Dynamic simulation and optimal heat management policy of a coupled solar reforming–heat storage process

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Abstract

This work is a first simplified approach on the exploitation of “direct” solar heat during on-sun operation, and stored solar-heat through thermochemical energy storage involving redox pair cycles during off-sun operation, for the production of solar hydrogen using concentrated solar energy. The coupling of the processes in a compact solar reforming-thermochemical heat storage system is conducted in terms of a lumped dynamic model; for the determination of the syngas composition in the reforming unit, thermodynamic equilibrium is assumed, while the required heat to facilitate the endothermic reforming reactions is provided by either solar heat (on-sun operation), or a combination of stored energy and an optimal linear profile of external heat provision (off-sun operation). The optimal heat management policy for the reduction or the oxidation step (during the solar heat storage and release process) ensures a steady H2 molar fraction for most of the operating time. It is revealed that the coupled scheme suggested is an in-principle viable option for sustainable H2 production, since reforming needs are entirely complemented by solar heat also supplying the required energy input for the storage unit, which in turn may provide almost 25% of the overall reforming energy needs under off-sun operation.

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1. Introduction

Concentrated solar power (CSP) technology has gained substantial worldwide attention from both industrial and research communities, with the aspiration of providing fully renewable energy (Pagkoura et al., 2014; Sakellariou et al., 2015). Complete exploitation of a CSP system requires the integration with thermal energy storage (TES) due to the intermittent nature of solar radiation; a category of TES systems is the thermochemical heat storage (TCS) based on reversible chemical reactions occurring in at least 2 steps. Combination of solar heat produced in CSP systems with TCS systems leads to solar thermochemical energy storage processes (Wu and Long, 2015). The TCS concepts have been applied in a number of different reactions schemes involving carbonation/decarbonation or hydration/dehydration of calcium oxide (CaO/CaCO3, CaO/Ca(OH)2) (Sakellariou et al., 2016), hydration/dehydration of magnesium oxide (MgO/Mg(OH)2) (Sakellariou et al., 2015), reduction/oxidation of cobalt, manganese or barium oxides (CoO/Co3O4, Mn3O4/Mn2O3 and BaO/BaO) (Agrafiotis et al., 2015a,b; Carrillo et al., 2014, 2016; Karagiannakis et al., 2014, 2016, Pagkoura et al., 2016). Block and Schmucker (2016) compared several metal oxide systems and concluded that systems containing cobalt oxide are promising as TCS materials. For a typical envisaged CSP-TCS coupled system, excess heat from the solar field during daylight can be directed to drive an endothermic...

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mic reaction in the TCS system (e.g. reduction of a high valence metal oxide to a lower valence one), thereby being stored as chemical energy. During off-sun operation, the reverse exothermic reaction (e.g. oxidation of the low valence oxide) is triggered so that previously stored energy is released to the heat transfer fluid and ultimately used to drive the power block. This concept can in-principle be extended to cover the requirements of solar-driven endothermic chemical reactions for the generation of useful products during periods that solar energy is not available. A prominent such example is steam methane reforming (SMR) for hydrogen production (Agrafiotis et al., 2014; Said et al., 2016).

SMR, which accounts for over 40% of the world’s H2 production (Pantoleontos et al., 2012), is a highly endothermic reaction scheme. Various efficiency values are reported in the literature for the SMR process depending on the operating conditions and the mode of thermal integration. Peng (2012) reported that the steam methane reforming process in industrial practice has a high thermal efficiency (excluding the electric power involved in the process) ranging from 80 to 90% on the higher heating value basis. Lutz et al. (2003) anticipate that the upper limit of thermal efficiency is 85% by conducting an equilibrium analysis of steam reforming, that is neglecting kinetic or diffusional limitations within the reforming reactor. Simpson and Lutz (2007) improved upon the previous model by using more detailed heat integration and calculated a maximum thermal efficiency of 66.7%.

Energy analyses reveal that 66% of the losses in the SMR process occur in the reforming unit (Hajjaji et al., 2012; Rosen, 1991). The majority (~30%) of the exergy destruction in the SMR process is attributable to the high irreversibility of combustion and heat transfer between reformer and furnace (Simpson and Lutz, 2007). Boyano et al. (2012) calculated that in an SMR plant ~60% of exergy destruction occurs in the combustion chambers and the reforming units. Furthermore, around 20–30% of CH4 is combusted as a fuel in the reformer furnace to support the endothermic reforming reactions resulting in additional energy penalty (Boyano et al., 2014). Apparently, it is essential to focus on the reforming unit performance, which can be further revised by providing heat coming from renewable (solar) sources, and thus, enhance the performance of reforming units in terms of process economics and carbon emissions avoided.

Coupling of TCS with solar reforming units has not been studied in the corresponding literature under a modelling and dynamic simulation framework. A prominent example of modelling CSP plants coupled with storage unit can be found in Ireland et al. (2014); similarities with dynamic process modelling studies are traced to the work by Jiang et al. (2005), who contemplated the coupled behaviour of a fuel cell with a hydrogen storage metal-hydride bed, a desalination unit coupled with solar collectors and a water storage tank (Ben Bacha et al., 2007), a coupled air receiver and a TCS system for solar thermal power plant (Li et al., 2016), and a solar driven membrane distillation desalination system (Chang et al., 2010).

The present study is an investigation on how a redox TCS scheme can be coupled, in an optimized way, to a solar methane reforming process in order to ensure that the requirements of the latter can be partially covered under off-sun conditions for as much time as possible. The overall novel approach (CONTISOL project) is based on a compact honeycomb receiver/reactor/heat exchanger configuration with non-porous channel walls (Fend et al., 2011; Hoffschmidt et al., 2008; Roeb et al., 2012), able to accommodate two distinct flows; namely a reforming feedstock and a heat transfer fluid (air) towards/from the redox TCS system with the inlet and outlet of the two flows separated to avoid gas mixing (depicted in Fig. 1). Operational experience so far has proven that honeycomb structures made of SiC or SiSiC are excellent candidates for high-temperatures processes. Similar SiC-based honeycomb structures are routinely used at industrial scale, such as the extensive commercial diesel particulate filters in automotive emission control. Another emerging application, already extensively validated at demo scale, is the use of SiC-based honeycomb-shaped modules as building blocks of open volumetric air receivers for high temperature solar

Figure 1 – Monolith structure counter-current flow configuration for reforming purposes. Adapted from Lange et al. (2015), Lange et al. (2016) and Roeb et al. (2012).
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