Novel graphical exergy analysis method for hydrogen production in a two-step solar thermochemical cycle

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ABSTRACT

The two-step solar thermochemical cycle for hydrogen production is one of the promising ways to alleviate current energy and environmental issues, and achieve carbon neutrality prospects in the future. Traditional graphical analysis methods investigate thermochemical cycles using temperature-entropy and temperature-enthalpy diagrams, without demonstrating the irreversibility of energy conversion processes in the looping of oxygen carriers. To solve this problem, a novel graphical exergy analysis method is proposed for two-step solar thermochemical cycles by illustrating material state in the looping of oxygen carriers and the exergy destruction quantitatively. The analysis process for describing the material state and exergy destruction with a diagram is introduced. The proposed graphical exergy analysis method is used to investigate a typical case of a solar ZnO/Zn two-step thermochemical cycle. The results show that the use of the inert sweeping gas during reduction to reduce the partial pressure of oxygen product to obtain a lower reduction temperature causes serious irreversibility. The proposed graphical exergy analysis method provides a useful tool for analyzing solar thermochemical cycles.

Keywords: Solar energy; Thermochemical cycles; Exergy destruction; Graphical analysis;

NONMENCLATURE

Abbreviations	
EUD Irr	Energy-utilization diagram Irreversibility
Symbols	
A	Energy level
С	Concentration solar ratio, 3000suns
ΔEXL	Exergy destruction
ΔG	Gibbs free energy
ΔH	Enthalpy change
1	Direct normal insolation, 1kW/m ²
ΔS	Entropy change
S	Area
Т	Temperature
<i>T</i> ₀	Surroundings temperature, 298K
σ	Boltzmann constant, 5.67x10 ⁻⁸ W/(m ² K ⁴)

1. INTRODUCTION

Efficient and reliable technologies for the use of solar energy are essential for sustainable development. Among the various technical routes, solar thermochemical cycles are considered to be one of the promising ways, due to the advantages of storing solar energy in the form of chemical energy of fuels, lowering the temperature of pyrolysis water process and eliminating the needs to separate the products of hydrogen and oxygen [1, 2]. Two-step thermochemical cycles are the simplest ones in which a metal oxide with

high valence is thermally reduced, releasing oxygen, and then the reduced lower valence metal oxide or metal element is oxidized by water, producing hydrogen and regaining the initial metal oxide. The chemical processes can be expressed as:

Reduction reaction: $MO_n \rightarrow MO_{n-\delta} + 0.5\delta O_2$

Oxidation reaction: $MO_{n-\delta} + \delta H_2 O \rightarrow MO_n + \delta H_2$

The graphical analysis for thermochemical cycles still relies on that of thermodynamic cycles, such as temperature-entropy (T-S) and temperature-enthalpy (T-H) diagrams. Lange et al. [3] conducted an energy analysis for a two-step thermochemical cycle, and presented it in a T-S diagram. However, some additional processes, which do not exist in practice, are introduced to obtain a closed curve, e.g. heating hydrogen product from the temperature of oxidation reaction to reduction reaction. Entropy changes resulting from the movement of materials in and out of the cycle system are also ignored. Bilgen et al. [4] and Nakamura [5] illustrated ZnO/Zn and Fe₃O₄/FeO thermochemical cycles with T-S and T-H diagrams. Different from thermodynamic cycles, the working fluid is only involved in the change of thermodynamic states, the thermochemical cycles are accompanied with the production and consumption of materials and the input and output of reactants and products. Traditional T-S and T-H diagrams can hardly illustrate the irreversibility and exergy destruction of complex cycles. The energyutilization diagram (EUD) proposed by Jin and Ishida [6] describes the exergy destruction in an A- ΔH diagram by introducing the concept of energy level, and is widely used to analyze complex physical and chemical processes from the viewpoint of exergy [7, 8]. However, this analysis method is not effective enough in graphing the looping of oxygen carriers in thermochemical cycles because of focusing on the energy process. A suitable graphical analysis method for solar thermochemical cycles is needed.

In order to fill this research gap, a novel graphical method for exergy analysis two-step solar thermochemical cycles is proposed, which illustrates the material state in the looping of oxygen carriers, and destruction. reveals the exergy А typical thermochemical cycle is investigated using the proposed graphical analysis method, and the results indicate that the proposed method is a useful tool for the analysis of solar thermochemical cycles.

2. PROPOSAL OF A NOVEL GRAPHICAL EXERGY ANALYSIS METHOD

2.1 Exergy analysis for a thermochemical cycle

A thermochemical cycle consists of several physical and chemical processes, mainly including metal oxide heating, reduction reaction, reduced products cooling, oxidation reaction, etc. Generally, the above processes take place in a reactor specially designed to switch between heating and cooling [9]. Fig.1 shows a simple flowsheet.



Fig. 1. Flowsheet of thermochemical cycles

According to the Second Law of Thermodynamics, the irreversible loss caused by heat transfer can be determined by:

$$Irr_{heat} = -\frac{\Delta H}{T} + \sum_{i} n_i \Delta S_i$$
 (1)

where $\sum_{i} n_i \Delta S_i$ is total entropy change; $\frac{\Delta H}{T}$ represents entropy flow derived from heat absorbed or released; the difference of the two is the entropy

generation triggered by the process irreversibility. The irreversibility of chemical reactions is mainly caused by the deviation of reaction from the condition

of $\Delta G=0$, which can be determined by [10] :

$$Irr_{rea} = -\sum_{i} \frac{n_i \Delta G_i}{T_i}$$
(2)

The total exergy destruction is therefore computed by:

$$\Delta EXL_{total} = T_0 \left(Irr_{heat} + Irr_{rea} \right)$$
(3)

2.2 A graphical exergy analysis method to diagram the material state and exergy destruction

Previous studies focused on the graphical analysis of thermochemical cycles and generally used *T-S* or *T*- ΔH diagrams. These methods can hardly show the exergy destruction, and depict a thermochemical cycle with many assumptions. The EUD diagram shows an explicit distribution of exergy destruction, but cannot display the looping of oxygen carriers. An advanced

graphical analysis method needs to solve two questions: presenting material actual state in the looping of oxygen carriers, and showing the distribution of exergy destruction.



Fig. 2. Exergy destruction in an A- ΔH diagram

Firstly, we focus on the presentation of the looping of oxygen carriers and the depiction of material state in an A- ΔH diagram, because the enclosed area between the difference of energy level of energy donator (A_{ed}) and acceptor (A_{ea}) and the enthalpy change can represent exergy destruction, see Fig 2. A is energy level, defined as the ratio of exergy to energy, which is usually used to evaluate the quality of energy. For thermal energy, the energy level is equal to the Carnot efficiency according to the Second Law of Thermodynamics, i.e., A=1- T_0/T .





AH

Plotting the different states of material on an $A-\Delta H$ diagram leads to Fig 3. Path $1\rightarrow 2$ is metal oxide, MO_n , heated from A_3 to A_2 (from the temperature of oxidation reaction T_3 to reduction reaction T_2) Path $2\rightarrow 3$ represents MO_n reduced to $MnO_{n-\delta}$ and O_2 at A_2 . Path $3\rightarrow 4$ is the reduced products cooled from A_2 to A_3 . Point 4 represents $MO_{n-\delta}$ and O_2 at A_3 . However, the point 4', i.e., $MO_{n-\delta}$ and H_2O at A_3 , is needed rather than point 4, because the oxidation reaction occurs between $MO_{n-\delta}$ and H₂O. The discontinuity of the curve in Fig.3 leads to the failure of the oxygen carrier looping illustration, because we believe that the looping of the oxygen carrier should have a closed curve, like thermodynamic cycle in the *T-S* diagram. In order to overcome this problem, the thermochemical cycle is initially analyzed in an *A-H* diagram, see Fig. 4.

In Fig.4, H_2 and MO_n at the energy level of A_3 are considered to be the beginning of the thermochemical cycle, i.e., point 1. Path $1 \rightarrow 2$ presents metal oxide heated from A_3 to A_2 , but H_2 stays at the energy level of A_3 . In other words, each point at the path $1 \rightarrow 2$ is the total state of H₂ at A₃ and MO_n at A (A₃ \leq A \leq A₂). Path $2 \rightarrow 3$ is MO_n thermally decomposed into MnO_{n- δ} and O₂ at A_2 , in which the energy change refers to the reduction reaction enthalpy. The state of H₂ in the process of $2 \rightarrow 3$ is also constant. Path $3 \rightarrow 4$ is the reduction reaction products cooled from A₂ to A₃, and the energy change is derived from the heat released from $MO_{n-\delta}$ and O_2 . The constant state of H_2 at A_3 in the path $3 \rightarrow 4$ does not contribute to any energy change. Point 4 includes the states of $MO_{n-\delta}$, H_2 and O_2 at the energy level of A_3 . One of the oxidation reactants, H_2O , can be acquired though a virtual reaction between H₂ and O_2 , corresponding to path $4\rightarrow 5$. Thus, we simultaneously obtain oxidation reactants, $MO_{n-\delta}$ and H₂O, at the energy level of A_3 at point 5. Path 5 \rightarrow 1 is the oxidation reaction process, by which H_2 and MO_n at A_3 are regained, and another cycle can start over again.



 $0 \qquad H_{\rm MOn} \qquad H_{\rm MOn-\delta} + \delta H_{\rm H2O} \qquad (H_{\rm MOn-\delta} + 0.5 \delta H_{\rm O2}) @A_2 + \delta H_{\rm H2} @A_3 \qquad H \label{eq:MOn-def}$ Fig. 4. Analysis of the looping of oxygen carrier in an A-H diagram

Based on the above discussion, H_2 at the energy level of A_3 participates in the looping of the oxygen carrier to achieve a closed curve in the *A*-*H* diagram. The point on the cycle curve in Fig. 4 represents the total state of the oxygen carrier and H_2 . This is not realistic. On the other hand, we are more concerned on the energy change in each process. In order to improve and simplify the graphical thermochemical cycle, the *A*- *H* diagram can be changed to be an *A*- Δ *H* diagram through taking the point ($H_{MOn}+\delta H_{H2}$, 0) in Fig. 4 as the origin of coordinates, see Fig. 5. In the *A*- Δ *H* diagram, the amount of the energy change is considered, and the unchanged state of H₂ considered in the *A*-*H* diagram does not affect the curve in the *A*- Δ *H* diagram. The variation of energy is only from the state change of materials, i.e., MO_n, MO_{n- δ} and O₂. The material state in the looping of the oxygen carrier is illustrated in a diagram.



Fig. 5. Illustration of the looping of the oxygen carrier in an A ΔH diagram

Next, we concentrate on presenting the exergy destruction in the above $A-\Delta H$ diagram. The EUD diagram is a widely used tool to show the amount of exergy destruction caused by the mismatching energy level of the energy donator and acceptor in a process. In the $A-\Delta H$ diagram (see Fig. 6), the path $1\rightarrow 2\rightarrow 3$ is thermal energy absorbed by the thermochemical cycle. The energy acceptor of the path $1\rightarrow 2$ and the path $2\rightarrow 3$ is MO_n and reduction reaction, while the energy donator is a constant temperature heat source at $A_{\text{heat,souce}}$. The enclosed areas of S_1 and S_2 are the exergy destruction in the endothermic processes. The paths $3\rightarrow 4$ and $5\rightarrow 1$ are thermal energy released by the products of reduction reaction and oxidation reaction respectively.

Generally, the sensible heat carried by $MO_{n-\delta}$ and O_2 after reduction reaction is used to heat H_2O (path $6\rightarrow7$, the phase change of H_2O is ignored) from 0 to A_3 . The exergy destruction of the heat exchange process is represented as area S_3 . As no heat is recovered from the oxidation reaction, the thermal exergy released by the oxidation process is completely lost, which is denoted as area S_4 . Area S_5 represents the exergy destruction of cooling H_2 and O_2 (path $8\rightarrow9$) from A_3 to 0. The path $4\rightarrow5$ is an unreal process for the sake of achieving the looping of the oxygen carrier, which does not cause any

exergy destruction. The sum of areas S_1 , S_2 , S_3 , S_4 , and S_5 is the exergy destruction resulting from heat exchange in the thermochemical cycle.



In addition to the exergy destruction of heat transfer, there is also exergy destruction from chemical reactions. This loss will appear when the reaction temperature deviates from the temperature ∆G=0 (called corresponding to equilibrium temperature), which can be illustrated with area S₆ and S_7 in Fig. 7. The material state during the looping of the oxygen carrier and the exergy destruction of each process in the thermochemical cycle are both illustrated in Fig. 7.



Fig. 7. Qualitative graphical analysis of a thermochemical cycle

3. CASE STUDY WITH THE NOVEL ANALYSIS METHOD

3.1 Illustrated thermochemical theoretical cycle

The ZnO/Zn thermochemical cycle is studied by the proposed novel graphical exergy analysis method for verifying its practicability, see Fig. 8.

The thermal absorbed energy by the thermochemical cycle is provided by a heat source at the constant energy level of 0.90 (A_{heat source}). The reduction and oxidation reactions proceed at the energy level of 0.88 and 0.60. In Fig. 8, it can be found that the largest exergy destruction takes place during the heat exchange between the reduction reaction products and H_2O , corresponding to area S_3 . This exergy destruction mainly includes two parts: one is caused by heat transfer with temperature difference between the reduction reaction products (Zn and O₂) and H₂O, due to the mismatching of their energy level; the other is resulted from heat dissipation because of the heat released by Zn and O₂ larger than that absorbed by H₂O from 0 to A_3 . The thermal exergy discharged by the oxidation reaction also accounts for a larger proportion, as compared with the exergy destruction in heating and reaction processes. In addition, the exergy destruction in reactions is lower than that of heat transfer in the thermochemical theoretical cycle. The application of effective heat recuperation can reduce this loss. Though the above graphical analysis, the theoretical exergy efficiency of the ZnO/Zn two-step thermochemical cycle is 47.6%.



Fig. 8. ZnO/Zn thermochemical cycle diagram

However, such high theoretical efficiency can hardly be achieved in practice. The high temperature in the reduction reaction leads to a severe re-radiation loss, if the thermochemical cycle is driven by solar energy [11]. The oxygen partial pressure of the reduction reaction is generally reduced by inert gas sweeping and vacuum pumping in order to decrease the inaccessible high temperature, introducing extra energy penalty.

3.2 Inert sweeping gas assisted solar two-step thermochemical cycle

The inert gas (Ar) sweeping is used to reduce the partial pressure of oxygen in the reduction reaction. The inert sweeping gas assisted solar thermochemical cycle is shown in Fig. 9. The theoretical amount of Ar can be obtained from ref. [12]. The re-radiation exergy loss, corresponding to area S_6 in Fig. 9, can be obtained by:

$$\Delta EXL_{\text{re-rad}} = (1 - \eta_{\text{abs}}) Q_{\text{solar}} A_{\text{heat source}}$$
(4)

where Q_{solar} is the total solar radiation energy; η_{abs} refers to the absorption efficiency of the reactor [11], which can be determined by:

$$\eta_{\rm abs} = 1 - \frac{\sigma T_2^4}{IC}$$
(5)

where σ is the Boltzmann constant; *I* refers to direct normal insolation, 1kW/m²; *C* is solar concentration ratio, 3000suns.

Although the inert sweeping gas does not participant in the reduction reaction, it enters the reactor together with ZnO for diluting the concentration of oxygen product. The solar heat absorbed and released by the inert sweeping gas causes the largest exergy destruction in the solar thermochemical cycle, leading to the increase of the areas of S_1 , S_3 and S_5 in Fig. 9 as compared with that in Fig. 8. Thus, operating the reduction reaction at a low reduction temperature without a low partial pressure of oxygen for preventing inert gas sweeping is beneficial to achieving efficient hydrogen production through solar thermochemical cycles. In addition, the re-radiation exergy destruction is represented as the area S_6 . It may be larger when the exergy loss of heat conduction and convection is considered. The areas of S_8 and S_9 represent the theoretical separation work and separation loss of inert sweeping gas (Ar).



Fig. 9. Graphing the inert sweeping gas (Ar) assisted solar ZnO/Zn thermochemical cycle

4. CONCLUSIONS

In order to overcome the limit of traditional graphical analysis methods in illustrating two-step solar thermochemical cycles, a novel graphical exergy analysis method is proposed. The innovative method introduces a virtual reaction between H_2 and O_2 and energy level applied to the graphical analysis, and can simultaneously present the material state in the looping of oxygen carrier and exergy destruction in an $A-\Delta H$ diagram. The important factors, including material state, energy change, the distribution of exergy destruction are all actually graphed and revealed, which provides a new way for the analysis of thermochemical cycles. A solar ZnO/Zn two-step thermochemical cycle is analyzed using the proposed graphical exergy analysis method. The use of the inert sweeping gas during reduction to reduce the partial pressure of oxygen product to obtain a lower reduction temperature causes serious irreversibility. The results indicate that the proposed graphical exergy analysis method is a useful tool for the analysis of solar thermochemical cycles.

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