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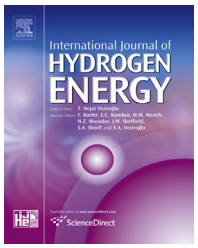

Efficiency assessment of a two-step thermochemical water-splitting process based on a dynamic process model

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ABSTRACT

Solar hydrogen production via two-step thermochemical redox cycles a promising candidate for green fuel production in the future energy market. In a European consortium, the Hydrosol concept has been developed to split water in such a thermochemical cycle. We developed a transient reactor model in order to predict the upper-limit efficiency of a large-scale process based on the Hydrosol reactor concept. The analysis shows that the state-of-the-art ferrite-based redox material properties need to be improved considerably in order to reach competitive efficiency. The two main properties that need improvement are the reaction kinetics on the one hand and the amount of oxygen that can be incorporated into and released from the redox material on the other hand.

Introduction

The reduction of greenhouse gas emissions is one of the greatest challenges the world community is facing today. Many energy transition scenarios use renewably generated hydrogen as a potential replacement for fossil fuels in the transportation sector. In addition to the potential future application, already today over 50 million metric tons of hydrogen are produced yearly. A substantial part of this goes into ammonia synthesis. This hydrogen originates from the conversion of fossil sources such as natural gas, oil and coal. In order to replace the current hydrogen production with climate neutral technologies and to support the application of hydrogen as a fuel, a great field of today's research is dedicated to the development of efficient, cost-effective and especially sustainable technologies for hydrogen production.

One path to produce renewable hydrogen is to use solar heat to drive a two-step thermochemical cycle based on redox materials. Such a process was first proposed by Nakamura et al. [1]. The reactions corresponding to this group of two-step cycles are

$$\text{Thermal reduction step (TR):} \quad MO_{ox} \rightarrow MO_{red} + \frac{1}{2}O_2 \tag{1}$$

$$\text{Water} - \text{splitting step (WS):} \quad MO_{red} + H_2O \rightarrow MO_{ox} + H_2 \tag{2}$$

In the first, endothermic thermal reduction step, the metal oxide (MO) is activated in order to split water in the second step. To run the process, mainly thermal energy is required. In order to keep the temperature of the reduction step at a

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technically reasonable level, the oxygen partial pressure in the gas phase needs to be reduced. Therefore, in this step either inert sweep gas or a vacuum need to be applied. Either option requires additional energy which has to be considered in the efficiency calculation.

The properties of the material denoted by MO impact the process efficiency substantially. To show in what direction the material development should be focused, an upper-limit efficiency analysis of a water-splitting process was carried out, varying the metal oxide properties. In this paper, the Hydrosol concept was used as a reference. The concept is based on honeycomb structure which consists of or is coated with the reactive metal oxide material. As a metal oxide, nickel ferrite is used, but that may vary in future development. To avoid any hot moving parts, the process is run in batch mode. Thus, reduction and oxidation take place successively in the same reaction chamber. The development of this concept started in 2002 and has been ongoing continuously until today [2–7]. In the current project, Hydrosol_PLANT, a 750 kW_{th} plant will be set up and test-operated at the Plataforma Solar de Almería in Spain.

The upper limit of the efficiency of thermochemical water-splitting processes has been discussed in literature before. The most generic way is to define the Carnot efficiency as the upper limit [8,9], which is true for any process driven by thermal energy. More sophisticated approaches have been elaborated for thermochemical cycles in general [10–12] and also specifically for solar-driven processes [13] and analysing specific materials or process strategies [14–17]. Although the aforementioned analyses are essential for a general understanding of the process, the absolute values of the upper-limit efficiency are rather interesting from an academic point of view. Real applications have shown considerably lower efficiencies [18,19].

In this paper, we strive to become more specific in the efficiency calculation method, making use of a reactor model and simulation runs instead of general thermodynamic considerations. Thus, the results are less universal, because they only apply to this specific process concept. However, the outcome is also considerably closer to reality. The simulation results shall guide material research by quantitatively showing what certain material improvements have on the efficiency.

Modelling

As solar receiver-reactors are not considered standard unit operations, they are not part of the model libraries of common process simulation tools, such as Aspen Plus – the tool we used for the following analysis. Therefore we developed a new model of the Hydrosol reactor. It is written in the equation-based modelling language Aspen Custom Modeler. As the Hydrosol process is subject to strong inherent dynamic behaviour, the model allows for dynamic simulation.

Reactor model

In literature, several models of the honeycomb structure are available from the field of catalytic converters [20,21]. However, they differ from the model needed for the present task. In catalytic converters, a different reaction takes place and no incoming radiation needs to be accounted for. Further, they only work at temperatures up to 600 °C. In addition to the catalytic converter models, some approaches to model the Hydrosol reactor are reported. Kostoglou et al. [22] present the most elaborate modelling work of the honeycomb, using differently-scaled models. They conclude that a 1D approach for the description of the honeycombs is sufficient. Since their work is focused only on the honeycomb, the model cannot predict the behaviour of a complete reactor.

Dersch et al. [23] created a model of the single-chamber Hydrosol reactor in the Modelica language. The model is written in two dimensions, i. e. it is rotationally symmetric. Noglik et al. adapted the model for the simulation of an SO_3-splitting reactor [24]. Neises et al. [25] changed the model by Dersch et al. to the geometry of the Hydrosol pilot reactor. As that reactor is not rotationally symmetric, all three dimensions are resolved. The model validation resulted to be not satisfactory above 1000 °C and moreover, computational speed was not acceptable for a profound analysis of the influence of different redox material properties. The model presented in this paper is designed similar to the Modelica models. However, computational speed and smooth integration into a complete flowsheet were emphasized in the present case. Therefore, a new model was developed for this study.

Fig. 1 shows the reactor design of interest. It was developed in the project Hydrosol 3D [7]. A similar design will be constructed in the successor project Hydrosol PLANT which started in January 2014. As the reactor has not been built so far, no data is available to validate the model. Therefore, a previous reactor design which has been tested extensively was modelled first for validation [26]. The design is shown in Fig. 2. In a second step, the model was adapted to the Hydrosol 3D geometry which is described by Houaijia et al. [7]. All results presented later in this paper are based on the Hydrosol 3D geometry.

In the following, the main equations describing all relevant reactor components are presented. First, the conservation equations and the discretization of the different components are described, starting at the reactor front. After that, the boundary conditions and the implementation of the kinetic formulation are presented.

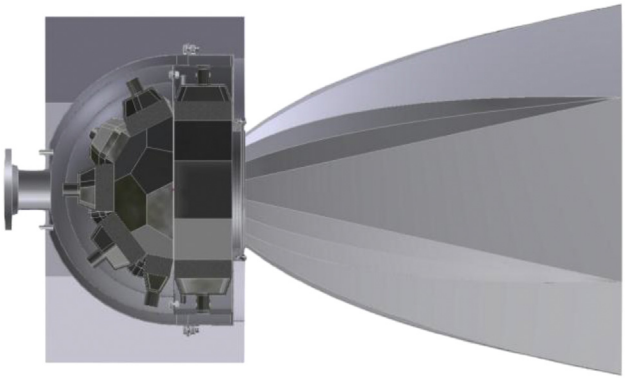

Fig. 1 – Design of the Hydrosol 3D reactor which is the final design for the simulation work.