



# State of the art on gas–solid thermochemical energy storage systems and reactors for building applications



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## ABSTRACT

Thermal energy storage (TES) is moving towards thermochemical materials (TCM) which present attractive advantages compared to sensible and phase change materials. Nevertheless, TCM are more complex to characterize at lab scale and also the implied technology, which belongs to the chemical engineering field, needs to be contextualized in the TES field. System configurations for thermochemical energy storage are being divided into open/closed storage system and separate/integrated reactor system. Reactors, which are the core of the system, are the focus of this paper. Different gas–solid thermochemical and sorption reactors for building applications are reviewed from lab to pilot plant scale, from 0.015 to 7850 dm<sup>3</sup>. Fixed bed reactors are the most used ones. Mainly, mass transfer is limiting to achieve the expected energy density. The geometry of the reactor and contact flow pattern between phases are key parameters for a better performance.

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## 1. Introduction

There is a global aim to reduce energy consumption since humans are using finite resources and contributing to environmental

pollution. A part of becoming aware of this problem, engineers and scientists are focused on renewable energy sources and on improving energy efficiency of heating and cooling systems. Thermal energy storage (TES) is needed to capture thermal energy when available and to release it when demanded and for temperature control. Thermal storage applications have been proved to be efficient and financially viable, yet they have not been exploited sufficiently [1].

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Regarding TES systems for building comfort applications, several big projects are being carried out, for instance Dronninglund Solar District Heating Plant in Denmark is now established. It consists of 37,000 m<sup>2</sup> collectors (26 MWh) and 60,000 m<sup>3</sup> seasonal storage. In February 2014, the Dronninglund Solar District Heating Plant started operation serving the 1400 connected customers. The collector field together with the seasonal storage covers around 50% of the total annual heat load [2]. Present heat production in kW and W/m<sup>2</sup> is available in [3].

TES systems can be classified by the process undergone by the storage material: sensible, latent and thermochemical. Sensible storage is based on transferring heat to the material which leads to an increase of the material temperature itself. Latent storage implies storing heat when a phase change of the material (PCM) occurs. This last process usually carries also sensible heat storage, before and after the phase change process. Then, thermochemical storage is based on thermochemical materials (TCM) undergoing either a physical reversible process involving two substances or reversible chemical reactions (Eq. (1)). Endothermic processes absorb energy (heat), which can be stored as long as desired until the reverse (exothermic) process is forced. When the exothermic process takes place, the released heat can be then used for instance, for domestic hot water (DHW) and heating building applications. Since the storage is based on the molecular bonds formation, the energy is neither lost to the ambient nor transformed if the material is kept at certain conditions. This great advantage makes the TCM suitable for long-term storage, also known as seasonal storage, since heat from summer can be stored to provide heat at winter times.



TCM materials have other advantages when compared to sensible and phase change materials (PCM). TCM present higher energy densities [4], which lead to a lower volume of the storage tank, thus compact systems. On the other hand, corrosion of metals used to build up reactors containing TCM is one of the main drawbacks to overcome. From a material point of view mass transfer is a key issue when selecting the material. Salt hydrates (which are one big group of TCM) tend to form a compact block which is inhibiting the reversibility of the reaction. Furthermore, additional heat is needed to reach the discharging reaction temperature.

Depending on the system configuration that is chosen to implement TCM for building applications (see Section 2), the equipment is composed of the reactor, heat exchangers, vessels, evaporator/condenser, solar collectors, valves and piping. In order to design the main equipment, the reactor, several steps need to be followed. From the system design further research is still needed to resolve practical aspects before commercial implementation [5]. And focusing on the reactor, there is still a big field of research to promote mass and heat transfer playing with the inside geometry and/or reactor kind. The design and operation of reactors nowadays require computer skills, but such computation must be based on a firm grasp of the principles of chemical reaction engineering. First, reaction kinetics, thus reaction rate, is needed to be experimentally determined for the specific operating conditions [6]. Then, once the equation of reaction rate is experimentally obtained, mass and heat balances are formulated depending on the reactor type. All these equations gathered give variables profiles (concentration, pressure, temperatures, etc.), volume, and let do predictions for further cases as well as optimization.

The main objective of this paper is to review the available equipment currently used for thermochemical energy storage, concerning all system configuration and especially gas–solid reactors for building comfort applications, providing obtained results, at lab and pilot plant scale. Furthermore, gas–solid chemical reactors already available in the literature and industry are exposed to be related with the developed ones for TES by TCM.

## 2. Gas–solid TCM reactors and system

Different concepts and applications based on TCM have arisen to fulfil the global aim to reduce energy consumption and to efficiently use renewable energies or to use waste heat. Prototypes for both high temperature and building applications are being built up to test this concept. For instance, directly irradiated rotary kiln for high temperature reactions (around 900 °C) has been set up and performed for thirty cycles with no evident degradation of the material [7].

More effort is needed in the system design part regarding TCM reactors for building comfort. This application implies that a solar collector should be able to provide the charging reaction temperature (maximum 150 °C) to the reactor containing the TCM. Also, a big challenge is that the volume of the final system should fit in a single family house and be cost competitive to the actual heating systems.

As shown in Section 4.1, reactors can be classified by the present phases of the reactant materials. Here, the aim is to focus on gas–solid TCM (Eq. (2)) and building comfort applications (i.e. heating, cooling, and domestic hot water (DHW)), and being water the gas reactant (working fluid).



In TCM TES field, the chemical reaction is used for the production of energy instead of a specific product. The operating principle is to charge (dehydrate) the solid TCM with solar heat from a solar collector. This endothermic reaction releases water vapour. The storage process is therefore based on maintaining separately released water from the dehydrated TCM. When combining again the dehydrated TCM and water vapour, heat is released and can be used for space heating and DHW.

Despite the reactor is the core of the system, other essential concepts and components are needed to be considered for TES: the working fluid, a low heat source and an evaporator/condenser (depending on the system).

The working fluid is usually water because of its high vaporization enthalpy, availability, non-toxicity and low price. Ammonia is also a candidate [8], but then another heat exchanger (ammonia/water or ammonia/air) is needed to provide the heating fluid to the building.

### 2.1. TCM systems classification

The existing thermochemical energy storage system configurations can be divided following an overall vision of the complete system.

#### 2.1.1. Separate or external vs. integrated reactor

In the integrated reactor system, the absorption/release of energy (reaction) occurs within the storage vessel while the separate reactors concept consists in transporting the TCM from the storage vessel to the reactor and to another storage vessel, after reacting, as illustrated in Fig. 1.

The integrated concept requires no solid material transport, thus less pump power consumption (see Fig. 2, left). Nevertheless, all the material, instead of a portion, needs to be preheated to reach the discharging temperature and the control of the reaction is more complex. In the separate reactor concept the material is transported between the reactor and the material storage vessel, therefore more vessels are needed (at least two more). The advantage of being in separate vessels is that the reaction is reduced to only a small part of the total material amount [9], so the reactor volume is much smaller which leads to a lower pressure drop and less complex process control.

Another possible classification would look at the type of reactor (see Section 4.2): fixed bed reactor, moving bed, and fluidized bed. Specifically, in TCM, fixed bed is the most used one.

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