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## Adsorption cooling utilizing the "LiBr/silica – ethanol" working pair: Dynamic optimization of the adsorber/heat exchanger unit



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#### ABSTRACT

Owing to encouraging energy saving potential, adsorption heat transformers are considered as promising alternative to compression systems. However the enhancement of their specific power is required for their broader dissemination. This paper aims at the dynamic optimization of the Ad-HEx (adsorber/heat exchanger) unit operating with the novel working pair "LiBr/silica – ethanol", which is characterized by high sorption difference under typical conditions of ice making and air conditioning cycles. The comparative investigation of various Ad-HEx configurations, namely thin beds of loose sorbent grains located on a flat metal plate and loaded into finned flat-tube heat exchangers was carried out. The effects of the adsorbent grain size, Ad-HEx geometry were explored in detail, and the main factors affecting sorption dynamics were revealed. The intra-particle diffusion of ethanol vapor and heat transfer between the support and the sorbent bed were shown to affect the sorption rate for flat sorbent bed configuration. For the configurations based on finned flat-tube heat exchangers, additional effects of the inter-particle diffusion or/and residual air were detected. On the base of the main findings obtained the practical recommendations on optimization of the Ad-HEx unit were formulated in order to enhance the specific cooling power of the adsorptive chiller.

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#### 1. Introduction

Recently AHTs (adsorption heat transformers) have attracted an increasing attention due to their heat storage potential and to the use of environmentally friendly refrigerants [1,2]. A number of advanced solid sorption cycles have been developed for refrigeration [3–5], ice making [6], deep freezing [7] and thermal energy storage [8–10]. Contrary to conventional compression systems, the AHTs can produce cooling/heating effect utilizing waste or renewable heat as driving energy source that can lead to an essential reduction of primary energy consumption. Despite the known advantages of this technology (environmental friendly, noiseless, etc.), it still presents crucial problems and troubles to be overcome for its implementation. Large efforts have been applied to study the thermodynamic aspects related to the enhancement of the AHTs performance [11]. The research activity in this direction is aimed to the development of new sorbent materials or improvement of the existent working pairs [11,12].

Among common refrigerants used in AHTs (water, methanol, ethanol and ammonia), ethanol is gaining interest owing to its low freezing point (159 K) and ecological compatibility. Typical ethanol adsorbents used in AHTs are activated carbons [13,14]. Recently new composites "salt/silica gel" with advanced sorption capacity have been proposed as ethanol sorbents for adsorption cooling [15]. The affinity of the sorbent LiBr/silica to ethanol is moderate that allows the regeneration of the composite at relatively low temperature of 363–368 K. The main sorbing component of the composite is LiBr, the ethanol vapor is absorbed according to the reaction [16]:

 $\text{LiBr} + 4\text{C}_2\text{H}_5\text{OH} = \text{LiBr} \cdot 4\text{C}_2\text{H}_5\text{OH}.$  (1)

Further sorption leads to the formation of salt-ethanol solution inside the silica pores. The LiBr/silica composites are characterized by a large variation in the uptake  $\Delta w = 0.3-0.5$  g g<sup>-1</sup> under conditions of typical AC (air conditioning) and IM (ice making) cycles.



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Nomenclature		U	heat transfer coefficient, W m <sup><math>-2</math></sup> K <sup><math>-1</math></sup>
		V	volume, m <sup>3</sup>
Α	heat flux, W	$V_p$	pore volume, $\text{cm}^3 \text{ g}^{-1}$
COP	Coefficient of Performance	W	HEx width, mm
$C_{\rm LiBr}$	LiBr content, wt. %	$W_c$	cooling power, Wk $g^{-1}$
$c_p$	specific heat, J/gK	w	mass of ethanol adsorbed, g $g^{-1}$
$d_{av}$	average pore diameter, nm		
$d_{ m tr}$	transport pore diameter, mm	Greek symbols	
D	diffusivity, m <sup>2</sup> /s	$\eta$	dynamic viscosity, Pa•s
G	grain diameter, mm	ρ	density, g cm <sup>-3</sup>
$\Delta H$	enthalpy, kJ g <sup>-1</sup>	au	characteristic time, s
Н	HEx height, mm		
L	HEx length, mm	Subscripts	
1	path of inter-particle mass transfer, mm	0.8	corresponding to conversion $q = 0.8$
М	molar mass, g	ads	sorption
т	mass, g	com	composite
Р	pressure, mbar	con	condenser
q	conversion	des	desorption
R	universal gas constant, kJ mol $^{-1}$ K $^{-1}$	ev	evaporation
r	ratio of characteristic times	HEx	heat exchanger
S	heat transfer surface, m <sup>2</sup>	max	maximum
S <sub>sp</sub>	specific surface area, $m^2 g^{-1}$	mel	melting
Т	temperature, K	tr	transport
t	time, s		

The cooling COP (Coefficient of Performance) of adsorptive chiller based on the "LiBr/silica – ethanol" working pair was estimated to be 0.66 and 0.61 for AC and IM cycles, respectively [15], which is comparable with the COP of the best water sorbents [1,2].

Nowadays, the AHT dynamic optimization is gaining more attention by researchers since it represents an indispensable requirement in the development and subsequent commercialization of compact units [17]. The adsorption dynamics commonly is affected by heat and mass transfer between the HEx (heat exchanger) and the adsorbent bed, inside the bed and the grains. For composite sorbents "salt inside porous matrix" an additional factor, affecting the adsorption dynamics, can be a chemical reaction between the salt and the vapor [18].

In this paper the results of dynamic study of ethanol sorption on the LiBr/silica composite are presented. Dynamics of ethanol sorption on the LiBr/silica composite was studied by a LTJ (Large Temperature Jump) method that simulates the real conditions of isobaric stages of the cooling cycles. We studied very usable adsorber configurations, consisting of the loose adsorbent grains located on a flat metal plate, and loaded into small scale versions of common finned flat-tube heat exchanger. The ethanol sorption dynamics was studied under typical conditions of two cooling cycles, namely IM and AC. The results obtained allow practical recommendations on the optimization of the Ad-HEx (adsorbent heat exchanger) unit to be made. These recommendations might promote the enhancement of the specific cooling power of the adsorptive chillers utilizing the "LiBr/silica — ethanol" working pair and their efficient implementation.

#### 2. Experimental

#### 2.1. Materials

The silica gel KSK ("Salavatnefteorgsyntes", Russia) with the specific surface area  $S_{\text{sp,SiO}_2} = 280 \text{ m}^2 \text{g}^{-1}$ , the pore volume  $V_{p,\text{SiO}_2} = 1.0 \text{ cm}^3 \text{g}^{-1}$ , the average pore size  $d_{\text{av,SiO}_2} = 15 \text{ nm}$  and the grain size G = 2-5 nm was used as a porous matrix. The composite sorbent LiBr/silica was prepared by dry impregnation of the silica

gel with a LiBr aqueous solution followed by thermal drying. The silica gel was dried at 473 K for 4 h to remove adsorbed water, cooled to ambient temperature and impregnated with aqueous LiBr solution (2.7 M). The solution volume was equal to the pore volume of the matrix. The wet composite was kept for 16 h to reach uniform distribution of the salt inside grains and then dried at 433 K for 4 h. The LiBr content  $C_{\text{LiBr}}$  in the anhydrous composite was 19 wt.%. Characteristics of porous structure of the LiBr/silica composite, that have been investigated by nitrogen physisorption technique (ASAP 2020 by Micromeritics), are as follows:  $V_{p,\text{com}} = 0.73 \text{ cm}^3 \text{ g}^{-1}$ ,  $S_{\text{sp,com}} = 181 \text{ m}^2 \text{ g}^{-1}$  and  $d_{\text{av,com}} = 15 \text{ nm}$ . The pore volume of the composite per 1 g of the initial silica  $V_{p,\text{com}} = 0.9 \text{ cm}^3 \text{ g}^{-1}$  This value is very close to the pore volume of the silica gel  $V_{p,\text{SiO}_2}$  subtracted by the volume  $V_{\text{LiBr}}$  of the LiBr confined to 1 g of silica ( $V_{\text{LiBr}} = C_{\text{LiBr}}/\rho_{\text{LiBr}}/(100-C_{\text{LiBr}}) = 0.07 \text{ cm}^3 \text{ g}^{-1}$  where  $\rho_{\text{LiBr}}$  is the density of LiBr)



Fig. 1. Isosteric chart of the LiBr/silica composite with ethanol vapor.

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