Applied Energy 183 (2016) 113–120

Contents lists available at ScienceDirect

Applied Energy

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

Systematic search algorithm for potential thermochemical energy storage systems

Markus Deutsch [a,*], Danny Müller [b], Christian Aumeyr [b], Christian Jordan [a], Christian Gierl-Mayer [c], Peter Weinberger [b], Franz Winter [a], Andreas Werner [d]

[a] Institute of Chemical Engineering, Vienna University of Technology, 1060 Vienna, Austria
[b] Institute of Applied Synthetic Chemistry, Vienna University of Technology, 1060 Vienna, Austria
[c] Institute of Chemical Technologies and Analytics, Vienna University of Technology, 1060 Vienna, Austria
[d] Institute for Energy Systems and Thermodynamics, Vienna University of Technology, 1060 Vienna, Austria

HIGHLIGHTS

- An automated search for reaction systems suitable for thermochemical energy storage was performed.
- Algorithm to build reaction systems for thermochemical energy storage is presented.
- Close to 1000 possible reaction systems for 5 different reactive gases were found.
- The VIENNA TCES-database for thermochemical energy storage materials is presented.

ARTICLE INFO

Article history:
Received 3 June 2016
Received in revised form 16 August 2016
Accepted 25 August 2016

Keywords:
Thermochemical energy storage
Database
Systematic search
Storage material

ABSTRACT

Thermochemical energy storage (TCES) is considered as an emerging green technology for increased energy utilization efficiency, thereby achieving a reduction of greenhouse gases. Various reaction systems based on different substance classes (e.g. hydrates, hydroxides, oxides) were suggested and investigated so far. Nevertheless, the number of know reactions which are suitable is still limited, as the main focus concentrates on the investigation of a handful known substances, their further improvement or applicability. To find novel promising candidates for thermochemical energy storage and also to allow for a broader view on the topic, this work present a systematic search approach for thermochemical storage reactions based on chemical databases. A mathematical search algorithm identifies potential reactions categorized by the reactant necessary for the reaction cycle and ranked by storage density. These candidates are listed in the online available VIENNA TCES-database, combined with experimental results, assessing the suitability of these reactions regarding of e.g. decomposition/recombination temperature, reversibility, cycle stability, etc.

1. Introduction

Research on the topic of thermochemical energy storage (TCES) has experienced an increased perception in the last few years. This is primarily driven by the possibility to reduce CO_2 emission by energy savings in buildings and industrial sectors and reducing waste thermal energy on a national and continental scale [1]. In this context TCES is of special interest due to is applicability in a wide temperature range and for a variety of applications.

The International Energy Agency (IEA) distinguishes three temperature levels for heat: low (<100 °C), medium (100–400 °C) and high (>400 °C) [2].

The low temperature level represents the typical household application. There, TCES can be used for heating and cooling, often in combination with solar energy [3].

The medium temperature level comprises mainly waste heat sources from industrial applications, which are a major cause of energy inefficiency [4]. Waste heat occurs when heat is used within production processes either in form of process steam or in fired furnaces [5]. In electricity production about 66% of the total primary energy input are lost during the conversion from heat to electricity [6]. A higher conversion rate to electricity is hampered by the comparably low efficiency of the available processes (e.g.

* Corresponding author.
E-mail address: markus.deutsch@tuwien.ac.at (M. Deutsch).

http://dx.doi.org/10.1016/j.apenergy.2016.08.142
0306-2619/

the energy efficiency of the organic rankine cycle (ORC) process at the cement plant in Lengfurt, Germany, is at only 12.8% [7]). The use of waste heat as heat itself is often not possibly due to the fact that supply and demand cannot be matched temporally or the distances between producer and customer are too large [8]. TCES can be used to improve the energy efficiency of processes, by bridging the temporal and/or spacial gap between the producer of waste heat and potential consumer (e.g. from the heat production site to a local heating district or in a batch process, from the cool down of one cycle to the heat up of the next) [9].

In the high temperature level TCES can be used for specialized applications. In cars 60% of the fuel energy are lost as heat, mostly through the exhaust at a temperature up to 800 °C [10]. TCES can be used to recuperate parts of this energy and use it for minimizing the warm-up period of the exhaust track at the next cold start [11]. TCES can also be combined with concentrating solar plants to increase their production into times with low sunlight (e.g. when the sun is blocked by clouds or after sunset) [12,13]. For this application materials for temperatures of 800 °C or higher are needed.

TCES is based on a reversible chemical reaction (1). Heat is consumed, while decomposing material A into two products B and C, thus storing the reaction energy ΔH_R in the products. To discharge the system, both products B and C react under formation of A, now releasing the stored energy.

$$\nu_A A + \Delta H_R \rightleftharpoons \nu_B B + \nu_C C \tag{1}$$

The direction of the reaction, which strongly depends on temperature, is given by the sign of the Gibbs energy ΔG_R:

$$\Delta G_R^T = \Delta H_R^T - T\Delta S_R^T \tag{2}$$

with $\Delta H_R^T = \sum_i \nu_i \Delta H_i^T$ and $\Delta S_R^T = \sum_i \nu_i \Delta S_i^T$, where ΔS_R^T being the reaction entropy (it can be assumed that $\Delta S_R > 0$ for the given notation of reaction (1)). If the reaction is in equilibrium then $T = T_{equ}$ and $\Delta G_R = 0$. For $T > T_{equ}$ follows that $\Delta G_R < 0$, which means the system reacts from left to right (decomposition), if $T < T_{equ}$ then $\Delta G_R > 0$ and the system reacts form right to left (recombination). The equilibrium temperature T_{equ} can be calculated iteratively from (2) by

$$T_{equ} = \frac{\Delta H_R^{T_{equ}}}{\Delta S_R^{T_{equ}}} = \frac{\sum_i \nu_i \Delta H_i^{T_{equ}}}{\sum_i \nu_i \Delta S_i^{T_{equ}}} \tag{3}$$

Since ΔH_i^T and ΔS_i^T differ for each substance, each reaction system has a specific T_{equ}. For an efficient use of TCES it is crucial that the equilibrium temperature of the applied reaction system fits to the temperature level of the heat source.

The fundamental process for TCES is depicted in Fig. 1. The charging reaction occurs in reactor 1, thereby decomposing the storage material A to B following reaction (1). Depending on the reaction system it may be necessary to store the produced gas C. The heat input is generally realized using a carrier gas. It is obligatory that the carrier gas is inert in terms of the reaction system, so no side reactions occur. The charged material B reacts with C back to A in reactor 2, releasing the previously stored energy. Again, in most processes a heat carrier gas will be used to transport the heat out of the reactor 2, which can be the reactive gas itself or an inert gas. It has to be noted that the temperature in reactor 1 T_1 has to be above T_{equ} of the reaction kinetic of the reaction system, while in reactor 2 it has to be vice versa ($T_2 < T_{equ}$) at the given process conditions. The required temperature spread $T_2 - T_1$ strongly depends on the reaction system and the process conditions. Reactors 1 and 2 can be located at different sites with a material transport system between them, e.g. trucks transporting the material. Another possibility would be to use only one reactor for both charging and discharging at different times in a batch process. Thus, on-site material storage would be needed for this case.

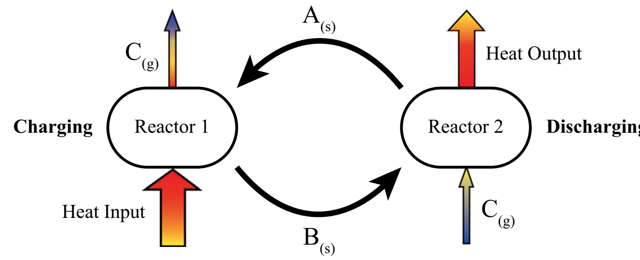

Fig. 1. Schematic principle of TCES.

There are various reaction systems in development at the moment. For the low and middle temperature level mainly salt hydrates [14], like $CaCl_2 \cdot 6H_2O/CaCl_2$ [15,16] and $MgSO_4{\cdot}7H_2O/MgSO_4$ [17,18] are currently investigated. Pardo et al. [19] concluded that the most promising reaction systems for the high temperature level are $Ca(OH)_2/CaO$ [20] and $PbCO_3/PbO$ [21]. For solar applications, also reactions of metal oxides are shifting in the focus of the research [22,23].

The wide temperature range in which TCES can be utilized and the diversity of the reactions applicable for TCES create the necessity of a comprehensive database with different TCES reaction systems. This database helps the consumer to select an appropriate TCES reaction system for a given application purpose. The basis for such a database is a systematic screening to find reaction systems for a wide temperature range. So far, only one systematic approach to screen for TCES materials is known to the authors. N'Tsoukpoe et al. performed a systematic evaluation of 125 salt hydrates for TCES at low temperature levels with the main focus on a household application. They first discriminated based on material safety and past experiences, then focused on thermal analysis to find suitable candidates for TCES. The 125 salt hydrates where identified using a thermochemical database, but no detailed information on how they were identified was given [24]. In this work, reaction systems were identified for a broad temperature range (25–1000 °C). The use of an algorithm to find reaction systems results in an objective, comprehensive list, which is not based on prior knowledge of the researcher.

2. Search for potential storage systems

2.1. Goal of the search

With this systematic search approach for potential TCES systems the goal of the authors is the provision of an TCES database, where different kinds of principally suitable TCES reactions, sorted by temperature regime regarding their potential applicability, are listed. The entries in the database include products and educts of the reaction, equilibrium temperatures and, for selected promising candidates, also experimental data regarding material properties, reversibility of the TCES reaction, cycle stability and storage density. In a second step thermodynamic data and kinetic information will be supplemented. Below, the database search algorithm yielding potential TCES systems is described, for further details on the database see Section 3.

2.2. Basis of the search

The focus of this work lies on the search for potential TCES systems. In this first approach the search was narrowed to reactions of solid inorganic substances with a reactive gas, following general reaction

$$\nu_A A_{(s)} \rightleftharpoons \nu_B B_{(s)} + \nu_C C_{(g)} \tag{4}$$