



# T–S diagram efficiency analysis of two-step thermochemical cycles for solar water splitting under various process conditions



M. Lange\*, M. Roeb, C. Sattler, R. Pitz-Paal

Institute of Solar Research, German Aerospace Center (DLR), Linder Höhe, 51147 Köln, Germany

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## ABSTRACT

Temperature–entropy diagrams combined with a pinch point analysis are introduced, providing a vivid and detailed tool to analyse two-step thermochemical water-splitting processes. The impacts of different temperature and pressure conditions, as well as different water conversion rates, are studied. Further, requirements regarding the entropy change in the redox material to reach desired process conditions are presented. This paper provides insights on how future research shall be oriented to achieve optimal conditions for this challenging but also very promising class of reactions.

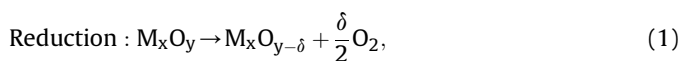
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## 1. Introduction

The efficient production of fuels from renewable energy sources is an important task to be solved for the changing energy economy. As solar radiation is by far the largest renewable energy resource on earth, it is important to put effort in developing technologies to convert solar radiation into fuels. Several possibilities are under development. Especially, thermal processes have the potential to be efficient, as on the one hand, they can use the complete solar spectrum available on the surface of the earth and on the other hand, high temperature processes can be realized, which may reach high efficiencies according to Carnot's law. Hydrogen is of special interest as it already is a mass-produced chemical, necessary for the production and upgrading of fossil fuels and fertilizers. Further, it has the potential to be used as an energy vector itself by efficient conversion in fuel cells.

Many different paths for thermochemical hydrogen production are currently being investigated [1]. In the field of high temperature processes for solar fuel production, a focus is set on two-step thermochemical cycles [2–4], as they are able to split water into

hydrogen and oxygen at much lower temperature than the pure one-step thermal decomposition. The two reaction steps are [5]



$M_xO_y$  represents a metal oxide with  $x$  metal atoms and  $y$  oxygen atoms. Typical candidates that are used as redox material are mixed iron oxides [6], ceria [7,8] and zinc oxide [9]. In one cycle,  $\delta$  atoms of oxygen can be incorporated in and released from the metal oxide resulting in a yield of  $\delta$  hydrogen molecules. Several different reactor designs have been proposed for this process. In the most prominent approaches, the metal oxide can appear as rotating discs [10,11], rotating tubes [12], particles in fluidized beds [13,14] or moving beds [3], honeycombs [15,16] and foam structures [4,17]. Concepts with rotating parts and particles provide a good opportunity to realize heat recovery of the solid material when cycling the temperature. However, those concepts are challenging from an engineering point of view, as the moving parts typically need to reach temperatures above 1400 °C. On the contrary, honeycomb and foam structures can be operated more easily, but the possibility of solid heat recovery is very limited. So the efficiency of those concepts is expected to be lower.

\* Corresponding author.

E-mail addresses: [matthias.lange@dlr.de](mailto:matthias.lange@dlr.de), [matthias\\_lange@outlook.com](mailto:matthias_lange@outlook.com) (M. Lange), [martin.roeb@dlr.de](mailto:martin.roeb@dlr.de) (M. Roeb), [christian.sattler@dlr.de](mailto:christian.sattler@dlr.de) (C. Sattler), [robert.pitz-paal@dlr.de](mailto:robert.pitz-paal@dlr.de) (R. Pitz-Paal).

Thermochemical cycles for hydrogen were introduced by Funk et al. in the 1960s [18,19]. Thereafter, several studies of the general thermodynamics of thermochemical cycles were carried out [20,21]. More than 100 different possible cycles were examined [22]. As most studies assumed the primary heat source to be provided by nuclear reactors, the upper temperature limit of the publications of that time is about 1000 °C [23]. As no two-step cycle could be identified to be possibly operated below that temperature [20], the detailed thermodynamic analyses of that time focused on cycles with three or more steps, like for example the Westinghouse cycle [24], the sulphur iodine cycle [25] or methanol-sulphuric acid water splitting cycle [26].

Despite the nuclear energy trend of that time, already in the mid-1970s the use of solar energy was proposed to power thermochemical hydrogen generation processes [27–29]. The most prominent cycle in solar research today is the two-step cycle as shown in Equations (1) and (2), first introduced by Nakamura [5] using the example of iron oxide as the redox material. Nakamura already provided basic thermodynamic considerations of the cycle. After the second oil crisis, investigation on solar thermochemical water splitting was neglected. Renewed effort was put in research only starting from the year 2000 [30,31].

Diver et al. [10] introduced a thermodynamic model based on energy balances to stress the importance of solid heat recovery when performing the two reaction steps at different temperatures. Later studies have used more sophisticated methods to calculate the process efficiency when using specific metal oxides [32,33]. A recent trend in process operation is to perform both oxidation and reduction at the same temperature. This isothermal operation results in a lower conversion of water, which has been analysed thermodynamically by Bader et al. and Muhich et al. [33,34].

While some of the aforementioned studies include the solar to thermal efficiency, we excluded it from this analysis, thus only the thermochemical conversion efficiency  $\eta_{tc}$  is dealt with. This decoupling gives a clearer view on the thermodynamic effects occurring in the conversion process. To include the solar to thermal efficiency, one can proceed in an analogous way as described by Fletcher and Moen [35] by multiplying the maximum possible thermochemical efficiency ( $\eta_{tc}$ ) with the maximum possible absorption efficiency when assuming the absorber to be a black body. The resulting idealized system efficiency is formulated as

$$\eta_s = \left(1 - \frac{\sigma T^4}{IC}\right) \times \eta_{tc}. \quad (3)$$

This study closes the gap between the very generic work from the 1970s which provides the basic thermodynamic principles [19,20] and recent thermodynamic studies which have been applied to optimize or analyse a specific process based on a specific material and reactor concept [33,3,10]. While the focus of the following analysis is put only on two-step cycles, still a general approach is used to systematically determine the influence of process parameters on the process efficiency of two-step thermochemical cycles for water splitting. To ensure the general character, the process is analysed in a completely idealized way, only applying thermodynamic principles. Efficiency penalties that occur when operating a reactor in reality are excluded from this analysis, because the loss mechanisms depend very much on the reactor type and the process layout. The scope of this paper is limited to theoretical considerations, having two objectives. First, the paper shall extend the understanding of the thermodynamic principles that underlie two-step thermochemical cycles, especially elaborating the necessity of the second step in a vivid way by applying  $T$ – $S$  diagrams. Second, this study shall support the orientation of ongoing research in order to achieve optimal conditions for this class of reactions. Only once,

the example of ceria is used, otherwise either material-independent trends are discussed or entropy requisites towards yet unspecified materials are revealed.

## 2. $T$ – $S$ diagrams and Carnot efficiency

To determine the theoretical upper limit of the efficiency, all state changes have to be assumed reversible. Thus, the reversible, special case of the second law formulation

$$\delta Q = T dS \quad (4)$$

holds for all state changes, if not denoted otherwise. According to Eq. (4), the amount of heat  $\delta Q$  associated to an entropy change  $dS$  at a given temperature  $T$  is known. Based on this insight, the representation of thermodynamic cycles in a  $T$ – $S$  diagram is very vivid: Any process proceeding in clockwise direction receives heat at higher temperatures and releases it at lower temperatures.

Since the heat associated to an entropy change at a temperature  $T_H$  has a larger absolute value than at a lower temperature  $T_L$ , more heat is introduced than rejected. The integral of a closed curve in the  $T$ – $S$  diagram represents this difference between heat input  $Q_{in}$  and heat output  $Q_{out}$  of the process.

In order to satisfy the first law of thermodynamics, work  $W_{use}$  needs to be withdrawn to make up for the difference in heat input  $Q_{in}$  and heat output  $Q_{out}$ :

$$Q_{in} = Q_{out} + W_{use}. \quad (5)$$

The efficiency of such a process is the quotient of the work  $W_{use}$ —being pure exergy and thus the useful output—and the required heat input  $Q_{in}$ :

$$\eta_{cycle} = \frac{W_{use}}{Q_{in}}. \quad (6)$$

In the following sections, this concept of efficiency analysis will be applied on water splitting by thermochemical cycles. The influence of material properties and process conditions will be discussed. However, the analysis may not lead to the conclusion that the discussed processes can be realized. In addition to the fact that reversible processes are practically impossible, this analysis does not allow for identifying materials that are able to follow such temperature and entropy profiles. In general,  $T$ – $S$  diagrams cannot predict if a material is capable of water splitting, because the enthalpy of formation of the materials and water is not taken into account. This can be done, for example, using Ellingham diagrams, as first suggested by Bilgen et al. [36].

Wherever material properties of real substances were used, they were calculated with the software FactSage [37].

## 3. One step cycles

### 3.1. Thermolysis

In a first step, direct thermal decomposition (thermolysis) of water is examined as a starting point for the following analysis. Fig. 1 shows a theoretical process representing direct water splitting in a  $T$ – $S$  diagram, similar to the one proposed by Abraham and Schreiner [20]. The pressure is constant at 1 bar. From point 1 to point 2, liquid water is heated to its boiling temperature. Then, it is evaporated isothermally to saturated steam (point 3) which is subsequently heated to 4300 K (point 4). This is the temperature at which thermodynamics predicts water, oxygen and hydrogen to be in equilibrium, if all were at 1 bar. From point 4 to point 5, the reversible water splitting reaction takes place. Subsequently, the

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