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# Isothermal or Non Isothermal Modeling in a Pellet Adsorbent: Application to Adsorption Heat Pumps

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## Abstract

Understanding the interaction between a fluid and a solid phase is of fundamental importance to design of an adsorption process. Because the heat effects associated with adsorption are comparatively large, the assumption of isothermal behaviour is a valid approximation only when uptake rates are relatively slow. In this article, we propose to determine when it is needed to choose the isothermal or non isothermal assumptions according to two physical parameters  $\alpha$  (ratio convection/capacity) and  $\beta$  (ratio quantity of energy/capacity). The proposed problem was solved by a mathematical method in the Laplace domain.

**Keywords:** Adsorption, Non Isothermal, Energy, Pellet.

## 1. Introduction

A basic adsorption heat pump cycle consists of four main parts: an adsorber, which is a container filled with an adsorbent (such as zeolite, active carbon, silica gel, etc.); a condenser; an evaporator; and an expansion valve. Basically, adsorption heat pump operates by cycling adsorbate between adsorber, condenser, and evaporator. In the adsorption heat pump cycle, adsorption phenomena play the same role of mechanical power, so that the working fluid can be circulated in the cycle without any mechanical power (Demir et al., 2008).

In recent years, the importance of adsorption heat pumps and adsorption refrigeration systems has increased since these kinds of systems can directly utilize the primary thermal energy sources and additionally the waste heat generated in various industrial processes. The important advantages of the adsorption heat pumps can be described as follows (Demir et al., 2008):

- they can operate with thermal driving energy sources such as waste heat, solar, and geothermal energies, etc.;
- they can work with low temperature driving energy sources;
- they do not require moving parts for circulation of working fluid;
- they have long life time;
- they operate without noise and vibration;
- they have simple principle of working;
- they do not require frequent maintenance;
- they are environmental friendly since they do not contain any hazardous materials for environment; and
- they can be employed as thermal energy storage device.

On the contrary, the main disadvantages of the adsorption heat pump systems are as follows (Demir et al., 2008):

- they have low COP values;
- they are intermittently working principles;
- they require high technology and special designs to maintain high vacuum; and
- they have large volume and weight relative to traditional mechanical heat pump systems

AHPs are thermally driven and can, therefore, make use of waste heat as well as thermal renewable energy resources. Moreover, AHPs can utilize high energy fuels more effectively than modern condensing boiler heating systems and, consequently, a reasonable amount of the resulting environmental pollution could be avoided. One of the most interesting working pairs for AHPs is zeolite-water. This working pair is non-poisonous, non-flammable and, moreover, has no ozone depletion potential. The adsorption of water vapour into a porous solid adsorbent, such as zeolite, results in the release of the heat of adsorption. Accordingly, the temperature of the adsorbent particle rises, which reduces its water uptake capacity. Therefore, the heat of adsorption has to be removed before a further vapour mass transfer into the adsorbent particle may take place. The evaluation of the heat and mass transfer rates accompanying such an adsorption process is therefore a very important aspect in designing and optimizing the operation of an adsorption heat pump.

In this study, a methodology to choose a good adsorbent in particular according to its thermodynamic properties is presented. We focused our attention on the interaction fluid/solid. The simplest case to consider is a single microporous adsorbent particle exposed to a step change in sorbate concentration at the external surface of the particle at time zero. Heat transfer is assumed to be sufficiently rapid, relative to the sorption rate, so that temperature gradients both through the particle and between particle and surrounding fluid are negligible. Two cases were developed in this article, firstly the isothermal conditions and secondly adsorption behaviour with temperature effect. A mathematical development is presented for each case. According to two developed parameters  $\alpha$  (ratio convection/capacity) and  $\beta$  (ratio quantity of energy/capacity), the difference between isothermal and non-isothermal was analysed.

## **2. Isothermal Assumptions**

During adsorption, heat generated is partly transferred to the surrounding fluid and partly accumulated in the particle leading to an increase of the temperature. The calculation of the temperature uptake curves is based on mathematical model of different complexity depending on the simplifying assumptions being made. Since adsorption is exothermic and the heat of sorption must be dissipated by the heat transfer, there is, in general, a difference in temperature between an adsorbent particle and the ambient fluid when sorption is taking place. Whether or not this temperature difference is significant depends on the relative rates of mass and heat transfer. By the simple theoretical analysis it may be shown that in a batch adsorption experiment it is the dissipation of heat from the external surface of the adsorbent sample, rather than the conduction of heat within the adsorbent, which is generally the rate limiting heat

transfer process. The conditions under which heat transfer resistance may be neglected and the system treated as isothermal case.

Firstly, we considered some isothermal conditions in the pellet and the isotherm was  $q = q_0$ . The isotherm is supposed to relate the concentration  $q$  inside the pellet (or at the external boundary) to the concentration of the external fluid. Another basic assumption is that the pellet is treated as a homogenous medium (contact with the fluid occurs only at the external boundary). So, the diffusivity  $D_c$  is constant in the pellet.

The system was modeled by the following equations (1):

$$\begin{cases} \frac{\partial q}{\partial t} = D_c \left( \frac{\partial^2 q}{\partial r^2} + \frac{2}{r} \frac{\partial q}{\partial r} \right) & \forall t > 0, \forall r (0^+ < r < r_c) & (1-a) \\ q(r, t = 0) = q'_0 & \forall r (0^+ < r < r_c) & (1-b) \\ q(r_c, t) = q_0 & \forall t > 0 & (1-c) \\ \left. \frac{\partial q}{\partial r} \right|_{r=0^+} = 0 & \forall t > 0 & (1-d) \end{cases}$$

The value  $q(r_c, t)$  is equal to  $q_0 \neq 0$ , for solving the system analytically.

With  $\tau = D_c t / r_c$ , the analytic solution is given by the familiar expression

$$\frac{m_t}{m_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{e^{-n^2 \pi^2 \tau}}{n^2} \quad (2)$$

Where  $m_t$  represents the quantity adsorbed in the pellet at time  $t$  and  $m_\infty$  the quantity adsorbed in the pellet at final time. We denote  $\bar{Q}(\tau) = m_t / m_\infty$ . In practice  $m_t / m_\infty$  will

be approximated by (Ruthven et al. 1980):  $\bar{Q}_N(\tau) = 1 - \frac{6}{\pi^2} \sum_{n=1}^N \frac{e^{-n^2 \pi^2 \tau}}{n^2}$

Let us check by the following simple error estimation:

$$\begin{aligned} |\bar{Q}(\tau) - \bar{Q}_N(\tau)| &= \frac{6}{\pi^2} \sum_{n=N+1}^{\infty} \frac{e^{-n^2 \pi^2 \tau}}{n^2} \leq \frac{6}{\pi^2} \sum_{n=N+1}^{\infty} \frac{1}{n^2} \\ &\leq \frac{6}{\pi^2} \int_N^{\infty} \frac{dx}{x^2} = \frac{6}{\pi^2 N} \end{aligned} \quad (3)$$

This inequality gives for  $N=5$  an absolute error of approximately 0.12. But, notice that, in reality, the error is much smaller at least if  $\tau$  stays away from zero. Indeed, if  $\tau \geq \tau_0 \geq 0$ , then the upper estimation can be improved to the following exponential error bound:

$$|\overline{Q}(\tau) - \overline{Q}_N(\tau)| = \frac{6}{\pi^2} \int_N^{\infty} \frac{e^{-n^2 \pi^2 \tau_0}}{x^2} dx \leq \frac{3}{\pi^4 \tau_0} \frac{e^{-N^2 \pi^2 \tau_0}}{N^3} \quad (4)$$

For example, if the reduced time is at least  $\tau_0 = 0.01$  and if again  $N = 5$  then we get for the absolute error a much better approximation of 0.000418.

### 3. Non Isothermal Assumptions

In this case, we assume that intracrystalline diffusion is the only significant resistance to the mass transfer. The sorbate concentration at the surface of each particle in the sample is therefore always in equilibrium, at the temperature of the sample with the sorbate concentration in the ambient fluid. In addition, the thermal conductivity is assumed to maintain an essentially uniform temperature throughout the entire adsorbent particle. The rate of heat transfer between the adsorbent and the ambient fluid which is assumed to obey Newton's law, was finite, so that during the course of the transient adsorption there was a time-dependent temperature difference between the adsorbent and ambient fluid. The system was subjected at time zero, to a small difference step change in ambient sorbate concentration from a previously established equilibrium condition. We assume that concentration equilibrium between fluid phase and adsorbed phase is established quickly at the free surface of the pellet and the equilibrium adsorbed phase concentration is assumed to vary linearly with both temperature and fluid phase concentration. Subject to these approximations, the system may be described by the following equation (10) in reduced value ( $Q=q(t)/q_{\infty}$ ,  $\eta=r/r_c$  and  $\tau=D_c t/r_c^2$ ).

In opposite to the previous part, the reduced value permitted to find an analytic solution in the Laplace domain.

$$\frac{\partial Q}{\partial \tau} = \frac{1}{\eta^2} \frac{\partial}{\partial \eta} \left( \eta^2 \frac{\partial Q}{\partial \tau} \right) \quad (5-a)$$

$$Q(\eta, \tau) = 0, (\tau < 0) \quad Q(\eta, 0^+) = 0, (0 \leq \eta < 1) \quad (5-b)$$

$$Q(1, \tau) = Q_s(T) \quad (5-c)$$

$$\left. \frac{\partial Q}{\partial \eta} \right|_{\eta=0} = 0 \quad (5-d)$$

$$\rho(-\Delta H) \frac{d\overline{Q}}{d\tau} = \frac{\rho C_p}{q_{\infty} - q_0} \frac{dT}{d\tau} + \frac{ha}{q_{\infty} - q_0} \frac{(T - T_0)}{D/r_c} \quad (5-e)$$

The equilibrium relationship at the crystal surface is assumed to be linear with respect to both concentration and temperature:

$$Q_s = 1 + \frac{\partial q^*}{\partial T} \left( \frac{T - T_0}{q_{\infty} - q_0} \right) \quad (5-f)$$

The final result is similar to Ruthven(1984), and the mathematical discussion is described in L. Montastruc (2009) then:

$$\bar{Q}(\tau) = 1 + \sum_{n=1}^{\infty} \frac{-9 \left( \frac{q_n \cot(q_n) - 1}{q_n^2} \right)^2 e^{-q_n^2 \tau}}{\frac{1}{\beta} + \frac{3}{2} \left[ (q_n \cot(q_n)) \left( \frac{(q_n \cot(q_n)) - 1}{q_n^2} \right) + 1 \right]} \quad q_n \in \Re \quad (6)$$

where  $q_n$  are the roots of the equation

$$(\alpha - q_n^2 - 3\beta) \sin(q_n) + 3\beta q_n \cos(q_n) = 0 \quad (7)$$

$$\text{With } \alpha = \frac{ha}{\rho Cp D} \frac{r_c}{D} \text{ and } \beta = \frac{\Delta H}{Cp} \left( \frac{\partial q^*}{\partial T} \right)$$

The parameters  $\alpha$  and  $\beta$  were in a first approach variables used to solve the PDE system. These two parameters represent respectively the ratio between the conductivity and the heat capacity and the ratio between the quantity of energy and heat capacity.

#### 4. Non Isothermal and Isothermal Comparison

In the non-isothermal model, the uptake curve commonly shows a rapid initial uptake followed by a slow approach to equilibrium because the external heat transfer controlled the adsorption. Let us recall that the isothermal model represents the ideal condition in the heat adsorption process.

In fact, in the isothermal case, the equilibrium was reached very quickly. The maximum difference between the two models is obtained in the first phase of the batch adsorption. This phenomenon is due to the fast temperature rising when the adsorption starts. The heat of adsorption produced in the pellet is not transferred into the fluid due to the external heat transfer. In the figure 1, different graphs represent the square distance between the adsorbed quantity with an isothermal model and a non isothermal assumption at different reduced time. To calculate, the  $N$  choice terms is 20, the  $\alpha$  value is comprised between 0 to 40 and  $\beta$  between 0 to 10. If  $\alpha$  is near zero and  $\beta$  is large, we observed that when the reduced time is lower that 0.25, the calculated errors increased with the reduced time. And when the reduced time is higher than 0.25, the calculated errors decreased.

To increase the process efficiency, it is necessary to raise the external heat transfer. It can be modified by the hydrodynamics around the pellet. The values of  $\alpha$  and  $\beta$  can determine the "efficiency" of the heat adsorption process. In fact, if the  $\beta$  value is small and /or near to zero, the adsorption curve can be analyzed as in the isothermal case. But it means that the heat pump process cannot be operated because it will not produce enough heat. The  $\alpha$  value is more significant, because it represents the ratio between the convection and the thermal capacity. To reach the ideal case,  $\alpha$  should be very large. The external heat transfer will then not be a limiting phenomenon, and the adsorption is closed to the isothermal case.

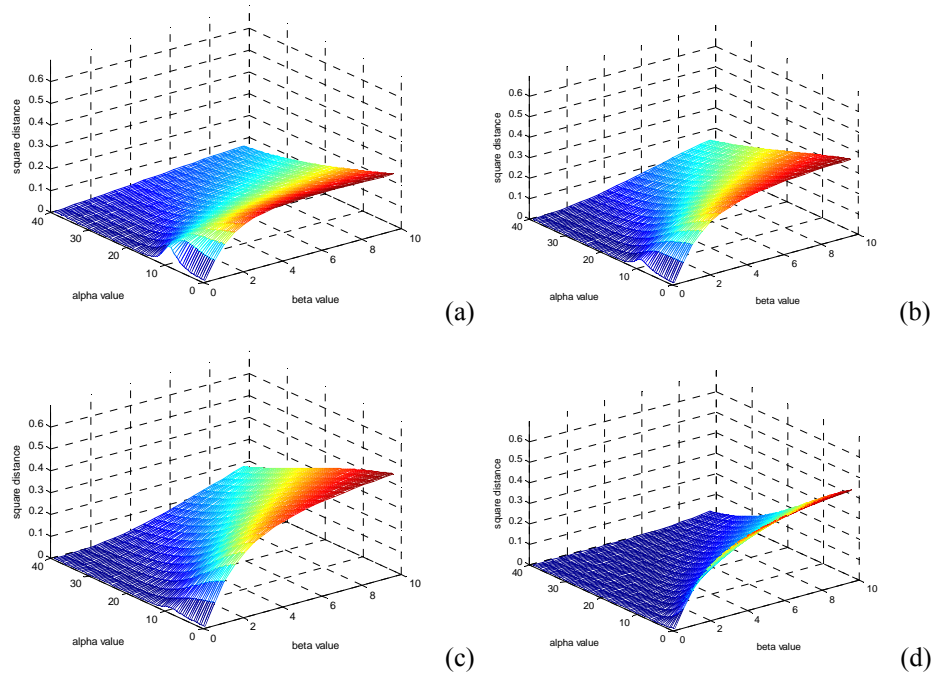


Figure 1. Square distance between the isothermal and the non isothermal model for different  $\alpha$  value between 0 to 40 and for different  $\beta$  value between 0 to 10((a) reduced time = 0.01, (b) reduced time = 0.05, (c) reduced time = 0.1, (d) reduced time = 0.5)

## 5. Conclusion

In this article, we show the importance of the pellet adsorption study before designing a heat adsorption process. The difference between the two models - isothermal or non isothermal - could be measured by the value of two parameters  $\alpha$  and  $\beta$ . In fact, when  $\alpha \rightarrow \infty$  (infinitely high heat transfer coefficient) or  $\beta \rightarrow 0$  (infinitely large heat capacity), the limiting case was isothermal. When diffusion was rapid ( $\alpha$  small) the kinetics of sorption was controlled entirely by heat transfer. If the adsorption process might be used as a heat pump, it shall be represented by an isotherm model with  $\alpha$  and  $\beta$  as higher as possible. Then, these two parameters could determine if the couple adsorbant/ adsorbate can be used in the case of an adsorption heat pump process.

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