Thermochemical Copper Oxide – Copper Sulfate Water Splitting Cycle for Solar Hydrogen Production

R. Bhosale*, D. Dardor, A. Kumar, F. AlMomani, U. Ghosh

Department of Chemical Engineering
College of Engineering
Qatar University, Doha, Qatar, rahul.bhosale@qu.edu.qa

ABSTRACT

In this paper, the solar thermochemical copper oxide – copper sulfate (CO-CS) water splitting cycle is thermodynamically investigated. CO-CS cycle consists of two steps: first step – exothermic oxidation of CuO via water splitting reaction producing H₂, and second step – the CuSO₄ is thermally decomposed into CuO, SO₂, and O₂. The CuO is recycled back to first step and can be used in multiple steps. This study is divided into two steps: 1. Thermodynamic equilibrium analysis, and 2. Second law energy and exergy analysis. At the end, the efficiency of CO-CS cycle is calculated and the results of the thermodynamic analysis are reported in detail.

Keywords: solar energy, thermochemical, hydrogen, water splitting, copper oxide.

1 INTRODUCTION

Due to the thermodynamic constraints associated with the direct water splitting reaction, attempts are currently underway to achieve H₂ production via metal oxide (MO) based solar thermochemical water splitting reaction. In recent years, iron oxide cycle, zinc/zinc oxide cycle, tin/tin oxide cycle, mixed ferrite cycle, and ceria cycle [1-27] were extensively investigated towards solar H₂ production via thermochemical water splitting reaction. Although these cycles are promising, the sulfur-iodine cycle (reaction set I), and hybrid sulfue cycle (reaction set II) are more appealing as the required operating temperatures are lower.

Reaction set I: sulfur-iodine cycle

\[
\begin{align*}
H_2SO_4 & \rightarrow SO_3 + H_2O & (673K) \\
SO_3 & \rightleftharpoons SO_2 + \frac{1}{2} O_2 & (1123 – 1273K) \\
SO_2 + 2H_2O + I_2 & \rightarrow H_2SO_4 + 2HI & (393K) \\
2HI & \rightarrow H_2 + I_2 & (573 – 723K)
\end{align*}
\]

Reaction set II: hybrid sulfur cycle

\[
\begin{align*}
H_2SO_4 & \rightarrow SO_3 + H_2O & (673K) \\
SO_3 & \rightleftharpoons SO_2 + \frac{1}{2} O_2 & (1123 – 1273K) \\
SO_2 + 2H_2O & \rightarrow H_2SO_4 & (353 – 393K)
\end{align*}
\]

In this two-step process, the first non-solar step belongs to the exothermic oxidation of MO by SO₂ and H₂O producing metal sulfate (MSO₄) and H₂ production. The second solar step corresponds to the solar thermal reduction of MSO₄ into MO, SO₂, and O₂. The MO and SO₂ produced in step 2 are recycled back to step 1 and hence can be used in multiple cycles.

In this paper, the computational thermodynamic analysis of a ‘copper oxide – copper sulfate’ (CO-CS) solar thermochemical water splitting cycle is reported. This analysis is performed by using HSC Chemistry 7.0 software and its databases. This paper mainly deals with a) equilibrium composition analysis, and b) second law energy and exergy calculations. The maximum theoretical solar energy conversion efficiency of the CO-CS cycle is determined by performing the second law thermodynamic analysis and the obtained results are reported in this paper. A typical CO-CS solar thermochemical water splitting cycle is shown below.
2 CHEMICAL THERMODYNAMIC ANALYSIS

The equilibrium thermodynamic chemical compositions of the solar thermal reduction of CuSO$_4$ are reported in Figure 2. As per the thermodynamic modeling, the complete thermal reduction of CuSO$_4$ into CuO, SO$_2$ (g) and O$_2$ (g) is possible at or above 1215 K in presence of Ar = 10 mol/sec.

Figure 2. Solar thermal reduction of CuSO$_4$ (Ar = 10 mol/sec).

The equilibrium molar compositions associated with the H$_2$ production via water splitting reaction via CO-CS solar thermochemical cycle is shown in Figure 3. As per the shown results, H$_2$ production via oxidation of CuO by SO$_2$ and H$_2$O is possible at 310 K.

Figure 3. Water splitting reaction using CO-CS cycle.

3 ENERGY AND EXERGY ANALYSIS

The energy and exergy analysis of the solar thermochemical CO-CS water splitting cycle was performed by following the second law analysis. The process flow diagram for the CO-CS cycle is presented in Figure 4. This cycle comprises of:

1. Solar reactor performing thermal reduction
2. A water splitting reactor (CuO oxidizer)
3. Ideal H$_2$/O$_2$ fuel cell (theoretical)
4. Two coolers
5. A gas separator

To perform the energy and exergy analysis of the solar thermochemical CO-CS water splitting cycle, the methodology and the governing equations employed in the previous MO cycles, are utilized in this study. As mentioned earlier, all the thermodynamic data and properties are extracted from HSC Chemistry 7.0 software and databases. In addition, the molar flow rate of CuSO$_4$ entering the solar reactor is assigned to 1 mol/sec for the entire thermodynamic analysis.

To start with the energy and exergy analysis, the solar energy absorption efficiency ($\eta_{absorption}$) for the CO-CS cycle is determined by:

$$\eta_{absorption} = 1 - \left( \frac{\sigma T R}{IC} \right)$$  \hspace{1cm} (10)

Where, $\sigma$ = Stefan-Boltzmann constant, $I$ = normal beam insolation 1(kW/m$^2$), C = solar flux concentration ratio of the solar concentrating system (5000 suns), $Q_{reactor-net}$ = net energy absorbed in the solar reactor, $Q_{solar}$ = solar energy input. For CO-CS water splitting cycle, at $T_R$ = 1215 K, the $\eta_{absorption}$ is observed to be 97.53%.
For the heating of inert Ar from ambient conditions upto 1215 K and for thermal reduction of CuSO₄, solar energy input is required. To determine the solar energy input, at first the net energy required to run the solar reactor needs to be calculated as:

\[ Q_{\text{reactor-net}} = Q_{\text{CuSO₄-reduction}} + Q_{\text{Ar-heating}} \]  

(11)

According to the thermodynamic analysis, to achieve the 100% thermal reduction of CuSO₄ at 1215 K, 10 mol/sec of inert Ar is needed. According to Eq.(12), 190.61 kW of heat energy is required to raise the Ar temperature from 298 K to 1215 K.

\[ Q_{\text{Ar-heating}} = \dot{n} \Delta H |_{\text{Ar(g)}}@298K\rightarrow\text{Ar(g)}@T_R \]  

(12)

Furthermore, the energy required for the complete reduction of CuSO₄ (at 1215 K) into CuO, SO₂(g), and O₂(g) is given by Eq.(13) and observed to be equal to 437.97 kW.

\[ Q_{\text{CuSO₄-reduction}} = \dot{n} \Delta H |_{\text{CuSO₄@298K}}\rightarrow\text{CuO+SO₂(g)+1/2O₂(g)}@T_R \]  

(13)

According to Eq.(11), the \( Q_{\text{reactor-net}} \) for the CO-CS cycle at \( T_R = 1215 \) K is equal to 628.58 kW.

Total amount of solar energy input required to run the CO-CS cycle can be calculated according to Eq. (14) and observed to be 644.51 kW.

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

(14)

As the operation of the solar reactor is carried out at higher operating temperatures, the radiation losses are inevitable. Radiation heat losses and % re-radiation from the solar reactor conducting the thermal reduction of CuSO₄ can be calculated by equations (15) and (16):

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

(15)

\[ \% \, \text{re-radiation losses} = \frac{Q_{\text{re-radiation}}}{Q_{\text{solar}}} \times 100 \]  

(16)

The thermodynamic calculations indicate that at \( T_R = 1215 \) K, the re-radiation losses from the CO-CS solar reactor is equal to 15.93 kW (2.47% of solar energy is lost by re-radiation).

After performing thermal reduction in the CO-CS solar reactor, the exiting products includes solid CuO and gaseous SO₂, O₂ and Ar. As the water splitting needs to be carried out below 310 K, the solid CuO is cooled down from 1215 K to 298 K. During this cooling step, 52.11 kW of heat energy is released by cooler – 2. Likewise, cooling of gases i.e. SO₂, O₂ and Ar from 1215 K to 298 K releases 259.09 kW of heat energy (cooler – 1).

The H₂ production via water splitting reaction can be carried out by transferring the CuO produced via CuSO₄ reduction to the water splitting reactor. In this reactor, the CuO is allowed to react with H₂O and SO₂(g) at 298 K and H₂ formation is achieved with subsequent production of CuSO₄. By assuming 100% oxidation of CuO producing CuSO₄ and H₂ via water splitting reaction, the rate of heat rejected to the surrounding by CuO oxidizer is estimated as 31.539 kW according to equation (17).

\[ Q_{\text{CuO-oxidizer}} = -\dot{n} \Delta H |_{\text{CuO+H₂(g)+SO₂(g)}@298K\rightarrow\text{CuSO₄+H₂(g)}@298K} \]  

(17)

The maximum work can be extracted from the produced H₂ is calculated by employing an ideal H₂/O₂ fuel cell with 100% work efficiency. The rate of theoretical work performed by the ideal fuel cell in case of CO-CS cycle can be calculated according to Eq. (18). Likewise, the rate of heat energy released by the ideal fuel cell is determined by Eq. (19). Both calculations yield into \( W_{\text{FC-Ideal}} = 237.05 \) kW and \( Q_{\text{FC-Ideal}} = 48.56 \) kW, respectively.

\[ W_{\text{FC-Ideal}} = -\dot{n} \Delta G |_{\text{H₂(g)+0.5O₂(g)}@298K\rightarrow\text{H₂O(l)}@298K} \]  

(18)

\[ Q_{\text{FC-Ideal}} = -(298) \times \dot{n} \Delta S |_{\text{H₂(g)+0.5O₂(g)}@298K\rightarrow\text{H₂O(l)}@298K} \]  

(19)

CO-CS cycle efficiency can be calculated as the ratio of theoretical work performed by the ideal fuel cell to the solar energy input:

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

(20)

Furthermore, the solar-to-fuel energy conversion efficiency of the solar thermochemical CO-CS water splitting process is defined as the ratio of higher heating value (HHV) of the H₂ produced to the solar energy input:

\[ \eta_{\text{solar-to-fuel}} = \frac{\text{HHV}_{\text{H₂}}}{Q_{\text{solar}}} \]  

(21)

Where,

\[ \text{HHV}_{\text{H₂}} = -\dot{n} \Delta H |_{\text{H₂(g)+0.5O₂(g)}@298K\rightarrow\text{H₂O(l)}@298K} \]  

(22)

As per the HSC computational thermodynamic modeling, \( \eta_{\text{cycle}} \) and \( \eta_{\text{solar-to-fuel}} \) equal to 36.80% and 44.35%, respectively.

4 CONCLUSIONS

In this paper, the energy and exergy analysis of the solar thermochemical H₂ production via CO-CS water splitting cycle was performed. The equilibrium thermodynamic analysis of this cycle indicate that the complete thermal reduction of CuSO₄ is feasible at or above 1215 K (Ar = 10 mol/sec) and H₂ production via water splitting reaction is possible below 310 K, respectively. The second law thermodynamic analysis indicate that indicate \( \eta_{\text{absorption}} = 97.53\% \), \( Q_{\text{solar}} = 644.54 \) kW, \( Q_{\text{reactor-net}} = 628.58 \) kW, \( Q_{\text{re-radiation}} = 15.93 \) kW, \( Q_{\text{cooler-1}} = 259.09 \) kW, \( Q_{\text{CuO-oxd}} = 31.539 \) kW, and \( \eta_{\text{cycle}} = 36.80\% \), and \( \eta_{\text{solar-to-fuel}} = 44.35\% \), respectively.
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REFERENCES
