Adsorption heat pumps for heating applications: A review of current state, literature gaps and development challenges

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\textbf{ABSTRACT}

A review of the most relevant work on the field of adsorption heat pumps with emphasis on heating applications is presented, covering the working principle, physical models, adsorption equilibrium and kinetics, adsorbent material physical and thermodynamic properties, adsorbent bed designing and operating conditions. The major literature gaps and development challenges of adsorption heat pumps for heating applications are identified and discussed. A bridge between materials and system level studies is lacking. The simultaneous investigation of the adsorption kinetics, adsorbent bed specifications, operating conditions and interaction between all the system components is missing in the literature. Detailed information required for the development and validation of physical models is often not provided in the experimental studies. A physical model that considers an entire adsorption heat pump system, which is required for performance predictions and system's optimization, cannot be found in the literature. To improve the adsorption heat pump system's performance the heat and mass transfer resistances need to be minimized by developing new adsorbent materials and better interaction between the adsorbent bed and the wall of the duct where the heat transfer fluid flows. In addition, operation modes optimized for the desired application can also contribute to improving the system's performance.

\section{1. Introduction}

Due to their low environmental impact, adsorption heat pumps (AHPs) have attracted researchers and heating market attention over the last years. Compared to the conventional vapour compression heat pumps, which rely on high global warming potential (GWP) refrigerants (HFCs and HCFCs), AHPs may work with natural refrigerants that have zero GWP such as water and ammonia\cite{1}. Moreover, contrary to the vapour compression heat pumps that run on electrical energy, AHPs can make mainly use of waste heat and renewable energies like solar and geothermal energy\cite{2}.

Nowadays, almost 50\% of Europe's energy consumption is channelled to heat and cold production. More than 35\% of the overall consumption is used by the building sector alone, from which 75\% is employed on domestic hot water production and room heating\cite{3}. Since most of this energy is from non-renewable and environmentally harmful energy sources, AHPs can significantly contribute to decrease humanity's dependence on these harmful energy sources.

AHP's application was first demonstrated by Tchernev\cite{4} in 1976 for domestic hot water production and space heating. Since then, much research has been done in order to increase their coefficient of performance (COP), operating with lower desorption temperatures and providing continuous heating or cooling process. Finding new working pairs or enhance the existing pairs to increase the COP, the adsorption rate and to decrease desorption temperature are among the most studied subjects at the adsorbent material level. In addition, the development of more accurate and efficient numerical models, optimization of heat and mass transfer by designing of adsorbent beds and operating conditions have also been investigated\cite{2}. However, studies of a complete AHP system considering all its aspects and components cannot be found in literature.

In the following sections, an overview of the recent studies on adsorption heat pumps with emphasis on heating applications is presented. The main objective is to identify the bridges that need to be built between the adsorption kinetics, bed designing, operating conditions and remaining system components instead of being a repertory of previous work on the field. Thus, the identification of the major challenges and setting directions for the development of future work, attempting to fill the existing gaps, are discussed in this review. In addition, this paper comprises information about the AHP working...
principle, physical models, adsorption equilibrium and kinetics of typical and new adsorbent-adsorbate working pairs, adsorbent material thermodynamic and physical properties, adsorbent bed designing and operating conditions. Overall, it can help researchers working on the field or it can be used as a guide for researchers that are new to the AHPs subject, covering the main usually dispersed information required to start developing work in AHP systems.

2. Working principle

Heat pumps work by extracting heat from a low temperature level and delivering it at an intermediate temperature level, driven by a third energy source [5]. In AHPs, this third energy source is heat from a higher temperature level source that in practice can be, for example, waste heat, gas burners, electricity, geothermal and solar energy. A simple AHP consists on an adsorbent material packed or coated on an adsorbent bed (metallic structure where the adsorbent is placed), an evaporator, a condenser, an expansion valve and a heat transfer system or fluid to provide/withdraw heat to/from the adsorbent bed. In heating applications, the evaporator makes use of a free of charge low temperature level heat source (ambient, geothermal or waste heat) to vaporize the adsorbate, which is fed to the adsorbent bed during the adsorption phase. Useful heat of adsorption is collected by the heat transfer system, normally through a heat transfer fluid (HTF). On the other hand, during desorption phase heat has to be provided to the bed in order to release the adsorbate from the adsorbent in vapour state. The adsorbate is driven through the condenser, where it condenses before returning to the evaporator. Useful heat of condensation, Qc, is released during the process. A scheme of an AHP system is presented in Fig. 1.

The ideal thermodynamic cycle of an AHP is presented in Fig. 2 in the Clapeyron diagram. It consists of four phases, namely isobaric adsorption (1–2), isosteric heating (2–3), isobaric desorption (3–4) and isosteric cooling (4–1).

During the isobaric adsorption phase (1–2) the valve between the evaporator and the adsorbent bed is open and the valve between the adsorbent bed and the condenser is closed. The vaporized adsorbate is adsorbed by the adsorbent releasing heat Q_{1-2} in the process, which has to be removed until the bed temperature reaches T_2 (~ T_c). The cycle maximum adsorbate uptake, X_{\text{max}} is achieved at the end of the phase and it is dependent on the bed pressure, which is normally at the evaporator pressure, P_e. The heat released by the adsorbent bed during this phase can be calculated through the following equation [2]:

\[ -Q_{1-2} \approx \int_{T_1}^{T_2} [m_i(C_i + X_{\text{c,p}}) + m_{\text{bed}}C_{\text{ads}}]dT - \int_{X_{\text{max}}}^{X_{\text{min}}} m_i \Delta H_{\text{ads}}dX \]

(1)

After the isobaric adsorption phase (1–2), the isosteric heating phase (2–3) starts. The valve between the evaporator and the adsorbent bed is closed and heat is provided to the bed. Since both bed valves are closed, the adsorbate uptake remains constant throughout this phase. The pressure inside the bed increases with temperature until it reaches the condenser pressure, P_c, when the phase is terminated. The amount of heat provided during this process is given by [2]:

\[ Q_{2-3} \approx \int_{T_2}^{T_3} [m_i(C_i + X_{\text{max}}C_{p,a}) + m_{\text{bed}}C_{\text{bed}}]dT \]

(2)

The isobaric desorption phase (3–4) follows continuing the heating process with the valve between the bed and the condenser open. The adsorbate is desorbed and flows from the bed to the condenser, where it condenses releasing useful heat of condensation, Q_c. The pressure remains constant during this phase, being at the condenser pressure. When desorption temperature, T_{\text{des}} = T_4, is achieved the valve is closed and the next phase follows. The heat that must be provided to the bed during this phase is given by [2]:

\[ Q_{3-4} \approx \int_{T_3}^{T_4} [m_i(C_i + X_{\text{max}}C_{p,a}) + m_{\text{bed}}C_{\text{bed}}]dT - \int_{X_{\text{max}}}^{X_{\text{min}}} m_i \Delta H_{\text{ads}}dX \]

(3)

The last phase of the cycle is the isosteric cooling (4–1). The valves between the adsorbent bed and the condenser and evaporator are closed and the temperature of the bed is lowered. The uptake remains constant during the process and the pressure inside the bed decreases along with the temperature. When the pressure drops to the evaporator pressure, P_e, the phase ends and the subsequent isobaric adsorption phase follows. The heat withdrawn from the bed during the isosteric cooling is [2]:

\[ -Q_{4-1} \approx \int_{T_4}^{T_1} [m_i(C_i + X_{\text{max}}C_{p,a}) + m_{\text{bed}}C_{\text{bed}}]dT \]

(4)