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Adsorptive transformation and storage of renewable heat: Review of current trends in adsorption dynamics

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ABSTRACT

The main shortage of emerging technology of adsorptive transformation and storage (ATS) of heat is a low specific power that leads to large-size units poorly competitive so far with common compression systems. Significant intensification of heat and mass transfer in ATS units would allow an overcoming of this drawback. This is especially urgent for transformations driven by renewable heat sources for the following reasons: (i) the driving temperature is low, hence temperature losses in adsorbent – heat exchanger unit must be strictly minimized; (ii) solar heat can be highly variable in time, therefore good desorption dynamics is very important to accept high insolation regimes; (iii) the rate of heat recovery during winter time is essentially restricted by low vapour pressure in an evaporator coupled to the ambient. Current trends of ATS dynamic optimization are considered in the manuscript.

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1. Introduction

The world community has realized the gravity of the problems arising from CO_2 emissions and global warming, and has taken initiatives to alleviate or reverse this situation. Fulfilment of these initiatives requires, first of all, the replacement of fossil fuels with renewable energy sources (the Sun, wind, ocean, etc) and, besides, sustainable use of heat in industry, transport and dwellings (re-use of waste heat, heat storage and transformation, etc.). These new heat sources have significantly lower temperature potential than that achieved by burning fossil fuels which opens a niche for applying adsorption technologies for heat transformation and storage [1].

Current progress in this field is essentially related to the development of Adsorptive Transformation and Storage (ATS) of low temperature heat that is an emerging technology offering both economic and ecological advantages [2,3]. It uses benign working fluids which reduce the direct emissions of greenhouse gases. Moreover, renewable and waste heat can be utilised to reduce the consumption of fossil fuel and, therefore, indirect emissions [2].

The main shortage of ATS technology is a low specific power (SP) that leads to large-size ATS units that are purely competitive with common compression systems. Significant intensification of heat and mass transfer (HMT) in ATS units would allow an overcoming of this drawback. This is especially urgent for ATS units driven by renewable heat sources, at least, but not last, for the following reasons:

(i) the driving temperature difference is low, hence temperature losses in adsorbent – heat exchanger (Ad-HEx) unit must be strictly minimized. It means that the Ad-HEx unit has to be intelligently optimized to anyway get good adsorption dynamics and acceptable SP-values;
(ii) solar heat can be highly variable in time, therefore fast desorption dynamics is very important to follow these alterations and accept high insolation regimes;
(iii) the rate of recovery of stored solar heat during winter time is essentially restricted by low vapour pressure in an evaporator coupled to the ambient. This can be a real problem in countries with cold climate, thus requiring thorough optimization of vapour adsorption dynamics in ATS units working under these severe conditions.

For typical cycle of adsorptive air conditioning with the temperatures of evaporator T_e, condenser T_c and regeneration T_r equal to 10 °C (283 K), 35 °C (308 K) and 90 °C (363 K), respectively, the Carnot efficiency $\eta_{max} = (1/T_c - 1/T_r)/(1/T_e - 1/T_c)$ [4] is calculated to be 1.715. In real ATS units with non-zero power there is a

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temperature loss ΔT in the evaporator, condenser and adsorber which drives appropriate processes of evaporation, condensation and desorption. This loss is higher if HMT is slower. For brief estimation, we considered this difference equal for all these three units and calculated the limiting ATS efficiency corrected by accounting for the temperature loss ΔT: $T_e - \Delta T$, $T_c + \Delta T$ and $T_r - \Delta T$ (Fig. 1) which takes into account dynamic imperfections of real ATS units. Even at $\Delta T = 2$ K, the efficiency reduces down to 1.38 that is only 80% of the maximal efficiency. At typical $\Delta T = 5$ K, the reduction is as much as 42%.

Another example concerns a novel cycle HeCol (Heat from Cold) for transformation of ambient heat recently presented in Refs. [5,6]. Two main features of this temperature amplification cycle are a) regeneration is performed by dropping the vapour pressure over adsorbent, this pressure drop being ensured by low ambient (air) temperature; and b) this cycle can produce heat that has commercial value, by using for free an ambient (renewable) heat from natural heat sources at low temperature (air, water basins, soil, etc). For typical HeCol cycle, the boundary temperatures are −25 °C (248 K), 2 °C (275 K) and 30 °C (303 K), therefore, the Carnot amplification efficiency [4] $\eta = (1/T_e - 1/T_c)/(1/T_e - 1/T_r)$ is low (0.54), and further reduces to 0.35 at the temperature loss $\Delta T = 5$ K. What's more, the ad/desorption rate in HeCol units has to be carefully optimized to reach acceptable specific power (related to the adsorbent mass/volume) and reasonable unit size. Indeed, the isothermal adsorption and desorption stages of the HeCol cycle occur at very low vapour pressure P_o corresponding to saturation temperatures of −25 °C and +2 °C (for methanol, 7 and 45 mbar, respectively). On the whole, intelligent optimization of HMT and adsorption rate is prerequisite for making ATS units, especially working at low temperatures and pressures, competitive with traditional compression heat transformers.

In this paper, we consider dynamic aspects of Adsorptive Transformation and Storage of low temperature heat from renewable and waste heat sources, and, first of all, heat and mass transfer in ATS systems. This is because intrinsic adsorption that is interaction between a gas molecule and a surface is fast and the kinetics of ad/desorption is dictated either by gas or heat transport through the adsorbent grain/bed, or by both. The only exception is related to ATS systems in which heat is stored/release due to the vapour interaction with an active salt [7,8]. Such gas-solid reaction can be slow and may require a "driving force" to rearrange the salt crystalline structure.

Both open and closed systems are used for ATS. The HMT in open ATS units [9] is similar to common adsorption systems for gas separation and purification, therefore vast accumulated knowledge and experience [10,11] can be directly applied to analyze open ATS units. Therefore, in this review we shall deal only with closed ATS systems, HMT in which can significantly differ from that in the open systems. At least, but not last, the following essential distinctions are:

- adsorption/desorption is usually initiated by a large drop/jump of temperature, not pressure increase/decrease;
- gas phase contains only one component, that is a vapour of water, methanol, ammonia, etc.;
- little amounts of residual non-adsorbable gas (air, hydrogen, etc) can dramatically affect the dynamic performance;
- gas pressure can be significantly below 1 bar that may reduce both heat and mass transfers;
- adsorbent can be used as consolidated layer/coating.

In this paper, we consider these and other peculiarities of closed ATS systems in the context of renewable and waste heat utilization.

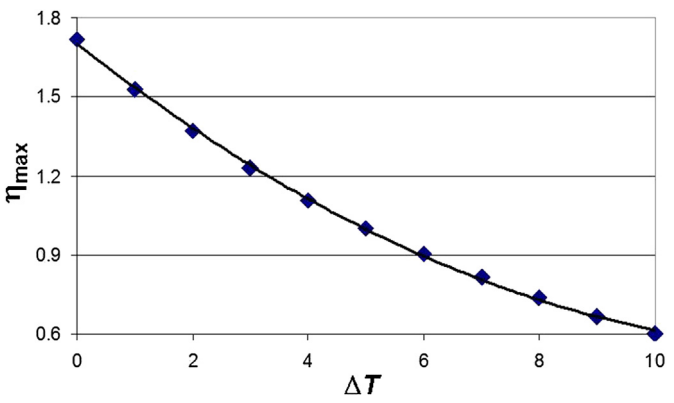

Fig. 1. The ATS limiting efficiency corrected for the temperature loss ΔT (see text).

2. Measurement of adsorption dynamics: two ways to initiate adsorption

Principle feature of closed ATS systems is that the vapour adsorption/desorption is initiated by a drop/jump of temperature of a metal plate that is in mechanical and thermal contact with an adsorbent bed (Temperature-initiation or *T*-initiation). This is quite different from a common ad/desorption initiation by the increase/decrease of gas/vapour pressure over an adsorbent (Pressure-initiation or *P*-initiation).

2.1. P-initiation

Ad/desorption dynamics under the *P*-initiation was studied in many papers, and important analytical solutions are summarized e.g. in Refs. [10,12,13]. The most famous and useful solution was suggested for dynamics of isothermal adsorption initiated by a small jump of gas pressure over an adsorbent grain (*Isothermal Differential Step*, IDS method) [12]. This solution gives a linear dependence of the gas uptake on the square root of time at short adsorption times $m_t/m_\infty = A\sqrt{t}$. This approximation is valid at $m_t/m_\infty < 0.3$ (see an exact solution in Refs. [10,12]). The diffusion constant

$$k_D = D_{ap}/R^2 \quad (1)$$

is much larger for smaller grains, where D_{ap} is the apparent gas diffusivity, R is the grain radius. The IDS approach provides a theoretical foundation for experimental measuring the apparent diffusivity $D_{ap} = A^2\,\pi R^2/36$ (for spherical grains) [10]. Thermogravimetric version of the IDS method was used to measure the apparent water diffusivity for two adsorbents interesting for ATS, namely, Fuji silica RD [14] and SWS-1L ($CaCl_2$ in mesoporous silica KSK) [15]. The ethanol apparent diffusivity on activated carbon fibre A-15 was measured in Ref. [16]. A "constant volume - variable pressure" IDS version was applied in Ref. [17] to determine the apparent diffusivity of R134a and R507A onto pitch based activated carbon of Maxsorb III type.

Another useful approximation of the IDS model concerns long adsorption times (or $m_t/m_\infty > 0.7$): $m_t/m_\infty = 1 - \frac{6}{\pi^2}\exp\left(-\pi^2\frac{D_{ap}t}{R^2}\right)$ [10]. It was used e.g. for determining the apparent diffusivity of ethanol vapour on spherical phenol resin [18].

The apparent diffusivity

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