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Research Paper

Comparative analysis of promising adsorbent/adsorbate pairs for adsorptive heat pumping, air conditioning and refrigeration

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HIGHLIGHTS

- Working pairs are evaluated for adsorptive heat pumping, air conditioning and refrigeration applications.
- A model was developed to evaluate the performance for different sorption cycles.
- Results of simulation showed the importance of selecting the optimal adsorbent for a given application.
- Design of the adsorber must take into account both thermodynamic and dynamic aspects.

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ABSTRACT

In this study, the most promising working pairs are evaluated for utilization in thermal driven adsorptive heat pumping, air conditioning and refrigeration applications employing water, ethanol and methanol as refrigerant. With this aim, a comparative study was carried out for different currently available (silica gels, zeolites, aluminophosphates, activated carbons) and recently developed materials (composite adsorbents). A simple mathematical model was developed in order to evaluate the performance of various working pairs for different sorption cycles. Among the considered adsorbents, the Mitsubishi product AQSOA®-FAM-Z02, the composite adsorbents LiBr–silica and $CaCl_2$–silica appeared the best water adsorbents for air conditioning and heat pumping purpose, providing heating/cooling COP up to 1.62/0.71 and heating/cooling enthalpy up to 1080/570 kJ kg^{-1}. Also the LiCl–silica/methanol working pair showed high performance for air conditioning cycles, especially in terms of cooling enthalpy (Q_{ev} = 640 kJ kg^{-1}).

The composite LiBr–silica showed to be the most promising methanol and ethanol sorbent for refrigeration purpose, permitting cooling COP in the range 0.53–0.59 and cooling enthalpy in the range 180–360 kJ kg^{-1}.

The noticeable influence of the metal-to-adsorbent mass ratio on the sorption cycle performance was also demonstrated, showing that utilization of compact finned tube aluminum heat exchanger types (typical m_{met}/m_{ads} = 0.9–1.6) allows a 15–30% cooling COP higher than a traditional stainless steel tube-and-shell exchanger (m_{met}/m_{ads} = 2.4–3.1). Additionally, some brief dynamic considerations are done for most interesting working pairs.

1. Introduction

Nowadays, adsorption heating and cooling (AHC) systems are a promising alternative to conventional vapor compression systems, due to the high energy efficiency referred, which results in a significant reduction of primary energy demand, and a low environmental impact. Details on the operating principles of AHC systems are reported elsewhere [1,2]. Looking at the current state of art, it appears evident that many advancements in the field have been achieved, with an increasing number of sorption chillers and heat pumps available on the market in small to medium sizes [3]. However, still large room for further improvement exists, especially in terms of mass and volume reduction and energy density enhancement [4]. Indeed, the first adsorption machines employed common adsorbents, such as silica gel or 4A zeolite, resulting in bulky machines, and still today, a very limited number of adsorbents is used. Accordingly, a major trend of the research involves the development of new or modified adsorbents with enhanced adsorption and thermo-physical properties, low cost and high stability. Possible adsorbent classes for application in AHC are zeolites, silica gels, activated carbons, MOFs, composite adsorbents [5].

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Nomenclature

$A(w)$, $B(w)$	polynomials for adsorbent/adsorbate equilibrium (see Eqs. (2), (3a) and (3b))
$C(w)$, $D(w)$	polynomials for equivalent specific heat (see Eqs. (17), (18a) and (18b))
c_p	specific heat (J kg^{-1} K^{-1})
COP	coefficient of performance
$L(T)$	latent heat at the temperature T (J kg^{-1})
m	mass (kg)
M_v	molecular mass of adsorbate (kg kmol^{-1})
P	pressure (Pa)
Q	heat for unit mass of adsorbent (J kg^{-1})
R	universal gas constant (8314.5 J kmol^{-1} K^{-1})
S	adsorber heat transfer surface area (m^2)
t	time (s)
T	temperature (K)
w	uptake (kg kg^{-1})
ΔH	adsorption enthalpy (J kg^{-1})
Δw	uptake variation (kg kg^{-1})
W	specific cooling power (W kg^{-1})

Greek symbols

α, β, γ	flags (0 or 1)
ϕ	metal/adsorbent mass ratio (kg kg^{-1})

Subscripts

1–4	phase number of the thermodynamic cycle
ads	adsorbent
avg	*average value*
c	condenser
eq	equivalent (i.e., referred to adsorbent plus adsorbate)
eV	evaporator
i	phase index (1–4)
met	metal
v	**vapor phase (adsorbate)**

Moreover, various AHC applications need different adsorbent/adsorbate pairs depending on the specific operating conditions and the field of application (i.e. stationary or mobile). Accordingly, the search for the optimal adsorbent should not preclude from boundaries on the system, therefore requiring a profound understanding of the different potentialities of the possible working pairs.

Aim of this work is the evaluation of the adsorption performance of several working pairs and the identification of the best one for specific AHC cycles. Firstly, a concise state-of-art on working pairs is presented. Then, a comparative thermodynamic study is carried out on several promising working pairs, by means of a thermodynamic model which takes into account the adsorption parameters as well as the adsorber thermal capacity including the heat exchanger mass. Simulations were carried out for different operating conditions, based on literature or author's experimental data on adsorption equilibrium, adsorption heat and equivalent specific heat measured for various conventional and novel adsorbents employing water, ethanol and methanol as working fluids. Results are given in terms of cooling/heating COP and cooling/heating enthalpy. Finally, in order to highlight the importance of combining thermodynamic and dynamic optimization of the adsorber, some brief dynamic considerations are done for the most interesting working pairs.

2. Working pairs

2.1. Refrigerants

Among possible refrigerants, water is the most used for air conditioning and heat pumping applications, due to the high latent heat and the self-evident environmental benefits. For ice making or refrigeration below 0 °C, methanol or ethanol can be utilized, due to the lower freezing point. Ammonia is an alternative high-pressure refrigerant proposed for refrigeration and heat pumping, which will not be subject of this study, that is focused on low-pressure fluids (water, ethanol and methanol). Main properties, advantages and drawbacks of various refrigerants are discussed elsewhere [6].

2.2. Classical adsorbents

Microporous silica gel [7] is the standard adsorbent of water widely and historically used in adsorption chillers driven by low temperature heat sources (60–100 °C), the advantages being in its low cost and its sufficient reliability for practical application if the temperature lift between evaporator and condenser is not too large. However, silica gel is generally considered less stable than crystalline zeolites due to its amorphous nature. Zeolites can be used with all the major refrigerants, even if most of research has been done on zeolite/water pair. The commercial products commonly used are the alumino-silicate zeolites of type 4A and 13X [8]. These zeolites have a strong hydrophilic character that results in a high water adsorption capacity and high ad/desorption heat. Such alumino-silicate zeolites, however, have the disadvantage of requiring high regeneration temperature, limiting their use to applications where a high temperature driving heat source (200–300 °C) is available.

2.3. (Silico)aluminophosphates

Accordingly, R&D on adsorbent materials for "low temperature" applications focused on new classes of zeolite-like materials, denominated AlPO and SAPO, able to combine a moderate hydrophilicity with a high capacity of adsorption of water vapor, resulting in moderately low regeneration temperature (60–100 °C), while maintaining high performance [9]. A number of studies were carried out on different types of (silico)aluminophosphates (AlPO-5, AlPO-18, SAPO-34, etc.) [10,11], confirming the interesting properties of such materials for adsorption cycles.

Novel adsorbent materials "AQSOA®", belonging to the class of (Silico)aluminophosphates, have been developed and commercialized by Mitsubishi Plastic Inc. (MPI) for desiccant and AHP systems [12]. Adsorption equilibrium and durability studies of adsorbents AQSOA®-FAM-Z01 and AQSOA®-FAM-Z02 are presented in [13–16]. Both materials present S-shaped isotherms, are able to exchange large amount of water (up to 0.25 g g^{-1}) within narrow temperature and humidity ranges and conveniently low desorption temperature (60–90 °C). A general issue of AlPO and SAPO zeolite-like materials is the high capital cost, as the synthesis process is more expensive than standard commercial zeolites and no industrial mass-production has yet been established.

2.4. Special Y-type zeolites

Y-type zeolites have partially hydrophilic character, and may therefore represent a cheaper alternative to AlPO and SAPO. Some years ago, UOP Llc., a Honeywell Company, developed a novel