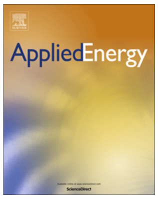
Applied Energy xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy



Thermochemical energy storage by consecutive reactions for higher efficient concentrated solar power plants (CSP): Proof of concept

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HIGHLIGHTS

- The feasibility of a novel concept for TCS for CSP is presented.
- The new concept is based on consecutive reactions.
- One cycle and two coupled cycles of consecutive reactions are exemplified.
- Poor reversibility is overcome and thus the overall CSP efficiency is improved.
- A better material stability and hence longer operational plant can be achieved.

ARTICLE INFO

Article history:
Received 4 July 2016
Received in revised form 25 September 2016
Accepted 25 October 2016
Available online xxxx

Keywords:
Thermal energy storage (TES)
Thermochemical materials (TCM)
High temperature
Concentrated solar power plant (CSP)
Consecutive reactions

ABSTRACT

Concentrated solar power plants (CSP) combined with thermal energy storage (TES) offers the benefit to provide continuous electricity production by renewable energy feed. There are several TES technologies to be implemented, being the thermochemical energy storage the less studied and the most attractive since its volumetric energy density is 5 and 10 times higher than latent and sensible TES, respectively. Thermochemical energy storage technology is based on reversible chemical reactions, also named thermochemical materials (TCM). One of the main challenges of TCM is to achieve a proper reversibility of the reactions, which in practical conditions leads to lower efficiencies than the theoretically expected. A new concept based on changing from reversible TCM reactions towards TCM consecutive reactions aims to eliminate reversibility problems and therefore improve the overall efficiency. Consecutive TCM reactions can either be based in one cycle, where reactants are needed to feed the reaction, or two coupled cycles which offer the possibility to work without any extra mass reactants input. The plausibility of the implementation of both concepts in CSP is detailed in this paper and case studies are described for each one.

1. Introduction

The fact of taking profit from renewable energies, like solar energy, and turning to sustainable and competitive energy systems is in agreement with the current world wide directives and H2020 [1]. The general target is focused on reducing fossil fuel consumption for electricity production, heating, and cooling in order to decrease CO_2 emissions and thus support climate change goals. Regarding electricity production, concentrated solar power (CSP) plants are attractive alternative technologies. CSP technologies generate electricity by concentrating the solar radiation beam onto a small area, where a heat transfer fluid (HTF) is heated up and this energy is ultimately transferred to the steam. Electricity is then generated by an electric generator which is driven by a steam turbine with the efficiency limited by the Carnot cycle [2].

Today, several countries such as USA or Spain have developed commercial CSP plants [3,4] which are using different technologies to concentrate the solar beam. Nowadays, four CSP technologies are represented at pilot and commercial scale: parabolic-trough collectors (PTCs), linear Fresnel reflector (LFR) systems, power towers or central receiver systems (CRS), and dish/engine systems (DE). All existing plants imitate parabolic geometries with large surface area for the mirrors [4].

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http://dx.doi.org/10.1016/j.apenergy.2016.10.093
0306-2619/

Energy production is restricted when sun shines, therefore, a system that allows storing solar heat is required. In case of not having problems with sun shine, a producer company might want to store the energy as a function of the price of kWh on the market (to increase company benefits). For this purpose a thermal energy storage system (TES) is essential. TES is becoming particularly important for electricity storage in combination with concentrating solar power (CSP) plants where solar heat can be stored for electricity production when sunlight is not available [5,6].

Proposed mechanisms to store thermal energy are based on different physical or chemical principles: sensible heat (molten salts, solid particle materials, etc.), latent heat by means of phase change materials (PCM), and thermochemical heat storage (TCS) using thermochemical materials (TCM) [7–13]. Nowadays, the use of molten salts is the most viable alternative for TES coming from solar heat to supply intermittent power demand. Nevertheless, molten salts cannot provide a temperature or an energy density as high as the TCS due to the mechanism itself. From a theoretical point of view the use TCS is a challenge that can provide higher storage of energy for longer periods and operate at higher temperatures compared to the other mentioned systems. Consequently, implementing TCS technology would allow increase efficiency of a CSP plant [5,6]. This topic has experienced a remarkable increased perception in the last few years and thus several studies are being published. For instance, modeling of redox reactions where the model is shown to track complex trends in measured non-stoichiometry data, specific heat capacity, and global heats of reaction with respect to changes in T and p_{O2} [14], novel concepts based coupling a CSP-CaL process and CO_2 power cycle [15], cascade thermochemical storage with internal condensation [16], algorithm for searching potential thermochemical energy storage for a wide temperature range (25–1000 °C) [17], etc.

Actually, TCS for CSP is based on reversible reactions with high enthalpy of reaction but these reactions presented low efficiency and poor reversibility. The trend is to use heterogeneous reactions (solid-gas) to facilitate the removal and transport of the gases involved in the reaction. Redox systems based on oxide pairs, i.e. Mn_3O_4/Mn_2O_3 [12,13] are the most used to achieve the requirements and maintain material stability. The storage mechanism can be defined as depicted in Eq. (1):

$$A_{(s)} \underset{\text{heat release exothermic reaction}}{\overset{\text{heat storage endothermic reaction}}{\rightleftarrows}} B_{(s)} + C_{(g)} \tag{1}$$

During the charging process (endothermic reaction), solar thermal energy is used to move the reaction from the solid reactant (A) (sometimes together with a gas reactant) to products B (solid) and C (gas). During this step, the TCM is absorbing the heat concentrated at the solar receiver. The storage process consists on keeping B and C products separated. In order to discharge the system (exothermic reaction), the former solid product, B, is placed in contact with the gas C, to react and thus release the chemical reactions energy between the product stored.

The problem that is seen from the TCS systems prototypes is that the reaction must be reversible and this premise is not being fully achieved. This implies that the chemical conversion and reversibility of the reaction [18,19] is not fulfilled and therefore the storage capacity differs from the expected. This makes difficult to find a TCM that can be adjusted to the theoretical model and in all, it will be difficult to implement TCS systems with the established premises.

The main objective of this paper is to demonstrate the feasibility of a new concept of a CSP plant with solar central receiver reactors technology implementing thermochemical materials. This concept overcomes the drawback of the poor reversibility and low efficiencies in high temperature storage by changing from the reversible reactions towards TCM consecutive reactions. To illustrate this, two case studies are shown, one for a one cycle of TCM consecutive reactions and another for two coupled cycles of TCM consecutive reactions.

2. Consecutive TCM reactions

Two different concepts, one based on one cycle and the other based on two coupled cycles of consecutive TCM reaction were developed [20,21] and are presented in this section.

2.1. One cycle TCM consecutive reaction, a case study Zn + CO_2

2.1.1. General concept

The general concept of one cycle of TCM consecutive reactions is depicted in Fig. 1. The initial solid A is transformed into another solid B and a gas C, this last solid reacts with another gas D, giving the initial solid A and a gas E. The consecutive reaction can be running being the only input the gas D in the second reaction.

2.1.2. Case study: chemical basis

As an example of this concept, the ZnO/Zn cycle is considered. The first step is the endothermic thermal reduction ($\Delta H_{298K} = 350.85\ \text{kJ·mol}^{-1}$) of zinc oxide and can be referred as the solar step (Eq. (2)). The second step, the non-solar step (Eq. (3)), is the exothermic reduction ($\Delta H_{298K} = -67.87\ \text{kJ·mol}^{-1}$) of CO_2 with zinc to generate CO and ZnO [22,23].

$$ZnO_{(s)} \rightarrow Zn_{(g)} + \frac{1}{2}O_{2(g)} \tag{2}$$

$$Zn_{(g)} + CO_{2(g)} \rightarrow ZnO_{(s)} + CO_{(g)} \tag{3}$$

The thermal reduction of ZnO can be performed at 1627–1727 °C [24,25] at 1 bar and inert atmosphere (N_2 or Ar). After this thermal reduction, zinc is obtained in gas form (T_b = 912 °C) [26]. Afterwards, in the non-solar step, the produced Zn gas reacts with CO_2 giving the initial oxide (solid) and CO. This second reaction may be performed at temperatures below ZnO thermal decomposition. However, it presents a high resistance due to the formation of an oxide layer which slows the reaction (Fig. 2) which drops the chemical conversion [23]. This phenomenon can determine the working temperature, because at temperatures lower than 912 °C it has a low rate and conversion, but above 912 °C it would work in the gas phase. Some studies that perform CO_2 splitting using liquid Zn achieved less than 50% of Zn conversion at 500 °C [22,23,27,28]. Having a phase change can facilitate the reduction of the thermal reduction temperature through decreasing the system pressure.

Table 1 shows the enthalpy of each reaction of the thermochemical heat storage system. The optimal working temperature (T_w) and the maximum chemical efficiency (X) calculated in bibliography or estimated have been taken into account. Therefore, three values of enthalpy are shown at 25 °C, at optimum Tw and,

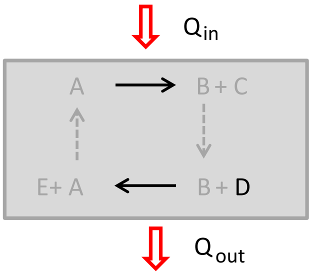

Fig. 1. Simplified scheme of the consecutive reactions concept: one cycle.

Please cite this article in press as: Cabeza LF et al. Thermochemical energy storage by consecutive reactions for higher efficient concentrated solar power plants (CSP): Proof of concept. Appl Energy (2016), http://dx.doi.org/10.1016/j.apenergy.2016.10.093