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Ethanol adsorption onto carbonaceous and composite adsorbents for adsorptive cooling system

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ABSTRACT

The aim of the present paper is the experimental characterization of adsorbent materials suitable for practical applications in adsorption refrigeration systems, employing ethanol as refrigerant. Different commercial activated carbons as well as a properly synthesized porous composite, composed of LiBr inside a silica gel host matrix, have been tested. A complete thermo-physical characterization, comprising nitrogen physi-sorption, specific heat and thermo-gravimetric equilibrium curves of ethanol adsorption over the sorbents, has been carried out. The equilibrium data have been fitted by means of the Dubinin – Astakhov equation.

On the basis of the experimental data, a thermodynamic evaluation of the achievable performance of each adsorbent pair has been estimated by calculating the maximum COP (Coefficient of Performance) under typical working boundary conditions for refrigeration and air conditioning applications. The innovative composite material shows the highest thermodynamic performances of 0.64–0.72 for both tested working conditions. Nevertheless, the best carbonaceous material reaches COP value comparable with the synthesized composite.

The results have demonstrated the potential of the chosen adsorbents for utilization in adsorption cooling systems.

1. Introduction

With the rapid development of economy and society, our modern life and industry consume large amounts of energy for cooling. Furthermore, the depletion of fossil fuels and the threat of global warming over the last decades have challenged air conditioning industry to develop new cooling technologies alternative to the conventional vapor compression systems. Heat driven adsorption cooling cycles have the great energy saving potential due to utilization of the solar energy and low grade waste heat, e.g. engine exhaust, industrial waste heat, etc. [1,2].

The interest in adsorption cooling systems first is started to the oil crisis in the 1970s, and then later, in the 1990s, because of ecological problems related to the use of CFCs and HCFCs as refrigerants. Accordingly, systems that can recover waste heat at low temperature levels – such as adsorption systems – can be an interesting alternative to common vapor compression ones, for a wiser energy management [3].

Sorption refrigeration technologies are thermally driven systems, in which the conventional mechanical compressor of the common vapor compression cycle is replaced by a 'thermal compressor' [4]. This technology could be suitable, for instance, for fishing boat using waste heat discharged from the internal combustion engine.

A sorption refrigeration system is noise-free, easy controllable, environmental friendly and virtually maintenance-free [3]. However the main drawback of these systems, which hinder their practical dissemination, is their reduced performance in terms of specific cooling capacity and COP, as well as cooling power [5,6].

The adsorption characteristics of the adsorbent/refrigerant pair are one of the most essential parameters that affect the system performance [7–9]. An adsorbent must have the ability to adsorb large quantities of an adsorbate in a narrow range of temperatures and to desorb it easily when temperature rises. Its properties

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should not change with age and use (i.e. high hydrothermal stability).

Water, ammonia, methanol and ethanol are typical refrigerants of the adsorption refrigerator. While silica gel, zeolites and activated carbons are the most common adsorbents used in these systems.

Among the common refrigerants, ethanol is one of the most interesting due to its low freezing point (−114 °C) and to its ecological compatibility. Respect to methanol, ethanol has a similar saturation pressure, but its latent heat is about 30% lower than methanol. Nevertheless, methanol is characterized by high toxicity and inflammability compared to ethanol and for this reason special care must be used during the phases of storage, handling and use. Methanol also shows the problem of dissociation above 120 °C, especially in the presence of copper. The typical ethanol adsorbents used in adsorption applications are activated carbons, in fact these latter have a large surface area and exhibit good affinity towards ethanol.

A good number of papers related to ethanol adsorption refrigeration have already been published.

The activated carbons are common materials proposed as ethanol adsorbents for adsorption cooling [10]. Accordingly, other authors further investigated the features of this activated carbon as discussed below. El-Sharkawy et al. [11] measured the adsorption isotherms Maxsorb III/ethanol pair. They found that this pair is attractive for solar cooling application. Indeed, a cooling cycle realized with this adsorption pair can achieve a specific cooling effect as high as 420 kJ/kg at evaporator temperature of 7 °C in combination with heat source and heat sink of temperatures 80 and 30 °C, respectively. Maxsorb III/ethanol as adsorption pair was investigated also by Uddin et al. [12]. They studied the characteristics of ethanol adsorption onto "parent" Maxsorb III and surface treated Maxsorb III with controlled oxygen content. Experimental results show that adsorption capacity improves in H_2 treated Maxsorb III, the KOH−H_2 treated Maxsorb III highlights faster adsorption kinetics but the isosteric heat of adsorption remains higher in the parent Maxsorb III/ethanol pair. Loh et al. [13] have presented the performance analysis of both ideal single-stage and single-effect double-lift adsorption cooling cycles working at partially evacuated and pressurized conditions of six specimens of adsorbents and refrigerant pairs. They found that the activated carbon fibers (AC/20)/ethanol pair provides the highest value of specific cooling effect among the tested pairs.

El-Sharkawy et al. [14] have also investigated the activated carbon fibers/ethanol pairs for adsorption cooling system. They have studied the adsorption capacity and adsorption rate of the ACF A-15 and A-20. They found that the equilibrium adsorption capacity of A-20/ethanol pair is considerably larger than that of A-15/ethanol pair and that the ACF A-20 seems to be a promising adsorbent as it has large ethanol adsorption capacity related per gram of the adsorbent. However the low packing density of ACF reduces their capacity related per the unit volume. The same authors [15] have also analyzed the adsorption characteristics of ethanol onto two promising adsorbents based on spherical phenol resin treated with different mass ratios of KOH named as KOH4-PR and KOH6-PR. They found that the adsorption uptake of ethanol onto the sorbents are 1.43 and 2 kg/kg, respectively. This result shows that the newly developed adsorbents have promising adsorption characteristics with ethanol that may lead to the development of next generation of adsorption chillers, in particular for air conditioning cycles. Under conditions of ice making cycle, means at evaporation temperature −3 °C the ethanol uptake on KOH4-PR and KOH6-PR is much lower 0.3−0.4 g/g. Recently, Rezk et al. and [16] Saha et al. [17] have been presented the experimental and theoretical investigations of adsorption characteristics of ethanol onto metal organic framework namely MIL-101Cr. The adsorption capacity of MIL-101Cr reaches as high as 1.1 g/g at ethanol relative pressure of 1, while under conditions of the typical air conditioning cycle (evaporation and adsorption temperatures of 10 and 30 °C, respectively) it is 0.9 g/g. At ice making cycle (evaporator temperature of −3 °C) the uptake falls down but remains quite high − 0.45 g/g. The results demonstrate that the MIL-101Cr − ethanol is promising working pair, however more studies on the durability, thermal properties (namely the heat capacity, thermal conductivity) etc. are required for evaluation of its practical potential for the adsorption cooling applications. Recently, a new adsorbent, namely composites sorbent salt/silica gel, have been proposed for ethanol sorption cooling. Gordeeva et al. [18] found that the composite $LiBr/SiO_2$ is the promising composite ethanol adsorbent due to the large variation in the ethanol uptake for both air conditioning and ice making cycles.

Thus, the data available in the literature shows that various carbonaceous materials, MIL-101Cr and composite $LiBr/SiO_2$ are the most promising ethanol adsorbents in the adsorption cooling. However, the major part of the studies are related to the conditions of air conditioning cycle. The materials having the greatest potential in terms of ethanol uptake, namely KOH4-PR, KOH6-PR, and MIL-101Cr are not commercially available, and consequently can hardly be considered for practical application in the adsorption chillers. As regards the traditional ethanol adsorbents, activated carbons, it was shown by Li et al. [19] that an activated carbon − ethanol working pair cannot allow ice production. Therefore, an empty room still exists for the search of ethanol adsorbents suitable for practical application in the adsorption chillers.

The goal of the present paper is the investigation of the adsorption characteristics of ethanol on some on-purposely selected commercially available activated carbons, produced from different bases (coal, coconut shell) and having different morphology (grains, pellets, fibers) with the aim to find the most suitable material for a sorption cooling system, in particular, for an ice making cycle. Additionally, the previously mentioned novel composite $LiBr/SiO_2$ was investigated and compared with the selected activated carbons. The ethanol sorption isobars of the selected samples were valued by a thermo-gravimetric system, specifically realized for alcohols adsorption measurement under real adsorption cooling conditions. The measured adsorption data were correlated with the nitrogen physi-sorption results and they were analyzed according to the Dubinin−Astakhov theory in order to evaluate the equilibrium adsorption coefficients and sorption heat. Calorimetric measurements were carried out for all the samples to evaluate the specific heat. The evaluated experimental data were used to carry out thermodynamic analysis with the aim to estimate the performance of a refrigeration and air conditioning cycle in terms of cooling COP.

2. Experimental

2.1. Selected materials

Five different commercial activated carbons, supplied by different companies, have been characterized and evaluated for the use in adsorption refrigeration systems. The samples are chosen with different bases, ranging from coconut shell to coal based, and with different shapes, from grains to fibers. Table 1 reports the list of the tested samples.

In addition, the innovative composite sorbent LiBr/silica gel (SG/LiBr) has been studied. The silica gel KSK ("Salavatnefteorgsyntes", Russia) with the specific surface area $S_{sp} = 280\ m^2/g$, the pore volume $V_p = 1.0\ cm^3/g$, the average pore size $d_{av} = 15$ nm was used as a porous matrix. The composite sorbent SG/LiBr was prepared