

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

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## ABSTRACT

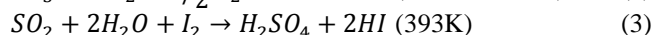
In this paper, the solar thermochemical copper oxide – copper sulfate (CO-CS) water splitting cycle is thermodynamically investigated. CO-CS cycle consists of two steps: first step – exothermic oxidation of CuO via water splitting reaction producing H<sub>2</sub>, and second step – the CuSO<sub>4</sub> is thermally decomposed into CuO, SO<sub>2</sub>, and O<sub>2</sub>. 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 H<sub>2</sub> 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 H<sub>2</sub> production via thermochemical water splitting reaction. Although these cycles are promising, the sulfur-iodine cycle (reaction set I), and hybrid sulfur cycle (reaction set II) are more appealing as the required operating temperatures are lower.

Reaction set I: sulfur-iodine cycle

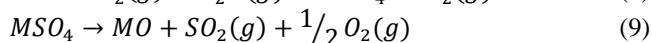
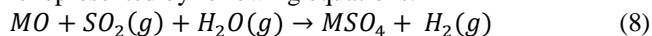


Reaction set II: hybrid sulfur cycle



In previous studied, a noble metal catalyst was used in case of sulfur-iodine and hybrid sulfue cycles. Utilization of metal oxides as the catalytic materials (instead of noble metal catalysts) and converting the sulfur-iodine and hybrid sulfur cycle into a ‘metal oxide – metal sulfate’ cycle operated using concentrated solar energy is one of the

alternative to achieve H<sub>2</sub> production at moderate temperatures. The solar ‘metal oxide – metal sulfate’ cycle is represented by following equations.



In this two-step process, the first non-solar step belongs to the exothermic oxidation of MO by SO<sub>2</sub> and H<sub>2</sub>O producing metal sulfate (MSO<sub>4</sub>) and H<sub>2</sub> production. The second solar step corresponds to the solar thermal reduction of MSO<sub>4</sub> into MO, SO<sub>2</sub>, and O<sub>2</sub>. The MO and SO<sub>2</sub> 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.

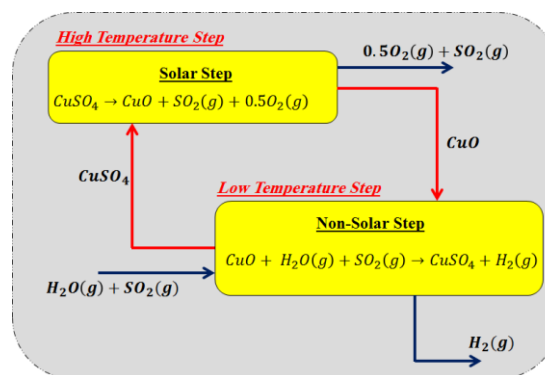


Figure 1. A typical CO-CS solar thermochemical water splitting cycle.

## 2 CHEMICAL THERMODYNAMIC ANALYSIS

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

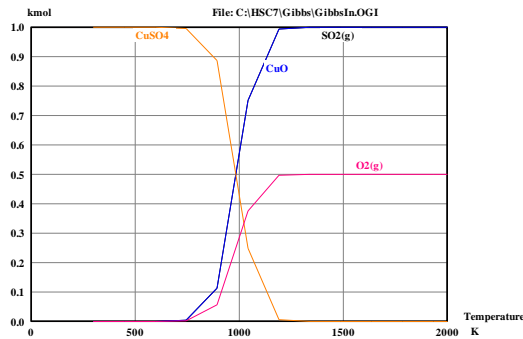


Figure 2. Solar thermal reduction of  $\text{CuSO}_4$  ( $\text{Ar} = 10 \text{ mol/sec}$ ).

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

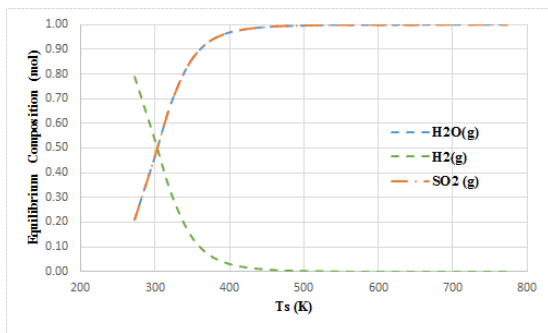


Figure 3. Water splitting reaction using CO-CS cycle.

## 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 ( $\text{CuO}$  oxidizer)
3. Ideal  $\text{H}_2/\text{O}_2$  fuel cell (theoretical)
4. Two coolers
5. A gas separator

In addition to this, several assumptions were made (similar to previous studies) during performing energy and exergy analysis of solar thermochemical CO-CS water splitting cycle which are mentioned below:

1. The solar reactor is assumed to be a perfectly insulated blackbody absorber
2. No convective/conductive heat losses
3. Effective emissivity and absorptivity equal to unity
4. All the products separate naturally without expending any work
5. All reactions reach 100% completion
6.  $\text{H}_2$  production is carried out at atmospheric pressure and at steady state conditions
7. Viscous losses and variation in the kinetic and potential energies are neglected
8. Energy required for the separation of gaseous products such as separation of  $\text{SO}_2$  from  $\text{O}_2$  and  $\text{Ar}$  are not accounted during the efficiency calculation
9. Heat exchangers required for recovering the sensible and latent heat are omitted from thermodynamic considerations

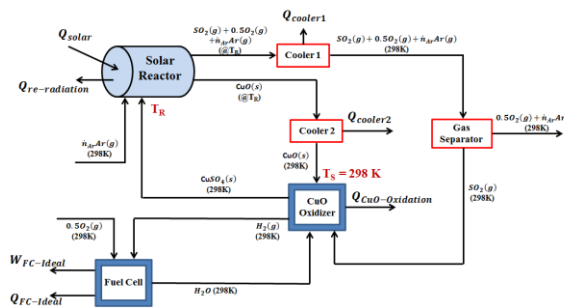


Figure 4. Process configuration for  $\text{H}_2$  production via solar thermochemical CO-CS water splitting cycle.

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  $\text{CuSO}_4$  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 ( $\eta_{\text{absorption}}$ ) for the CO-CS cycle is determined by:

$$\eta_{\text{absorption}} = 1 - \left( \frac{\sigma T_R^4}{IC} \right) \quad (10)$$

Where,  $\sigma$  = Stefan-Boltzmann constant,  $I$  = normal beam insolation ( $\text{kW}/\text{m}^2$ ),  $C$  = solar flux concentration ratio of the solar concentrating system (5000 suns),  $Q_{\text{reactor-net}}$  = net energy absorbed in the solar reactor,  $Q_{\text{solar}}$  = solar energy input. For CO-CS water splitting cycle, at  $T_R = 1215 \text{ K}$ , the  $\eta_{\text{absorption}}$  is observed to be 97.53%.

For the heating of inert Ar from ambient conditions upto 1215 K and for thermal reduction of CuSO<sub>4</sub>, 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:

$$Q_{reactor-net} = Q_{CuSO_4-reduction} + Q_{Ar-heating} \quad (11)$$

According to the thermodynamic analysis, to achieve the 100% thermal reduction of CuSO<sub>4</sub> 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.

$$Q_{Ar-heating} = \dot{n}\Delta H|_{Ar(g)@298K \rightarrow Ar(g)@T_R} \quad (12)$$

Furthermore, the energy required for the complete reduction of CuSO<sub>4</sub> (at 1215 K) into CuO, SO<sub>2</sub>(g), and O<sub>2</sub>(g) is given by Eq.(13) and observed to be equal to 437.97 kW.

$$Q_{CuSO_4-reduction} = \dot{n}\Delta H|_{CuSO_4@298K \rightarrow CuO+SO_2(g)+\frac{1}{2}O_2(g)@T_R} \quad (13)$$

According to Eq.(11), the  $Q_{reactor-net}$  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.

$$Q_{solar} = \frac{Q_{reactor-net}}{\eta_{absorption}} \quad (14)$$

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 CuSO<sub>4</sub> can be calculated by equations (15) and (16):

$$Q_{re-radiation} = Q_{solar} - Q_{reactor-net} \quad (15)$$

$$\% \text{ re - radiation losses} = \frac{Q_{re-radiation}}{Q_{solar}} \times 100 \quad (16)$$

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 SO<sub>2</sub>, O<sub>2</sub>, 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. SO<sub>2</sub>, O<sub>2</sub> and Ar from 1215 K to 298 K releases 259.09 kW of heat energy (cooler – 1).

The H<sub>2</sub> production via water splitting reaction can be carried out by transferring the CuO produced via CuSO<sub>4</sub> reduction to the water splitting reactor. In this reactor, the CuO is allowed to react with H<sub>2</sub>O and SO<sub>2</sub>(g) at 298 K and

H<sub>2</sub> formation is achieved with subsequent production of CuSO<sub>4</sub>. By assuming 100% oxidation of CuO producing CuSO<sub>4</sub> and H<sub>2</sub> 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).

$$Q_{CuO-oxidizer} = -\dot{n}\Delta H|_{CuO+H_2O(g)+SO_2(g)@298K \rightarrow CuSO_4+H_2(g)@298K} \quad (17)$$

The maximum work can be extracted from the produced H<sub>2</sub> is calculated by employing an ideal H<sub>2</sub>/O<sub>2</sub> 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  $W_{FC-ideal} = 237.05$  kW and  $Q_{FC-ideal} = 48.56$  kW, respectively.

$$W_{FC-ideal} = -\dot{n} \Delta G|_{H_2(g)+0.5O_2(g)@298K \rightarrow H_2O(l)@298K} \quad (18)$$

$$Q_{FC-ideal} = -(298) \times \dot{n} \Delta S|_{H_2(g)+0.5O_2(g)@298K \rightarrow H_2O(l)@298K} \quad (19)$$

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

$$\eta_{cycle} = \frac{W_{FC-ideal}}{Q_{solar}} \quad (20)$$

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 H<sub>2</sub> produced to the solar energy input:

$$\eta_{solar-to-fuel} = \frac{HHV_{H_2}}{Q_{solar}} \quad (21)$$

Where,

$$HHV_{H_2} = -\dot{n} \Delta H|_{H_2(g)+0.5O_2(g)@298K \rightarrow H_2O(l)@298K} \quad (22)$$

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

## 4 CONCLUSIONS

In this paper, the energy and exergy analysis of the solar thermochemical H<sub>2</sub> production via CO-CS water splitting cycle was performed. The equilibrium thermodynamic analysis of this cycle indicate that the complete thermal reduction of CuSO<sub>4</sub> is feasible at or above 1215 K (Ar = 10 mol/sec) and H<sub>2</sub> production via water splitting reaction is possible below 310 K, respectively. The second law thermodynamic analysis indicate that indicate  $\eta_{absorption} = 97.53\%$ ,  $Q_{solar} = 644.54$  kW,  $Q_{reactor-net} = 628.58$  kW,  $Q_{re-radiation} = 15.93$  kW,  $Q_{cooler-1} = 259.09$  kW,  $Q_{CuO-oxd} = 31.539$  kW, and  $\eta_{cycle} = 36.80\%$ , and  $\eta_{solar-to-fuel} = 44.35\%$ , respectively.

## ACKNOWLEDGEMENT

This publication was made possible by the NPRP grant (NPRP8-370-2-154) and UREP grant (UREP18-146-2-060) from the Qatar National Research Fund (a member of Qatar Foundation). The statements made herein are solely the responsibility of author(s). The authors also gratefully acknowledge the financial support provided by the Qatar University Internal Grant QUUG-CENG-CHE-14\15-10.

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