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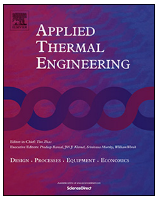

Research Paper

Analysis of equilibrium and kinetic parameters of water adsorption heating systems for different porous metal/metalloid oxide adsorbents

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HIGHLIGHTS

- Modelled/simulated water AHSs using different porous metal/metalloid oxides.
- Zeolite 13X/water is the most promising pair with $COP = 1.48$ and $SHP = 1232\ \mathrm{W\ kg_s^{-1}}$.
- Good prediction of the performance of AHSs using constant $\lambda_{\mathrm{eff,s}}$, Q_{ads} and K_{LDF}.
- Performance of AHS not significantly influenced for d_p up to 0.6 mm.

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ABSTRACT

The performances of well-known porous metal/metalloid oxide adsorbents (zeolite 13X, zeolite 4A and silica gel) and less explored Engelhard titanosilicate ETS-10 for water adsorption heating systems (AHSs) were compared with the aid of computational modelling and simulations. The developed model contemplated adsorption equilibrium, one-dimensional heat and mass transfer in the bed, external heat transfer limitations, and intraparticle mass transport. The pair zeolite 13X/water seemed most promising for the AHS partly due to a higher amount of heat generated per cycle, and favourable water-adsorption isotherm features. Based on sensitivity studies, for zeolite particle diameters in the range 0.2–0.6 mm, the coefficient of performance was 1.48 and the specific heating power was in the range 1141–1254 W $\mathrm{kg_s^{-1}}$. Aiming at inferior computational and numerical efforts, the impact of considering some simplified postulations (e.g. constant thermal conductivity of the adsorbent; constant isosteric heat of adsorption; constant linear driving force coefficient), while ensuring comparable predictions of the performances of the AHSs, was successfully investigated.

1. Introduction

During the last 35 years thermally-driven adsorption cycles have been widely investigated, namely adsorption systems for heating/cooling applications, due to their lower environmental impact compared to that of conventional vapour compression systems. While the latter use hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs), adsorption-based systems utilize benign refrigerants, such as water, which have zero global warming potential, and can be powered by solar energy or waste heat instead of mechanical power [1–3].

In terms of energy demand in Europe, almost 50% of the final energy consumption is used for heating and cooling. The building sector accounts for more than 35% of the overall consumption, of which 75% is for domestic hot water production and room heating [4]. Therefore, efficient and cost effective heat production is important not only to meet the market needs, but also to decrease the consumption of fossil fuels in the building sector. In this respect, adsorption-based heating systems using e.g. porous metal/metalloid oxides as adsorbents, such as zeolites/zeotype materials, have been pointed as promising technology [1,4,5].

The cyclic operation of an adsorption heating system (AHS), such as an adsorption heat pump (AHP), consists of four stages (Fig. 1), namely, isobaric adsorption ($1 \rightarrow 2$), isosteric heating ($2 \rightarrow 3$), isobaric desorption ($3 \rightarrow 4$), and isosteric cooling ($4 \rightarrow 1$). A detailed description of the working principles of adsorption cycles can be found elsewhere [6,7]. The selection of the most appropriate working adsorbent/adsorbate pair is one of the main factors determining the efficiency of adsorption systems, and it depends on various factors such as the desirable operating conditions and the heat source

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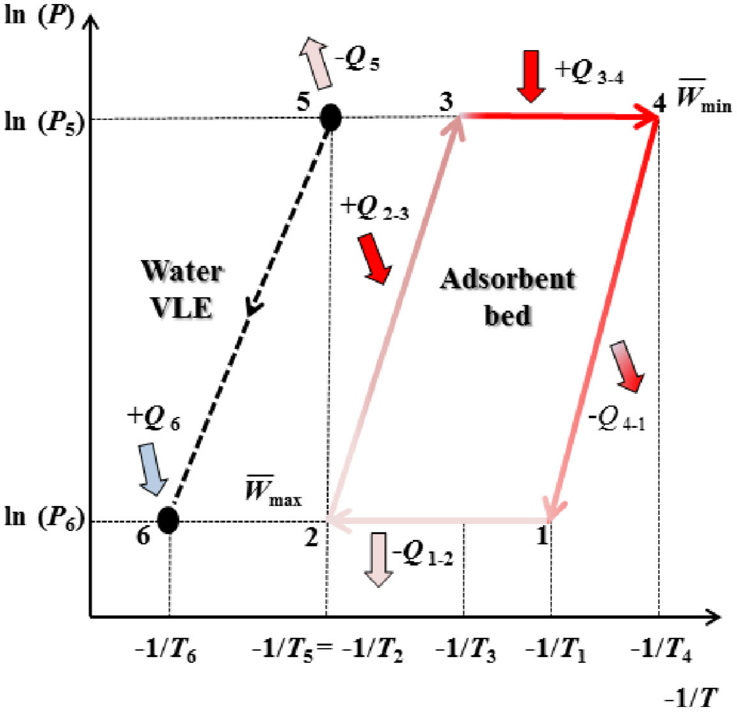

Q_{1-2}, Q_{4-1} and Q_5 - heats generated during isobaric adsorption, isosteric cooling and in the condenser, respectively;

Q_{2-3}, Q_{3-4} and Q_6 - heats consumed during isosteric heating, isobaric desorption and in the evaporator, respectively;

P_5 and P_6 - pressures of condenser and evaporator, respectively;

T_5 and T_6 - temperatures of condenser and evaporator, respectively;

T_1 and T_2 - temperatures of adsorbent bed at the beginning and at the end of isobaric adsorption, respectively;

T_3 and T_4 - temperatures of adsorbent bed at the beginning and at the end of the isobaric desorption, respectively;

$\overline{W}_{min}$ and $\overline{W}_{max}$ - average minimum and maximum adsorbate loadings, respectively.

Fig. 1. Clapeyron diagram of an adsorption heating system (AHS).

temperature. It is important that the solid possesses a large adsorption capacity, is easily regenerated, and exhibits good hydrothermal stability, while the refrigerant fluid should have a large specific latent heat of condensation, good thermal stability, no toxicity and no flammability [8]. An important parameter to evaluate working pairs is the heat of adsorption (Q_{ads}) which has a direct influence on the cycled heat [9]. While a high value is favourable for generating heat in the adsorption stage, this may be levelled-off by more demanding conditions required for the regeneration of the adsorbent, and thus good compromises between the two are important for improved performances of heating processes.

Zeolites, namely those of the faujasite framework type (X and Y zeolites), have been considered for AHP applications since the 1980s [9]. In particular, zeolite/water pairs have been reported as very suitable for AHPs due to the non-linear pressure dependence of their adsorption isotherms, and their fairly high water adsorption capacity [10]. Other investigated pairs include activated carbon/methanol [11] and activated carbon/ammonia [12], albeit the use of eco-friendlier adsorbates is desirable.

Relatively high adsorption capacities of zeolites result at least partly from relatively strong adsorbent/adsorbate interactions, and therefore high desorption temperatures may be required (200–300 °C), presenting limitations for many applications [13]. More recently, efforts have been made to develop zeolitic adsorbents requiring less demanding regeneration conditions for AHPs, such as zeolite DDZ-70 from UOP and AQSOA^{TM}-FAM-Z02 from Mitsubishi Plastics [14]. The use of Engelhard titanosilicate number 10 (ETS-10) with water as adsorbate for use in AHSs has been recently reported [15]. The isotherms of the ETS-10/water pair feature benefits in terms of moderate regeneration conditions.

The overall performance of an AHS depends on the equilibrium properties of the pair and also on the mass and heat transfer processes within the adsorbent bed. Concerning equilibrium, large adsorption capacity at low relative pressures (characteristic of type I isotherms) and desorption of most of the adsorbate even at high relative pressures are particularly important [10]. Regarding mass transfer processes, adsorption kinetics can strongly affect the dynamic behaviour of an AHS and hence its specific heating power (SHP). The Linear Driving Force (LDF) model has often been used for describing intraparticle mass transfer kinetics. It includes an overall mass transfer coefficient (K_{LDF}) dependent on the effective diffusivity (D_{eff}) of the adsorbate in the porous solid [16,17]. The D_{eff} varies not only with temperature but also with adsorbate loading, which tends to be discarded [18,19]. Intraparticle mass transport and vapour permeability through the bed are both affected by particle diameter (d_p); larger particle sizes increase internal diffusion limitations, and, on the other hand, decrease the vapour transport resistances through the bed. Previous studies have reported on the strong impact of d_p on the mass transfer processes in adsorbent beds [2,16,20]. Regarding thermophysical properties, the thermal conductivity of the adsorbent ($\lambda_{eff,s}$) influences the efficiency of adsorbent beds [10,21]. It may vary along the cycle, depending on adsorbate loading, temperature and pressure [21–23], although most modelling and simulation studies of adsorption refrigeration systems reported in the literature consider constant $\lambda_{eff,s}$ [10,24,25].

In this work, modelling and simulation studies were carried out aiming at the comparison of the heating performance of ETS-10, zeolites 13X and 4A, and silica gel for AHSs with water as adsorbate. The cyclic adsorption process was rigorously simulated, and the overall heating performance of each system was evaluated by means of the coefficient of performance (*COP*) and specific heating power (*SHP*). A comparison of the heat generated and consumed on the different stages of the cycle by each working pair was carried out, and the heating performances were discussed accounting for the shape of the isotherms. In addition, given the importance of equilibrium, kinetic and thermophysical parameters for the estimation of the performance of AHSs, simulation studies were carried out in order to gain insights into the influence of using: constant or variable $\lambda_{eff,s}$; constant Q_{ads} or adsorbate loading-dependent Q_{ads}; D_{eff} varying with temperature and adsorbate loading; constant K_{LDF} in the whole adsorption cycle. A sensitivity analysis was made in order to investigate the impact of the particle size on the overall performance of an AHS.