



## Research Paper

# Dynamic optimization of adsorptive chillers: Compact layer vs. bed of loose grains



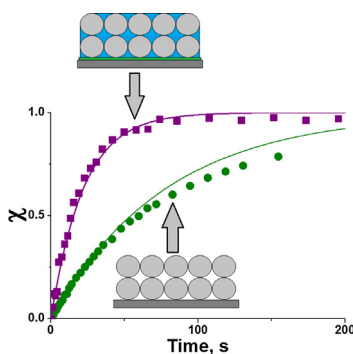
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## HIGHLIGHTS

- This is the first V-LTJ study on adsorption dynamics in compact adsorbent layers.
- Methanol is adsorptive, carbon ACM-35.4 is adsorbent, polyvinyl alcohol is binder.
- The initial part of the uptake/release curves is exponential.
- The invariance with respect to the ratio (heat transfer surface)/(adsorbent mass).
- Ad/desorption in the compact layers is faster than in the grain beds by 1.5–2.2 times.

## GRAPHICAL ABSTRACT



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## ABSTRACT

This paper addresses the dynamic study on methanol ad-/desorption in compact adsorbent layers, performed by a Volumetric Large Temperature Jump (V-LTJ) method, appropriate for dynamic examination of adsorptive chillers. The commercial active carbon ACM-35.4 was used as an adsorbent, and polyvinyl alcohol as a binder. The influence of the carbon grain size and the layer thickness on the V-LTJ dynamics was studied at a fixed binder content of 12 wt%. To single out the effect of consolidation, a detailed comparison was made with reference beds of the loose carbon grains, having the same configuration, however, containing no binder.

The following findings are reported for the compact layers: (i) near-exponential shape of the dynamic curves of methanol adsorption; (ii) invariance of the dynamics with respect to the ratio  $(S/m) = \langle \text{heat transfer surface} \rangle / \langle \text{adsorbent mass} \rangle$ ; (iii) linear relationship between the maximal specific power and this ratio. For the compact layers, the process becomes faster by a factor of 1.5–3.5 as compared to the reference beds.

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## 1. Introduction

Adsorptive chillers (ACs) are attracting an increasing attention due to their encouraging potential for effective utilization of waste

and renewable heat for heating and cooling [1–3]. Improvement of ACs dynamics would make them more competitive with compression and absorption machines [4]. The common way to do this is an intensification of heat transfer by consolidating adsorbent grains with each other and with heat exchanger (HEX) walls by using a binder/glue [5,6]. A compact layer has a larger density as compared to a bed of the loose grains that leads, in turn, to higher thermal conductivity [7,8], however, impedes vapour transport in the layer.

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## Nomenclature

$A$	slope coefficient ( $\text{kW m}^{-2}$ )
$B$	constant ( $\text{kW kg}^{-1}$ )
$d$	pore size (nm)
$D$	grain size (mm)
$\Delta H$	heat of evaporation ( $\text{J g}^{-1}$ )
$m$	adsorbent mass (g)
$N$	number of layers
$P$	pressure (mbar)
$q$	adsorption uptake ( $\text{g g}^{-1}$ )
$R$	initial sorption rate ( $\text{g g}^{-1} \text{s}^{-1}$ )
$S_{sp}$	specific surface area ( $\text{m}^2 \text{g}^{-1}$ )
$S$	heat transfer surface ( $\text{m}^2$ )
$T$	temperature (K)
$t$	time (s)
$U$	coefficient of heat transfer ( $\text{W m}^{-2} \text{K}^{-1}$ )
$V_p$	pore volume ( $\text{cm}^3 \text{g}^{-1}$ )
$W$	specific power ( $\text{W kg}^{-1}$ )

## Greek symbols

$\chi$	dimensionless conversion
$\tau$	characteristic time (s)

## Subscripts

0	initial
2	stage 2
4	stage 4
$a$	adsorption
$av$	average
$c$	condensation
$d$	desorption
$e$	evaporation
$gr$	grain
$H$	high
$L$	low
$max$	maximal
$M$	middle

Therefore, the consolidation procedure should be intelligent to find a compromise between heat and mass transfer in the layer, and further research on this subject is welcome.

The aim of this work was to elucidate the effect of adsorbent grains consolidation with a binder/glue on the dynamics of isobaric stages of the typical AC cycle. Methanol was used as adsorbate, and active carbon ACM-35.4 as adsorbent [9]. This carbon is a modern analogue of the carbon AC-35 widely studied for AC cycles [10]. A Volumetric Large Temperature Jump (V-LTJ) method [11] was applied for this dynamic study. This is the *first* LTJ-study of the adsorption dynamics on *compact* adsorbent layers. To single out the effect of consolidation, a detailed comparison was made with the reference beds of loose grains, having the same configuration, however, containing no binder. To the best of our knowledge, such a detailed comparison has never been performed before. The reference equilibrium and dynamic data were taken from [9]. The consolidation effect was studied depending on the carbon grain size  $D_{gr}$  and the layer thickness (measured as a number  $N$  of adsorbent grains in the direction perpendicular to the metal support) at fixed binder content.

## 2. Experimental

### 2.1. Adsorbent characterization and sample preparation

Activated carbon ACM-35.4 (CECA Arkema group) with the average pore size  $d_{av} = 2.3$  nm, the specific surface area  $S_{sp} = 1200 \text{ m}^2 \text{g}^{-1}$ , and the specific pore volume  $V_p = 0.69 \text{ cm}^3 \text{g}^{-1}$  is characterized by advanced microporous structure leading to large methanol adsorption. The isotherms of methanol adsorption on ACM-35.4 were measured in [9].

The carbon was milled and sieved in two fractions with  $D_{gr} = 0.8\text{--}0.9$  mm and  $1.6\text{--}1.8$  mm. Compact layers were prepared by using polyvinyl alcohol (PVA) as a binder. For this purpose, 1 g of ACM-34.5 was mixed with 2 ml of 15 wt% aqueous solution of PVA. This mixture was used to prepare tablets (Fig. 1a) with fixed mass of the adsorbent ( $m = 0.50$  g) and various ratios of  $(S/m) = 3.2, 1.6, 0.8,$  and  $0.4 \text{ m}^2 \text{kg}^{-1}$ , where  $S$  is the heat transfer surface.

These tablets were dried in air for 24 h at room temperature, for 2 h at  $100$  °C and calcined at  $400$  °C for 4 h in argon flow to carbonize PVA. The content of the binder (formed carbon) was calculated to be 12 wt% (dry base). The tablets were glued to a metal

support of the measurement cell by a Zalman ZM-STG2 thermal paste to reduce the thermal resistance between the sample and the support (Fig. 1b). Comparison of the consolidated layers was made with appropriate beds of 1, 2, 4, and 8 layers of loose ACM-35.4 grains (Fig. 2). Fixing this ratio is obligatory for correct comparison of the granulated and consolidated beds, because the LTJ dynamics is invariant with respect to the  $(S/m)$ -value as shown in [9] for the beds of loose grains.

### 2.2. Volumetric large temperature jump method

The detailed V-LTJ procedure was described in [11] whereas the experimental test rig used in this study was presented in [9]. The samples were placed on a metal support subjected to a jump/drop of temperature as it takes place in real AC. The chosen boundary temperatures were typical for isobaric stages of the chilling cycle:  $T_L = 5$  °C,  $T_M = 30$  °C,  $T_H = 90$  °C (Fig. 3) and equal to those used in [9]. To initiate methanol adsorption, the temperature was dropped from the initial temperature  $T_2 = 56$  °C down to the final adsorption temperature  $T_c = 30$  °C at almost constant vapour pressure  $P_e = 54$  mbar that corresponds to an evaporator temperature  $T_L$  of  $5$  °C. For the desorption runs, the temperature was jumped from the initial temperature  $T_2 = 54$  °C to the final desorption temperature  $T_3 = 90$  °C at almost constant methanol pressure  $P_c = 214$  mbar, corresponding to the condenser temperature  $T_M = 30$  °C. The amount of methanol, exchanged in this cycle, was  $0.184 \text{ gg}^{-1}$ . It did not depend on the binder presence and was in good agreement with data of [9].

The methanol ad-/desorption initiated a slight variation  $\Delta P(t)$  of the vapour pressure over the adsorbent. Evolution of the vapour pressure  $P(t) = P_o + \Delta P(t)$  for desorption and  $P(t) = P_o - \Delta P(t)$  for adsorption was measured by an absolute pressure transducer Barocel™ 600 with an accuracy of  $\pm 0.15\%$ . Data on the pressure evolution  $P(t)$  required for calculating the methanol uptake/release  $q(t)$  were recorded each 1 s by a data acquisition system. The dimensionless uptake was calculated as [11]

$$\chi = q_t / \Delta q = [q(t) - q(0)] / [q(t \rightarrow \infty) - q(0)] \\ = [P(t) - P(0)] / [P(t \rightarrow \infty) - P(0)]. \quad (1)$$

The accumulated error in the absolute methanol loading was  $\pm 10^{-3} \text{ kg/kg}$  that leads to the accuracy of the differential methanol loading  $q(t)$  equal to  $\pm 3\%$ . Relative variation  $\Delta P/P_o$  of the total

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