Catalytic CO₂ conversion via solar-driven fluidized bed reactors

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Abstract
Converting CO₂ and steam (H₂O) into synthesis gas is a new route to recycle them to fuels. Conversions are performed via a two-step conversion method in which catalysts are heated up and cooled down repeatedly with CO and H₂ as the products. To make the method economic, solar energy is employed to drive conversion systems. A solar-driven system with fluidized bed reactors is proposed for CO₂ conversion in this paper, and numerical models are built to study its performance and find out the optimum working condition. The investigation proves that system is a competent candidate to power the two-step conversion of CO₂ for the carbon recycle and the syngas production.

Keywords: CO₂ conversion; solar energy; numerical model; system assessment

INTRODUCTION
The current energy system based on the utilization of fossil fuels has apparent and potential environmental impacts [1]. Among the impacts, greenhouse effect from CO₂ emission is vital [2]. Carbon capture and sequestration have been proposed as the main technique to counterbalance the CO₂ emission. Sequestration of atmospheric CO₂ in underground reservoirs or in deep oceans has been studied and tried. Nevertheless, there are political and technical difficulties that may delay the introduction of such solutions in the near future [3].

Conversion of carbon dioxide into valuable products such as high-energy-content fuels and chemicals is a complement to the sequestration approach. However, CO₂ is a very stable molecule with unfavorable thermodynamics in conversions. The dissociation of CO₂ only happens above 2500 K [4]. Besides, the products of the dissociation are CO and O₂, which are easily explosive [5]. Thus, chemical conversions of CO₂ have been developed. The hydrogenation of CO₂ has been investigated widely [6]. This method requires hydrogen or hydrocarbons, which are fuels and important materials for chemical industries. To eliminate these limitations, the two-step conversion of CO₂ has been proposed [7]. The method does not require the same high-energy input or input of hydrogen and hydrocarbons [8], but careful preparation of catalysts, reactor optimization and exploration of reaction mechanisms. It utilizes homogenous or heterogeneous catalysts as intermediaries for the reaction [9] and relies on the oxygen storage and transport capabilities of the catalysts. Catalysts normally refer to the oxides of Ce, Zn, Zr, Mg, Au, Ni, Rh, etc. Furthermore, cerium oxide (ceria, with chemical formula CeO₂) also works as an important material supporting other catalysts to enhance the overall performance.
These catalysts go through a redox (reduction–oxidation) cycle. The cycle begins with an endothermic reduction process of the catalysts, releasing O₂. Then, the reduction is followed by an exothermic re-oxidation process of the catalysts. The catalysts are oxidized by CO₂ or H₂O, with CO or H₂ formed as the raw material of syngas [10]. The chemical equations describing the processes are listed below:

\[ \text{MO} \rightarrow \text{MO} + 0.5 \text{O}_2 \]  \hspace{1cm} (1)
\[ \text{MO} + \text{CO}_2 \rightarrow \text{MO}_2 + \text{CO} \]  \hspace{1cm} (2)
\[ \text{MO} + \text{H}_2\text{O} \rightarrow \text{MO}_2 + \text{H}_2 \]  \hspace{1cm} (3)

The compound MO₂ refers to the involved catalysts of metal oxides. Reaction of Equation (1) requires an extensive energy input since the reaction is strongly endothermic. The temperature needed for reducing the catalysts varies from 1000–2200 K. The method is not cost-efficient, and alternative energy resources should be considered. Solar energy is the prime candidate since it is a clean, cheap, renewable and abundant energy resource. The two-step conversion method will be lucrative once solar energy is utilized for the chemical reactors. Syngas
production via solar energy by a two-step redox cycle based on Zn/ZnO and FeO/Fe₃O₄ was studied [11–14].

In those studies, catalysts were heated by direct solar radiation in solar receivers. However, the use of those reactors is limited by the solid–gas contact and residence time depending on the flow velocity, the size and structure of the chemical reactor, and the varied sun radiation. In this work, a twin-bed reactor system is suggested. The system avoids the mentioned limitations and provides an accurate control of the reaction conditions. The theoretical basis and the design details are described in the methodology section, followed by the description of the numerical model to analyze and evaluate the system.

**METHODOLOGY**

**The structure of the system**

The schematic of the proposed twin-bed solar-driven reactor system is shown in Figure 1. The solar rays are concentrated by a solar concentrator and reflected into a volumetric solar receiver. The inert gas flows through the solar receiver and gets heated up. Afterwards, it enters the reduction reactor (Reactor 1) and heats up the catalyst particles. The catalyst particles are fluidized and reduced during the heating process, with O₂ released. The particles are blown out to Cyclone 1 after the reduction. Cyclone 1 collects the reduced particles and transfers them to the oxidation reactor (Reactor 2), where the particles are fluidized and cooled down by CO₂ flow or steam flow. The catalysts are then oxidized, with CO or H₂ produced. At last, catalysts return to Reactor 1 through Cyclone 2. In this study, ceria is used as the catalyst, because of its high redox rate and unique capability of oxygen transport [15]. The commercial ceria undergoes a mass loss of 3.2% as released O₂ at 1700 K [16]. Nitrogen is used as the inert gas and heat carrier from solar receiver to Reactor 1.

**The solar section**

The value of solar radiation changes with time and depends on the location [17]. It is normally assumed to be 800 W/m² in calculations. Parabolic dishes are chosen as solar concentrators for their high concentration ratios [18], and their efficiency ƞₑₑₑ depends on the specifications. Contemporary volumetric receivers can already supply hot gas flow of >1300°C [19]. The efficiency of a receiver ƞₑₑₑ depends on the concentration ratio and the operation temperature. Their relationships are expressed as Equation (4). It drops when the concentration ratio C decreases or the operation temperature Tmp increases. The flow rate of the gas depends on the fluidization in Reactor 1, and it will be discussed in the next section. I represents the solar irradiance.

\[
ƞₑₑₑ = 1 - \frac{σ T₄^4}{IC}
\]

**Reactor 1**

Reactor 1 is based on fluidization technique to promote the endothermic reactions reducing the ceria particles. Fluidized reactors have many advantages, including the optimum phase-contact and heat transfer between gas and solid phases. The ceria particles are settled at the bottom of the reactor. The heat carrier gas of N₂ enters the reactor through the inlet of the reactor below the particles bed. The heat loss along the gas line is neglected, so the temperature of the N₂ leaving the solar receiver is equal to that of the N₂ entering the reactor. The temperature of the N₂ entering the reactor T₄ is equal to that of the N₂ leaving the solar receiver. The flow velocity of N₂ depends on the requirement of the fluidization of the particles. The terminal velocity Uₜ for the fluidization is determined by the following three equations:

\[
Uₜ = \sqrt{\frac{4(ρ_p - ρ_g)gd_p}{3Cd_pρ_g}}
\]

\[
Cd = a + b/Re + c/Re^2
\]

\[
Re = d_pUₜρ_g/μ
\]

Figure 1. The diagram of the solar-driven system for the two-step conversion method.
where \( \rho_g \) is the density of the solid phase ceria; \( \rho_g \) and \( \mu \) are the density and the viscosity of \( \text{N}_2 \) at the temperature \( T_g \); \( d_p \) is the diameter of ceria particles; \( C_d \) is the drag force; \( R_e \) is the Reynolds number at the terminal velocity. The empirical constants \( a = 1.22, b = 29.17, c = 3.9 \). The Reynolds number \( R_e_{mf} \) at the minimum fluidization velocity \( U_{mf} \) is calculated with Equation (8):

\[
1823 R_e_{mf}^{1.07} + 21.27 R_e_{mf}^2 = Ar
\]

(8)

\( Ar \) is the dimensionless number of Archimedes number:

\[
Ar = \frac{\rho_g (\rho_g - \rho_s) g d_p^3}{\mu}
\]

(9)

The minimum fluidization velocity \( U_{mf} \) can be calculated by Equations (7) and (8). The operation velocity of \( \text{N}_2 \) flow \( U_g \) is normally 4–5 times of \( U_{mf} \). Calculations of the fluidization are performed with the software Ergun 6.2. The heat transferred between the two phases is equal to the heat released from \( \text{N}_2 \), and the heat absorbed by ceria particles. The heat transfer in the reactor can be described by Equations (10–17):

\[
h A_s (T_g - T_p) + \frac{1}{2} \left( \frac{d T_g}{dt} - \frac{1}{2} \frac{dT_p}{dt} \right) = \frac{d Q_h}{dt} = \frac{d Q_p}{dt} \frac{d T_g}{dt}
\]

(10)

\[
\frac{d Q_p}{dt} = \rho_g U_g A_s C_p \frac{dT_p}{dt}
\]

(11)

\[
A_s = \rho_p A_t H_b (1 - e_0) A_{sp}
\]

(12)

\[
h = 6 k g \varepsilon (1 - \varepsilon) N u / d_p^2
\]

(13)

\[
N u = (7 - 10 \varepsilon + 5 \varepsilon^2)(1 + 0.7 R e^{0.2} Pr^{1/3}) + (1.33 - 2.4 \varepsilon + 1.2 \varepsilon^2) R e^{0.7} Pr^{1/3}
\]

(14)

\[
Pr = C_g \mu / k_g
\]

(15)

\[
\frac{H - H_b}{H_b} = \frac{e_0 - e}{1 - e} = 10.978 \left( \frac{U_g - U_{mf}}{U_{mf}} \right)^{0.937} \frac{\rho_{129} d_p}{U_{mf}^{0.129} \rho_{129}}
\]

(16)

where \( Q_h \) is the heat transferred between the gas and the solid phases; \( h \) is the heat transfer coefficient; \( A_s \) is the surface area of all the particles; \( A_{sp} \) is the specific surface area of the particles; \( T_p \) is the temperature of the particles; \( Q_h \) is the heat released from \( \text{N}_2 \); \( Q_p \) is the heat absorbed by the particles; \( C_g \) and \( C_p \) are the specific heat capacities of \( \text{N}_2 \) and ceria; \( t \) is the physical time since the fluidization begins; \( H_b \) is the initial height of the fluidized bed; \( H \) is the transient height; \( k_g \) is the thermal conductivity of the gas \( \text{N}_2 \); \( \varepsilon \) is the transient porosity of the fluidized bed; \( e_0 \) is the initial porosity of the bed; \( Nu \) is the Nusselt number; \( Pr \) is the Prandtl number. The model of Gunn describes the granular heat transfer phenomenon here [20].

The efficiency \( \eta \) of Reactor 1 can be calculated by Equations (18–20), in which \( Q_{gr} \) refers to the heat absorbed by \( \text{N}_2 \) in the solar receiver:

\[
Q_p = \int_0^t \rho_p A_t H_b (1 - e_0) C_p d T_p dt
\]

(18)

\[
Q_{gr} = \int_0^t \rho_g U_g A_s C_p (T_g - T_{g0}) dt
\]

(19)

\[
\eta = Q_p / Q_{gr}
\]

(20)

Reactor 2

Reactor 2 is also of fluidized type, for \( \text{CO}_2 \) flow to cool down and oxidize the reduced ceria particles. When particles in Reactor 1 reach the target temperature \( T_{in} \), they will be blown out and collected in the cyclone separator 1 with a collection efficiency \( \eta_{cy1} \). Afterwards, they are transported to Reactor 2. The physical phenomena of the fluidization and heat transfer between the \( \text{CO}_2 \) and ceria particles are similar to those in Reactor 1 between \( \text{N}_2 \) and the particles, except that heat is transferred from particles to \( \text{CO}_2 \) in Reactor 2. Mathematical models in previous section can also be used here, with the properties of \( \text{N}_2 \) replaced by \( \text{CO}_2 \). When the temperature of ceria particles drops to a required value and the oxidation is completed, the particles are blown away and collected by Cyclone 2 with a collection efficiency \( \eta_{cy2} \). The collected particles are transported back to Reactor 1 or to a storage stack.

The numerical model

The numerical model was built with Matlab/simulink, which is a powerful toolbox for dynamic simulation of various systems. The highest-level diagram of the model is shown as Figure 2.

The model simulates the actual components in the system: solar concentrator, solar receiver, Reactor 1, Cyclone 1, Reactor 2 and Cyclone 2. It also includes three virtual components: control unit 1, control unit 2 and parameter settings. The control unit 1 has the following functions: initiating the whole system, activating the blowing out of the particles, waking up the cyclone separator 1 and loading the next batch of catalyst particles into Reactor 1. There are delay settings in the cyclone units to define the time needed for separation. Control unit 2 functions to initiate Reactor 2 and activates the blowing out of the particles to Cyclone 2. All the initial values are given in the 'Parameter settings' unit.

The crucial parameter settings in the case of converting \( \text{CO}_2 \) with catalysts ceria are given in Table 1.

The concentration ratio \( C \) is first set as 1000 here. The efficiency of the concentrator \( \eta_{scr} \) is set as 80% [21, 22]. The efficiency of the solar receiver \( \eta_{scr} \) is ~70% at the operation temperature of 1300 K, and 38% at the operation temperature of 1700 K. The temperature of \( \text{N}_2 \) leaving the solar receiver is set as 1300 K at first and then changed to higher values in the further investigations. The two reactors are assumed to have the same geometry. The collection efficiencies of the cyclone separators are supposed to be 100%. The initial bed heights \( H_b \) of ceria particles in the reactors are also the same. The initial porosity of the
is 0.376 basing on the assumption that all the ceria particles are perfect spheres. The properties of N$_2$ are chosen with its values at the temperature of 1273 K and assumed to be constants. The specific surface area $A_{sp}$ is set as 10 m$^2$/g for commercial ceria particles. The diameter of ceria particles is set as 300 µm aiming at a sufficient fluidization.

The heating performance of Reactor 1 is the primary objective of investigation. The temperature of the particles is recorded, and the efficiency of the reactor is calculated with Equation (20). The heat loss in the receiver is mainly affected by the radiation instead of convection at high temperatures. Based on this fact, the influence of the velocity of N$_2$ on the operation temperature and efficiency of the solar receiver is neglected. The total energy utilization efficiency $\eta_{tol}$ from solar to particles is calculated with Equation (21).

$$\eta_{tol} = \eta_{sc} \eta_{rec} \eta_{r}$$

**RESULTS AND DISCUSSION**

The effects of N$_2$ velocities and bed heights of ceria

The effects of velocities of N$_2$ on the heat transfer are investigated first. The temperature of N$_2$ entering Reactor 1 is 1300 K, and the target temperature for heating the particles is 1273 K. The initial bed height of ceria particles is 0.01 m, and the velocities of N$_2$ change with the values of 0.1, 0.2, 0.3, 0.4 and 0.5 m/s.
The results are shown in Table 2, and the temperature curves of ceria are shown in Figure 3a. Subsequently, the effects of the bed heights of ceria particles are investigated with the same settings. The velocity of N₂ is set as 0.5 m/s, and the bed heights are set as 0.01, 0.02, 0.03, 0.04 and 0.05 m, respectively. The results are shown in Table 3, and the temperature curves of ceria are shown in Figure 3b.

The time needed for heating up ceria particles to the target temperature increases proportionally as the bed heights of ceria grow but decreases proportionally as the velocity of N₂ grows, because the augmentation of ceria requires more heat to enhance its temperature and results in a longer heating time. On the contrary, the N₂ flow with a higher velocity brings more heat and reduces the heating time. The heat brought by N₂ flow at the velocity of 0.5 m/s is just 210 W, but the heat transfer coefficient $h$ is $9.89 \times 10^6$ W/m². Besides, the weight of ceria particles is 56.6 g when the bed height is 0.01 m, corresponding to a surface area $A_s = 566$ m². The maximum heat transfer capacity between the two phases is 7 orders of magnitude larger than the heat brought by N₂ flow. It means the total heat transfer capacity is not the barrier limiting the heating performance, but the flow rate of N₂ is. The relations are based on Equation (22).

$$Q = hA_s(T_g - T_p)$$  \hspace{1cm} (22)

The velocity of N₂ flow cannot increase without limits, because the operation velocity of is suitable to be 4–5 times of the minimum fluidization velocity $U_{mf}$. To find other ways to improve the heat transfer performance, the effects of N₂ temperatures on the heat transfer performance are also investigated.

### Table 2. The effects of velocities of N₂ on the heat transfer.

| Parameters                  | Units | Test 1 | Test 2 | Test 3 | Test 4 | Test 5 |
|-----------------------------|-------|--------|--------|--------|--------|--------|
| Velocity of N₂              | m/s   | 0.1    | 0.2    | 0.3    | 0.4    | 0.5    |
| Heat transfer coefficient $h$ | W/m²  | $7.64 \times 10^6$ | $8.43 \times 10^6$ | $9.01 \times 10^6$ | $9.49 \times 10^6$ | $9.89 \times 10^6$ |
| Time for reaching target temperature | s    | 2337   | 1171   | 782    | 588    | 471    |
| Efficiency $\eta_r$         | %     | 26.1   | 26.1   | 26.1   | 26.1   | 26.1   |

### Table 3. The effects of bed heights of ceria particles on the heat transfer.

| Parameters                  | Units | Test 1 | Test 2 | Test 3 | Test 4 | Test 5 |
|-----------------------------|-------|--------|--------|--------|--------|--------|
| Bed heights of ceria        | m     | 0.01   | 0.02   | 0.03   | 0.04   | 0.05   |
| Heat transfer coefficient $h$ | W/m²  | $9.89 \times 10^6$ | $9.89 \times 10^6$ | $9.89 \times 10^6$ | $9.89 \times 10^6$ | $9.89 \times 10^6$ |
| Time for reaching target temperature | s    | 471    | 938    | 1404   | 1870   | 2337   |
| Efficiency $\eta_r$         | %     | 26.1   | 26.1   | 26.1   | 26.1   | 26.1   |

Figure 3. The effects on the heat transfer by (a) the flow velocities of N₂; (b) the bed heights of ceria particles.
The effects of N₂ temperatures and the concentration ratio
The effects of the temperature of N₂ on the heat transfer are shown in Table 4. The temperature curves of ceria are shown in Figure 4. The height of the bed of ceria particles is 0.01 m, the velocity of N₂ is 0.1 m/s and the temperatures of N₂ entering the reactor change from 1300 to 1700 K. Raising the temperature of N₂ can reduce the time needed for heating up ceria particles to the target temperature 1273 K. The efficiency \( \eta_r \) is higher if the temperature of N₂ is enhanced. The curve of the efficiency \( \eta_r \) during the heating process Test 1 is given in Figure 5. It shows that the efficiency \( \eta_r \) is high when the temperature difference between N₂ and ceria is large in the beginning of the heating process. It gets lower and lower as the temperature difference becomes smaller. The relation is also based on the heat transfer equation (Equation 22). For the receiver with a concentration ratio \( C = 1000 \), the efficiencies are shown in Table 5.

The total efficiency is calculated via Equation (21) with the efficiency of solar concentrator \( \eta_{sc} \) assumed as 80%. A higher temperature of N₂ does not ensure a higher total efficiency if the solar receiver is considered, because the efficiency of the solar concentrator drops largely when the operation temperature of the receiver is high [23]. The increase in the efficiency \( \eta_r \) is not enough to compensate the drop of the efficiency \( \eta_{rec} \) at high temperatures. In this case, the peak of the total efficiency \( \eta_{tot} \) is 20.9% when the temperature of N₂ entering the reactor is 1500 K. However, the drop of the efficiency \( \eta_{rec} \) at high temperatures is not notable when the concentration ratio is quite high. The efficiencies are shown in Table 6 when the concentration ratio \( C \) is 10 000.

| Parameters                                    | Units | Test 1 | Test 2 | Test 3 | Test 4 | Test 5 |
|-----------------------------------------------|-------|--------|--------|--------|--------|--------|
| Temperature of N₂ entering Reactor 1          | K     | 1300   | 1400   | 1500   | 1600   | 1700   |
| Heat transfer coefficient \( h \)             | W/m²  | \( 7.64 \times 10^6 \) | \( 7.64 \times 10^6 \) | \( 7.64 \times 10^6 \) | \( 7.64 \times 10^6 \) | \( 7.64 \times 10^6 \) |
| Time for reaching target temperature           | s     | 2337   | 1397   | 1078   | 894    | 769    |
| Efficiency \( \eta_r \)                       | %     | 26.1   | 39.9   | 47.5   | 53.0   | 57.3   |

Figure 4. The effects of the temperatures of N₂ flow on the heat transfer.

Figure 5. The change of the efficiency of Reactor 1 during the heating process.

Table 5. The effects of temperatures of N₂ on efficiencies (when \( C = 1000 \)).

| Parameters                                    | Units | Test 1 | Test 2 | Test 3 | Test 4 | Test 5 |
|-----------------------------------------------|-------|--------|--------|--------|--------|--------|
| Temperature of N₂ entering Reactor 1          | K     | 1300   | 1400   | 1500   | 1600   | 1700   |
| Efficiency of solar receiver \( \eta_{rec} \) | %     | 70     | 64     | 55     | 45     | 35     |
| Efficiency of Reactor 1 \( \eta_r \)         | %     | 26.1   | 39.9   | 47.5   | 53.0   | 57.3   |
| Total efficiency \( \eta_{tot} \)             | %     | 14.6   | 20.4   | 20.9   | 19.8   | 16.0   |

Table 6. The effects of temperatures of N₂ on efficiencies (when \( C = 10 000 \)).

| Parameters                                    | Units | Test 1 | Test 2 | Test 3 | Test 4 | Test 5 |
|-----------------------------------------------|-------|--------|--------|--------|--------|--------|
| Temperature of N₂ entering Reactor 1          | K     | 1300   | 1400   | 1500   | 1600   | 1700   |
| Efficiency of solar receiver \( \eta_{rec} \) | %     | 88     | 87     | 86     | 85     | 83     |
| Efficiency of Reactor 1 \( \eta_r \)         | %     | 26.1   | 39.9   | 47.5   | 53.0   | 57.3   |
| Total efficiency \( \eta_{tot} \)             | %     | 18.4   | 27.8   | 32.7   | 36.0   | 38.0   |
Table 7. The influence of the reaction temperatures on the efficiencies ($C = 10 000$).

| Parameters                        | Units | Test 1 | Test 2 | Test 3 | Test 4 | Test 5 |
|-----------------------------------|-------|--------|--------|--------|--------|--------|
| Temperature of reaction           | K     | 1273   | 1373   | 1473   | 1573   | 1673   |
| Time for reaching the reaction    | s     | 769    | 942    | 1178   | 1553   | 2554   |
| Efficiency of solar receiver $\eta_{\text{rec}}$ | %     | 83     | 83     | 83     | 83     | 83     |
| Quantity of released $O_2$        | mol   | 0.0035 | 0.0106 | 0.0346 | 0.0424 | 0.0566 |
| Weight of equivalent CO           | g     | 0.196  | 0.594  | 1.938  | 2.374  | 3.170  |
| Heating value of equivalent CO $Q_{\text{CO}}$ | J     | 2000   | 6059   | 19 768 | 24 215 | 32 334 |
| Efficiency of heating in Reactor 1 $\eta_t$ | %     | 57.3   | 51.6   | 45.1   | 37.1   | 24.3   |
| Heat absorbed by $N_2$ in receiver $Q_{\eta}$ | J     | 44 915 | 55 020 | 68 805 | 90 707 | 1 491 73 |
| Heat-to-fuel efficiency $\eta_{\text{h-f}}$ | %     | 4.5    | 11.0   | 28.7   | 26.7   | 21.6   |
| Solar-to-fuel Efficiency $\eta_{\text{s-f}}$ | %     | 3.0    | 7.3    | 19.1   | 17.7   | 14.3   |

It can be seen that the total efficiency keeps increasing as the temperature of $N_2$ increases to 1700 K, but the increase in the total efficiency is slowing down. The reason is that the efficiency of solar receiver is eventually dropping, but the increase in the efficiency $\eta_t$ is slowing down. Generally, the concentration ratio should be as large as possible. When the concentration ratio is fixed, there is a maximum total efficiency determined by the temperature of $N_2$ entering the reactor. The temperature of the turning point is higher when the concentration ratio increases.

The influence of the temperature of reactions

The preceding results are based on the prerequisite that the target temperatures for the reduction of ceria are all 1273 K. However, the chemical reaction rates and the productivity change if the temperature of the reaction changes [16]. The influence of the reaction temperature on the efficiencies is shown in Table 7. The temperature of $N_2$ entering Reactor 1 is 1700 K, and the concentration ratio $C$ is assumed to be 10 000. The velocity of $N_2$ flow is 0.1 m/s, and the bed height of ceria is 0.01 m, corresponding to a mass of 56.6 g. The heat brought by $N_2$ flow is 58.38 W, and the heating value of CO is 1.02 × 10^4 J/g. With the total heating value of produced CO, the heat-to-fuel efficiency $\eta_{\text{h-f}}$ can be calculated with Equation (23), and the solar-to-fuel efficiency $\eta_{\text{s-f}}$ can be defined as Equation (24):

$$\eta_{\text{h-f}} = \frac{Q_{\text{CO}}}{Q_{\eta}}$$

$$\eta_{\text{s-f}} = \eta_{\text{rec}} \eta_{\text{tol}} \eta_{\text{h-f}}$$

When ceria is reduced, the released $O_2$ increases as the reaction temperature increases from 1273 to 1673 K. The equivalent CO is calculated with the hypothesis that all the reduced ceria could be re-oxidized by CO$_2$. The peak of the heat-to-fuel efficiency appears at the target temperature of 1473 K and then drops, because the heating efficiency is decreasing and the heat brought by $N_2$ is not sufficiently utilized. At the temperature of 1473 K, 0.0346 mol of $O_2$ is released by 56.6 g of ceria, and then 1.938 g of CO could be produced. 19.1% of the solar energy is converted into chemical energy in CO. The trend largely depends on the kinetics of the reduction of specific catalysts.

CONCLUSIONS

The two-step conversion method of CO$_2$ is an attractive choice to recycle CO$_2$ for CO production. In this work, solar energy is employed as the energy source. The twin-bed system successfully avoids the inconvenience of the systems combining the solar receivers and chemical reactors as one body. The reactors are designed with fluidization technique, which is suitable for gas-solid reactions and heat transfer. The mathematical model in Simulink has been built to simulate the operation and evaluation of the system.

The conversion of CO$_2$ by ceria investigated in the article shows that the system can successfully heat up the catalyst particles of 56.6 g to 1273 K in 8 min. The efficiency of the reactor $\eta_t$ decreases during the heating processes. When ceria reaches the target temperature of 1273 K, the reactor efficiency $\eta_t$ is ~26.1%, and it increases to 57.3% as the temperature of $N_2$ entering the reactor increases from 1300 to 1700 K. However, the efficiency is not affected by the change of $N_2$ flow rate or load of ceria.

The efficiency of the solar receiver $\eta_{\text{rec}}$ drops when the operation temperature increases. Considering this, the total efficiency of the system $\eta_{\text{tol}}$ demonstrates a convex profile as the temperature of $N_2$ entering the reactor increases. There is a peak of the efficiency $\eta_{\text{tol}} = 20.9\%$ when the temperature is 1473 K. The increase in the concentration ratio can enhance the efficiencies. For a concentration ratio $C = 10 000$, the total efficiency increases from 20.9 to 32.7%.

The $O_2$ released by ceria increases when the reaction temperature increases from 1273 to 1673 K, meaning more CO can be produced. At the temperature of 1673 K, 3.17 g of CO could be produced by 56.6 g of ceria. The maximum solar-to-fuel efficiency $\eta_{\text{s-f}}$ of 19.1% appears at the reaction temperature of 1473 K, because the heating efficiency decreases in the heating processes. The system is proved to be competent for solar-driven CO$_2$ conversions with considerable efficiencies. The model successfully simulated and evaluated the case of converting CO$_2$
with ceria catalysts and could be used for the design and evaluation of other systems.

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REFERENCES

[1] Lange J, Solutions SG. Lignocellulose conversion: an introduction to chemistry, process and economics. *Biofuels Bioprod Biorefining* 2007;1:39–48.
[2] IEA. CO₂ emission from fuel combustion. International Energy Agency, 2012.
[3] Pires JCM, Martins FG, Alvim-Ferraz MCM, et al. Recent developments on carbon capture and storage: an overview. *Chem Eng Res Des* 2011;89:1446–60.
[4] Steinfield A, Zurich C, Palumbo R. Solar thermochemical process technology. *Encycl Phys Sci Technol* 2001;15:237–56.
[5] Nakamura T. Hydrogen production from water utilizing solar heat at high temperatures. *Sol Energy* 1977;19:467–75.
[6] Najafabadi AT. CO₂ chemical conversion to useful products: an engineering insight to the latest advances toward sustainability. *Int J Energy Res* 2013;37:485–99.
[7] Loutzenhisier PG, Meier A, Steinfield A. Review of the two-step H₂O/CO₂-splitting solar thermochemical cycle based on Zn/ZnO redox reactions. *Materials (Basel)* 2010;3:4922–38.
[8] Steinfeld A, Kuhn P, Keller A, et al. Solar-processed metals as clean energy carriers and water-splitters. *Int J Heat Mass Transf* 1998;33:767–74.
[9] Dorner RW, Hardy DR, Williams FW, et al. Heterogeneous catalytic CO₂ conversion to value-added hydrocarbons. *Energy Environ Sci* 2010;3:884–90.
[10] Charvin P, Abanades S, Beche E, et al. Hydrogen production from mixed cerium oxides via three-step water-splitting cycles. *Solid State Ionics* 2009;180:1003–10.
[11] Loutzenhisier PG, Elena Gálvez M, Hirschier I, et al. CO₂ splitting in an aerosol flow reactor via the two-step Zn/ZnO solar thermochemical cycle. *Chem Eng Sci* 2010;65:1855–64.
[12] Abanades S, Villafan-vidales I. CO₂ valorisation based on Fe₂O₄/FeO thermochemical redox reactions using concentrated solar energy. *Int J Energy Res* 2013;37:598–608.
[13] Carotenuto A, Nocera U, Tecchio P. Thermal behaviour of a multi-cavity volumetric solar receiver: design and test results. *Sol Energy* 1993;50:113–21.
[14] Anikeev VI, Bobrin AS, Ortner J, et al. Catalytic thermochemical reactor/receiver for solar reforming of natural gas: Design and performance. *Sol Energy* 1998;63:97–104.
[15] Bedrane S, Descorme C, Duprez D. Investigation of the oxygen storage process on ceria- and ceria–zirconia-supported catalysts. *Catal Today* 2002;75:401–5.
[16] Zhou Y, Rahaman MN. Effect of redox reaction on the sintering behavior of cerium oxide. *Acta Mater* 1997;45:3635–9.
[17] Radosavljevic JDA. Defining of the intensity of solar radiation on horizontal and oblique surfaces on Earth. *Facta Univ Ser Work Living Environ Prot* 2001;2:77–86.
[18] Kalogirou SA. Solar thermal collectors and applications. *Prog in Energy and Combust Sci.* 2004;30:231–95.
[19] Ávila-Marín AL. Volumetric receivers in solar thermal power plants with central receiver system technology: a review. *Sol Energy* 2011;85:891–910.
[20] Gunn DJ. Transfer of heat or mass to particles in fixed and fluidised beds. *Int J Heat Mass Transf* 1978;21:467–76.
[21] Jaffe LD. Test results on parabolic dish concentrators for solar thermal power systems. *Sol Energy* 1984;42:173–87.
[22] Wu SY, Xiao L, Cao Y, et al. A parabolic dish/AMTEC solar thermal power system and its performance evaluation. *Appl Energy* 2010;87:452–62.
[23] Spelling JD. *Hybrid Solar gas-Turbine Power Plants*. Kungliga Tekniska Högskolan, 2013.