Research Article

Solar Thermochemical Hydrogen Production via Terbium Oxide Based Redox Reactions

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The computational thermodynamic modeling of the terbium oxide based two-step solar thermochemical water splitting (Tb-WS) cycle is reported. The 1st step of the Tb-WS cycle involves thermal reduction of TbO₂ into Tb and O₂, whereas the 2nd step corresponds to the production of H₂ through Tb oxidation by water splitting reaction. Equilibrium compositions associated with the thermal reduction and water splitting steps were determined via HSC simulations. Influence of oxygen partial pressure in the inert gas on thermal reduction of TbO₂ and effect of water splitting temperature (T₁₂) on Gibbs free energy related to the H₂ production step were examined in detail. The cycle (η_cycle) and solar-to-fuel energy conversion (η_solar-to-fuel) efficiency of the Tb-WS cycle were determined by performing the second-law thermodynamic analysis. Results obtained indicate that η_cycle and η_solar-to-fuel increase with the decrease in oxygen partial pressure in the inert flushing gas and thermal reduction temperature (T₁₁). It was also realized that the recuperation of the heat released by the water splitting reactor and quench unit further enhances the solar reactor efficiency. At T₁₁ = 2280 K, by applying 60% heat recuperation, maximum η_cycle of 39.0% and η_solar-to-fuel of 47.1% for the Tb-WS cycle can be attained.

1. Introduction

H₂ is considered as one of the most promising future energy sources as it is characterized by a very high energy density (143 MJ/kg) and environmentally clean utilization. H₂ can be produced by gasification and reforming of fossil fuels [1–3], pyrolysis and reforming of biomass [4–7], ethanol and methanol decomposition [8–11], and so forth. Literature survey indicates that, in recent years, the researchers are attracted more towards production of H₂ from water by using solar energy as the heat source.

Solar radiation is an essentially inexhaustible energy source that delivers about 100,000 TW to the earth. Harvesting the solar radiation and converting it effectively into renewable H₂ fuel from H₂O provide a promising path for a future sustainable energy economy. Solar H₂ production via metal oxide (MO) based thermochemical H₂O splitting reaction is considered as one of the capable new technologies for fulfillment of future energy requirement. In comparison to the high temperature direct thermolysis of H₂O, the MO based thermochemical cycle is advantageous as (a) this cycle needs lower temperatures as compared to thermolysis, (b) it has no explosive mixture formation as the production of H₂ and O₂ can be carried out in two different steps, and (c) it is environmentally and thermodynamically more feasible compared to thermolysis.

Production of solar H₂ via MO based thermochemical reactions is a two-step process. In the first step, the MO is reduced into a lower valence MO or metal with the help of solar energy. The reduced MO is further reoxidized in the second step via H₂O splitting reaction. Several MO based redox systems were theoretically and experimentally studied towards thermochemical water splitting reaction which includes ZnO/Zn cycle [12–15], Fe₂O₃/FeO cycle [16–20], SnO₂/SnO cycle [21–23], ferrite cycle [24–30], ceria cycle [31–36], and perovskite cycle [37–41]. Previous investigations indicate that these cycles are promising towards solar water splitting reaction but possess certain limitations also. The ZnO/Zn and SnO₂/SnO cycles are volatile in nature and hence material loss during multiple cycles is inevitable. On the other hand, Fe₂O₃/FeO, ferrite, ceria, and perovskite cycles depend upon the nonstoichiometry of the redox...
materials and hence the complete reduction and oxidation were not observed which resulted in the fact that smaller amounts of H₂ production were observed. Due to these reasons, investigations are underway to explore new thermochemical cycles for the production of H₂ via water splitting reaction.

In this study, computational thermodynamic modeling of a new terbium oxide based two-step solar thermochemical water splitting (Tb-WS) cycle was performed to determine its thermodynamic efficiency by using HSC Chemistry software and databases (HSC 7.1). Thermodynamic equilibrium composition of the solar thermal reduction of terbium oxide (step 1) and water splitting reaction (step 2) were determined. Effect of oxygen partial pressure in the inert flushing gas used inside the solar reactor during thermal reduction step on thermodynamic efficiency of the process was explored in detail. Furthermore, the effect of water splitting temperature (\(T_H\)) on Gibbs free energy associated with the oxidation of Tb (via water splitting reaction) was also explored. In addition to the thermodynamic equilibrium analysis, the solar reactor thermodynamic modeling was also carried out. Absorption efficiency of the solar reactor, solar energy input required to run the Tb-WS cycle, heat losses due to radiation, rate of heat rejected by the quench unit and water splitting reactor, Tb-WS cycle efficiency, and solar-to-fuel energy conversion efficiency were estimated. Typical redox reactions involved in the Tb-WS cycle are presented in Figure 1.

The redox reactions involved in the Tb-WS cycle are as follows:

\[
\text{TbO}_2 \rightarrow \text{Tb(g) + O}_2(g) \quad (1) \\
\text{Tb} + 2\text{H}_2\text{O(g)} \rightarrow \text{TbO}_2 + 2\text{H}_2 \quad (2)
\]

Thermodynamic data associated with \(\text{TbO}_2\), \(\text{Tb, O}_2\), \(\text{H}_2\text{O}\), and \(\text{H}_2\) as the reactive species were taken from HSC and the analysis was performed by assuming continuous operation of the solar reactor with inlet molar flow rate of \(\text{TbO}_2\) equal to 1 mol/sec. The boiling and fusion points for Tb are 1629 and 3396 K, respectively. Similar to other lanthanides, Tb possesses low toxicity. According to Patnaik [42], the crust global abundance of Tb is estimated to be 1.2 mg/kg.

2. Equilibrium Thermodynamic Analysis

Previous investigations associated with the production of solar fuels via MO based thermochemical reactions indicate that the heat energy that is thermal reduction temperature (\(T_H\)) required to achieve complete reduction of MOs can be decreased if ultra-high purity inert flushing gas with lower oxygen partial pressures in the range of \(10^{-5}\) to \(10^{-8}\) atm is used during the reduction step inside the solar reactor [43, 44]. The effect of oxygen partial pressure in the inert flushing gas on thermal reduction of \(\text{TbO}_2\) was examined in this study and the results are reported in Figure 2. The reported findings indicate that, similar to the previous MO cycles, \(T_H\) required for the thermal reduction of \(\text{TbO}_2\) can be lowered due to the drop in the oxygen partial pressure in the inert flushing gas. For example, at oxygen partial pressure of \(10^{-5}\) atm, \(T_H\) required for the complete dissociation of \(\text{TbO}_2\) is equal to 2780 K. \(T_H\) can be decreased by 80, 260, and 500 K if the oxygen partial pressure in the inert flushing gas is reduced to \(10^{-6}\), \(10^{-7}\), and \(10^{-8}\) atm, respectively.

In addition to \(T_H\), the effect of oxygen partial pressure in the inert flushing gas on equilibrium compositions associated with the thermal reduction of \(\text{TbO}_2\) was also investigated. HSC simulations reported in Figure 3 indicate that the slope of the decrease in the equilibrium concentration of \(\text{TbO}_2\) and increase in the equilibrium concentration of \(\text{Tb(g)}\) is shifted significantly towards the lower \(T_H\) due to the decrease in the oxygen partial pressure in the inert flushing gas. The possible reason behind this shift is the reduction in the entropy of the product gases due to the drop in the oxygen partial pressure in the inert flushing gas used inside the solar reactor.

As per the HSC simulations, formation of \(\text{Tb}_2\text{O}_3\) is an intermediate step in the thermal reduction of \(\text{TbO}_2\) into \(\text{Tb(g)}\) and \(\text{O}_2(g)\). In addition, it was observed that the Tb formation is achieved only after decomposition of \(\text{Tb}_2\text{O}_3\). Hence, as we are dealing with the final products, there is no need to consider \(\text{Tb}_2\text{O}_3\) in the thermodynamic analysis. Therefore, \(\text{Tb}_2\text{O}_3\) is not included in this study.
Figure 3: Influence of oxygen partial pressure in the inert flushing gas on equilibrium compositions associated with the thermal reduction of TbO\(_2\).

Figure 4: Variation in Gibbs free energy as a function of \(T_L\) for Tb-WS cycle.

Figure 5: Process flow diagram for H\(_2\) production via Tb-WS cycle.

(a) The Tb-WS solar reactor considered as a perfectly insulated blackbody absorber with effective emissivity and absorptivity equal to 1 and negligible conductive convective heat losses.

(b) Atmospheric H\(_2\) production and steady state conditions with negligible viscous losses and kinetics/potential energies.

(c) Complete conversion of all the reactions associated with the Tb-WS cycle.

(d) Products separating naturally without laying out any work.

(e) Omission of heat exchanger required for recovering the sensible latent heat from the thermodynamic modeling.

Previously reported methodology was employed to perform the solar reactor modeling [20]. HSC Chemistry software and databases were used to get the thermodynamic properties of the reactive species and the calculations are normalized to the TbO\(_2\) molar flow rate (1 mol/sec) entering the solar reactor.

The solar reactor absorption efficiency (\(\eta_{\text{absorption}}\)), which is defined as the net rate at which energy is being absorbed by the solar reactor divided by the solar energy input through the aperture, can be calculated as per

\[
\eta_{\text{absorption}} = 1 - \left( \frac{\sigma T_H^4}{I C} \right),
\]

where \(I\) is direct-normal solar irradiance (normal beam insolation) (W/m\(^2\)), \(C\) is solar flux concentration ratio (ratio of the solar flux intensity achieved after concentration to the normal beam insolation, dimensionless number) (suns), \(T_H\) is solar reactor temperature required for the thermal reduction of TbO\(_2\) (K), and \(\sigma\) is Stefan-Boltzmann constant which is equal to 5.6705 × 10\(^{-8}\) (W/m\(^2\)·K\(^4\)).

Figure 6 indicates a significant improvement in \(\eta_{\text{absorption}}\) due to the reduction in \(T_H\) and oxygen partial pressure in the inert flushing gas used inside the solar reactor decreases.
oxygen partial pressure in the inert flushing gas of $10^{-5}$ atm, the required $T_H$ is 2780 K and corresponding $\eta_{absorption}$ is 66.1%. As the oxygen partial pressure in the inert flushing gas is further lowered to $10^{-7}$ atm, $T_H$ can be decreased to 2520 K and $\eta_{absorption}$ can be increased up to 77.1%. As per the conditions employed in this study, the maximum $\eta_{absorption}$ that can be achieved is equal to 84.7% (oxygen partial pressure in the inert flushing gas is $10^{-8}$ atm and $T_H$ is 2280 K).

In addition to the oxygen partial pressure in the inert flushing gas and $T_H$, $C$ also has a significant impact on $\eta_{absorption}$. At oxygen partial pressure of $10^{-8}$ atm and $T_H$ of 2280 K, the lower values of $C$ (2000 suns) yield $\eta_{absorption}$ of 23.4%. As the value of $C$ increases up to 3000 to 5000 suns, $\eta_{absorption}$ can get enhanced up to 48.9% and 69.3%, respectively.

The net energy required to operate the Tb-WS solar reactor can be determined according to the following equations:

\[ Q_{\text{reactor-net}} = Q_{\text{TbO}_2-\text{heating}} + Q_{\text{TbO}_2-\text{reduction}} \tag{4} \]

\[ Q_{\text{TbO}_2-\text{heating}} = \dot{n} \Delta H \mid _{\text{TbO}_2(g) \rightarrow \text{TbO}_2(s) + \text{O}_2(g)} \tag{5} \]

\[ Q_{\text{TbO}_2-\text{reduction}} = \dot{n} \Delta H \mid _{\text{TbO}_2(s) \rightarrow T_L \rightarrow \text{Tb} + \text{O}_2(g)} \tag{6} \]

The variation in $Q_{\text{reactor-net}}$ with respect to the change in $T_H$ is presented in Figure 7. Presented results indicate that the required $Q_{\text{reactor-net}}$ decreases with the drop in $T_H$ and oxygen partial pressure in the inert flushing gas. As $T_H$ is reduced from 2780 K (oxygen partial pressure in the inert flushing gas of $10^{-8}$ atm) to 2280 K (oxygen partial pressure in the inert flushing gas of $10^{-9}$ atm), $Q_{\text{reactor-net}}$ is also lowered from 1543.0 kW to 1499.2 kW, respectively.

By using the calculated $\eta_{absorption}$ and $Q_{\text{reactor-net}}$, total amount of solar energy required for the operation of the Tb-WS cycle can be estimated as

\[ Q_{\text{solar}} = \frac{Q_{\text{reactor-net}}}{\eta_{absorption}} \tag{7} \]

The decrease in $Q_{\text{solar}}$ as a function of reduction in $T_H$ and oxygen partial pressure in the inert flushing gas is shown in Figure 7. 2333.2 kW of solar energy is required for the operation of Tb-WS cycle when the oxygen partial pressure in the inert flushing gas is equal to $10^{-5}$ atm ($T_H = 2780$ K). $Q_{\text{solar}}$ is reduced to 1970.3 kW as the oxygen partial pressure in the inert flushing gas is lowered to $10^{-7}$ atm ($T_H = 2280$ K). As per the modeling conditions employed in this study, the minimum $Q_{\text{solar}}$ (1770.5 kW) is possible at oxygen partial pressure in the inert flushing gas of $10^{-8}$ atm ($T_H = 2280$ K). The reason behind this drop in $Q_{\text{solar}}$ is the elevation in $\eta_{absorption}$ due to the fall in $T_H$ from 2780 to 2280 K as the oxygen partial pressure in the inert flushing gas is reduced from $10^{-5}$ to $10^{-8}$ atm.

Radiation heat losses from the Tb-WS solar reactor are unavoidable as the operating temperatures are very high. These losses can be calculated as

\[ Q_{\text{radiation}} = Q_{\text{solar}} - Q_{\text{reactor-net}} \tag{8} \]

The radiation heat losses associated with the Tb-WS cycle are presented in Figure 8(a). The plot shown indicates that, at $T_H = 2780$ K, 790.2 kW of heat is lost from the solar reactor due to the reradiation. However, the radiation losses are decreased due to the lowering of $T_H$. For instance, at $T_H = 2280$ K, only 271.3 kW of reradiation losses is reported as per the thermodynamic modeling. This is again due to the fact that $\eta_{absorption}$ of the Tb-WS solar reactor is higher at lower $T_H$.

Solar thermal reduction of $\text{TbO}_2$ yields $\text{Tb}(g)$ and $\text{O}_2(g)$. As the operating temperatures are very high, these compounds will try to recombine and reform the $\text{TbO}_2$. Therefore, it is highly essential to quench these compounds from $T_H$ to $T_L$ to avoid any recombination. During quenching, it is assumed that the chemical composition of the products remains unaltered. Due to quenching $\text{Tb}(g)$ is cooled down to solid Tb and automatically gets separated from $\text{O}_2(g)$. Also, during quenching, latent and sensible heat will be lost to the surroundings from the quench unit which can be estimated as

\[ Q_{\text{quench}} = -\dot{n} \Delta H \mid _{\text{Tb}(g) + \text{O}_2(g) \rightarrow \text{Tb}(s) + \text{O}_2(g)} \tag{9} \]

The data reported in Figure 8(b) indicates that higher amount of heat is lost due to quenching (571.4 kW) when $T_H$ is 2780 K (oxygen partial pressure in the inert flushing gas is $10^{-7}$ atm).
However, as $T_H$ is decreased to 2280 K due to the lowering of oxygen partial pressure in the inert flushing gas ($10^{-8}$ atm), the heat lost is reduced by 43.8 kW.

Because of the irreversible chemical transformations and reradiation losses, the irreversibilities generated in the solar reactor and the quench unit can be determined as

\[
\text{Irr}_{\text{reactor}} = \left(\frac{-Q_{\text{solar}}}{T_H}\right) + \left(\frac{Q_{\text{reradiation}}}{298}\right) + \dot{n}\Delta S_{\text{TbO}_2 \rightarrow \text{Tb}(g)+O_2(g)@T_H}
\]

\[
\text{Irr}_{\text{quench}} = \left(\frac{Q_{\text{quench}}}{298}\right) + \dot{n}\Delta S_{\text{Tb}(g)+O_2(g)@T_H \rightarrow \text{Tb}(s)+O_2(g)@T_L}
\]

Table 1 lists the $\text{Irr}_{\text{reactor}}$ and $\text{Irr}_{\text{quench}}$ values as a function of $T_H$. From the reported numbers, it can be seen that, in case of both the Tb-WS solar reactor and quench unit, $\text{Irr}_{\text{reactor}}$ and $\text{Irr}_{\text{quench}}$ values are maximum at higher $T_H$ and decrease with the reduction in $T_H$. For instance, $\text{Irr}_{\text{reactor}}$ and $\text{Irr}_{\text{quench}}$ can be lowered by 73.8% and 7.8% due to the drop in $T_H$ from 2780 to 2280 K.

H$_2$ generation via water splitting reaction can be carried out at $T_L$ of 298 K by transferring the Tb obtained after the quench unit to the water splitting reactor. The water splitting is an exothermic reaction and hence the rate of heat rejected to the surroundings from the water splitting reactor is estimated as being equal to 399.8 kW according to

\[
Q_{\text{Tb oxidation}} = -\dot{n}\Delta H_{\text{Tb+2H}_2\text{O} \rightarrow \text{TbO}_2+2\text{H}_2(g)@T_L}
\]

Similarly, the irreversibility associated with the water splitting reaction is estimated (1.5 kW/K) by solving

\[
\text{Irr}_{\text{Sm oxidation}} = \left(\frac{Q_{\text{Sm oxidation}}}{298}\right) + \dot{n}\Delta S_{\text{Tb+2H}_2\text{O} \rightarrow \text{TbO}_2+2\text{H}_2(g)@T_L}
\]

To determine the maximum work that can be extracted from the H$_2$ generated, an ideal H$_2$/O$_2$ fuel cell with 100% work efficiency is added to the Tb-WS cycle. According to (14) and (15), it was observed that the theoretical work performed and heat energy released by the ideal fuel cell are equal to 473.9 and 97.3 kW:

\[
W_{\text{FC-Ideal}} = -\dot{n}\Delta G_{\text{2H}_2(g)+O_2(g) \rightarrow 2\text{H}_2\text{O}(l)@298 K} \tag{14}
\]

\[
Q_{\text{FC-Ideal}} = -(298)\dot{n}\Delta S_{\text{2H}_2(g)+O_2(g) \rightarrow 2\text{H}_2\text{O}(l)@298 K} \tag{15}
\]

The cycle ($\eta_{\text{cycle}}$) and solar-to-fuel conversion ($\eta_{\text{solar-to-fuel}}$) efficiency of the Tb-WS cycle can be defined as

\[
\eta_{\text{cycle}} = \frac{W_{\text{FC-Ideal}}}{Q_{\text{solar}}} \tag{16}
\]

\[
\eta_{\text{solar-to-fuel}} = \frac{\text{HHV}_\text{H}_2}{Q_{\text{solar}}} \tag{17}
\]

Variation in $\eta_{\text{cycle}}$ and $\eta_{\text{solar-to-fuel}}$ of the Tb-WS cycle as a function of $T_H$ is presented in Figure 9. The data reported
indicate $\eta_{\text{cycle}}$ of 20.3% and $\eta_{\text{solar-to-fuel}}$ of 24.5% at $T_H$ of 2780 K. However, at lower $T_H$ (2280 K), higher $\eta_{\text{cycle}}$ (26.8%) and $\eta_{\text{solar-to-fuel}}$ (32.3%) can be achieved. $\eta_{\text{solar-to-fuel}}$ of the Tb-WS cycle at $T_H$ of 2280 K is comparable to the efficiency values reported by previous investigators in case of ZnO/Zn cycle (29%), SnO$_2$/Sn cycle (29.8%), Fe$_3$O$_4$/FeO cycle (30%), and ceria cycle (20.2%).

$\eta_{\text{cycle}}$ and $\eta_{\text{solar-to-fuel}}$ of Tb-WS cycle can be increased further by reutilizing the heat released by the water splitting reactor and quench unit. The amount of heat that can be recuperated is calculated as

$$Q_{\text{recuperable}} = Q_{\text{quench}} + Q_{\text{Sm oxidation}}.$$  \hspace{1cm} (18)

As the heat released by the water splitting reactor and quench unit is recycled to run the Tb-WS cycle, the amount of solar energy required will be decreased as

$$Q_{\text{solar, with recuperation}} = Q_{\text{solar}} - [(\text{recuperation}) Q_{\text{recuperable}}].$$  \hspace{1cm} (19)

In case of $T_H$ of 2280 K, Figure 10 shows that as the % heat recuperation increases, $Q_{\text{recuperable}}$ enhances whereas $Q_{\text{solar, with recuperation}}$ diminishes. At 10% heat recuperation, $Q_{\text{solar, with recuperation}}$ is equal to 1677.8 kW, which can be decreased to 1306.8 kW due to the increase in the heat recuperation up to 50%.

After applying the heat recuperation, $\eta_{\text{cycle}}$ and $\eta_{\text{solar-to-fuel}}$ associated with the Tb-WS cycle can be calculated as

$$\eta_{\text{cycle}} = \frac{W_{\text{FC-Ideal}}}{Q_{\text{solar, with recuperation}}}.$$  \hspace{1cm} (20)

$$\eta_{\text{solar-to-fuel}} = \frac{\text{HHV}_{H_2}}{Q_{\text{solar, with recuperation}}}.$$  \hspace{1cm} (21)

Table 2 reports $\eta_{\text{cycle}}$ and $\eta_{\text{solar-to-fuel}}$ of Tb-WS cycle for different $T_H$ and by applying 10 to 50% heat recuperation. For the data listed, it can be seen that, due to the inclusion of heat recuperation, both $\eta_{\text{cycle}}$ and $\eta_{\text{solar-to-fuel}}$ of Tb-WS cycle are significantly improved. For instance, by applying...
20% heat recuperation at $T_H$ of 2280 K, $\eta_{\text{cycle}}$ and $\eta_{\text{solar-to-fuel}}$ can be increased up to 23.5 and 28.4%. Likewise, at heat recuperation of 60% and $T_H$ of 2280 K, $\eta_{\text{cycle}}$ and $\eta_{\text{solar-to-fuel}}$ can get enhanced up to 39.0 and 47.1%.

According to the previous studies, the heat recuperation is highly essential to achieve higher efficiency values in case of metal oxide based solar thermochemical cycles [12, 14, 15, 17, 18, 43, 44]. In the past, attempts were made to achieve the heat recuperation in a real-life solar reactor system. For instance, Diver et al. [45] developed a heat recovery system for iron oxide cycle by using a stack of counter-rotating rings with the reactive material along the perimeter of each ring. In this system, the reactive surfaces act as extended heat transfer surfaces to achieve heat recuperation. Similarly, in case of Tb-WS cycle, heat exchangers can be coupled with the quench unit and water splitting reactor to recover the latent and sensible heat rejected by these units. Suitable heat exchanger fluid needs to be selected and the heat rejected by quench unit (due to the cooling of the thermal reduction products) and water splitting reactor (due to the exothermic splitting of water) can be stored in this fluid. This fluid can be recirculated throughout the process configuration shown in Figure 5 and the captured heat can be reutilized to run the Tb-WS cycle.

The solar reactor thermodynamic modeling performed in this paper is also verified by performing an energy balance and by evaluating the maximum achievable efficiency from the total available work and from the total solar power input. The energy balance performed in case of Tb-WS cycle (for all $T_H$) confirms that

$$W_{\text{FC-Ideal}} = Q_{\text{solar}} - (Q_{\text{reradiation}} + Q_{\text{quench}} + Q_{\text{Sm oxidation}} + Q_{\text{FC-Ideal}}). \quad (22)$$

As an example, at $T_H$ of 2280 K, (22) indicates $W_{\text{FC-Ideal}}$ of 473.9 kW which is equal to $W_{\text{FC-Ideal}}$ determined by (14). Furthermore, the maximum cycle efficiency is also calculated according to

$$\eta_{\text{cycle, maximum}} = \frac{W_{\text{FC-Ideal}} + T_l (\text{Irr}_\text{reactor} + \text{Irr}_\text{quench} + \text{Irr}_\text{Sm oxidation})}{Q_{\text{solar}}}. \quad (23)$$

For all $T_H$, it was observed that $\eta_{\text{cycle, maximum}}$ is equal to the Carnot heat engine operating between hot and cold temperature reservoirs:

$$\eta_{\text{cycle, maximum}} = 1 - \frac{T_l}{T_H} = \eta_{\text{carnot}}. \quad (24)$$

For instance, at $T_H$ of 2280 K and $T_l$ of 298 K, $\eta_{\text{cycle, maximum}}$ is 86.9% which is equal to $\eta_{\text{carnot}} = 86.9$.

4. Summary and Conclusions

Solar reactor efficiency analysis of the Tb-WS cycle for the production of H$_2$ via water splitting reaction was conducted by using HSC Chemistry software and databases. Simulation results indicate that the heat energy required for the complete reduction of TbO$_2$ into Tb and O$_2$ can be reduced significantly from 2780 to 2280 K by decreasing the oxygen partial pressure in the inert flushing gas from $10^{-5}$ to $10^{-8}$ atm. According to the simulations, the water splitting reaction via Tb oxidation is feasible below 5400 K.

Exergy analysis shows that $\eta_{\text{absorption}}$ of the Tb-WS solar reactor can be increased by a factor of 1.28 due to the decrease in $T_H$ from 2780 to 2280 K. It was also observed that $Q_{\text{reactor-net}}$ and $Q_{\text{solar}}$ can be reduced by 43.8 and 562.7 kW with the lowering of $T_H$ from 2780 to 2280 K. Similarly, due to the similar fall in $T_H$, the quenching and reradiation heat losses can be dropped by 7.7 and 65.7%, respectively. The reason for the lower amounts of solar energy requirement and reduction in the heat loss via quenching and reradiation is due to the fact that $\eta_{\text{absorption}}$ of the Tb-WS solar reactor improves with the decrease in $T_H$. $\eta_{\text{cycle}}$ of 23.5% and $\eta_{\text{solar-to-fuel}}$ of 28.4% of Tb-WS cycle at $T_H$ of 2280 K are observed to be comparable to the previously investigated MO cycles. Furthermore, $\eta_{\text{cycle}}$ and $\eta_{\text{solar-to-fuel}}$ can be further increased up to 39.0% and 47.1% by recuperating 60% of the heat rejected by the quench unit and water splitting reactor.

Nomenclature

- C: Solar flux concentration ratio, suns
- HHV: Higher heating value
- I: Normal beam solar insolation, W/m$^2$
- MO: Metal oxide
- $i_\text{r}$: Molar flow rate, mol/sec
- $Q_{\text{quench}}$: Heat rejected to the surrounding from quench unit, kW
- $Q_{\text{FC-Ideal}}$: Heat rejected to the surrounding from ideal fuel cell, kW
- $Q_{\text{Tb oxidation}}$: Heat rejected to the surrounding from water splitting reactor, kW
- $Q_{\text{TbO}_2\text{-heating}}$: Energy required for heating of TbO$_2$, kW
- $Q_{\text{TbO}_2\text{-reduction}}$: Energy required for the thermal reduction of TbO$_2$, kW
- $Q_{\text{reactor-net}}$: Net energy input required for the operation of Tb-WS cycle, kW
- $Q_{\text{reradiation}}$: Radiation heat loss from the solar reactor, kW
- $Q_{\text{recuperable}}$: Total amount of heat that can be recuperated, kW
- $Q_{\text{solar}}$: Solar energy input, kW
- $Q_{\text{solar,with recuperation}}$: Solar energy input after heat recuperation, kW
- $\Delta G_{\text{WS}}$: Gibbs free energy change for water splitting reaction, kJ/mol
- $\Delta H_{\text{WS}}$: Enthalpy change for water splitting reaction, kJ/mol

...
\[ \Delta S_{WS}: \text{ Entropy change for water splitting reaction, } J/\text{mol-K} \]
\[ \sigma: \text{ Stefan-Boltzmann constant, } 5.67 \times 10^{-8} \text{ (W/m}^2\cdot\text{K}^4) \]
\[ \text{Irr}_{\text{reactor}}: \text{ Rate of entropy produced across solar reactor, kW/K} \]
\[ \text{Irr}_{\text{quench}}: \text{ Rate of entropy produced across quench unit, kW/K} \]
\[ \text{Irr}_{\text{Sm oxidation}}: \text{ Rate of entropy produced across water splitting reactor, kW/K.} \]

**Conflict of Interests**

The authors declare that there is no conflict of interests regarding the publication of this paper.

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