HEAT AND MASS RECOVERY IN AN ACTIVATED CARBON-METHANOL ADSORPTIVE CHILLER

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Abstract. This paper presents the first results of a transient model of the heat and mass transfers of an activated carbon-methanol adsorption chiller. The chiller's functioning is based on two adsorptive beds (adsorbers), one condenser and one evaporator. They are operating in alternated turns, or else, if one adsorber is adsorbing, the other is desorbing. The adsorber model takes into account the geometry of the finned-tube liquid-adsorbent heat exchanger. Keeping the cycle period constant, some heat recovery and mass recovery time were tested. The simulation results show an increment of both coefficient of performance and specific cooling power of 16.23% and 8.17%, respectively.

Keywords: heat and mass recovery, adsorption chiller, transient simulation.

1. INTRODUCTION

As a rule, the cooling systems requiring thermal energy as their main power input for the production of frigorific effect are most dependable on sorption processes. For sorption cycles, the input energy can come from the thermodynamic conversion of low-grade thermal sources. A comparative study between the three sorption cooling systems (liquid, chemical reaction and adsorption) was published by Meunier (1998). In all these systems the mechanical energy consumption is kept to a minimum or null, i.e. they utilize mainly thermal energy that comes from various sources, as such, process heat, thermal waste or solar energy. This represents a great advantage over the conventional vapor compression systems, especially in countries like Brazil whose energy consumption depends mainly on hydroelectric power.

The adsorption technology applicable to cooling systems differs significantly from that of absorption on account of its unsophisticated functioning. In adsorption, there occurs the interaction between a solid and a fluid, the transportation of the latter being thermal gradient dependable, i.e. it does not require the use of pumps. In the case of liquid absorption cycle, however, a solution interacts with a refrigerating fluid, calling for a number of electromechanical devices in order to move both the solution and the fluid. Moreover, the adsorption cycle depends on fewer electromechanical components (heat exchangers, valves). On the other hand, adsorption refrigeration has shown performance coefficients lower than those obtained by liquid absorption. In the field of the adsorption refrigeration, there have been considered various kinds of fluid-solid pairs. Zeolite-water and silica gel-water are used for cold storage and air conditioning, whereas activated carbon-methanol and activated carbon-ammonia are used for obtaining low negative temperatures.

Solar energy is abundant over large areas of northeast Brazil (annual average being over 6 kWh/m^{2}day), securing, therefore, a great potential supply for use on helium-thermal conversion systems applicable for either heating or cooling purposes. In this region, the energy consumption for air conditioning is very high and we notice an increasing demand, especially in the industrial and tertiary sectors. This paper presents some fundamentals of adsorption and the related refrigeration cycles, with or without mass and heat recovery, and results from numerical simulations for an activated carbon-methanol adsorptive chiller.

2. ADSORPTION FUNDAMENTALS

Adsorption is a solid sorption process where the binding forces between fluid molecules (the adsorbate) and the solid medium (the adsorbent) come from an electrostatic origin or from dispersion-repulsion forces. It is an exothermic process due to the gas-liquid phase change. The energy liberated in adsorption processes is called isosteric heat, and it depends on the nature of the adsorbent-adsorbate pair.

To describe the thermodynamic equilibrium of adsorption, several state equations known as "isotherms of adsorption" are proposed. These functions correlate the temperature T, the pressure P and the concentration of the adsorbed phase a, so that f(T, P, a) = 0. The main isotherms of adsorption are: (a) Henry's law, valid only for weak concentrations; (b) Langmuir's approach, which considers adsorption in monomolecular layers and that there is a dynamic equilibrium between the phases; (c) Gibbs' theory, based on the perfect gas equation, in which the adsorbate is treated in the microscopic and bidimensional form; and (d) Eucken and Polany's theory, the so-called "potential adsorption theory", in which it is assumed that in the space around each solid one may find some isopotential surfaces delimiting adsorbate that is adsorbed at pressures (or concentrations) lower than those corresponding to the potential value and that such isopotential surfaces

are specific for a given solid surface (Polanyi, 1916). Dubinin and Radushkevich proposed the "micropore volume filling theory" that is related to Eucken-Polanyi potential theory. The Dubinin-Radushkevich isotherm describes adsorption on a single type of uniform pores that is similar to Langmuir-like local isotherms in adsorption on energetically heterogeneous solids. This theory was later extended by Stoeckli, allowing it to describe adsorption on energetically heterogeneous solids with a continuous distribution of pore sizes. A detailed analysis of the thermodynamics of adsorption and its different isotherms is given by Leite (1998).

2.1 Adsorption cycles with mass and heat recovery

An adsorptive cooling system can base its operation on a basic intermittent - or a mass and heat recovery free cycle - which may be described by one stage in which a gaseous adsorbate fluid is transported from the evaporator to the adsorber, and a next stage when the fluid is transported from the adsorber to the condenser, where it liquefies and flows down into the evaporator, completing then the cycle. The corresponding ideal thermodynamic cycle is represented by two isosteres (iso-lines with constant adsorbed phase concentration) and two isobars, as shown in Fig. 1a. The 1-2 and 2-3 processes describe the adsorber's cooling and the adsorption, while the 3-4 and 4-1 processes describe the regeneration of the adsorber, i.e., its heating and desorption. Points 2 and 4 (Fig. 1a) represent the initial states of the adsorption and the desorption, respectively.
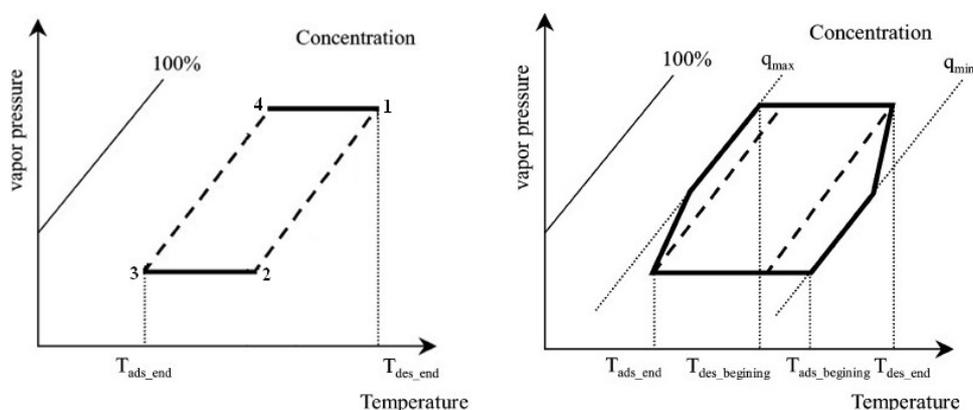

Figure 1. Dühring diagram for the ideal basic cycle (a) and for the mass recovery cycle (b)

In order to improve the COP of adsorption cooling systems, various operation procedures of the adsorbers can be considered, as such continuous two or four-adsorber heat recovery cycles, mass recovery with sensible heat recovery, and mass recovery with both sensible heat and heat of adsorption recoveries. A general scheme of the mass recovery cycle is shown in Fig. 1b. A widely description (numerically and experimentally) of mass recovery cycle was done by Poyelle *et al.* (1999) and, of heat recovery, by Douss *et al.* (1988).

Wang *et al.* (2005) have experimentally obtained an expressive COP-enhancing with a passive heat recovery scheme in a two-bed and four-bed chillers, without any effect on their cooling capacities. In another study, with a prototype heat-regenerative adsorptive air conditioning system (Gui *et al.*, 2002), they analyzed the effects of step times of the heat recovery, mass recovery and half-cycle on the COP and the specific cooling power (SCP). According to this study, the experimental COP and SCP increased 16% and 6%, respectively, with a very short time - 0.5 min - of mass recovery before the beginning of the heat-recovery process. They obtained as an appropriate half-cycle time for improving both COP and SCW about 20-25 minutes. Akahira *et al.* (2004) have investigated the performance of a two-bed silica gel-water adsorption refrigeration cycle with mass recovery process under different operating conditions. Results from computer simulation showed that, for a hot water temperature of 70řC and chilled water of 7řC, with the mass recovery cycle and any heat recovery the COP and SCP are, respectively, 28% and 9.5% larger than those obtained with the single cycle.

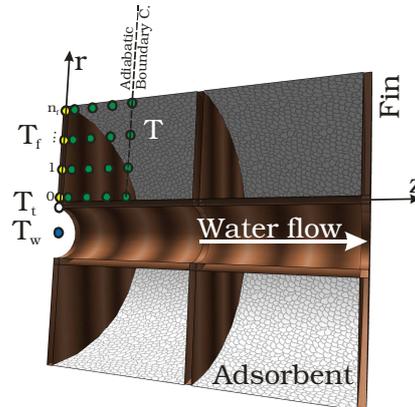## 3. SIMULATION DESCRIPTION

Figure 2. Finned-tube heat exchanger: simulation volume control

It is known that the thermal behaviour of the adsorber is strongly dependent on the adsorbent thermal conductivity, k, and the heat transfer coefficient of the interface metal/adsorbent, h. Therefore, a finned-tube heat exchanger was chosen to increase the heat transfer area. In the geometrical model of this heat exchanger, annular fins with adiabatic boundaries were used as simplification hypothesis, see Fig. 2, with the followings assumptions:

1. the heat transfer in the adsorbent medium is two-dimensional (axial and radial);
2. the thermal gradient in radial direction is neglected both for water flow and inside the tubes ($r_i \ll L$);
3. the fin thickness is small enough to consider the heat transfer only in radial direction;
4. a thermal contact resistance is considered at the interface tube/fin;
5. the convective effects and pressure drops are negligible in the adsorber bed;
6. no heat losses to the ambient are considered;
7. regarding thermal conductivity, the adsorbent is treated as a continuous medium;
8. all adsorbent particles have the same properties (including shape and size); they are uniformly distributed throughout the adsorbent, and in local thermal equilibrium with the adsorbate and the surrounding gaseous phase;
9. the gaseous phase behaves as an ideal gas;
10. the properties of the heat transfer fluid and the adsorbate are considered as temperature dependent.

The simulation is divided in n_x nodes that contain n_f fins, as shown in Fig. 2. It is calculated for each node one mean temperature to the water flow T_w, another to the tube T_t, n_r points to the fin and a thermal gradient in 2D to the adsorbent. The model take into consideration the thermal contact resistance between the fin and the tube. It can simulate fins smelted, pressed or even with a air-gap. The adsorber bed is under vacuum and it is big enough to make the pressure drops close to zero. This was also the reason to not consider heat losses to the ambient. As pellets are often used as adsorbent, assumption (vii) and (viii) are about the treatment of it as an unique solid in terms of heat conduction.

3.1 Adsorber, Condenser and Evaporator

The equations related to the adsorber, condenser and evaporator where widely described and experimentally validated on a previous paper (Riffel *et al.*, 2009). The adsorber corresponds to a multi-tubular system, whose inner surface exchanges heat with the water coming from a hot or cold source, depending on the stage of the cycle. The adsorbent occupies the space delimited by the external wall of the tube and the corrugated fins. The condenser/evaporator can be a finned-tube heat exchanger or also a tube heat exchanger, without fins.

3.2 Diffusion in the adsorbent

In 1920, Daynes proposed a method to determine the diffusion coefficients by mounting a porous medium between two chambers. One chamber is filled with gas and the other is kept under vacuum. Although the diffusion is started at $t = 0$, the pressure in the receiving chamber remains very low. This time lag in the response of the pressure is measured and used to extract kinetic parameters (Do, 1998). The same idea is used in the proposed model. The measured pressure on the adsorber chamber is corrected by a time lag, τ, and utilised as mean adsorbent pressure that can be given by the

following differential equation:

$$\frac{dP}{dt} = \frac{1}{\tau}\left(P_{ch} - P\right) \tag{1}$$

If Δt is small enough, it is right to consider that the adsorber bed pressure, P_{ch}, has a linear variation. Solving this equation in the Laplace domain and applying the inverse, the following equation can be founded:

$$P^t = P_{ch}^t - \frac{P_{ch}^t - P_{ch}^{t-\Delta t}}{\Delta t}\tau + \left[\frac{P_{ch}^t - P_{ch}^{t-\Delta t}}{\Delta t}\tau + P^{t-\Delta t} - P_{ch}^{t-\Delta t}\right]\exp\left\{-\frac{\Delta t}{\tau}\right\} \tag{2}$$

3.3 Chiller Simulation
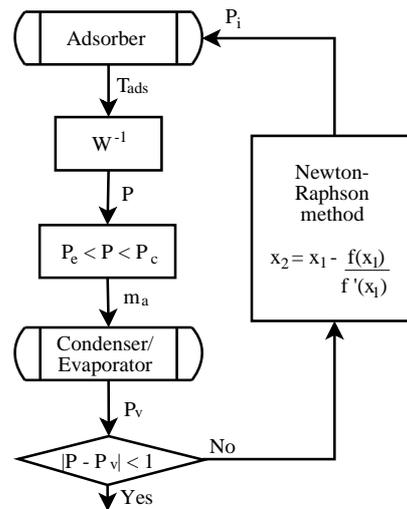
Figure 3. Chiller simulation flowchart.

The adsorption chiller is described by energy and mass balance. A set of differential energy equations for each component (adsorber, evaporator and condenser) are numerically solved and joined by the mass balance, as shown in Fig. 3. The iteration begins with the solution of the Adsorber energy equations and the calculation of the mean temperature in the solid adsorbent medium (T_{ads}), where the volume of each node is taking into account. With the help of the inverse of the characteristic curve (W^{-1}), the new pressure is obtained and corrected by the pressure of evaporator or condenser ($Pe < P < Pc$), depending on the stage of the cycle. The difference between the input and output uptake ($W\rho_s$) times the total mass of adsorbent is the mass of adsorbate that was adsorbed or desorbed (m_a). Now it is needed to evaluate if the Condenser/Evaporator is able to condensate or evaporate all this amount of adsorbate without great variation in the pressure P used in the beginning. If the pressure variation is small enough ($|P - P_v| < 1$ Pa), the mass balance was respected and the simulation can go ahead, otherwise, the Newton-Raphson method is used to compute the new pressure and the iteration restarts.
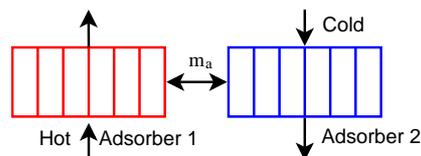
3.4 Mass Recovery Simulation

Figure 4. Mass recovery scheme.

The simulation were developed to build three independent blocks: adsorber, condenser and evaporator. It can also make multiple blocks of each. The only problem is the computational time, but with this strategy it could be solved by another processor (task parallelism), for example. Fig. 4 presents the mass recovery scheme, where one adsorber is hot and the other, cold. The water flow still being pumped, while the valve between adsorbers is open. In this stage, the condenser and the evaporator are both disconnected. The simulation steps of this process are shown in Fig. 5. It begins to simulate one adsorber with the pressure of the other. The pressure of both adsorber beds are, almost instantly, the same.

But, due to the diffusion on the adsorbent medium, the adsorbent pressure increases slowly. It is computed using the time lag. What the flowchart shows is that the pressure of the second adsorber is calculated in order to conserve the mass of the system.
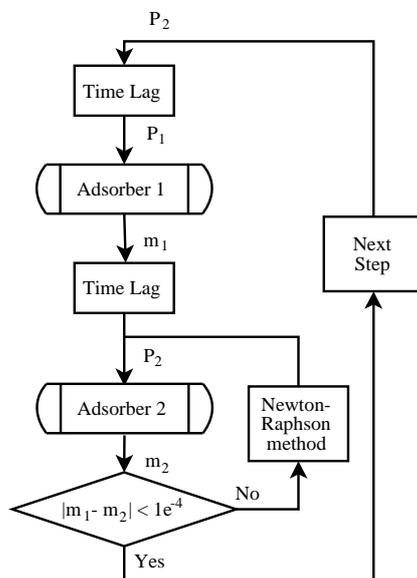

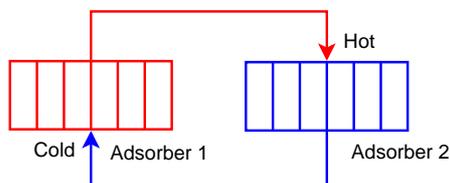Figure 5. Mass recovery: simulation flowchart.

3.5 Heat Recovery Simulation

Figure 6. Heat recovery scheme.

The heat recovery simulation is easier, the vacuum chamber of each adsorber bed are not interconnected. Only the water flow is the same for both adsorbers; the input of one adsorber is the output of the other. For the simulation, it means that at each time step the adsorber equations can be solved independently. The condenser and the evaporator are both disconnected, during the entire process.

4. RESULTS

An adsorption cycle with mass recovery can be seen at Fig. 7, where the period of mass recovery is highlighted. The shape of this curve is very difficult to measure, because the temperature and the pressure have to be obtained in the micropores of the adsorbent medium, that have a diameter smaller than 2 nm. What can be easily measured is the pressure in the vacuum chamber of the adsorptive bed, but than, this shape will look like a straight line to the equilibrium pressure and some fuzzy reactions, because both pressure and the temperature are not being measured in the right place. An example can be found in Wang *et al.* (2006).

This shape is obtained, basically, with a mass balance and a diffusion time lag. Both techniques are accepted for this case. However, for shorter cycles, the diffusion time lag should not be more valid, because this theory takes into consideration a local equilibrium.

Fig. 7 has another important information: his peak. This is exactly the optimally mass recovery time. That is exactly what the Pareto global optimisation method shows. It was found 5 minutes of mass recovery and 2 minutes of heat recovery, as shown in Fig. 8. That peak can also be noted here, on the interface of the dashed line of the heat recovery and the straight line of the mass recovery.

Some experimental results, collected by Wang *et al.* (2005), where used as reference on the analysis of the results. As shown in Fig. 9, the simulation results have a really good agreement with the experimental data. Unfortunately, detailed geometrical data is needed to make a deeper comparison, but qualitatively, the shapes of the curves are the same. Some
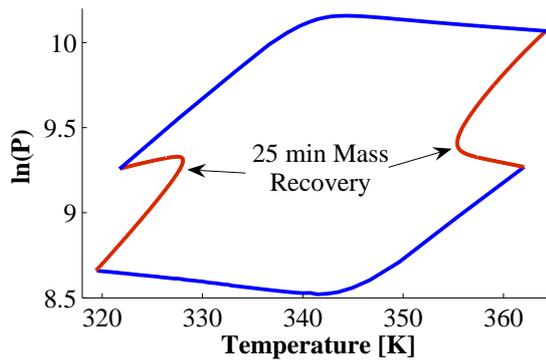
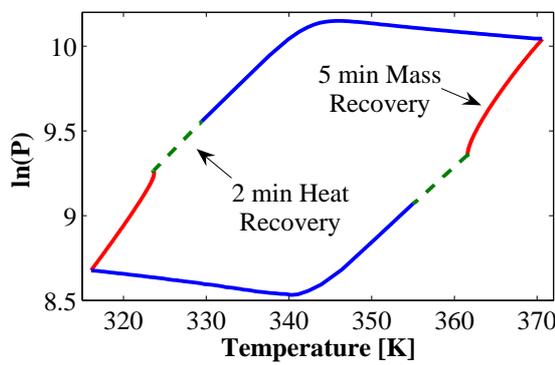Figure 7. Mass Recovery Simulation Results: clapeyron.

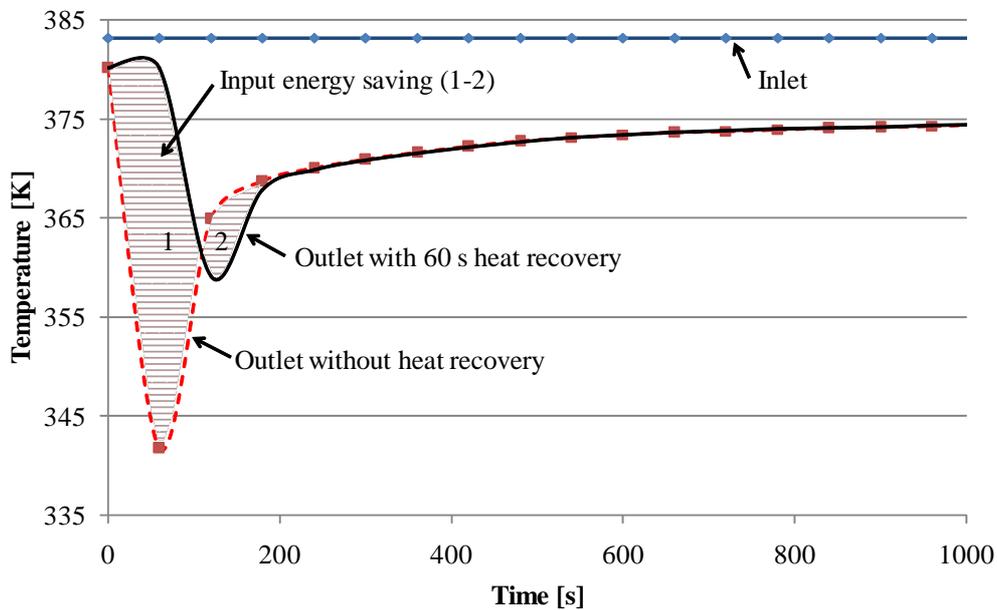Figure 8. Heat-Mass Recovery Simulation Results: clapeyron.

Figure 9. Heat Recovery Simulation Results: time response.

differences can be noted, like the time scale, but it can not be directly compared. The simulation results, presented here, are for a 20 kW activated carbon-methanol adsorption chiller that is being installed at University of Paraíba.

Wang *et al.* (2005) shows that, in their case, the COP is seen to have improved by 14% at long cycle times to 38% at short cycle times, with almost no cooling throughput of the chiller. The best improvement enhanced here where with the results of the Fig. 8, or else, 100 minutes of adsorption period, considering 5 minutes of mass recovery and 2 minutes of heat recovery. The simulation results shows a increment of 16.23% in the COP and 8.17% in the specific cooling power.

5. CONCLUSION

A local optimisation algorithm, based on Pareto, was runed. It keeps all the parameters constant, changing only the heat recovery and the mass recovery time. The simulation results show an increment of both coefficient of performance and specific cooling power of 16.23% and 8.17%, respectively. It was archived with 120 seconds of heat recovery and 300 seconds of mass recovery.

6. ACKNOWLEDGEMENTS

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