

Thermodynamic analysis on CSP integrated cerium oxide ($\text{CeO}_2 - \text{CeO}_{1.72/1.83}$) water splitting cycle for hydrogen production

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ABSTRACT

Solar thermochemical CeO_2 -based H_2O splitting cycle was thermodynamically analyzed to ascertain the optimal thermal reduction (T_H) and re-oxidation (T_L) temperatures and evaluate the solar-to-fuel conversion efficiency ($\eta_{\text{solar-to-fuel}}$) of the cycle. The equilibrium composition of CeO_2 , $\text{CeO}_{1.72}$, $\text{CeO}_{1.83}$ and O_2 exhibited that the thermal reduction initiated at 1400 K thereby attaining 100 % TR at 2734 K. The observed variations in Gibbs free energy (ΔG) correspond to the feasibility of the re-oxidation step of $\text{CeO}_{1.83}$ and $\text{CeO}_{1.72}$ at 1050 K and 1200 K respectively. It was reported that the absorption efficiency of solar reactor ($\eta_{\text{abs-solar-reactor-WS}}$) decreases from 95.6 % to 37 %, as the T_H increases from 1400 K to 2734 K. The results show that $\eta_{\text{solar-to-fuel}}$ reached the maximum value of 7.45 % for $\text{CeO}_{1.72}$ and 7.69 % for $\text{CeO}_{1.83}$ at 61.72 % TR of CeO_2 without heat recuperation. Further, the $\eta_{\text{solar-to-fuel}}$ attained the maximum value of 14.92 % and 13.54 % for $\text{CeO}_{1.83}$ and $\text{CeO}_{1.72}$, respectively at the %TR of CeO_2 of 80 % with 50 % heat recuperation. The solar-to-fuel conversion efficiency ($\eta_{\text{solar-to-fuel}}$) further can be increased with the optimization of oxygen partial pressure (P_{O_2}) and molar flow rate of reduction reagents (Ar or N_2).

1. Introduction

Solar fuels such as H_2 and syngas have been produced with extensive utilization of solar energy via thermochemical water-splitting cycles. Solar concentrated energy was utilized as the primary source of energy input and water as material input to produce solar fuels [1–6]. Researchers have exhaustively investigated different solar thermochemical cycles based on various metal oxide compounds such as zinc oxide [7,8], iron oxide [9,10], ferrites [11–13], tin oxide [14,15], ceria/doped ceria [16–19], perovskites [20–22], and others [23,24]. Similar cycles, such as sulfur iodine, the hybrid sulfur cycle [25,26], and the hybrid S-NH_3 cycle [27,28], have also been examined to generate solar fuels. Some of the rare earth metals have been explored in the water research to lower the ecological risks [29–32].

Loutzenhiser et al. studied the thermodynamic analysis of Zn/ZnO

WS cycle and reported the cycle efficiency reaches 31.5 % without heat recuperation and 52 % with heat recuperation [8]. The study carried out by Charvin et al. reported the conversion of 83 % Fe_2O_3 into FeO at 575 °C [9]. Scheffe studied the Cobalt ferrites/ Al_2O_3 and reported that it can be cycled at $T_H = 1200$ °C and $T_L = 1000$ °C and also significant quantities of H_2 can be produced at 1200 °C [12]. Study carried out on SnO_2/SnO reported that the thermal reduction can be carried out at 1600 °C and the re-oxidation can be performed at 500–600 °C with 90 % hydrogen yield [15]. Study performed on perovskite (LSM40) showed the conversion efficiency of 16 % at 1800 K and 13 % at 1600 K [21].

The combination of metal oxide and sulfate (MO-MS) based solar thermochemical cycle has been the center of attention in recent times due to their improved conversion efficiency performance [33]. Mainly, $\text{Fe}_2\text{O}_3 - \text{FeSO}_4$ [34], $\text{ZnO} - \text{ZnSO}_4$ [35], and $\text{SrO} - \text{SrSO}_4$ [36] WS cycles fall in this category.

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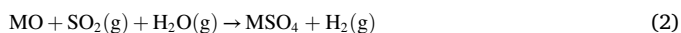
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Further it some other studied metal oxides have shown their potential in great potential for pollution control [37–41].

The standard thermochemical reactions of MO-MS based WS (water splitting) cycle can be written as follows:



The $\eta_{\text{solar-to-fuel}}$ of the MO-MS WS cycles such as $\text{Fe}_2\text{O}_3 - \text{FeSO}_4$, $\text{ZnO} - \text{ZnSO}_4$, and $\text{SrO} - \text{SrSO}_4$ was reported to be higher than the other solar thermochemical cycles explored earlier.

According to the reported results of the MO-MS water splitting cycles (IO-IS, ZO-ZS, and SrO-SrS), their conversion efficiency was considerably higher than that of the other solar thermochemical cycles. The MO-MS water splitting cycles are the most favorable method for producing hydrogen. Nevertheless, it is vital to identify an optimal and balanced combination of MO-MS that will provide the highest $\eta_{\text{solar-to-fuel}}$ at low reduction temperatures. Cerium oxide has been an outstanding candidate for solar thermochemical hydrogen production due to its non-volatile nature (volatile MO evaporates and blocks the porous matrix which leads to extreme pressure in solar reactor) and staller solar-to-fuel conversion efficiency [42].

The present study investigated the chemical equilibrium of the two-step thermochemical $\text{CeO}_2 - \text{CeO}_{1.72/1.83}$ water splitting cycle (as illustrated in Fig. 1), and evaluated the $\eta_{\text{solar-to-fuel}}$ with and without the implementation of heat recuperation techniques, thereby assessing the feasibility of solar fuel production. Ceria or cerium oxide (CeO_2) is a rare earth metal oxide which demonstrate the exemplary solar-to-fuel conversion efficiency due to relatively low thermal reduction and re-oxidation temperatures. Further, it's a non-volatile compound eliminates the sintering risk and its ability to convert non-stoichiometric to and stoichiometric back and fourth makes it a perfect candidate for continuous operation [43,44].

2. Mathematical modelling and system configuration for equilibrium analysis

The solar-assisted non-stoichiometric cerium oxide ($\text{CeO}_2 - \text{CeO}_{1.72/1.83}$) WS thermochemical cycle was analyzed thermodynamically using the HSC Chemistry software. HSC chemistry facilitates numerical investigation of chemical processes and a diverse range of variables, including change in enthalpy (ΔH), Gibbs free energy (ΔG), entropy (ΔS), and heat capacity (ΔC_p). HSC chemistry software database is inbuilt with 28,000 chemical species thus enabling the user to validate the feasibility of the chemical process.

In the presented thermodynamic analysis, the first step was per-

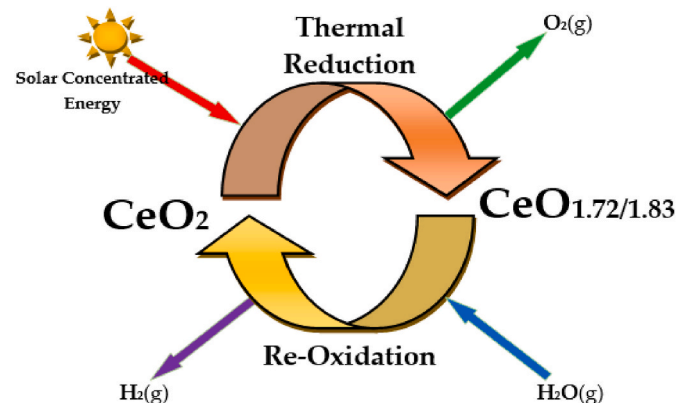


Fig. 1. Solar-driven thermochemical cerium oxide (CeO_2) WS cycle for hydrogen production.

formed to evaluate the equilibrium composition of the reactant species and the influence of (T_H) on the thermal reduction of CeO_2 . The second step was conducted to evaluate the $\eta_{\text{solar-to-fuel}}$ of the cycle. Consequently, primarily, equilibrium analysis was carried out as the first step of the thermodynamic analysis of solar-assisted ($\text{CeO}_2 - \text{CeO}_{1.72/1.83}$) cycle. The reduction of CeO_2 was carried out at oxygen partial pressure (P_{O_2}) of 1 bar. The equilibrium composition of CeO_2 , $\text{CeO}_{1.72/1.83}$, and O_2 reported in Fig. 2 exhibits that the thermal decomposition of CeO_2 started at 1400 K and the full extent of thermal reduction (100 % TR) was achieved at 2734 K.

Cerium oxide (CeO_2) is a non-volatile compound; therefore, this research focused on determining the influence of the thermal decomposition of CeO_2 on the overall efficiency of solar-to-fuel conversion. The results reported in Fig. 3 show that as T_H upsurges from 1412 K to 1622 K, the thermal reduction (TR) of CeO_2 initiates and moves forward gradually from 0.69 % to 4.08 %, respectively. However, as T_H further increases from 1622 K to 2315 K, the thermal reduction (TR) of CeO_2 upswings rather rapidly on a linear curve and go from 4.08 % to 76.03 %. The increase in thermal reduction of CeO_2 was reported to be quickest from 76.03 % to 100 % with T_H increases from 2315 K to 2734 K.

The equilibrium analysis continued by estimating the re-oxidation temperature (T_L) by analyzing the ΔG as a function of operating temperature as illustrated in Fig. 4. The temperature dependence of the ΔG was used to validate the feasible thermal reduction temperature (T_H) as well as the re-oxidation temperature (T_L). The reduction reaction is exothermic, thus ΔG is inversely bound with the temperature and eventually approaches zero value to sustain the chemical equilibrium. Subsequently, the re-oxidation reaction is an endothermic reaction and the ΔG value rises with the increasing temperature and approaches zero.

Given the ΔG is a function of operating temperature, the effects on the reduction reaction ($\text{CeO}_2 \rightarrow \text{CeO}_{1.72/1.83} + \text{O}_2$) and re-oxidation reaction ($\text{CeO}_{1.72/1.83} + \text{H}_2\text{O} \rightarrow \text{CeO}_2 + \text{H}_2$) are plotted in Fig. 4. The value of ΔG decreases from 600 kJ to -103.87 kJ and 590 kJ to -177.05 kJ for $\text{CeO}_{1.72}$ and $\text{CeO}_{1.83}$, respectively in the reduction step while it upsurges the value of ΔG decreases from 600 kJ to -103.87 kJ and 590 kJ to -177.05 kJ for $\text{CeO}_{1.72}$ and $\text{CeO}_{1.83}$, respectively with the increase in operating temperature from 300 K to 3000 K to achieve chemical equilibrium (see Table 1).

The reported data in Fig. 4 also suggest that the ΔG approaches zero at 2305 K and 2525 K for $\text{CeO}_{1.83}$ and $\text{CeO}_{1.72}$, respectively in thermal reduction reaction to attain the chemical equilibrium. However, in the re-oxidation reaction, the chemical equilibrium was achieved at 1100 K and 1290 K for $\text{CeO}_{1.83}$ and $\text{CeO}_{1.72}$, respectively. The aforementioned

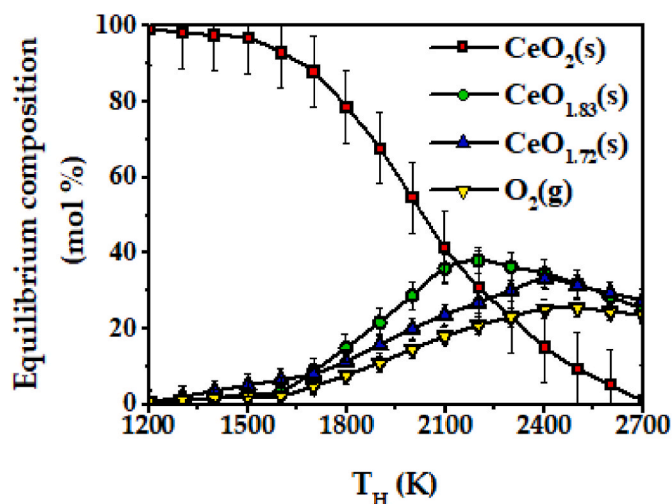


Fig. 2. Equilibrium composition of solid and gaseous species as a function of T_H .

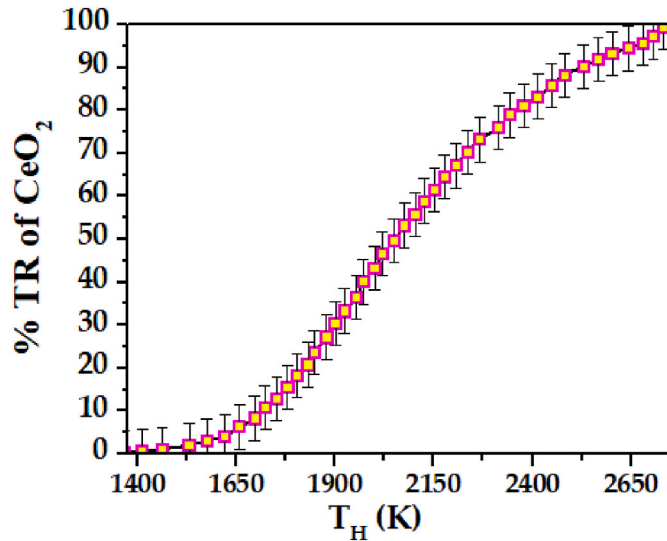


Fig. 3. Influence of T_H on %TR of CeO_2 .

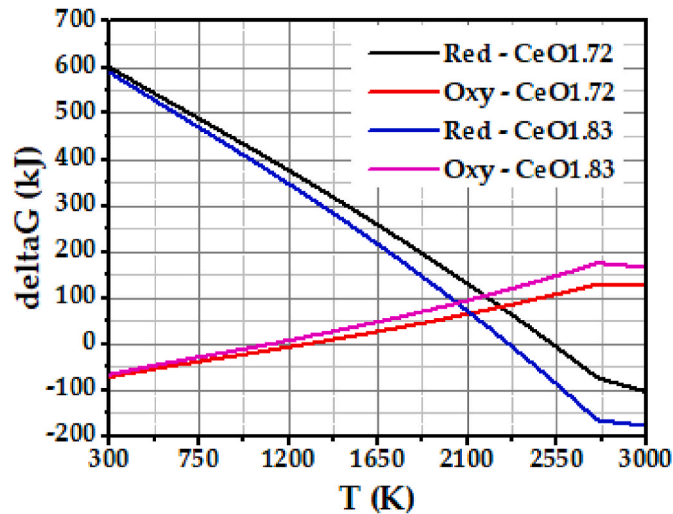


Fig. 4. The influence of T_H and T_L on change in Gibbs free energy (ΔG).

change in Gibbs free energy (ΔG) analysis suggests that the thermal decomposition is feasible at temperatures beyond 2305 K and 2525 K for $\text{CeO}_{1.83}$ and $\text{CeO}_{1.72}$, respectively while the WS reaction is practicable at a temperature lower than 1100 K and 1290 K for $\text{CeO}_{1.83}$ and $\text{CeO}_{1.72}$, respectively. Therefore, the re-oxidation temperature (T_L) opted to be 1050 K and 1200 K for $\text{CeO}_{1.83}$ and $\text{CeO}_{1.72}$, respectively.

The dynamic process configuration schematic is represented in Fig. 5. The essential components of the presented thermochemical system are the solar reactor, solar heater, cooler-A, cooler-B, cooler-C, and

WS reactor.

The thermal decomposition of ceria and H_2O splitting WS reaction of CeO_2 – WS cycles were performed in the solar reactor and WS reactor, respectively. The thermal reduction of CeO_2 into $\text{CeO}_{1.72}$ or $\text{CeO}_{1.83}$ takes place at high temperatures in a solar-driven solar reactor. The solid and gaseous species $\text{CeO}_2(\text{s})$, $\text{CeO}_{1.72}(\text{s})$ or $\text{CeO}_{1.83}(\text{s})$ and $\text{O}_2(\text{g})$ are directed into the cooler - A to reduce the temperature of the species from T_H to T_L and the excessive heat ($Q_{\text{cooler-A}}$) is released by the cooler - A to control the intermediate temperature.

The solid species i.e. $\text{CeO}_2(\text{s})$, $\text{CeO}_{1.72}(\text{s})$ or $\text{CeO}_{1.83}(\text{s})$ are fed into the WS reactor at operational re-oxidation temperature (T_L) and the gaseous species i.e. $\text{O}_2(\text{g})$ goes into cooler - B at the same temperature. Cooler - B is installed to further decrease the operational temperature of $\text{O}_2(\text{g})$ from T_L to 300 K and fed into a fuel cell. The solid species react with superheated steam $\text{H}_2\text{O}(\text{g})$ in the WS reactor and produce hydrogen gas at T_L . The hydrogen gas is further passed through cooler - C to bring it at atmospheric temperature and supplied to the fuel cell where it reacts with pre-existing $\text{O}_2(\text{g})$ and gets converted into $\text{H}_2\text{O}(\text{l})$.

Once the hydrogen is converted into steam at 300 K, it is passed through a heater to raise its temperature to T_L and directed to the WS reactor and the system process completes a closed-loop cycle.

The following assumptions were incorporated into the numerical thermodynamic calculations.

1. The solar reactor is operated at the molar flow rate ($\dot{m}$) of 1 mol/s of $\text{CeO}_2(\text{s})$.
2. All thermal losses through conduction and convection modes of heat transfer are omitted.
3. The full extent of thermal reduction of $\text{CeO}_2(\text{s})$ is assumed.
4. The changes in the kinetic and potential energies are negligible.
5. HEX calculations are not accounted for in the overall analysis.

2.1. Mathematical modelling

The first step of $\eta_{\text{solar-to-fuel}}$ assessment is the calculation of the solar absorption efficiency of the solar reactor ($\eta_{\text{abs-solar-reactor-WS}}$) and solar H_2O heater ($\eta_{\text{abs-solar-H}_2\text{O-heater-WS}}$) using Eqs. (3) and (4) mentioned below;

$$\eta_{\text{abs-solar-reactor-WS}} = \left[1 - \left(\frac{\sigma T_L^4}{\text{IC}} \right) \right] \quad (3)$$

$$\eta_{\text{abs-solar-H}_2\text{O-heater-WS}} = \left[1 - \left(\frac{\sigma T_H^4}{\text{IC}} \right) \right] \quad (4)$$

In the aforementioned equations, the values of I, C and σ are taken as 1000 W/m^2 , 3000 suns and $5.67 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4$, respectively.

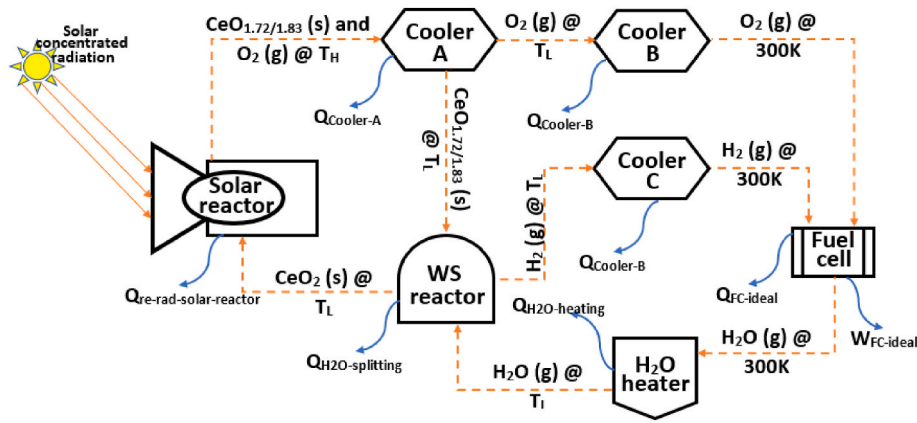
The input solar heat energy required to operate the solar reactor ($Q_{\text{solar-reactor-WS}}$) and solar H_2O heater ($Q_{\text{solar-H}_2\text{O-heater-WS}}$) was estimated using the following given Eq. (5) and Eq. (6);

$$Q_{\text{solar-reactor-WS}} = \frac{Q_{\text{CeO}_2\text{-partial-reduction-WS}}}{\eta_{\text{abs-solar-reactor-WS}}} \quad (5)$$

Table 1

Effect of reduction temperature on ΔH , ΔS and ΔG .

Thermal reduction of CeO_2 into $\text{CeO}_{1.83}$				Thermal reduction of CeO_2 into $\text{CeO}_{1.72}$			
T (K)	ΔH (kJ)	ΔS (J/K)	ΔG (kJ)	T (K)	ΔH (kJ)	ΔS (J/K)	ΔG (kJ)
1200	683.32	279.95	347.37	1200	682.71	255.22	376.45
1500	705.48	296.30	261.03	1500	697.96	266.47	298.26
1800	737.60	315.73	169.29	1800	720.02	279.81	216.36
2100	779.78	337.33	71.37	2100	748.91	294.61	130.22
2400	832.05	360.55	-33.27	2400	784.64	310.48	39.48
2700	894.44	385.01	-145.08	2700	827.23	327.18	-56.15
3000	-39.18	45.96	-177.06	3000	265.80	123.23	-103.87

Fig. 5. Process flow arrangement of the CeO₂ thermochemical cycle.

$$Q_{\text{solar-H}_2\text{O-heater-WS}} = \frac{Q_{\text{H}_2\text{O-heating-WS}}}{\eta_{\text{abs-solar-H}_2\text{O-heater-WS}}} \quad (6)$$

Further, the solar heat energy required to facilitate the partial reduction of CeO₂ ($Q_{\text{CeO}_2\text{-partial-reduction-WS}}$) is estimated by Eq. (7), while Eq. (8) is used to estimate the solar heat energy required for the H₂O heating ($Q_{\text{H}_2\text{O-heating-WS}}$).

$$Q_{\text{CeO}_2\text{-partial-reduction-WS}} = \dot{m}\Delta H|_{\text{CeO}_2(\text{s}) \text{ at } T_L \rightarrow a\text{CeO}_2(\text{s}) + b\text{CeO}_{1.72/1.83}(\text{s}) + c\text{O}_2(\text{g}) \text{ at } T_H} \quad (7)$$

$$Q_{\text{H}_2\text{O-heating-WS}} = \dot{m}\Delta H|_{\text{cH}_2\text{O}(\text{l}) \text{ at } 298 \text{ K} \rightarrow \text{eH}_2\text{O}(\text{g}) \text{ at } T_L} \quad (8)$$

The net solar energy required to operate the thermochemical cycle is

$$Q_{\text{Cooler-A-WS}} = -\dot{m}\Delta H|_{a\text{CeO}_2(\text{s}) + b\text{CeO}_{1.72/1.83}(\text{s}) + c\text{O}_2(\text{g}) \text{ at } T_H \rightarrow a\text{CeO}_2(\text{s}) + b\text{CeO}_{1.72/1.83}(\text{s}) + c\text{O}_2(\text{g}) \text{ at } T_L} \quad (16)$$

calculated by the addition of Eqs. (7) and (8) and it can be represented as Eq. (9) given below;

$$Q_{\text{cycle-net-WS}} = Q_{\text{CeO}_2\text{-partial-reduction-WS}} + Q_{\text{H}_2\text{O-heating-WS}} \quad (9)$$

Correspondingly, the addition of $Q_{\text{solar-reactor-WS}}$ from Eq. (5) and $Q_{\text{solar-H}_2\text{O-heater-WS}}$ from Eq. (6) results in the solar energy required to drive the complete solar cycle as shown in Eq. (10);

$$Q_{\text{solar-cycle-WS}} = Q_{\text{solar-reactor-WS}} + Q_{\text{solar-H}_2\text{O-heater-WS}} \quad (10)$$

The thermodynamic calculations in this study did not account for thermal losses resulting from conduction and convection in the solar reactor, solar heater, and water-splitting reactor. However, the re-radiation thermal losses are still considered and can be calculated using Eqs. (11) and (12);

$$Q_{\text{re-rad-solar-reactor-WS}} = Q_{\text{solar-reactor-WS}} - Q_{\text{CeO}_2\text{-partial-reduction-WS}} \quad (11)$$

$$Q_{\text{re-rad-solar-H}_2\text{O-heater-WS}} = Q_{\text{solar-H}_2\text{O-heater-WS}} - Q_{\text{H}_2\text{O-heating-WS}} \quad (12)$$

Accordingly, the energy losses via re-radiation from the WS cycle ($Q_{\text{re-rad-cycle-WS}}$) can be estimated by the summation of Eqs. (11) and (12) and can be expressed as Eq. (13);

$$Q_{\text{re-rad-cycle-WS}} = Q_{\text{re-rad-solar-reactor-WS}} + Q_{\text{re-rad-solar-H}_2\text{O-heater-WS}} \quad (13)$$

The $\eta_{\text{solar-to-fuel}}$ without heat recuperation can be estimated using the following given Eq. (14);

$$\eta_{\text{solar-to-fuel}} = \frac{\text{moles of H}_2 \times \text{HHV of H}_2}{Q_{\text{solar-cycle-WS}}} \quad (14)$$

However, if heat recuperation is taken into account, the roles of coolers and the WS reactor have to be taken into consideration. Therefore, the $Q_{\text{recuperation-WS}}$ can be calculated using the following mentioned Eq. (15);

$$Q_{\text{recuperation-WS}} = Q_{\text{Cooler-A-WS}} + Q_{\text{Cooler-B-WS}} + Q_{\text{WS-splitting-reactor-WS}} + Q_{\text{Cooler-C-WS}} \quad (15)$$

The value of $Q_{\text{recuperation-WS}}$ can be calculated by the following given Eq. (16)–(19);

$$Q_{\text{Cooler-B-WS}} = -\dot{m}\Delta H|_{\text{cO}_2(\text{g}) \text{ at } T_L \rightarrow \text{cO}_2(\text{g}) \text{ at } 298 \text{ K}} \quad (17)$$

$$Q_{\text{Cooler-C-WS}} = -\dot{m}\Delta H|_{\text{dH}_2\text{O}(\text{g}) \text{ at } T_L \rightarrow \text{dH}_2\text{O}(\text{l}) \text{ at } 298 \text{ K}} \quad (18)$$

$$Q_{\text{H}_2\text{O-splitting-reactor-WS}} = -\dot{m}\Delta H|_{a\text{CeO}_2(\text{s}) + b\text{CeO}_{1.72/1.83}(\text{s}) + \text{eH}_2(\text{g}) \text{ at } T_L \rightarrow \text{CeO}_2(\text{s}) + \text{dH}_2\text{O}(\text{g}) \text{ at } T_L} \quad (19)$$

Eq. (20) can be employed to determine the total solar energy demand for driving the water-splitting solar cycle;

$$Q_{\text{solar-cycle-HR-WS}} = Q_{\text{solar-cycle-WS}} - Q_{\text{recuperation-HR-WS}} \quad (20)$$

And $Q_{\text{recuperation-HR-WS}}$ can be calculated by Eq. (21);

$$Q_{\text{recuperation-HR-WS}} = (\% \text{HR}) \times Q_{\text{recuperable-WS}} \quad (21)$$

Thus, solar-to-fuel conversion efficiency ($\eta_{\text{solar-to-fuel-HR}}$) after taking the heat recuperation into taking account can be estimated by Eq. (22);

$$\eta_{\text{solar-to-fuel-HR}} = \frac{\text{moles of H}_2 \times \text{HHV of H}_2}{Q_{\text{solar-cycle-HR-WS}}} \quad (22)$$

The presented study is validated using the work output from the fuel cell ($W_{\text{FC-ideal-WS}}$) by the following mentioned Eqs. (23) and (24);

$$W_{\text{FC-ideal-WS}} = -\dot{m}\Delta G|_{\text{dH}_2\text{O}(\text{l}) + \text{cO}_2 \text{ at } 298 \text{ K} \rightarrow \text{eH}_2(\text{g}) \text{ at } 298 \text{ K}} \quad (23)$$

$$W_{FC-ideal-WS} = Q_{solar-cycle-WS} - (Q_{re-rad-cycle-WS} + Q_{Cooler-A-WS} + Q_{Cooler-B-WS} + Q_{Cooler-C-WS} + Q_{H_2O-splitting-reactor-WS} + Q_{FC-ideal-WS}) \quad (24)$$

where,

$$Q_{FC-ideal-WS} = -(298) \times \dot{m} \Delta S|_{dH_2O(l)+cO_2 \text{ at } 298 \text{ K} \rightarrow cH_2(g) \text{ at } 298 \text{ K}} \quad (25)$$

The feasibility of the exergy investigation conducted on the solar thermochemical IO-IS water splitting cycle was established by an energy balance analysis using Eq. (24). The energy balance analysis performed considering the thermal reduction temperature (T_H) = 1450 K, re-oxidation temperature (T_L) = 500 K validates the accuracy of the analysis as $W_{FC-ideal-WS}$ = 143.78 kW estimated from Eq. (23) equals the $W_{FC-ideal-WS}$ calculated from Eq. (24).

3. Results and discussion

3.1. Performance assessment of solar reactor and heaters

The thermodynamic equilibrium analysis was performed as the primary step to evaluate the $\eta_{solar-to-fuel}$ of the $CeO_2 - CeO_{1.72/1.83}$ thermochemical WS cycle. The calculation of the related parameters was performed systematically using the thermodynamic empirical correlations mentioned in section 2.

The absorption efficiency of the solar reactor ($\eta_{abs-solar-reactor-WS}$) and solar heater ($\eta_{abs-solar-H_2O-heater-WS}$) is estimated using Eqs. (3) and (4), respectively. The re-oxidation temperature (T_L) is kept constant since entering superheated steam will further fluctuate the WS reactor temperature. If the WS reactor temperature is consistent, it is easier to control unilateral temperature fluctuations in the system. Thus, the WS reactor operates at a constant temperature (T_L) of 1050 K and 1200 K for $CeO_{1.83}$ and $CeO_{1.72}$, respectively and the value of concentration ratio (C) is considered as 4000 suns.

Since the WS reactor operates at a constant re-oxidation temperature (T_L), the absorption efficiency of the solar heater ($\eta_{abs-solar-H_2O-heater-WS}$) was stabilized at 98.3 % and 97.06 % for $CeO_{1.83}$ and $CeO_{1.72}$, respectively. The solar reactor operates at a varying range of reduction temperatures (T_H) and demonstrates the inverse effect on the absorption efficiency i.e. the $\eta_{abs-solar-reactor-WS}$ decreases with the increasing thermal reduction temperature (T_H).

The $\eta_{abs-solar-reactor-WS}$ decreases from 95.6 % to 37 %, as the T_H

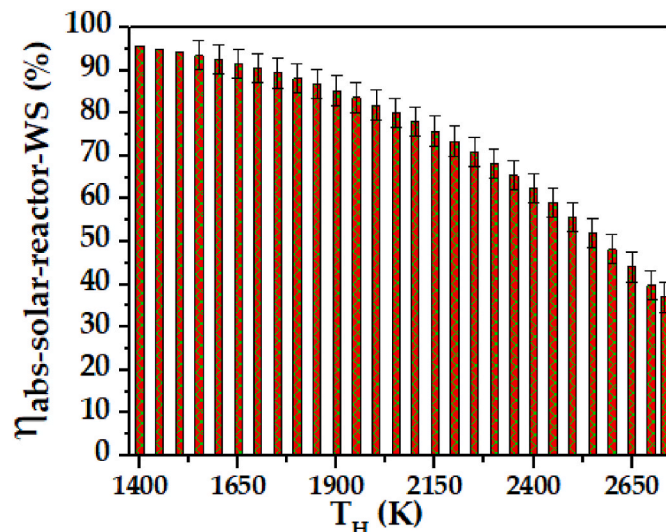


Fig. 6. The influence of T_H on the absorption efficiency of the solar reactor.

increases from 1400 K to 2734 K illustrated in Fig. 6. The statistical analysis of the absorption efficiency plot reveals that the drop in the $\eta_{abs-solar-reactor-WS}$ was 3.08 %, 4.47 %, 6.24 %, 8.42 %, 11.06 %, 14.20 % and 11.17 % for T_H increase from 1400 K to 1600 K, 1600–1800 K, 1800 K–2000 K, 2000 K–2200 K, 2200 K–2400 K, 2400 K–2600 K, and 2600 K–2734 K, respectively. The largest decline in absorption efficiency was reported from 2400 K to 2600 K T_H range.

The thermal reduction (TR) of CeO_2 is a directly proportional function of T_H which suggests that the increment in the thermal reduction temperature (T_H) results in the rapid reduction rate of CeO_2 . Similarly, the increase in T_H shows its effect on the required solar heat energy to reduce the CeO_2 and also to augment the temperature of steam from 298 K to T_L has been shown in Fig. 7. The observed trends indicate that elevating the thermal reduction temperature (T_H) results in an increase in the heat demand for partial reduction of CeO_2 ($Q_{CeO_2-partial-reduction-WS}$) and for the conversion of water (H_2O) into superheated steam ($Q_{H_2O-heating-WS}$).

As the reduction of CeO_2 proceeds from 0 to 100 % at two different re-oxidation temperatures 1050 K (for the formation of $CeO_{1.83}$) and 1200 K (for the formation of $CeO_{1.72}$), the solar heat energy essential for the partial reduction of CeO_2 ($Q_{CeO_2-partial-reduction-WS}$) increases from 108.19 kW to 2938.78 kW for $CeO_{1.72}$ and from 115.96 kW to 3055.12 kW for $CeO_{1.83}$. Apparently, for %TR of CeO_2 from 0 to 10.62 %, the $Q_{CeO_2-partial-reduction-WS}$ increases quite rapidly and goes from 108.19 kW to 780.6 kW for $CeO_{1.72}$ ($T_L = 1200$ K) and 115.96 kW–792.97 kW for $CeO_{1.83}$ ($T_L = 1050$ K). Subsequently, as the %TR of CeO_2 upturns from 10.62 % to 76.65 %, a slow rise in $Q_{CeO_2-partial-reduction-WS}$ from 780.6 kW to 2021.98 kW for $CeO_{1.72}$ and 792.97 kW–2103.18 kW for $CeO_{1.83}$ was seen on a linear curve. However, for the further %TR of CeO_2 from 76.65 % to 100 %, the rise in $Q_{CeO_2-partial-reduction-WS}$ for CeO_2 at $T_L = 1200$ K ($CeO_{1.72}$) and at $T_L = 1050$ K ($CeO_{1.83}$) was reported to be from 2021.98 kW to 2938.78 kW and 2103.18 kW–3055.13 kW, respectively. Statistically, the difference for input solar heat energy required for %TR of CeO_2 at the intervals of 0, 12.8 %, 36.44 %, 61.5 %, and 89.01 %–100 % was reported to be 7.78 kW, 20.96 kW, 33.2 kW, 48.85 kW, 84.48 kW and 116.34 kW for T_L of 1050 K ($CeO_{1.83}$) and 1200 K ($CeO_{1.72}$).

The heat required to drive the solar cycle ($Q_{cycle-net}$) is essentially a function of heat required to partially reduce the CeO_2

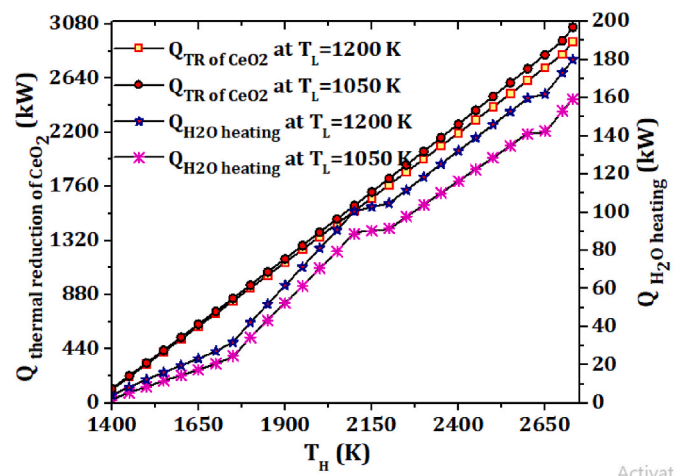


Fig. 7. Effect of %TR of CeO_2 on $Q_{partial\ reduction\ of\ CeO_2}$ and $Q_{H_2O\ heating}$ with increasing T_H .

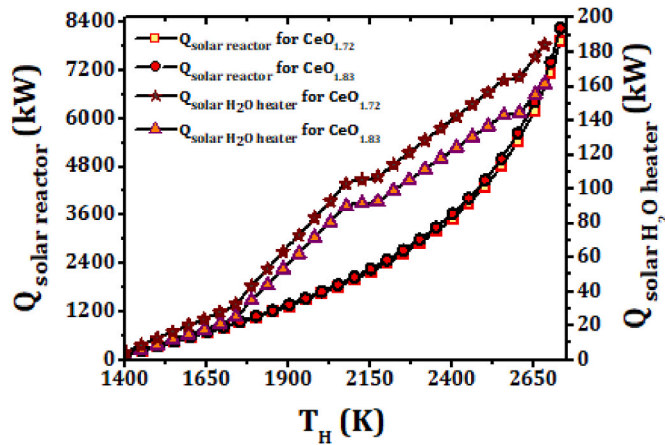


Fig. 8. Influence of T_H on $Q_{\text{solar reactor}}$ and $Q_{\text{solar steam generator}}$.

($Q_{\text{partial reduction of CeO}_2}$) and to heat the water ($Q_{\text{H}_2\text{O heating}}$) to convert it into steam to feed into the WS chamber to carry out the re-oxidation reaction and it can be mathematically expressed in Eq. (9). Therefore, it is interpreted that as the $Q_{\text{partial reduction of CeO}_2}$ and $Q_{\text{H}_2\text{O heating}}$ increased, the $Q_{\text{cycle-net}}$ also increased with the increasing T_H . Further, the analysis shows that as the T_H was amplified from 1400 K to 2750 K, the partial reduction of CeO_2 goes from 0 to 100 %. According to the reported data, the upswing in $Q_{\text{cycle-net}}$ for $\text{CeO}_{1.83}$ ($T_L = 1050$ K) and $\text{CeO}_{1.72}$ ($T_L = 1200$ K) resulted in the increase in the thermal reduction of CeO_2 from 0 to 100 % with the increment in T_H . As the reduction of CeO_2 increases from 0 to 7.74 %, the increase in $Q_{\text{cycle-net}}$ was reported to be from 112.41 kW to 645.76 kW for $\text{CeO}_{1.83}$ and from 117.74 kW to 656.06 kW for $\text{CeO}_{1.72}$. Furthermore, when the CeO_2 goes up from 7.74 % to 23.6 %, 43.08 %, 61.5 %, 75.22 %, 93.17 % and 100 %, the upsurge in $Q_{\text{cycle-net}}$ was reported as 1089.27 kW, 1431.74 kW, 1768.26 kW, 2100.46 kW, 2779.99 kW, and 3118.84 kW for $\text{CeO}_{1.83}$ and 1107.37 kW, 1457.95 kW, 1804.50 kW, 2148.64 kW, 2857.85 kW, and 3214.42 kW for $\text{CeO}_{1.72}$.

To estimate the necessary solar heat energy input for the solar reactor ($Q_{\text{solar reactor}}$) and solar steam generator ($Q_{\text{solar H}_2\text{O heater}}$) illustrated in Fig. 8, the mathematical expressions provided in Eqs. (5) and (6) were utilized, respectively.

The required solar heat energy input to the solar reactor ($Q_{\text{solar reactor}}$) and solar steam generator ($Q_{\text{solar H}_2\text{O heater}}$) presented in Fig. 8 was estimated using the mathematical expression given in Eqs. (5) and (6), respectively. It can be observed from Eq. (5) that the $Q_{\text{solar reactor}}$ is function of $Q_{\text{partial reduction of CeO}_2}$ and $\eta_{\text{abs-solar-reactor-WS}}$. As stated earlier, the upsurge in the T_H directly corresponds to the increase in %TR of CeO_2 which in turn increases the $Q_{\text{partial reduction of CeO}_2}$ but decreases the $\eta_{\text{abs-solar-reactor-WS}}$. Consequently, $Q_{\text{solar reactor}}$ being a function of %TR of CeO_2 increases with the increase of %TR of CeO_2 . In terms of values, it was reported that as %TR of CeO_2 upturns from 0 to 20 %, 40 %, 60 %, 80 %, 90 % and 100 %, the value of $Q_{\text{solar reactor}}$ upsurged from 121.25 kW to 1174.32 kW, 1642.10 kW, 2226.99 kW, 3455.78 kW, 4801.77 kW, 8254.60 kW for $\text{CeO}_{1.83}$ and from 113.12 kW to 1126.55 kW, 1576.70 kW, 2139.55 kW, 3322.07 kW, 4617.39 kW, 7940.25 kW for $\text{CeO}_{1.72}$, respectively.

Furthermore, the energy required to superheat the water (H_2O) by raising its temperature from 300 K to T_L and converting it into superheated steam in the H_2O heater is mathematically estimated by the expression given in Eq. (6). It was seen that the upsurge in $Q_{\text{solar H}_2\text{O heater}}$ was reported to be significantly less as compared to the $Q_{\text{solar reactor}}$. It is indicated in the expression that the $Q_{\text{solar H}_2\text{O heater}}$ is the function of $Q_{\text{H}_2\text{O-heating-WS}}$ and $\eta_{\text{abs-solar-H}_2\text{O-heater-WS}}$. It was seen from the results that the absorption efficiency of the solar water heater ($\eta_{\text{abs-solar-H}_2\text{O-heater-WS}}$) remains constant with the increasing %TR of

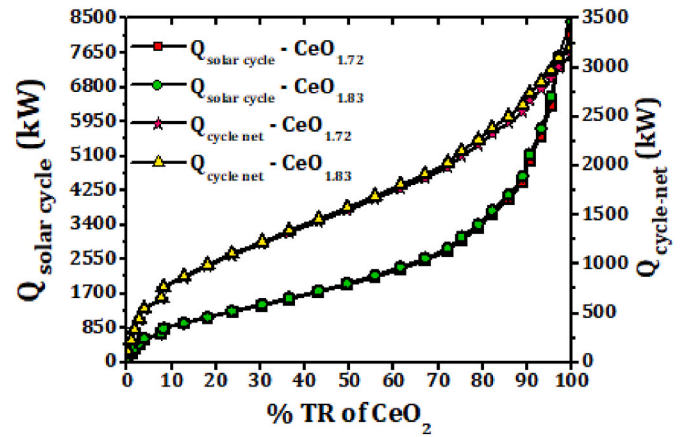


Fig. 9. Effect of %TR of CeO_2 on $Q_{\text{solar cycle}}$ and $Q_{\text{cycle net}}$.

CeO_2 . However, $Q_{\text{H}_2\text{O-heating-WS}}$ is also a function of %TR of CeO_2 and it is directly proportional to the %TR of CeO_2 which allows the $Q_{\text{H}_2\text{O-heating-WS}}$ to increase with the increasing %TR of CeO_2 . It was seen that the $Q_{\text{solar H}_2\text{O heater}}$ was increased by a factor of 12.94, 18.10, 24.77, 38.13, 50.86 and 89.65 for $\text{CeO}_{1.83}$ and 6.73, 9.05, 12.16, 18.37, 24.43 and 42.64 for $\text{CeO}_{1.72}$, as the %TR of CeO_2 upturns 20 %, 40 %, 60 %, 80 %, 90 % and 100 %, respectively.

The solar energy required in $Q_{\text{cycle-net-WS}}$ and $Q_{\text{solar-cycle-WS}}$ is mathematically expressed in Eqs. (9) and (10). According to Eq. (9), the addition of $Q_{\text{CeO}_2\text{-partial-reduction-WS}}$ and $Q_{\text{H}_2\text{O-heating-WS}}$ gives the $Q_{\text{cycle-net-WS}}$. Thus, the analysis of Fig. (9) reveals that as the %TR of CeO_2 upturns from 0 to 10 %, the $Q_{\text{cycle-net-WS}}$ goes up from 112.41 kW to 804.89 kW for $\text{CeO}_{1.72}$ and from 117.74 kW to 1095.18 kW for $\text{CeO}_{1.83}$. Further, as the %TR of CeO_2 increased to 20 %, 40 %, 60 %, 80 % and 100 %, the $Q_{\text{cycle-net-WS}}$ also upsurges to 1021.11 kW, 1388.50 kW, 1734.28 kW, 2253.32 kW, 2621.13 kW, and 3118.84 kW, respectively for $\text{CeO}_{1.72}$ and 1221.38 kW, 1446.74 kW, 1658.68 kW, 2011.23 kW, 2425.54 kW and 3214.43 kW, respectively for $\text{CeO}_{1.83}$. Moreover, the addition of $Q_{\text{solar-reactor-WS}}$ and $Q_{\text{solar-H}_2\text{O-heater-WS}}$ results in $Q_{\text{solar-cycle-WS}}$ as shown in Eq. (10). Therefore, the increase in $Q_{\text{solar-cycle-WS}}$ also has been plotted in Fig. 9 and it was seen that $Q_{\text{solar-cycle-WS}}$ upsurges with the increase in the %TR of CeO_2 . According to the reported data, the %TR of CeO_2 increases to 10 %, 20 %, 40 %, 60 %, 80 % and 100 % resulted in upsurge in $Q_{\text{solar-cycle-WS}}$ by the factor of 10.51, 11.92, 14.62, 17.44, 23.13, 32.15, and 69.18, respectively for $\text{CeO}_{1.72}$ and 10.20, 11.58, 14.22, 17.04, 22.61, 31.64, and 68.40,

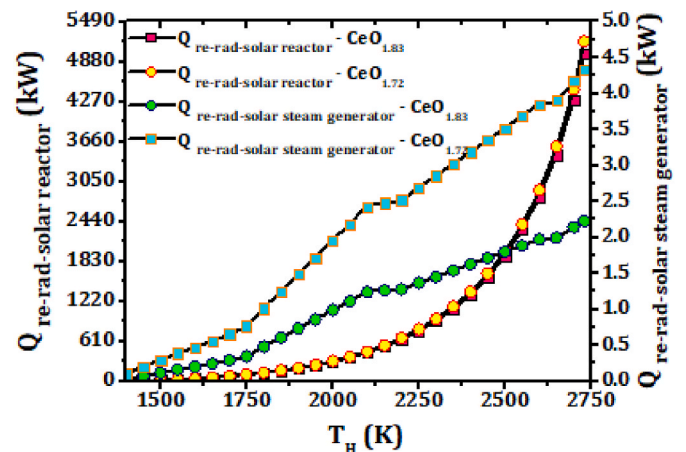


Fig. 10. Effect of T_H on the thermal losses from both solar reactor and H_2O heater.

respectively for $\text{CeO}_{1.83}$. It was observed that the absorption efficiency of the solar reactor ($\eta_{\text{abs-solar-reactor-WS}}$) decreases with increasing the oxidation temperature (T_L) and it is also a function of the %TR of CeO_2 which leads to $Q_{\text{solar-cycle-WS}}$ reach higher values as compared to $Q_{\text{cycle-net-WS}}$.

3.2. Estimation of re-radiation losses

Given the pre-established assumptions, the thermal losses in the form of conduction and convection from the solar heater and solar reactor had been chosen as negligible as compared to the re-radiation losses. The decreases in $\eta_{\text{abs-solar-reactor-WS}}$ with the increasing thermal reduction temperature (T_H) was the prime reason behind the re-radiation losses from the solar reactor as established in the expression given in Eq. (11). As the thermal reduction temperature (T_H) increased from 1400 K to 1600 K, 1800 K, 2000 K, 2200 K, 2400 K, 2600 K and 2730 K, the $Q_{\text{re-rad-solar-reactor-WS}}$ upsurged from 4.93 kW to 40.23 kW, 133.47 kW, 318.57 kW, 661.68 kW, 1344.29 kW, 2832.15 kW, 4290.85 kW and 5001.47 kW, respectively for $\text{CeO}_{1.83}$ and from 5.28 kW to 42.82 kW, 129.33 kW, 307.51 kW, 659.82 kW, 1367.47 kW, 2922.17 kW, 4465.2 kW and 5199.48 kW, respectively for $\text{CeO}_{1.72}$ as shown in Fig. 10.

The solar heater operates at the steady re-oxidation temperature (T_L) of 1050 K for $\text{CeO}_{1.83}$ and 1200 K for $\text{CeO}_{1.72}$ therefore, the $\eta_{\text{abs-solar-H}_2\text{O-heater-WS}}$ remained stabilized at 98.3 % and 97.06 % for $\text{CeO}_{1.83}$ and $\text{CeO}_{1.72}$, respectively. Consequently, re-radiative losses from the solar heater resulted from the temperature disparity between the re-oxidation temperature (T_L) and the ambient temperature. In numeric terms, with the upsurge in the thermal reduction temperature (T_H) to 1600 K, 1800 K, 2000 K, 2200 K, 2400 K, 2600 K, 2700 K and 2730 K, the $Q_{\text{re-rad-solar-H}_2\text{O-heater-WS}}$ increased to 0.20 kW, 0.48 kW, 0.98 kW, 1.28 kW, 1.62 kW, 1.97 kW, 2.14 kW and 2.23 kW, respectively for $\text{CeO}_{1.83}$ and 0.47 kW, 1.02 kW, 1.96 kW, 2.52 kW, 3.18 kW, 3.85 kW, 4.17 kW and 4.34 kW, respectively for $\text{CeO}_{1.72}$ as shown in Fig. 10.

The thermal losses resulting from the solar cycle were computed using the mathematical expression provided in Eq. (13). It was established from the expression that the re-radiative losses from the solar cycle ($Q_{\text{re-rad-cycle-WS}}$) are the combination of $Q_{\text{re-rad-solar-reactor-WS}}$ and $Q_{\text{re-rad-solar-H}_2\text{O-heater-WS}}$. The re-radiative losses from the solar cycle ($Q_{\text{re-rad-cycle-WS}}$) as a function of the %TR of CeO_2 for both $\text{CeO}_{1.72}$ and $\text{CeO}_{1.83}$ are reported in Fig. 11.

It was observed as the %TR of CeO_2 increased, the re-radiative losses from the solar cycle ($Q_{\text{re-rad-cycle-WS}}$) for both $\text{CeO}_{1.72}$ and $\text{CeO}_{1.83}$ also increased. According to the data reported in Fig. 11, the rise in

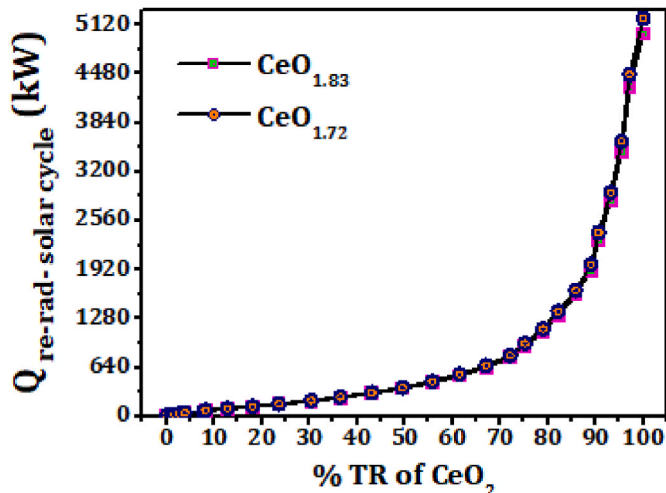


Fig. 11. Effect of %TR of CeO_2 on re-radiative losses from the solar cycle.

($Q_{\text{re-rad-cycle-WS}}$) was significantly low and occurred linearly for %TR of CeO_2 till 80 %. However, after the 80 % reduction of CeO_2 , the re-radiative losses increased exponentially. In numeric terms, as the %TR of CeO_2 goes up from 0 to 20 %, 40 %, 60 % and 80 %, the rise in $Q_{\text{re-rad-cycle-WS}}$ occurs from 4.95 kW to 146.99 kW, 298.51 kW, 540.64 kW, and 1188.25 kW, respectively for $\text{CeO}_{1.83}$ and 5.38 kW, 153.19 kW, 301.50 kW, 562.72 kW, 1236.18 kW, for $\text{CeO}_{1.72}$. Conversely, as the reduction of CeO_2 goes to 92 %, 95 %, 98 % and 100 %, the upturn in $Q_{\text{re-rad-cycle-WS}}$ was reported to be 2592.05 kW, 3347.91 kW, 455.76 kW, and 5003.72 kW, respectively for $\text{CeO}_{1.83}$ and 2694.94 kW, 3481.98 kW, 4717.21 kW and 5203.81 kW, respectively for $\text{CeO}_{1.72}$.

3.3. Performance assessment of coolers and WS reactor

Heat recuperation is the technique applied to reuse the dissipated heat in the solar thermochemical cycle and coolers and WS reactors are the equipment that was used for heat energy recuperation. The recuperated heat energy from cooler A, cooler B, cooler C, and WS reactor was estimated using the expression given in Eqs. (16)–(19), respectively.

Cooler A was installed to control the temperature swing of entities coming from the solar reactor (CeO_2 , $\text{CeO}_{1.72/1.83}$, and O_2) from T_H to T_L . According to the previously established relation, the %TR of CeO_2 directly correlates with the thermal reduction temperature (T_H) i.e. higher the T_H , the faster the %TR of CeO_2 . Therefore, as the T_H increases from 1400 K to 2730 K but the T_L remains constant at 1050 K ($\text{CeO}_{1.83}$) and 1200 K ($\text{CeO}_{1.72}$), the difference between T_H and T_L also increases. As a result, a wider temperature differential between T_H and T_L leads to increased heat dissipation by cooler-A, as illustrated in Fig. (12).

The findings presented in Fig. (12) suggest that heat energy dissipated from cooler-A ($Q_{\text{Cooler-A}}$) rises from 83.51 kW to 110.83 kW, 345.63 kW, 500.57 kW, 929.14 kW, 1262.78 kW, 1646.62 kW, and 1908.71 kW for $\text{CeO}_{1.83}$ and 72.25 kW–73.69 kW, 282.27 kW, 410.96 kW, 813.34 kW, 1120.72 kW, 1478.40 kW and 1720.82 kW for $\text{CeO}_{1.72}$, with the T_H increase from 1400 K to 1600 K, 1800 K, 2000 K, 2200 K, 2400 K, 2600 K and 2734 K, respectively.

Correspondingly, the heat energy dissipated from the cooler B ($Q_{\text{Cooler-B}}$) and the cooler-C ($Q_{\text{Cooler-C}}$) also increases with the increase in T_H . The reasons for the increase in heat dissipation were exposed to the production of a high amount of O_2 and H_2 during thermal decomposition and the H_2O dissociation step of the thermochemical cycle. Statistically, for the thermal reduction temperature (T_H) rise from 1400 K to 1800 K, 2200 K, 2600 K, and 2734 K, the $Q_{\text{Cooler-B}}$ upturns from 0.22 kW to 3.99 kW, 14.97 kW, 27.89 kW, and 32.44 kW, respectively for $\text{CeO}_{1.83}$ and 0.11 kW, 3.04 kW, 13.17 kW, 25.24 kW, and 29.46 kW, respectively for $\text{CeO}_{1.72}$. While the $Q_{\text{Cooler-C}}$ rises from 0.47 kW, 7.79 kW, 22.53 kW, 39.19 kW, and 45.15 kW, respectively for $\text{CeO}_{1.83}$ and

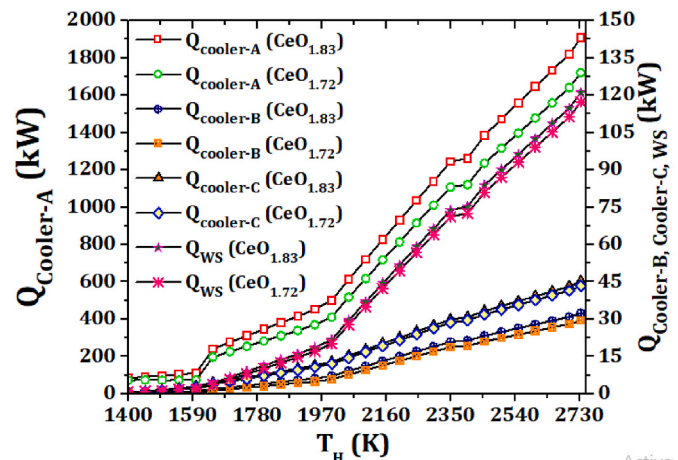


Fig. 12. Effect of T_H on $Q_{\text{Cooler-A}}$, $Q_{\text{Cooler-B}}$, $Q_{\text{Cooler-C}}$ and $Q_{\text{H}_2\text{O}}$ splitting WS.

0.28 kW, 7.22 kW, 21.46 kW, 37.64 kW, and 43.41 kW, respectively for $\text{CeO}_{1.72}$.

Furthermore, the re-oxidation is an exothermic reaction therefore, the WS reactor also emits a significant amount of heat energy. The heat energy released from the WS reactor depends on thermal reduction temperature. Increasing temperature favors the reduction process and leads to excess heat release. Proper control of thermal reduction temperature is crucial for optimal reactor performance, as excessive heat can cause material degradation and thermal stress.

The increase of T_H upturns the %TR of CeO_2 which is directly associated with the improved generation of O_2 during the TR step and H_2 generation during the WS step. Statistically, the $Q_{\text{H}_2\text{O-splitting-reactor-WS}}$ rises from 0.75 kW to 11.28 kW, 51.64 kW, 102.45 and 121.05 kW for $\text{CeO}_{1.83}$ and 0.84 kW–10.17 kW, 49.42 kW, 99.13 kW and 117.32 kW for $\text{CeO}_{1.72}$, for the T_H increase from 1400 K to 1800 K, 2200 K, 2600 K, and 2734 K, respectively.

3.4. Estimation of solar-to-fuel conversion efficiency

The $\eta_{\text{solar-to-fuel}}$ analysis was the most crucial and final step of the study. First, all the essential parameters required in the efficiency analysis were calculated systematically and then the $\eta_{\text{solar-to-fuel}}$ was estimated. According to Eq. (14), the $\eta_{\text{solar-to-fuel}}$ directly depends upon the HHV of H_2 produced and it inversely relates to the solar energy required to drive the solar thermochemical cycle ($Q_{\text{solar-cycle-WS}}$).

The variations in the $\eta_{\text{solar-to-fuel}}$ associated with the increase in %TR of CeO_2 for both $\text{CeO}_{1.72}$ and $\text{CeO}_{1.83}$ have been shown in Fig. 13. According to the reported data, the $\eta_{\text{solar-to-fuel}}$ rises quite rapidly from 0 to 2.41 % ($\text{CeO}_{1.83}$) and 2.32 % ($\text{CeO}_{1.72}$) for the %TR of CeO_2 from 0 to 5 %. Further, as the %TR of CeO_2 increased to 10 %, 20 %, 30 %, 40 %, 50 %, 60 %, the $\eta_{\text{solar-to-fuel}}$ gradually upturned to 3.53 %, 5.00 %, 6.19 %, 6.99 %, 7.48 %, 7.67 %, respectively and the maximum $\eta_{\text{solar-to-fuel}}$ of 7.69 % was attained at the %TR of CeO_2 of 61.72 % for $\text{CeO}_{1.83}$. Similarly, for the $\text{CeO}_{1.72}$, the $\eta_{\text{solar-to-fuel}}$ rises to 3.43 %, 4.85 %, 5.99 %, 6.77 %, 7.24 %, 7.42 %, respectively and it attains the maximum value of $\eta_{\text{solar-to-fuel}}$ of 7.45 % at the %TR of CeO_2 of 61.72 %. It was observed from the reported data that once the cycle reached its maximum efficiency, it preceded to decline with the increase in %TR of CeO_2 . At the %TR of CeO_2 of 70 %, 80 %, 90 %, 94 %, 97 % and 100 %, the $\eta_{\text{solar-to-fuel}}$ gradually decreased to the value of 7.57 %, 6.64 %, 5.30 %, 4.43 %, 3.85 % and 3.53 %, respectively for $\text{CeO}_{1.83}$ and 7.31 %, 6.41 %, 5.10 %, 4.26 %, 3.70 % and 3.38 %, respectively for $\text{CeO}_{1.72}$.

It has been stated that the $\eta_{\text{solar-to-fuel}}$ can be improved with the

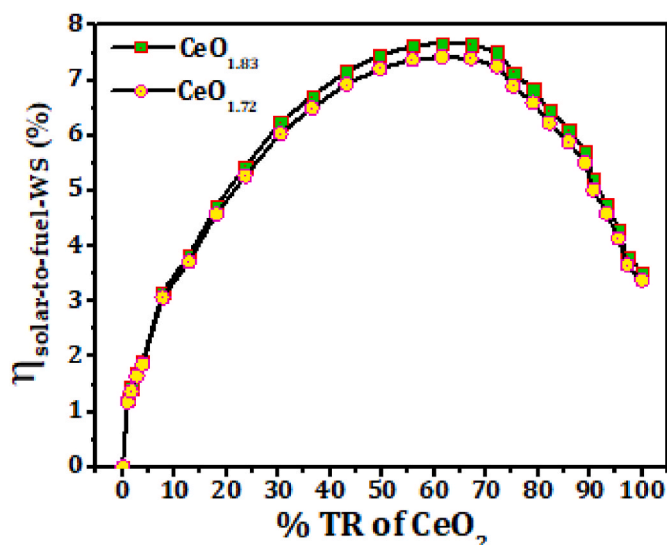


Fig. 13. Effect of %TR of CeO_2 on $\eta_{\text{solar-to-fuel}}$.

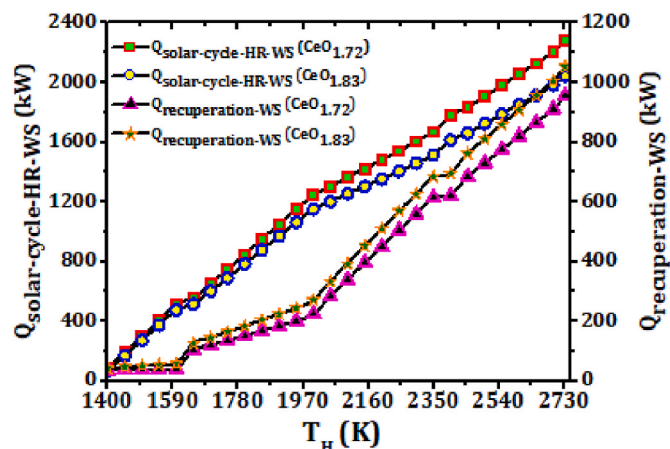


Fig. 14. Effect of thermal reduction temperature (T_H) on $Q_{\text{solar-cycle-HR-WS}}$ and $Q_{\text{recuperation-WS}}$.

utilization of the heat recovery technique where the heat released from the cooler-A, cooler-B, and WS reactor is re-used in the solar thermochemical cycle. The heat recuperation solar-to-fuel energy conversion efficiency ($\eta_{\text{solar-to-fuel-HR}}$) can only be estimated after the calculation of the $Q_{\text{recuperation-WS}}$ using the expression given in Eq. (15).

According to the obtained data, the $Q_{\text{recuperation-WS}}$ increased with the increased thermal reduction temperature (T_H). Statistically, as the T_H increased to 1600 K, 1800 K, 2000 K, 2200 K, 2400 K, 2600 K and 2734 K, the $Q_{\text{recuperation-WS}}$ increased to 39.42 kW, 151.35 kW, 224.39 kW, 448.70 kW, 621.00 kW, 820.20 kW, and 955.51 kW, respectively for $\text{CeO}_{1.72}$ and 58.71 kW, 184.35 kW, 271.12 kW, 509.14 kW, 695.15 kW, 908.09 kW and 1053.68 kW, respectively for $\text{CeO}_{1.83}$ as shown in Fig. 14.

After the estimation of $Q_{\text{recuperation-WS}}$, the calculation of $Q_{\text{solar-cycle-HR-WS}}$ was required which was done using Eq. (20). It was observed that the $Q_{\text{solar-cycle-HR-WS}}$ is a function of %HR and the T_H . Further, it was seen that the $Q_{\text{solar-cycle-HR-WS}}$ dropped to a significant value as compared to the $Q_{\text{solar-cycle-WS}}$. The reported data suggest that as the T_H increased to 1600 K, 1800 K, 2000 K, 2200 K, 2400 K, 2600 K, and 2734 K, the $Q_{\text{solar-cycle-HR-WS}}$ increased to 513.50 kW, 847.90 kW, 1244.13 kW, 1480.08 kW, 1778.44 kW, 2056.36 kW, and 2279.67 kW, respectively for $\text{CeO}_{1.72}$ and 475.05 kW, 783.34 kW, 1150.05 kW, 1353.12 kW, 1615.15 kW, 1853.18 kW, and 2044.41 kW, respectively

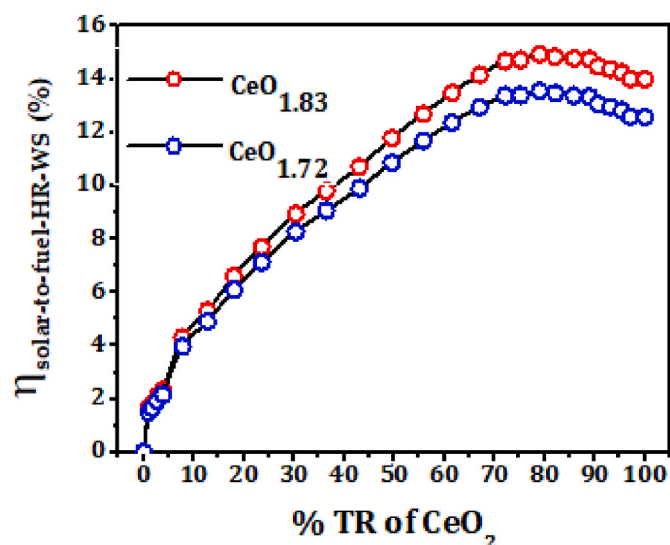


Fig. 15. Effect of %TR of CeO_2 on $\eta_{\text{solar-to-fuel-HR}}$.

for $\text{CeO}_{1.83}$.

The reduction in the $Q_{\text{solar-cycle-HR-WS}}$ improved the $\eta_{\text{solar-to-fuel-HR}}$ as shown in Fig. 15 by the employment of 50 % heat recovery. The reported data suggest that the increase in %TR of CeO_2 to 5 %, 10 %, 20 %, 40 %, 60 %, 70 %, 80 %, 90 % and 100 %, the upsurge in the $\eta_{\text{solar-to-fuel-HR}}$ to 2.88 %, 4.89 %, 6.91 %, 10.29 %, 13.34 %, 14.49 %, 14.92 %, 14.58 % and 13.99 %, respectively for $\text{CeO}_{1.83}$ and 2.73 %, 4.54 %, 6.42 %, 9.53 %, 12.25 %, 12.24 %, 13.54 %, 12.16 % and 12.55 %, respectively for $\text{CeO}_{1.72}$. Therefore, it was seen that the maximum efficiency with the 50 % heat recovery was 14.92 % and 13.54 % for $\text{CeO}_{1.83}$ and $\text{CeO}_{1.72}$, respectively at the %TR of CeO_2 of 80 %.

Even though the thermodynamic analysis of $\text{STC}_{|\text{CeO}_2-\text{CeO}_{1.72/1.83}}$ provide incredible solar-to-fuel conversion efficiency yield, experimentally continues operation (due to constant replacement of burnt metal oxides) of the $\text{STC}_{|\text{CeO}_2-\text{CeO}_{1.72/1.83}}$ is still a great challenge which needs to be resolved. The challenge can be resolved by lowering the thermal reduction and re-oxidation temperatures.

4. Summary and conclusion

This study thermodynamically investigated the conversion of H_2O into H_2 via solar thermochemical WS cycle and analyzed the effect of two different non-stoichiometric configurations $\text{CeO}_{1.72}$ and $\text{CeO}_{1.83}$. The chemical equilibrium analysis suggested that the %TR of CeO_2 increased from 0 to 8.2 %, 55.8 %, 82.2 %, 93.3 %, and 100 % with the increase in the T_{H} from 1400 K to 1700 K, 2100 K, 2400 K, 2600 K, and 2734 K, respectively. Further, it was seen that the $Q_{\text{partial reduction of CeO}_2}$, $Q_{\text{H}_2\text{O-heating-WS}}$, $Q_{\text{solar-H}_2\text{O-heater-WS}}$ and $Q_{\text{solar-reactor-WS}}$ was upturned up to 2834.48 kW ($\text{CeO}_{1.83}$) & 2944.03 kW ($\text{CeO}_{1.72}$), 153.12 kW ($\text{CeO}_{1.83}$) & 173.21 kW ($\text{CeO}_{1.72}$), 155.27 kW ($\text{CeO}_{1.83}$) & 177.38 kW ($\text{CeO}_{1.72}$) and 7133.54 kW ($\text{CeO}_{1.83}$) & 7409.23 kW ($\text{CeO}_{1.72}$), respectively when the thermal reduction temperature (T_{H}) increased to 2700 K. Furthermore, The increase in $Q_{\text{solar-reactor-WS}}$ and $Q_{\text{solar-H}_2\text{O-heater-WS}}$ caused an increase in $Q_{\text{solar-cycle-WS}}$ and $Q_{\text{re-rad-solar-cycle-WS}}$ from 7310.92 kW ($\text{CeO}_{1.72}$) & 7564.50 kW ($\text{CeO}_{1.83}$) and 4301.20 kW & 4469.37 kW with the increase in T_{H} up to 2700 K. Therefore, the solar-to-fuel conversion efficiency ($\eta_{\text{solar-to-fuel}}$) reached the maximum value of 7.45 % ($\text{CeO}_{1.72}$) and 7.69 % ($\text{CeO}_{1.83}$) at the %TR of CeO_2 of 61.72 % without heat recuperation and it attained the maximum value of 14.92 % and 13.54 % for $\text{CeO}_{1.83}$ and $\text{CeO}_{1.72}$, respectively at the %TR of CeO_2 of 80 % with the 50 % heat recuperation.

This thermodynamic analysis established the optimum thermal reduction and re-oxidation temperatures to achieve high solar-to-fuel conversion efficiency. This analysis will crucial to design the lab scale experimental Cerium oxide WS hydrogen production system.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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