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Thermodynamic analysis of reversible hydrogenation for heat storage in concentrated solar power plants

Christoph Krieger, Karsten Müller *, Wolfgang Arlt

Friedrich-Alexander-Universität Erlangen-Nürnberg, Institute of Separation Science and Technology, Germany

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Abstract

Heat storage in concentrated solar power plants is required to compensate for variable availability of solar radiation. The energy density achievable with thermochemical heat storage is higher than for molten salt which represents the state of the art technology. The efficiency of different reversible hydrogenation reactions as thermochemical heat storage systems have been examined, since they can be operated at appropriate temperatures. Thermal efficiency of reversible hydrogenation based thermal energy storage can reach values up to 65.9% and an overall efficiency of up to 23.1% compared to 25.7% without heat storage. The LOHC dibenzyltoluene and the metal hydride magnesium hydride turn out to be most suitable for this application.

Keywords: Thermal energy storage; LOHC; Metal hydride; Thermodynamics

1. Introduction

Four different types of collectors are used in concentrated solar plants (CSP): Parabolic trough collectors, Fresnel collectors, parabolic dish collectors and solar towers. In this contribution only CSP used for power generation, are examined. Parabolic dish collectors usually have a Stirling engine in the focus of the radiation if used for production of electricity. In all other collector systems the heat is transferred to a heat transfer fluid and afterwards to a thermal energy storage (TES) system or directly to a steam power station.

To adjust the supply of electricity to the demand either a storage system for electrical energy or a TES system is needed. TES has relatively low investment cost and exhibits high operating efficiencies (Kuravi et al., 2013). For CSP sensible heat storage is the state of the art technology, while latent heat storage is currently implemented on pilot scale and thermochemical system on laboratory scale (Gil et al., 2010). Kuravi et al. (2013) compared the temperature level and energy density of the different classes of TES in CSP, but not the energetic efficiency.

The most common collectors in CSP are parabolic trough. CSP systems based on Fresnel collectors reach a similar temperature level. Due to the similarity of these two collector systems only parabolic trough collectors are examined in this paper.

Oil heated by parabolic trough collectors can reach temperatures of about 390 °C (Gil et al., 2010). Molten salt (sodium (60%) and potassium nitrate (40%)) freezes at relatively high temperatures (120–220 °C), which should be prevented (Falchetta et al., 2010; Gil et al., 2010). The

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* Corresponding author. Tel.: +49 9131 8527455; fax: +49 9131 8527441.
E-mail address: karsten.mueller@fau.de (K. Müller).

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Nomenclature

h	enthalpy (J/mol)
n	amount of substance (mol)
P	pressure (Pa)
Q	heat (J)
T	temperature (K)
V	volume (m^3)
W	work (J)
X	conversion (–)
Greek letters	
Δ	difference (–)
η	efficiency (–)
Subscripts	
ads	adsorption
coll	collector
cool	cooling
compr	compressor
dehyd	at dehydrogenation reactor
el	electric
HE	heat exchanger
hyd	at hydrogenation reactor
isen	isentropic
L	liquid
pg	power generation
pre	preheating
r	reaction
rad	radiation
th	thermal
V	vapor
LRMH	low reaction enthalpy metal hydride
MS	molten salt
MSH	marlotherm
NEC	N-ethyl-carbazole
TOL	toluene

temperature difference between the system and its surroundings causes heat losses. Therefore, molten salt can require additional heating to prevent temperature drop below a certain level, which can occur during long storage times and service maintenance. Thermochemical TES offers the highest energy densities and no thermal losses over time. Hence, heat storage in CSP with thermochemical storage systems represents an interesting technology. Different systems for thermochemical heat storage on high temperature levels are currently under research, such as carbonates, hydroxides, ammonia and organic systems (Pardo et al., 2014). Metal hydrides, ammonia and some organic systems release hydrogen when used as a TES system. The storage density of these systems is close to each other. Felderhoff and Bogdanovic (2009) tested the storage of high temperature heat through metal hydrides and Lovegrove (Lovegrove and Luzzi, 1996; Lovegrove et al., 2004) et al. examined ammonia production and its dissociation for the same purpose. Pfeifer and Dittmeyer are currently testing liquid organic hydrogen carriers (LOHC) for TES applications (Kreuder et al., 2015; Ulmer et al., 2013). However, these systems are not compared to each other. In this contribution these systems are examined thermodynamically and the optimal system in terms of efficiency is determined.

2. Reversible hydrogenation for heat storage

2.1. Description of the systems

In a hydrogenation reaction hydrogen is bond to a carrier substance. The endothermic dehydrogenation reaction is performed when excess heat is generated in the collector. The exothermic hydrogenation reaction is performed when intensity of solar radiation is insufficient for power generation. Thermodynamically the hydrogenation reaction is done preferably at high pressures and low temperatures. However, high temperatures in the hydrogenation reaction are needed for high efficiencies in the steam power plant. Hydrogenation reactors, withstanding high temperatures and pressures, are well known e.g. from the Haber–Bosch process. In Fig. 1 the schematic of this process is shown.

Hydrogen has to be stored after the endothermic dehydrogenation reaction. Elemental gaseous hydrogen exhibits a very low density at atmospheric pressure. Therefore, density has to be increased to store hydrogen effectively.

In this study LOHC materials, metal hydrides and ammonia are compared to each other as TES systems. Below, the different TES systems examined and the storage possibilities of hydrogen after dehydrogenation are presented.

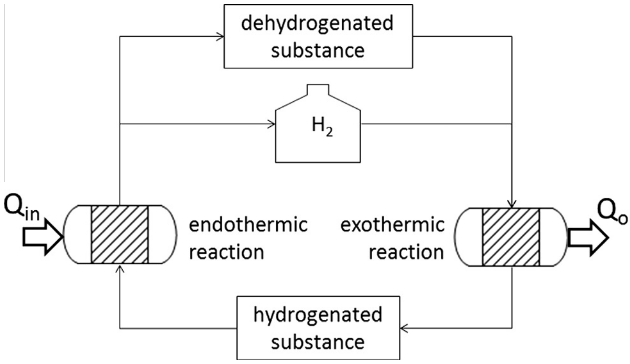

Fig. 1. Schematic of reversible hydrogenation for heat storage.