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Novel experimental methodology for the characterization of thermodynamic performance of advanced working pairs for adsorptive heat transformers

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ABSTRACT

This paper presents a novel experimental protocol for the evaluation of the thermodynamic performance of working pairs for application in adsorption heat pumps and chillers.

The proposed approach is based on the experimental measurements of the main thermo-physical parameters of adsorbent pairs, by means of a DSC/TG apparatus modified to work under saturated vapour conditions, able to measure the ads-/desorption isobars and heat flux as well as the adsorbent specific heat under real boundary conditions. Such kind of activity allows to characterize the thermo-dynamic performance of an adsorbent pair allowing the estimation of the thermal Coefficient Of Performance (COP) both for heating and cooling applications, only relying on experimental values.

The experimental uncertainty of the method has been estimated to be around 2%, for the COP evaluation.

In order to validate the proposed procedure, a first test campaign has been carried out on the commercial adsorbent material, AQSOA-Z02, produced by MPI (Mitsubishi Plastics Inc.), while water was used as refrigerant.

The proposed experimental methodology will be applied on several other adsorbent materials, either already on the market or still under investigation, in order to get an easy and reliable method to compare thermodynamic performance of adsorptive working pairs.

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1. Introduction

During recent years, an increasing interest in Adsorptive Heat Transformers (AHTs), especially in adsorption heat pumps and chillers, has been registered [1,2]. Indeed, as they are characterized by the use of heat as driving source, these technologies are considered as good opportunities to reduce the electrical consumption related to the widespread use of common vapour compression heating/cooling systems as well as to increase the differentiation of the consumption of primary energy sources [3,4].

Despite the depicted advantages, the commercial diffusion of these apparatuses is still in an early stage, due to several issues, like the reduced efficiency, the low power density and the high initial capital cost [5]. In general, the performance of an AHT heavily depend on the selection of the most appropriate adsorbent material, taking into account both thermodynamic [6] and dynamic

properties [7]. Historically, zeolites, silica gels and active carbons have been commonly employed as adsorbent materials for AHT applications [8]. More recently, thanks to the evolution of material science, several new classes of materials have been proposed, which seem to be really promising, namely, MOFs [9], Aluminophosphate [10,11], SWSs [12] etc. Some of these are already commercialized [13], showing higher performance compared to the commonly employed materials. Nevertheless, there is still a plenty of adsorbent materials whose characteristics have never been investigated for AHT applications. In literature, some studies were performed, aiming at the thermodynamic characterization of working pairs for AHT applications. For instance in Ref. [14] a comparison among several working pairs belonging to different thermally activated technologies (e.g. liquid absorption, physical adsorption) was performed. In this case the performance was calculated starting from experimentally measured thermo-physical properties, applying proper mathematical models, able to take into account also engineering parameters like the reactor configurations. A different approach proposed by Aristov [15] deals with the





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Fig. 1. Schematic drawing of the thermo-gravimetric apparatus installed at the CNR ITAE labs.

measurements of different thermo-physical working pairs properties, which are needed to create a database useful for mathematical modelling.

The approach proposed in the present paper is quite different. In this case, the idea is to characterize the thermodynamic performance of the working pair for AHT applications, only relying on experimental values. It is based on the employment of a modified DSC/TG apparatus, installed at the CNR ITAE, able to work under saturated vapour working conditions. Accordingly, it allows to measure both adsorption equilibrium curves and heat of adsorption under real working boundary conditions, thus perfectly replicating the main phases of the thermodynamic cycles of adsorption heat pumps or chillers. This means that the integral heat of adsorption/ desorption can be directly evaluated under isobaric conditions, typical of "active phases" of and AHT cycle, allowing the calculation of the ideal thermodynamic performance in terms of COP. In this manuscript, the characterization protocol is applied to the adsorbent material AQSOA-ZO2 [13] while water is used as refrigerant.

2. Thermo-gravimetric apparatus

The present protocol of characterization is mainly based on the employment of a modified DSC/TG apparatus. Actually, the core of the system is a Setaram Labsys-Evo analyser, equipped with a standard DSC rod, having a resolution of 10 μ W, and a TG probe characterized by 0.02 μ g of resolution and 0.02 mg of accuracy. The

saturated vapour pressure conditions. Fig. 1 shows the scheme of the thermo-gravimetric apparatus. It is mainly composed of a testing chamber (TestC), in which the sample (S) and the reference (R) crucibles are located. The furnace cooling rate is controlled by means of an external thermo-cryostat (TC2). The testing chamber can be evacuated, during the regeneration of the sample, employing a vacuum pump (VP), which is connected to the chamber by means of a preliminary valve, V5, and two vacuum valves arranged in parallel (V2 and V3), one of which is a needle valve (V3), employed during the first evacuation stage in order to avoid the elutriation of the sample. After test, air can be admitted to the system through the venting valve, V4. The generation of the refrigerant vapour is obtained by means of a glass evaporator (Evap) whose temperature is controlled by an external thermocryostat (TC1). Both the chamber pressure and the evaporator pressure are continuously monitored by means of two dedicated pressure sensors (P). Moreover, the system is placed into a thermostatic box (temperature max 45 °C), which allows to perform measurements at higher pressures, avoiding condensation on internal surfaces of the circuit as well as measuring chamber. Finally, an external data acquisition system (DAQ) is connected to the testing chamber and to the pressure sensors, in order to get the main parameters needed for the evaluation of the adsorbent material adsorption capacity under testing conditions.

 Table 1 reports the main features of the apparatus installed in the CNR ITAE lab.

3. Estimation of the thermodynamic performance

Evaluation of the achievable thermodynamic performance of adsorbent/adsorbate pairs for different applications is a crucial point for the development of efficient AHT systems. In the past, such a topic was analysed following different routes [14,15]. The present paper deals with the presentation of a novel approach, which is able to evaluate the achievable thermodynamic performance of working pairs under real working boundary conditions of adsorption heat pumps or chillers, experimentally measuring their main thermo-physical parameters.

A typical thermodynamic cycle of an adsorption heat pump/ chiller is reported in Fig. 2, plotted in a (T,w) plane where the main parameters needed for the performance evaluation are represented. During the isosteric heating phase (A–B) and isobaric desorption stage (B–C) the material is heated up and the refrigerant is desorbed from the material, thanks to the heat delivered to the adsorbent material $Q_{is_{-H}}$ and Q_{H} . During isosteric cooling down phase (C–D) and isobaric adsorption phase (D–A) the material is cooled down and the refrigerant is adsorbed by the material thanks to the heat extracted, $Q_{is_{-C}}$ and Q_{C} . More detailed description of the cycle can be found elsewhere [8,14].

For cooling cycle the thermodynamic efficiency is represented by the cooling COP, COP_{cool}, sometimes referred as EER (Energy Efficiency Ratio), which is defined as:

$$\operatorname{COP}_{\operatorname{cool}} = \frac{Q_{ev}}{Q_{is_H} + Q_H} = \frac{\left[L_{\operatorname{ref}}(T_{ev}) - \int_{T_{ev}}^{T_{\operatorname{con}}} cp_{l_ref} dT\right] \cdot (w_{\max} - w_{\min})}{\int_{T_C}^{T_{is_H}} cp_{\operatorname{ads}}(w_{\max}) dT + \left[\int_{T_{is_H}}^{T_H} \left(\int_{w_{\min}}^{w_{\max}} cp_{\operatorname{ads}} dw\right) dT + \int_{w_{\min}}^{w_{\max}} \Delta H_{\operatorname{des}} dw\right]}$$
(1)

testing chamber of the thermo-gravimetric system is able to reach up to 800 °C, and it has been modified in order to work under where Q_{ev} [kJ/kg_{ads}] represents the cooling effect, related to the refrigerant evaporation. Accordingly, it is evaluated as the product

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