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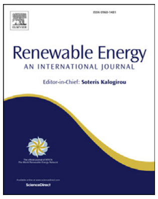

Adsorbent working pairs for solar thermal energy storage in buildings

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ABSTRACT

In this study, the thermodynamic analysis of several adsorption working pairs for adsorption heat storage applications at domestic level is presented. The selected working pairs employ different working fluids (i.e. water, ethanol, ammonia, methanol) and different adsorbent materials such as classical zeolites, silica gels, alumino-phosphates, composite sorbents and activated carbons. The simulations have been performed taking into account desorption temperatures in the range between 80 °C and 120 °C, compatible with non-concentrating solar thermal collectors, under seasonal heat storage working conditions. The composite sorbent MWCNT-LiCl with both water and methanol as working fluid showed the highest heat storage density under practical working boundary conditions. Among the standard adsorbents, the zeotype AQSOA Z02 showed promising achievable heat storage densities. Classical working pairs, such as zeolite 13X/water, commonly employed for heat storage applications, are not suitable for this working range. Finally, also the influence of the metal to sorbent mass ratio, due to the heat exchanger, was investigated, demonstrating that it can reduce the achievable amount of heat released to the user up to 30%.

1. Introduction

Renewable heating and cooling (RHC) sector, which mainly comprises solar thermal, geothermal and biomass energy, has been defined as the "sleeping giant" in 2011 by the European Renewable Energy Council (EREC) in the "Re-thinking 2050" document [1]. Indeed, it is expected that RHC will represent approximately 21% and 45% of the total final energy consumption in 2030 and 2050 respectively [1]. Among the RHC technologies, solar thermal seems the most promising thanks to its wide availability as well as to the reached technological maturity, which is making it as a valid alternative not only for standard applications (e.g. domestic hot water production, space heating), but also for more advanced applications (e.g. industrial heat, solar cooling) [2]. Nevertheless, there are still open research and development topics that may increase efficiency as well as cost effectiveness of solar thermal energy technology in order to promote and stimulate its deployment at large market scale. At the components level, the main fields of research are oriented towards solar thermal collectors, control and performance assessment and thermal energy storage [2]. Particularly, thermal energy storage (TES) is a crucial component in a solar thermal system, in order to cover the mismatch between energy supply and demand, thus increasing the achievable solar exploitation [3]. For this reason, it needs to be further investigated and optimized, in order to increase energy storage density and to limit energy losses through the environment during its operation [2]. Considering its working principle, thermochemical TES could be considered as the most promising solution to fulfil these technological needs [4]. Indeed, in a thermochemical TES, heat is stored as chemical potential deriving from the breaking of bonds between the sorbent material and the working fluid. This guarantees high-energy storage density, since the enthalpy of reaction can be order of magnitudes higher than specific heat, as well as no degradation of stored energy during time, since heat can remain stored as long as the sorbate and the working fluid are kept separated. Accordingly, thermochemical TES represents a viable way to enhance solar thermal systems performance both through high energy density daily heat storage [5,6] as well as for seasonal heat storage applications [7,8]. Main features of different thermochemical heat storage technologies have been recently discussed in a review [9]. Among the wider class of thermochemical TES, the adsorption one seems the most suitable for residential building applications. Indeed, it is characterized by good energy storage density, possibility to store energy at low-medium temperature (i.e. below 100 °C), typical of non-concentrating solar thermal collector technologies usually employed in this field, and ability to be

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Nomenclature

A	adsorption potential (kJ kg^{-1})
cp	specific heat (kJ kg^{-1} K^{-1})
E	characteristic energy of the working pair (kJ kg^{-1})
k	pre-exponential Dubinin factor (–)
M	mass (kg)
n	Dubinin exponent (–)
p	pressure (Pa)
Q	heat (kJ kg^{-1})
r	metal to sorbent mass ratio (kg kg^{-1})
R	universal gas constant (J mol^{-1} K^{-1})
T	temperature (K)
V	volume (m^3)
Y	slope of the saturated adsorbate line on the Clapeyron diagram (K)
w	uptake (kg kg^{-1})
ΔH	enthalpy (kJ kg^{-1})
Δs	entropy variation (kJ kg^{-1} K^{-1})
Δw	uptake variation (kg kg^{-1})

Greek symbols

ρ	density (kg m^{-3})

Subscripts

1, 2, 3, 4	cycle phases
ads	adsorption
amb	ambient
ave	average
disch	discharged
eff	effective
ev	evaporation
L	liquid
max	maximum
met	metal
min	minimum
s	sorbent
sat	saturation
sens	sensible
st	storage
v	vapour

operated both as daily and seasonal storage [10].

In order to develop an efficient adsorption TES, the first step is represented by the selection of the proper working pair. In the literature the performance of several adsorbent materials (e.g. zeolites, silica gels, composite sorbents) and working fluids (e.g. water, ammonia, alcohols) have been investigated, in the past, mainly for refrigeration and heat pumping applications [11,12]. More recently, Aristov [13] has reported an interesting review of available systems and adsorption working pairs for heat storage application in buildings. Nevertheless, a comprehensive thermodynamic analysis of different adsorption working pairs for heat storage applications has not been reported so far. Accordingly, the present paper aims at a thermodynamic comparison of the main adsorption working pairs available in the literature for adsorption heat transformer technologies. The analysis is carried out as a function of working boundary conditions.

2. Performance evaluation of the adsorption heat storage

Generally, there are two system configurations for adsorption TES: closed and open cycle. The present paper will mainly focus on closed adsorption systems. Deep analysis of open adsorption TES can be found elsewhere [14].

In the following, the closed adsorption TES working principle will be shortly introduced. More detailed analysis can be found elsewhere [10]. Fig. 1 reports the working cycle for a closed adsorption TES on the Clapeyron diagram. Fig. 2 schematically represents the typical adsorption TES architecture, made up of a closed reactor containing the adsorbent material put in contact with a heat exchanger (i.e. adsorber) and a closed reactor containing the liquid adsorbate, which acts as condenser/evaporator depending on the working phase. Furthermore, in Fig. 2, heat and working fluid (adsorbate) fluxes occurring during each working phase are highlighted.

During charging phase (i.e. desorption), the adsorber, in which the adsorbent material is saturated of adsorbate, is regenerated exploiting heat coming from the solar heat source, Q_{des}. This amount of energy can be distinguished, following the cycle in Fig. 1, in two different quantities: Q_1, usually known as isosteric heat, which represents the amount of sensible thermal energy spent to heat up the adsorbent material and the adsorbate under isosteric conditions, during which no desorption happens. This phase is needed in order to increase the pressure inside the adsorber to the same level of the condenser pressure. Q_2, which is the energy spent to desorb the adsorbate from the material, plus a small amount of specific heat to increase the adsorbent material temperature up to the final temperature, T_{max}. The desorbed vapour is continuously condensed in the condenser. The heat of condensation, Q_c, is usually dissipated in the ambient. Nevertheless, if needed, it can be also exploited by the user in daily heat storage applications, for instance by storing it in a buffer heat storage.

Once the charging process is completed, the connection between condenser and adsorber is closed. In this condition, the system can keep the stored energy for indefinite time, since the thermal energy is stored as adsorption potential between adsorbate and adsorbent material. In order to get back the stored thermal energy, the connection between liquid adsorbate reservoir, which in this phase acts as evaporator, and adsorber is again opened. During this discharging phase (i.e. adsorption), the adsorbate is evaporated adsorbing heat from the ambient, Q_{ev}, then the vapour fluxes to the adsorber, since the adsorption process is exothermic, heat is released to the user, Q_{ads}. Also in this case, Q_{ads} comprises two different components, Q_3 which represents the energy delivered during isosteric cooling down process, which brings the pressure down to the evaporator pressure and Q_4 which mainly represents the energy associated to the enthalpy of adsorption.

In the evaluation of an adsorption heat storage, two main quantities need to be taken into account, namely, the temperature lift, ΔT_{lift}, and the energy storage density, E_s (both per unit of mass and volume) [15].

The temperature lift represents the temperature difference between adsorber and evaporator during the adsorption phase and between adsorber and condenser during the desorption phase. Since the adsorption phase represents the discharging phase of the heat storage, it can be regarded as the achievable temperature upgrade from the low temperature heat source (evaporator) to the user. During the desorption phase, it can be considered as the temperature difference needed to drive the thermodynamic cycle. The energy storage density represents the amount of stored energy per unit of volume/mass.

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