CRR in the reduction zone and to keep rejecting released $O_2$ from porous media surfaces during the change from State 3 to State 4. The thermal energy of the product gas, the mixture of $N_2$ and $O_2$, is recovered to heat the inlet flow of $N_2$ by using an indirect gas-phase heat exchanger (HXer1). A reduction period finishes when the thermodynamic state $(T_{\text{red}}, P_{O_2,\text{red}})$ is reached. The settings of $T_{\text{red}}$ and $P_{O_2,\text{red}}$ values are discussed in “Results and Discussion” section. Because the solar-to-fuel efficiency is affected by the feeding strategy of $N_2$, the following simplified approach of controlling the $N_2$ flow rate per kilogram of ceria $r_{N_2}$ is used: (i) set an initial value of $r_{N_2} = 10^{-3}$ kg s$^{-1}$ kg$^{-1}$; (ii) continuously adjust $r_{N_2}$ to approximate the default final relative oxygen partial pressure. The $N_2$ feeding strategy is illustrated in detail in “Mathematical Model” section.

**Recuperation Zone**

The recuperation zone is composed of one gas-phase heat exchanger (HXer3) and 2N CRRs (yellow) with one half undergoing pre-cooling (from #1 to #N) and another half undergoing pre-heating (from #(N+1) to #2N) as labeled in Figure 3. $N_2$ is used as the sweep gas for oxygen scavenger and heat transfer fluid (HTF). A pure cold $N_2$ flow first goes into an indirect gas-phase heat exchanger (HXer3) where it is heated by the heat of product gases, namely, a mixture of $N_2$ and $O_2$. The

---

3One phase difference represents the angle difference between two adjacent cavities: $\Delta \theta = \frac{2\pi}{2N+2}$. 
mixture gas then flows continuously through the pre-cooling part from #1 to #N to cool the RPC material in each CRR. The sweep gas reaches the peak temperature when leaving #N, and then goes through the pre-heating part from #N+1 to #2N to heat the RPC material. The state of ceria in each CRR is updated from $(T_{n+1}^{f}, \delta_{n+1}^{w})$ to $(T_{n}^{f}, \delta_{n}^{w})$ during the change from States 3 to 4, where the subscript $i$ represents the $i$th CRR position (#$i$) in the recuperation zone. The superscript $rr$ indicates a time instant.\textsuperscript{4} Note that reduction may occur along with heat recovery processes in the recuperation zone. A detailed systematic study is presented in section “Mathematical Model”.

**Oxidation Zone**

According to Figure 3, the CRR in #1 position of the recuperation zone containing the reduced ceria ($\text{CeO}_2$-$\delta_{n}$) moves into the oxidation zone during the change from State 1 to State 2, where it will undergo the oxidation reaction. Then, $\text{CeO}_2$-$\delta_{n}$ is oxidized at constant oxidation temperature $T_{n}^{s}$ by water steam during the change from State 3 to State 4, while $\text{H}_2$ is generated. Note that ceria needs to be cooled before undergoing the oxidation process. Because the oxidation step is exothermic, the redundant heat generated during oxidation needs to be removed to keep the temperature constant. The heat may be further utilized in a distributed system such as a Rankine cycle power generation system, which is not discussed in this work.

**METHODOLOGY AND ASSUMPTIONS**

The methodology of modeling transient radiative fixed-bed reduction and cavity cascade heat recuperation is presented next. A lumped parameter model (LPM) and a linear matrix model (LMM) are, respectively, presented to describe the reducing and recuperating processes of the novel receiver-reactor redox system. For the LPM, the reduction is treated as a transient process and the numerical method is applied to solve the non-linear governing equation. For the LMM, mass and heat transfer between recuperation CRRs are expressed by a set of linear equations which is solved by matrix iteration. The main assumptions and settings are as follows:

1. Thermodynamic quasi-equilibrium is assumed for ceria reduction and oxidation.
2. Temperature difference between the RPC and sweep gases is neglected.
3. Lumped parameters of the RPC and gases, including temperature, relative oxygen partial pressure, non-stoichiometry, $N_2$ flow rate, are concluded for each CRR.
4. The relative oxygen partial pressure $p_{O_2}$ of the initial pure $N_2$ flow is set to $p_{O_2,0} = 1 \times 10^{-5}$ as a conservative estimate based on the existing industrial technologies (Häring, 2008).
5. The effectiveness of gas-phase heat exchanger is set to 95\% according to the literature (Blank and Wu, 1994; El-Ehwany et al., 2010).
6. The maximum operating temperature is set to 2,000 K, as ceria will undergo a phase change at temperatures $\geq 2,100$ K (Chueh and Haile, 1923; Bader et al., 2013).
7. The oxidation reaction is undergone constantly at 1,000 K.
8. For the LMM, the temperature of RPC (or sweep gases) in the recuperation zone varies linearly over time, namely, $T_{rr} = \frac{1}{\tau \int_{(n-1)\tau}^{n\tau} dt} (T_{n-1}^{s} + T_{n}^{s})/2$, and the $O_2$ generating rate is assumed as constant.

**MATHEMATICAL MODEL**

Figure 4 shows the schematic of the system model for the reaction process in the $n$th cycle from the $(n-1)$th to $n$th time instant. It corresponds to the process from State 3 to 4 in Figure 3. The red and blue blocks represent CRRs in the reduction and oxidation zones. In the recuperation zone, the CRRs are represented in a row of yellow rectangular boxes separated into the pre-cooling and pre-heating parts. All CRRs are enclosed by a frame in the solid line as the reactor boundary. For each CRR, the initial and final thermodynamic states of ceria in the $n$th cycle are given correspondingly. Thick solid arrows are used to show the direction of reactions. The flows of mass and energy are represented by thin solid arrows and thick hollowed arrows.

\textsuperscript{4}$\tau$ is omitted in the following text and equations for brevity.
respectively. The outermost dash frame denotes the boundary of the whole system. A steady thermodynamic state of temperature, \( T_0 = 298 \text{ K} \) and gauge pressure, \( p_0 = 1.013 \times 10^5 \text{ Pa} \) is assumed for the surroundings.

Energy conservation of the system undergoing one cycle (shown in Figure 4) is:

\[
Q_{\text{solar}} = Q_{\text{rad}} + Q_{\text{other}} + Q_{\text{gas}} + Q_{\text{quench}} + Q_{\text{fuel}} \tag{1}
\]

where \( Q_{\text{solar}} \) represents the total solar energy input during one cycle, including energy consumed by the reduction reaction \( Q_{\text{solar,red}} \) and energy for the recovery of heat losses \( Q_{\text{solar, recovery}} \). They can be expressed as:

\[
Q_{\text{solar,red}} = \int_{(n-1)t}^{nt} Q_{\text{solar,red}} \, dt \tag{2}
\]

\[
Q_{\text{red}} = \int_{(n-1)t}^{nt} \frac{\sigma T^4}{C \times \text{DNI}} \, Q_{\text{solar,red}} \, dt \tag{3}
\]

\[
Q_{\text{solar, recovery}} = Q_{\text{other}} = F (Q_{\text{solar}} - Q_{\text{red}}) \tag{4}
\]

where \( Q_{\text{solar,red}} \) is the incident solar power into the reduction cavity, \( Q_{\text{red}} \) and \( Q_{\text{other}} \) denote the radiative and other heat losses, respectively, \( \sigma \) is the Stefan–Boltzmann constant, \( \sigma = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4} \), \( C \) and DNI represent the concentration ratio and direct normal irradiation assumed equal to 3,000 and 1,000 W m\(^{-2} \), respectively, and \( F \) is the heat loss fraction of the entire system assumed to be equal to 0.2.

\[
Q_{\text{gas}} = Q_{\text{gas,HX}} + Q_{\text{gas,red}} + Q_{\text{gas,ox}} \tag{5}
\]

\[
Q_{\text{quench}} = m_{\text{RPC}} c_v (T - (n-1)t) - T_{\text{ox}} \tag{6}
\]

\[
Q_{\text{ox}} = n_{\text{H}_2} \left[ h_{\text{H}_2O}(T_{\text{ox}}) - h_{\text{H}_2}(T_{\text{ox}}) - \frac{\Delta h_{\text{O}_2}(\delta_{\text{ox}}, \delta_{\text{ox}})}{2} \right] \tag{7}
\]

\[
Q_{\text{reject}} = Q_{\text{ox}} + n_{\text{H}_2} \left[ h_{\text{H}_2O}(T_{\text{ox}}) - h_{\text{H}_2O}(T_{\text{ox}}) \right]
- \left( n_{\text{H}_2O} - n_{\text{H}_2} \right) \frac{\Delta h_{\text{O}_2}(\delta_{\text{ox}}, \delta_{\text{ox}})}{2}
+ \epsilon \left( n_{\text{H}_2O} - n_{\text{H}_2} \right)
\left[ h_{\text{H}_2O}(T_{\text{ox}}) - h_{\text{H}_2O}(T_{\text{ox}}) \right]
+ n_{\text{H}_2} \left[ h_{\text{H}_2}(T_{\text{ox}}) - h_{\text{H}_2}(T_{\text{ox}}) \right] \tag{8}
\]

\[
Q_{\text{fuel}} = n_{\text{H}_2} \left[ h_{\text{H}_2}(T_{\text{ox}}) - h_{\text{H}_2O}(T_{\text{ox}}) \right] \tag{9}
\]
Reduction Reaction

The governing equations of the LPM for simulating the non-linear solar reduction process are:

$$Q_{\text{gas,OX}} = m_{\text{N}_2,\text{H}_{2}}C_{\text{P},\text{N}_2}(1 - \epsilon)(T_{\text{ox}} + T_{\text{2N}} - T_{\infty})$$

$$Q_{\text{gas,OX}} = \int_{(m-1)r}^{\cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot 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\cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \·...
balance relates the pressure of oxygen at the outlet of the reactor, \( p_{\text{O}_2} \), to the rate at which oxygen is generated, \( \dot{n}_{\text{O}_2} \), by Eq. 16. \( \dot{m}_{\text{N}_2,\text{red}} \) is continuously adjusted throughout the reduction process to approximate a constant \( p_{\text{O}_2} \). A relaxation factor \( \chi \) is used to smooth the iteration of \( \dot{m}_{\text{N}_2,\text{red}} \) due to its high sensitivity to the results, namely \( \dot{m}_{\text{N}_2,\text{red}} = \chi \dot{m}_{\text{N}_2,\text{red}}^{(m-1)} + (1 - \chi)\dot{m}_{\text{N}_2,\text{red}}^{(m)} \). Figure 5 shows the computational accuracy and time as functions of the time step \( \Delta t \). The relative error \( \sigma_{\text{eff}} \) is defined as \( \sigma_{\text{eff}} \equiv \frac{\dot{m}_{\text{N}_2,\text{ref}} - \dot{m}_{\text{N}_2,\text{ref}}}{\dot{m}_{\text{N}_2,\text{ref}}} \), where \( \dot{m}_{\text{N}_2,\text{ref}} \) is calculated for a reference \( \Delta t = 0.01 \) s. Based on Figure 5, \( \Delta t \) is set to 0.1 s to ensure relatively higher accuracy.

### Heat Recuperation

For modeling the recuperating process, the LMM is established. The energy-balance equation for CRRs in the recuperation zone from State 3 to State 4 in a redox cycle is as follows:

\[
m_{\text{RPC}} c_{\text{p}} (T_i^{(n)} - T_i^{(n-1)}) + \dot{m}_{\text{RPC}} \frac{\delta_i^{(n)} - \delta_i^{(n-1)}}{2} \Delta h_{\text{O}_2} \left( \delta_i^{(n-1)}, \delta_i^{(n)} \right) = \dot{m}_{\text{N}_2,\text{HX} c_{\text{p}}} c_{N_2} \left[ \frac{1}{1 + \dot{m}_{\text{O}_2} c_{\text{p}} \dot{P}_{\text{O}_2,j}} \frac{\dot{P}_{\text{O}_2,j}^{(n)}}{\dot{m}_{\text{O}_2,j}} \frac{T_i^{(n)} + T_i^{(n-1)}}{2} - T_{\infty} \right] - \left( 1 + \frac{\dot{m}_{\text{O}_2} c_{\text{p}} \dot{P}_{\text{O}_2,j}}{\dot{m}_{\text{N}_2,\text{HX} c_{\text{p}}}} \frac{T_i^{(n)} + T_i^{(n-1)}}{2} - T_{\infty} \right)
\]

\( (1 < i \leq 2N) \)

where the subscript \( i \) represents the CRR position of the recuperation zone and the superscript \( n \) represents the \( n \)th redox cycle. As shown in Figure 3, \( X_i^{(n)} \) and \( X_i^{(n-1)} \) (X: \( T, \delta \)) correspond to thermodynamic parameter values of RPC in \( i \)th CRR position at State 4 and State 3 of the \( n \)th redox cycle, respectively. For \( X_i^{(n)} \) and \( X_i^{(n-1)} \), \( X_i^{(n-1)} \) corresponds to \( T_{\text{red}}, \delta_{\text{red}} \), and \( T_{\text{ex}}, \delta_{\text{ex}} \) respectively.

The LHS of Eq. 17 represents the change in internal energy of RPC material corresponding to \( i \)th position, and the RHS is the net amount of thermal energy input (or output) by \( N_2 \) from State 3 to State 4. For \( i = 1 \) position of the recuperation zone, the heat loss of gas-phase heat recovery should be considered, and the modified equation is:

\[
m_{\text{RPC}} c_{\text{p}} (T_1^{(n)} - T_1^{(n-1)}) + \frac{\dot{m}_{\text{RPC}} \delta_1^{(n)} - \delta_1^{(n-1)}}{2} \Delta h_{\text{O}_2} \left( \delta_1^{(n-1)}, \delta_1^{(n)} \right) = \dot{m}_{\text{N}_2,\text{HX} c_{\text{p}}} c_{N_2} \left[ \frac{\dot{P}_{\text{N}_2,j}^{(n)}}{\dot{m}_{\text{N}_2,j}} \frac{T_1^{(n)} + T_1^{(n-1)}}{2} - T_{\infty} \right]
\]

\( (18) \)

where \( \epsilon \) is gas-phase heat recovery effectiveness, \( \dot{P}_{\text{O}_2,j}^{(n)} \) is determined by the mass flow rate of \( N_2 \) and \( \dot{P}_{\text{O}_2,j}^{(n)} \), \( \dot{m}_{\text{N}_2,j} \) and \( \dot{m}_{\text{O}_2,j}^{(n)} \) can be calculated as:

\[
\dot{m}_{\text{N}_2,j}^{(n)} = \frac{\left( \delta_{1,j}^{(n)} - \delta_{i,j}^{(n-1)} + \sum_{j=2}^{i} (\delta_{j}^{(n)} - \delta_{j}^{(n-1)}) \right) m_{\text{RPC}} M_{\text{O}_2}}{2 M_{\text{RPC}} \tau}
\]

\( (19) \)

\[
\dot{P}_{\text{O}_2,j}^{(n)} = \frac{m_{\text{O}_2,j}^{(n)}}{m_{\text{O}_2,j}} + \frac{p_{\text{O}_2}}{m_{\text{O}_2,j}} + \frac{m_{\text{O}_2,j}^{(n)}}{m_{\text{O}_2,j}}
\]

\( (20) \)

where \( \beta = \frac{m_{\text{N}_2,\text{HX} c_{\text{p}}} c_{N_2}}{m_{\text{RPC}} c_{\text{p}}} \) and \( \gamma_{\text{RPC}} = \frac{m_{\text{RPC}} c_{\text{p}}}{m_{\text{RPC}} c_{\text{p}}} \).

A non-dimensional parameter \( \beta \), defined as the ratio of the speed of thermal front, \( \nu_{\text{TF}} = m_{\text{N}_2,\text{HX} c_{\text{p}}} c_{N_2} \), to the effective rotating speed of CRR-disk, \( \nu_{\text{rotating}} = \frac{m_{\text{RPC}} c_{\text{p}}}{\tau} \), is used. Three special cases, \( \beta = 0, 1 \), and \( \infty \), are discussed under simplified conditions: perfect gas-phase heat recovery and no chemical reaction.

**Figure 6** shows the steady-state temperature distributions of the CRR array, containing a reduction CRR, an oxidation CRR, and six recuperation CRRs, at the end of a cycle when reaching a steady running condition. For \( 0 < \beta < 1 \), the solid-phase heat recovery in the recuperation zone is insufficient, and the heat recovery efficiency can be improved by increasing \( \beta \). The highest heat recovery efficiency, \( \eta_{\text{recovery}} = \frac{T_4 - T_{\text{ex}}}{T_{\text{red}} - T_{\text{ex}}} \), is found at \( \beta = 1 \), where the final temperature distributions of the pre-heating and pre-cooling CRRs are identical (**Figure 6B**). Further increase of \( \beta \) leads to a detrimental effect on solid-phase heat recovery. Because the temperature of CRR in \( \#3 \) drops below 1675 K when \( \beta > 1 \), the CRR in \( \#4 \) will be cooled. Finally, the temperatures of all CRRs in the recuperation zone approach the same value of 1450 K when \( \beta = \infty \). In this study, \( \beta \) is set to 1.

Besides, as given in Eq. 21, \( \delta \) in each recuperation CRR is determined by \( \dot{P}_{\text{O}_2}, T \), and other constraints. During the
change from State 1 to State 2, the recuperation CRR containing CeO$_2$-δ with δ$_{i+1}^{(n)}$ is shifted counter-clockwise from #i to #i+1 and #i position as shown in Figure 3. Then, the CRR’s thermodynamic state moves from (P$_{O_2,i}$, T$_{i}^{(n)}$) to a new state, (P$_{O_2,i+1}$, T$_{i+1}^{(n)}$) during the change from State 3 to State 4. For the pre-heating CRRs, namely (N+1) $\leq i \leq 2N$, δ$_{i}^{(n)}$ is solely determined by (P$_{O_2,i}$, T$_{i}^{(n)}$). For the pre-cooling CRRs, namely $1 \leq i \leq N$, two possibilities should be discussed. The first possible condition is that δ determined by the new thermodynamic state (P$_{O_2,i}$, T$_{i}^{(n)}$), is larger than the previous non-stoichiometry δ$_{i}^{(n-1)}$. According to the assumption of thermodynamic quasi-equilibrium, a further reduction can occur and δ$_{i}^{(n)}$ is obtained by solving $f(P_{O_2,i}, T_{i}^{(n)}), \delta_{i}^{(n)} = 0$ which is similar to Eq. 15. The second possible condition is δ $< \delta_{i}^{(n-1)}$, and a re-oxidation should occur. However, this is inhabited due to the absence of O$_2$ in pure N$_2$ flows (P$_{O_2,0}$ = 1 x 10$^{-5}$). Because less O$_2$ can be regained by the ceria, the reaction extent is too small. It is found that the decrementation of $\Delta$δ is orders of magnitude smaller than δ$_{red}$. Therefore, δ$_{i}^{(n)}$ is assumed to be equal to δ$_{i}^{(n-1)}$ in the second condition.

$$\delta_{i}^{(n)} = \left\{ \begin{array}{ll} \text{max}\{\delta_{i}^{(n-1)}, f(P_{O_2,i}, T_{i}^{(n)})\}, & 1 \leq i \leq N \\ \text{f(P}_{O_2,i}, T_{i}^{(n)}), & N + 1 \leq i \leq 2N \end{array} \right\}$$

Equations 13 and 14 can be written in a matrix form as:

$$\mathbf{A} \cdot \mathbf{T}^{(n)} = \mathbf{B} \cdot \mathbf{T}^{(n-1)} + \mathbf{V}_{\text{trans}} - \mathbf{V}_{\text{chem}}$$

where

$$\mathbf{A} = \begin{bmatrix} 2 + \beta & 1 + \xi_i^{(n)} & 0 & \cdots & -\epsilon \beta \\ -\beta(1 + \xi_i^{(n)}) & 2 + \beta & 1 + \xi_i^{(n+1)} & \cdots & 0 \\ 0 & \cdots & -\beta(1 + \xi_{2N_i}^{(n)}) & 2 + \beta(1 + \xi_{2N_i}^{(n+1)}) & \cdots \end{bmatrix}$$

$$\mathbf{B} = \begin{bmatrix} \epsilon \beta & 2 - \beta(1 + \xi_i^{(n)}) & \cdots & 0 \\ 0 & \beta(1 + \xi_i^{(n+1)}) & 2 - \beta(1 + \xi_i^{(n+1)}) & \cdots \\ \cdots & \cdots & 0 & \beta(1 + \xi_{2N_i}^{(n+1)}) \end{bmatrix}$$

Vectors $\mathbf{T}^{(n)}$ and $\mathbf{T}^{(n-1)}$ contain the temperatures of 2N recuperation CRRs with respect to State 4 and State 3 in the nth cycle. $\mathbf{V}_{\text{trans}}$ and $\mathbf{V}_{\text{chem}}$ are vectors containing the themes related to the item of heat losses via gas-phase transport and the item of chemical enthalpy in the nth cycle. Finally, steady operation can be achieved as the iteration approaches a convergence solution, namely, $\lim_{n \to \infty} \mathbf{T}^{(n)} = \mathbf{T}$. The convergence criterion is:

$$\left| \frac{1}{2N} \sum_{i=1}^{2N} \left( \frac{T_i^{(n)} - T_i^{(n-1)}}{T_i} \right)^2 \right| < 10^{-6}$$

**Oxidation Reaction**

The process of oxidation involves two synchronous reactions: ceria re-oxidation and water splitting (WS). Similar to the reduction modeling, the lumped transient method is applied with the assumption of quasi thermodynamical equilibrium for each time step, namely $\Delta G_{\text{ox}} = 0$. The expression is given by:

$$\text{Oxidation Reaction}$$
TABLE 1 | Baseline model parameters.

| Parameter                                      | Value | Unit |
|------------------------------------------------|-------|------|
| Solar power input to the reduction reaction, $Q_{\text{fl}}$ | 1,000 | W    |
| Flux concentration ratio at the receiver-reactor aperture, $C$ | 3,000 | –    |
| Direct normal irradiance, DNI                  | 1,000 | W m$^{-2}$ |
| Oxidation temperature, $T_{\text{ox}}$         | 1,000 | K    |
| Reduction temperature, $T_{\text{red}}$        | 1900  | K    |
| Ambient temperature, $T_{\text{amb}}$          | 298   | K    |
| Relative oxygen partial pressure of reduction, $p_{O_2}$ | 0.01  | –    |
| CRR numbers, $N_{\text{crr}}$                 |       | –    |
| Reduction zone, $N_{\text{red}}$               | 1     | –    |
| Oxidation zone, $N_{\text{ox}}$                | 1     | –    |
| Recovery zone, $2N$                            |       | –    |
| Pre-cooling part, $N$                          | 10    | –    |
| Pre-heating part, $N$                          | 10    | –    |
| Gas-phase heat recovery effectiveness, $\varepsilon$ | 0.95  | –    |
| Loss factor, $F$                               | 0.2   | –    |

$$
\Delta G_{\text{ox}} = \left[ \Delta H_{WS}^* - T_{\text{ox}} \Delta S_{WS}^* \right] - \frac{\Delta H_{red}^* \left( \delta^{(m)} - \frac{1}{2} \right) - T_{\text{ox}} \Delta S_{red}^* \left( \delta^{(m)} - \frac{1}{2} \right)}{2} + RT_{\text{ox}} \ln \left( \frac{P_{H_2O}^{(m)}}{P_{H_2O}^{(H_2O)}} \right) = 0 \quad (24)
$$

where $\Delta H_{WS}^*$ and $\Delta S_{WS}^*$ are the standard reaction enthalpy and entropy for water splitting per mole of the released $H_2$. $T_{H_2O}$ and $T_{H_2}$ are the temperature of water at inlet and the generation rate of $H_2$, respectively. Here, the $P_{H_2O}$ is set equal to $\frac{\Delta H_{WS}}{\Delta S_{WS}}$. To re-oxidize ceria as much as possible, $n_{H_2O}$ is set to the maximum value calculated by Eq. 25, in which case the generated chemical heat is completely utilized for heating water. In addition, the connection of $r_{H_2}$ and $\delta$ is given by Eq. 26.

$$
n_{H_2O} = \frac{m_{\text{RPC}} \left( \delta_{\text{red}} - \delta_0 \right)}{M_{\text{RPC}} (1 - \varepsilon) \left( \bar{T}_{\text{H}_2O} (T_{\text{ox}}) - \bar{T}_{H_2O} (T_{\text{ox}}) \right)} \left\{ \left( \bar{T}_{\text{H}_2} (T_{\text{ox}}) - \bar{T}_{H_2O} (T_{\text{ox}}) \right) + (1 - \varepsilon) \left( \bar{T}_{\text{H}_2} (T_{\text{ox}}) - \bar{T}_{H_2O} (T_{\text{ox}}) \right) - \Delta \bar{T}_{\text{O}_2} \left( \delta^{(n-1)} \right) \right\} / 2 - \frac{M_{\text{RPC}}}{m_{\text{RPC}}} \int_0^T r_{\text{H}_2} \, dt \quad (25)
$$

$$
\delta = \delta_{\text{red}} - \frac{M_{\text{RPC}}}{m_{\text{RPC}}} \int_0^T r_{\text{H}_2} \, dt \quad (26)
$$

RESULTS AND DISCUSSION

In this section, we first present the verification of the described mathematical model and its assumptions. Then, we present the performance of the proposed receiver-reactor array. Finally, we show the results of a sensitivity study of the thermal-to-fuel efficiency as functions of the concentration ratio $C$, the number of CRRs in the pre-cooling or pre-heating part, $N$, the gas-phase heat recovery effectiveness $\varepsilon$, the reduction temperature, $T_{\text{red}}$, and the relative oxygen partial pressure, $p_{O_2}$. The baseline model parameters used in this study are listed in Table 1.

Model Verification

The present model is verified by comparing its selected predictions with the numerical and experimental results obtained by Venstrom et al. (2015) for the reduction reaction of a fixed-bed of ceria. Firstly, we compare the $O_2$ production rate, $r_{O_2}$. The same operating conditions are applied: (1) the ceria is heated from 1,013 to 1,748 K at a rate of 100 K min$^{-1}$ and then it kept isothermal for 4 min; (2) $N_2$ sweep gas flow is constant at 900 mL min$^{-1}$ $g_{\text{ceria}}^{-1}$; (3) the mass of ceria is 1.0245 g; and (4) the initial $\delta$ is assumed to be equal to $10^{-5}$. Figure 7 shows the $O_2$ production rates during the reduction reaction of fixed-bed ceria predicted by the two models. A good agreement has been found, indicating that the present model provides adequate accuracy to model the transient thermal reduction reaction of fixed-bed ceria. Secondly, experiments were conducted by Venstrom et al. (2015) to test a horizontal reactor under isothermal conditions in an infrared (IR) imaging furnace. The reactor comprised a packed-bed of porous ceria particles. The $N_2$ sweep gas flows were controlled with the high accuracy mass flow controllers. $r_{O_2}$ was measured in real-time using a Raman laser gas analyzer. The experimental data of $r_{O_2}$ are taken to compare with the results predicted from the present model, which is shown in Figure 8. The two sets of data correspond to $N_2$ sweep gas flows of 150 and 300 mL min$^{-1}$ g$^{-1}$ at a constant reduction temperature $T_{\text{red}} = 1773$ K. The shaded region in the plots indicates the range of rates predicted by the model due to the uncertainty in the initial $\delta$ (0.021 ± 0.002). Figure 8 shows a satisfactory agreement of $r_{O_2}$ predicted by the present model and measured by Venstrom et al. (2015).
In addition, according to the second law of thermodynamics, Gibbs's criterion should be followed at any time for chemical processes to spontaneously take place at specified thermodynamical conditions (Li et al., 2018a; Li et al., 2018b). In this study, we made an important assumption that for the recuperation step, the transient change of δ for each pre-heating cavity is linear during a cycle. Chemical reactions are assumed at equilibrium states at the beginning and the end of each cycle, namely ΔG = 0. As shown in the inset of Figure 9A, it takes N cycles to complete the pre-heating process for the cavity to move from #2N to #(N+1) position. The maximum δ at each temperature to reach thermodynamic equilibrium, δ_eq, is calculated and plotted in Figure 9 (the dashed curve in the inserted figure). The curve of δ_eq separates the full area into two regions: the gray region, ΔG < 0, and the white region, ΔG > 0. To meet the Gibbs’ criterion, δ should always be below δ_eq namely in the gray region. Figure 9A shows that the values of δ under the assumption of linear change of δ in the
recuperation process, $\delta_{\text{present}}$ exceed the values of $\delta$ under the equilibrium condition, $\delta_{\text{eq}}$, except for the initial and final states of cycles.

To examine the effect of the assumption of linear change of $\delta$ in the recuperation process, we introduce a correction factor $\alpha$ varying from 0 to 1. Instead of setting $\delta$ to $\delta_{\text{eq}}$ for the initial and final points of each cycle (marked with squares), $\delta$ is reduced to $\delta_{\text{revised}} = \alpha \delta_{\text{eq}}$ (marked with asterisks). $\alpha$ is adjusted by the trial-and-error method for different cavity positions to ensure $\delta_{\text{revised}}$ is always below $\delta_{\text{eq}}$, namely $\Delta G \leq 0$.

Figure 9B shows results of solar-to-fuel efficiencies using this correction for different numbers of pre-heating cavities. It is found that $\eta_{\text{th/present}}$ is larger than $\eta_{\text{th/revised}}$ due to the overestimation caused by neglecting the limit of the second law. However, the difference between the two efficiencies, $\Delta \eta_{\text{th}}$, is less than 0.3%. The relative error $\sigma_{\text{eff}}$ is $\sim 1\%$ for $N \leq 6$, and further decreases to $\sim 0.5\%$ for $N > 6$. The
linear assumption greatly increases the computational efficiency of the model with satisfactory accuracy. Hence, it is used to make the following predictions of the system performance.

**Recuperation Unit**

We first present the results of thermodynamic parameters, including temperature, relative oxygen partial pressure, and the non-stoichiometric number of ceria in CRRs in the recuperation unit when a steady state is reached.

The temperature distribution of CRRs in the recuperation unit is depicted in Figure 10. The recuperation unit consists of a cascade of
20 CRR positions, and the indexing numbers $i$ of the CRRs in the pre-cooling and pre-heating parts correspond to #1–10 and #11–20, respectively. For $1 \leq i \leq 10$, the temperature of the CRR in $i$ position drops from $T_{i}^{1}$ (State 1) to $T_{i}^{m}$ (State 4) after a complete cycle. The sensible heat in CRRs of the pre-cooling zone is captured and transported to the CRRs in the pre-heating part via the N$_2$ sweep flow. Therefore, for $11 \leq i \leq 20$, the CRR temperature increase is synchronized. Figure 10 also shows that the temperature peaks in the middle for $i = 10$ and decreases toward both sides. After 20 cycles, the target CRR, initially located in position #20, passes through all CRR positions and eventually arrives at position #1. The process can be separated into two stages. For the first 10 cycles, the temperature of the target CRR climbs up gradually. A peak value of 1,730 K can be reached at position #11 of the pre-heating part. For the next 10 cycles, the target CRR is cooled down step by step from the reduction temperature, $T_{red} = 1900$ K. The minimum value, 1038 K, is obtained as the CRR moves to position #1. The small temperature difference between $T_1$ and $T_{red}$ reduces the quenched heat loss, $Q_{quench}$ prior to the water-splitting process. Therefore, a high solid-phase heat recovery efficiency of 81% can be reached, as calculated by Eq. 25.

Figure 11 shows the thermodynamic parameters $\delta$ and $p_{O_2}$ as a function of recuperation CRR position at the end of a cycle. Pre-reduction may occur in the CRRs of the pre-heating part (11 $\leq i \leq 20$). $\delta$ can increase rapidly and reach a peak value of 0.015 when $i$ approaches 11. Because of pre-reduction, O$_2$ is generated and gradually accumulated in the sweep gas. $p_{O_2}$ of the gas flow increases from $2.4 \times 10^{-3}$ to $3.4 \times 10^{-3}$ when $i$ varies from 11 to 20. The pre-reducing effect enables storing 10% of the sensible heat in the form of chemical energy by increasing $\delta_{O_2}(\delta)$ during pre-heating. Figure 11 shows that $\delta$ can increase by 6% as compared to $\delta_{rad}$, and finally reach 0.036.

**Sensitivity Analysis**

Here we present the results of sensitivity study relative to change of a single key parameter, including number of CRRs in the pre-cooling or pre-heating part, $N$, reduction temperature $T_{red}$, relative oxygen partial pressure at the end of reduction $p_{O_2}$, and mass of RPC per cavity $m_{RPC}$, on the receiver–reactor array performance characterized by solid-phase heat recovery effectiveness $\varepsilon_{solid}$, solar-to-fuel efficiency $\eta_{th}$, hydrogen production rate $\dot{H}_2$ gas-phase heat recovery loss fraction $F_{gas}$ and reaction duration $\tau$. Then, the results of sensitivity study of the effects of changing parameters, including concentration ratio, $C$, gas-phase heat recovery effectiveness, $\varepsilon$, $N$, $T_{red}$, and $p_{O_2}$, respectively, on the system performance are presented. $C$ directly affects the cavity radiative heat loss, $Q_{rad}$. Increasing $C$ decreases $Q_{rad}$ for the same $T_{red}$. $N$ and $\varepsilon$ are key factors influencing the heat recovery efficiency during gas-solid- and gas-gas-phase heat exchange. $T_{red}$ and $p_{O_2}$ are the driving forces for reduction and affect the cavity heat loss and the heat recovery efficiency during gas-phase heat exchange.

According to Figure 12, $\varepsilon_{solid}$ and $\eta_{th}$ vary from 63% and 15% to 83% and 30%, respectively, by increasing $N$ from 2 to 16. This is because that a large $N$ leads to a small temperature difference between the reduction CRR and the CRR in the $(N+1)$ position, namely $(T_{red} - T_{N+1})$, which improves the solid-phase heat recovery and thus the total solar-to-fuel efficiency. The improvement magnitude is relatively larger when $N$ is increased from 2 to 4 that $\varepsilon_{solid}$ and $\eta_{th}$ are increased by 17% and 33%, respectively. $\varepsilon_{solid}$ and $\eta_{th}$ increase with $N$ at diminishing rates, as limited by other factors such as $T_{red}$, $p_{O_2}$, $\varepsilon$, and $C$. On the other hand, a large $N$ also leads to a large required CRR disk diameter, and thereby a large tilt angle of the tower reflector axis, decreasing the system optical efficiency (Li et al., 2020b). Here, $N$ is set to 10 in the baseline receiver–reactor system.

Figure 13 shows the increase of hydrogen production rate per kilogram of ceria, $r_{H_2}$, and total solar-to-fuel efficiency, $\eta_{th}$, with reduction temperature, $T_{red}$, which is attributed to the robust reduction capacity of non-stoichiometric ceria at high temperatures. The rate and efficiency increases are slower when $T_{red}$ further increases due to the rapidly increasing emission losses. For example, increasing $T_{red}$ from 1,600 to 1,700 K yields the increment of $r_{H_2}$ and $\eta_{th}$ of $2.3 \times 10^{-3}$ mol kg$^{-1}$ s$^{-1}$ and 5.7%, respectively, whereas increasing $T_{red}$ from 1,900 to 2,000 K yields the increment of $r_{H_2}$ and $\eta_{th}$ of only 0.2 $\times$ 10$^{-3}$ mol kg$^{-1}$ s$^{-1}$ and 0.6%, respectively. The improvement in the total thermal performance is insignificant for $T_{red} > 1,900$ K.

The relative oxygen partial pressure, $p_{O_2}$, also affects the thermal performance of the receiver–reactor system. As previously mentioned, ceria reduction is favored at atmospheres of low $p_{O_2}$, which can be created by a certain flow of pure N$_2$ to keep removing O$_2$ generated in the ceria. The benefit gained by reducing $p_{O_2}$ should be weighed against the penalty of thermal losses associated with imperfect gas-phase heat recovery. Figure 14 shows solar-to-fuel efficiency, $\eta_{th}$, and gas-phase heat recovery loss fraction, $F_{gas}$, as a function of $p_{O_2}$. A peak $\eta_{th}$ of 27% is found at relatively high $p_{O_2}$ (0.01–0.1). As $p_{O_2}$ decreases, the gas-phase heat recovery loss gradually becomes the major factor of system heat losses, and $\eta_{th}$ declines sharply. $F_{gas}$ rapidly increases from 0.14 to 0.65 when $p_{O_2}$ drops from 0.08 to 10$^{-4}$. $\eta_{th}$ is only 2% at $p_{O_2} = 10^{-4}$.

Figure 15 shows the effects of the mass of RPC, $m_{RPC}$, on reaction duration per cycle, $\tau$, shifting frequency of reactor disk $f = 1/\tau$, and thermal efficiency $\eta_{th}$. $\tau$ is proportional to $m_{RPC}$, indicating that for higher $m_{RPC}$, longer time is needed to finalize the reaction, and the required $f$ is lower. Based on Figure 15, $m_{RPC}$ has little impact on $\eta_{th}$. Figures 16, 17 show the effects of $C$ and $N$ on $\eta_{th}$ for selected values of $T_{red}$ and assuming $\varepsilon = 1$. $\eta_{th}$ is calculated based on selected $T_{red}$ varying from 1600 to 2000 K in 50 K increments for a fixed $p_{O_2}$ of 5 $\times$ 10$^{-3}$. As shown in Figure 16, optimal $T_{red}$ for maximized $\eta_{th}$ increases with the increase of $C$. Peak values of $\eta_{th}$ are found at $T_{red}$ of between 1,600 and 2,000 K for $C \leq 3,000$. For instance, for $C = 1,000, 2,000,$ and 3,000, the maximum $\eta_{th}$ of 22%, 33%, and 38%, respectively, are obtained at $T_{red} = 1,700$ K, 1,900 K, and 2,000 K. Further increasing $C$ leads to higher optimal $T_{red}$ and the corresponding $\eta_{th}$ increases at a diminishing rate with $C$. Moreover, aiming at high $C$ can lower optical efficiency of the optical sub-system (Li et al., 2016; Li et al., 2020a; Li et al., 2020b). Figure 17 shows that $\eta_{th}$ increases monotonically with increasing $T_{red}$ for given $N$. The maximum $\eta_{th}$ of 29%, 33%, 35%, 37%, and 38% are obtained at maximum $T_{red} = 2,000$ K, corresponding to $N = 2, 4, 6, 8$ and 10, respectively. Increasing $N$ leads to higher $\eta_{th}$ under the fixed $T_{red}$ and $p_{O_2}$, but $\eta_{th}$ increases at a diminishing rate with $N$. For instance, $\eta_{th}$ grows 4.6% and 1.1%, when increasing $N$ from 2 to 4, and 8 to 10 at $T_{red} = 1,900$ K, respectively. In addition, as mentioned in Section 5.2, increasing $N$ leads to a larger tilt angle of the tower reflector axis and reduces the optical efficiency of the system (Li et al., 2020b).
Figure 18 shows the effect of gas-phase heat transfer effectiveness, $\varepsilon$, on total solar-to-fuel efficiency $\eta_{th}$ in different levels of relative oxygen partial pressure, $p_{O_2}$, with a concentration ratio $C$ of 3,000 at $T_{red} = 1,900$ K. The top dashed line shows the limit of $\eta_{th}$ for perfect gas-phase heat exchange.

Figure 18 | Effect of gas-phase heat transfer effectiveness, $\varepsilon$, on total solar-to-fuel efficiency $\eta_{th}$ in different levels of relative oxygen partial pressure, $p_{O_2}$, with a concentration ratio $C$ of 3,000 at $T_{red} = 1,900$ K. The top dashed line shows the limit of $\eta_{th}$ for perfect gas-phase heat exchange.

Figure 19 shows the contour map of $\eta_{th}$ in different levels of non-dimensional reduction temperature, $\theta^*$, and relative oxygen partial pressure $P^*$ for $\varepsilon = 0.95$ and $C = 3,000$.

Figure 19 | Total solar-to-fuel efficiency, $\eta_{th}$, as a function of non-dimensional gas-phase heat transfer effectiveness, $\varepsilon^*$, and concentration ratio $C^*$ at fixed $T_{red} = 1,900$ K and $p_{O_2} = 0.01$.

Figure 20 shows the contour map of $\eta_{th}$ for selected $\varepsilon$ varying from 0.81 to 0.99 and $C$ from 1,000 to 4,000 at $T_{red} = 1,900$ K and $p_{O_2} = 0.01$. For the sake of comparison, normalized variables $\varepsilon^*$ and $C^*$ are defined as

$$
\varepsilon^* = \frac{\varepsilon - \varepsilon_{\min}}{\varepsilon_{\max} - \varepsilon_{\min}}, \quad C^* = \frac{C - C_{\min}}{C_{\max} - C_{\min}}
$$

where $\varepsilon_{\min}$, $\varepsilon_{\max}$, and $C_{\min}$, $C_{\max}$ are set to 0.8, 1, 0.001, and 1,000, 4,000, respectively. The colored contour lines present the different levels of $\eta_{th}$. The gradient of $\eta_{th}$ is given by $\nabla \eta_{th} = \left( \frac{\partial \eta_{th}}{\partial \varepsilon^*} \right) \hat{i} + \left( \frac{\partial \eta_{th}}{\partial C^*} \right) \hat{j}$.
As shown in Figure 19, \( \eta_{th} \) increases when increasing \( C^* \) or \( \varepsilon^* \). The maximum and minimum values of \( \eta_{th} \) are 31% and 10%, which are found at (0.95, 1) and (0.05, 0), respectively. The magnitude of the gradient of \( \eta_{th} \), \( \nabla \eta_{th} \), decreases when increasing \( C^* \) or decreasing \( \varepsilon^* \). For the region of low \( C^* \), \( \nabla \eta_{th} \) is much larger than \( \nabla \eta_{th} \). \( \nabla \eta_{th} \) tends to point upwards. For instance, \( \nabla \eta_{th} \) equals 0.5 at \( \varepsilon^* = 0.05 \), \( C^* = 0 \), which is fourteen times higher than \( \nabla \eta_{th} \). Hence, \( C^* \) is the critical parameter for \( \eta_{th} \) for low \( C^* \).

As \( C^* \) increases, \( \frac{\nabla \eta_{th}(C^*)}{\nabla \eta_{th}(\varepsilon^*)} \) will gradually increase. It approaches 2.4 and 2.3 at \( \varepsilon^* = 0.05 \) and 0.95, when \( C^* = 1 \). Since \( \eta_{th} \) is more sensitive to the change of \( \varepsilon^* \) rather than \( C^* \) for high \( C^* \), \( \varepsilon^* \) is more important than \( C^* \) for \( \eta_{th} \) under these conditions.

Figure 20 shows the contour map of \( \eta_{th} \) for selected \( T_{red} \) varying from 1,600 to 2,000 K and \( p_{O_2} \) from \( 10^{-4} \) to 0.096 when \( \varepsilon = 0.95 \) and \( C = 3,000 \). Non-dimensional reduction temperature and relative oxygen partial pressure, \( \theta^* \) and \( P^* \), are defined as

\[
\theta^* = \frac{T_{red} - T_{max}}{T_{max} - T_{min}}, \quad P^* = \frac{\ln \left( \frac{p_{O_2}(\varepsilon)}{p_{O_2,\min}} \right)}{\ln \left( \frac{p_{O_2,\max}}{p_{O_2,\min}} \right)}
\]

where \( p_{O_2,\min}, p_{O_2,\max} \) and \( T_{max}, T_{min} \) are set to 10\(^{-5}\), 0.1 and 1,000, 2,000 K, respectively. As shown in Figure 20, \( \eta_{th} \) is low for low \( P^* \). The values are less than 4% for \( P^* = 0.25 \). For the range 0.25 < \( P^* < 0.55 \), increasing \( p_{O_2} \) improves \( \eta_{th} \). For instance, when increasing \( P^* \) from 0.25 to 0.55 for \( \theta^* = 1 \), \( \eta_{th} \) is gradually improved from 2% to 16%. The average growth rate of \( \eta_{th} \) is 0.29 for the increase from 2% to 6%, which is then improved to 0.67 for the increase from 6% to 16%. By contrast, \( \eta_{th} \) is much less sensitive to the change of \( \theta^* \) for low \( P^* \). The differences of \( \eta_{th} \) are <2% when varying \( \theta^* \) over the range of 0.6–1 for \( P^* = 0.25 \). As \( P^* \) increases over 0.55, the increasing magnitude of \( \eta_{th} \) along the \( y \)-axis slows down. Meanwhile, the influence of \( \theta^* \) on \( \eta_{th} \) is enhanced. \( \theta^* \) becomes the major factor for \( \eta_{th} \) when further increasing \( P^* \) to high values. For the range of high \( P^* \) and low \( \theta^* \), increasing \( \theta^* \) may lead to a rapid increase of \( \eta_{th} \). It is shown that \( \eta_{th} \) is doubled as \( \theta^* \) increases from 0.6 to 0.8 for \( P^* = 1 \), while the change in \( \eta_{th} \) is insignificant for \( P^* \) between 0.92 and 1 and \( \theta^* = 0.6 \). In addition, the gradient of \( \eta_{th} \) points downwards in the region of high \( P^* \) and \( \theta^* \) toward a point corresponding to the optimal solution with the maximum of \( \eta_{th} = 29\% \) at \( \theta^* = 1 \) and \( P^* = 0.85 \).

**CONCLUSION**

In this study, a conceptual fixed-bed solar thermochemical cavity receiver–reactor array has been proposed and numerically studied for water-splitting via ceria-based redox cycling. Heat recuperation was modeled by a linear matrix model while reduction and oxidation were modeled by a lumped parameter model. Thermal performance characterized by solid-phase heat recovery effectiveness and total solar-to-fuel efficiency was studied for selected parameters of the proposed system such as the reduction temperature, relative oxygen partial pressure, number of receiver–reactor, concentration ratio, and gas-phase heat recovery effectiveness.

Under the assumptions made in this study, the solid-phase heat recovery effectiveness and the total solar-to-fuel efficiency were found to be 80% and 27%, respectively, for the baseline system. Along with the pre-heating process, pre-reduction occurs simultaneously, resulting in ceria non-stoichiometry of 0.015, which was attributed to the dual function of \( N_2 \) as HTF and oxygen scavenger during recuperation. A solar-to-fuel efficiency of 27% was found with a reduction temperature at 1,900 K and relative oxygen partial pressure of 0.01. The concentration ratio and gas-phase heat recovery effectiveness for the baseline case were assumed to be 3,000 and 0.95, respectively. A higher thermal efficiency can be achieved by increasing the total number of receiver–reactors.

Sensitivity analysis demonstrated that the solar-to-fuel efficiency is highly sensitive to the concentration ratio and the gas-phase heat recovery effectiveness at high reduction temperature and low relative oxygen partial pressure conditions. Increasing the concentration ratio and gas-phase heat recovery effectiveness simultaneously improves the system performance. The total solar-to-fuel efficiency was found to be 42% with a concentration ratio of 5,000 and perfect gas-phase heat recovery. In addition, for the baseline values of the concentration ratio and the gas-phase heat recovery effectiveness, the overall solar-to-fuel efficiency can be effectively increased by increasing relative oxygen partial pressure at low temperature or by increasing temperature at high relative oxygen partial pressure.

**DATA AVAILABILITY STATEMENT**

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

**AUTHOR CONTRIBUTIONS**

SY concept, analysis, writing. LL concept, writing. BW writing. SL writing, JW funding, supervision, writing PL writing WL funding, supervision, concept, writing.

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**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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NOMENCLATURE

\( C \) concentration ratio

\( c_p \) specific heat at constant pressure, \( \text{kJ} \text{kg}^{-1} \text{K}^{-1} \)

\( c_v \) specific heat at constant volume, \( \text{kJ} \text{kg}^{-1} \text{K}^{-1} \)

\( F \) heat loss fraction

\( f \) shifting frequency, min\(^{-1}\)

\( \overline{n} \) molar specific enthalpy, \( \text{kJ} \text{mol}^{-1} \)

\( \Delta n_{\text{O}_2} \) change in molar enthalpy of the non-stoichiometric ceria per \( n_{\text{O}_2} \), \( \text{kJ} \text{mol}^{-1} \)

\( \Delta T \) temperature difference \( T_{\text{red}} - T_{\text{ox}} \), K

\( M \) molar mass, \( \text{kg} \text{mol}^{-1} \)

\( m \) mass, kg

\( \dot{m} \) mass flow rate, \( \text{kg} \text{s}^{-1} \)

\( n \) amount of substance, mol

\( N \) cavity number in the pre-cooling (or pre-heating) part of recuperation zone

\( p \) pressure, Pa

\( p_{\text{O}_2} \) relative oxygen partial pressure

\( P^* \) non-dimensional oxygen partial pressure defined in Eq. 28

\( Q \) heat, kJ

\( \dot{Q} \) power, kW

\( r_{\text{O}_2} \) rates of oxygen production, \( \text{mL} \text{min}^{-1} \text{g}_{\text{ceria}}^{-1} \)

\( T \) temperature, K

\( r \) gas flow rate per unit mass of ceria, \( \text{kg} \text{s}^{-1} \text{kg}_{\text{ceria}}^{-1} \)

GREEK SYMBOLS

\( \alpha \) correction factor

\( \varepsilon \) heat recovery effectiveness

\( \beta \) non-dimensional number defined in Eq. 20

\( \gamma \) non-dimensional number defined in Eq. 20

\( \delta \) non-stoichiometry

\( \varepsilon^* \) non-dimensional heat recovery effectiveness defined in Eq. 27

\( \eta_{\text{th}} \) solar-to-fuel efficiency

\( \theta^* \) non-dimensional reduction temperature defined in Eq. 28

\( \xi \) non-dimensional number defined in Eq. 22

\( \tau \) reaction duration per cycle, min

\( \Delta \tau \) time step, s

\( \chi \) relaxation factor

\( \Delta \delta \) change in non-stoichiometry

SUBSCRIPTS

\( H \) high

\( HX \) heat exchange

\( L \) low

\( \text{chem} \) chemical item

\( \text{gas} \) gas-phase transport heat loss

\( \text{fuel} \) fuel

\( \text{input} \) input

\( \text{other} \) other heat loss

\( \text{ox} \) oxidation

\( \text{quench} \) quenching heat loss

\( \text{rad} \) radiative heat loss

\( \text{recovery} \) recovery of conductive heat loss

\( \text{red} \) reduction

\( \text{ref} \) reference

\( \text{reject} \) rejecting heat loss

\( \text{shift} \) shifted from the previous phase

\( \text{solar} \) solar energy

\( \text{solid} \) solid-phase

\( \text{trans} \) transport item

\( \infty \) ambient