

## OPTIMAL TEMPERATURES FOR THE PERIODIC STEADY STATE IN A CASCADE OF STIRRED ADSORBERS

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Received June 9th, 1981

A cascade of stirred adsorbers with a cyclic mode of operation under which adsorbers are periodically removed for activation and replaced by reactivated ones is considered. A method of computation of temperatures maximizing the period under the requirement that the outlet concentration is below a given level is presented.

In the preceding paper<sup>1</sup>, we have studied the problem of designing the temperature control in a stirred adsorber in such a way that the time for which the outlet adsorbate concentration does not exceed a given level is maximal. In case the adsorption process should not be interrupted, a cascade is frequently employed rather than a simple adsorber. Periodically the first adsorber of the cascade is removed for activation and simultaneously a reactivated one is added to the cascade as its last member (Fig. 1). The advantages of this mode of operation of the process (also called "merry-go-round") were discussed in<sup>2</sup>.

Naturally, for a given cascade, one would like to choose the operation parameters in such a way as to have this period as long as possible. An optimization problem for a cascade of tubular reactors under the same mode of operation with a different optimality criterion has been solved in<sup>3</sup>. As in<sup>1</sup> we shall deal with temperature as a control variable. However unlike in<sup>1</sup>, we keep the temperature constant in each particular adsorber during one period. This gives rise to a finite dimensional maximization problem with the temperatures in the particular adsorbers as variables and length of the period as the function to be maximized.

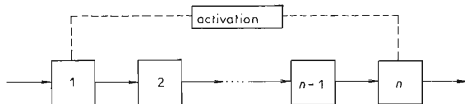


FIG. 1

Cascade with periodic activation

In this paper, we solve this problem by the gradient method. The main difficulty lies in the computation of the periodic steady state and its derivatives with respect to the temperatures. For the former one has to solve a coupled system of partial and ordinary differential equations, for the latter a coupled system of their adjoints.

## THEORETICAL

### *Problem Formulation*

As cascade members we consider continuous stirred adsorbers with the sorbent in the form of spherical particles of approximately equal diameter with the following properties: *a*) The concentration of the adsorbate in the gaseous phase at a given time is constant over the adsorber and equal to that in the outflowing stream (a consequence of perfect mixing). *b*) The temperature in a given member of the cascade is constant. *c*) The distribution of the concentration of the adsorbate in the particles at a given time is the same for every particle. *d*) The resistance against mass transfer from the gaseous phase to the sorbent particle is negligible.

It follows from<sup>1</sup> that under the above conditions the *i*-th adsorber,  $i = 1, 2, \dots, n$ , of the cascade can be modelled by the following system of dimensionless equations:

$$\delta(d\phi_i/d\tau) = \theta_{i-1}\phi_{i-1} - \theta_i\phi_i - (dq_i/d\tau) \quad (1)$$

(the equation of material balance),

$$q_i(\tau) = 3 \int_0^1 \varrho^2 c_i(\tau, \varrho) d\varrho \quad (2)$$

(the formula for adsorbed amount),

$$\frac{\partial c_i}{\partial \tau} = \bar{D}_i \left( \frac{\partial^2 c_i}{\partial \varrho^2} + \frac{2}{\varrho} \frac{\partial c_i}{\partial \varrho} \right); \quad (3)$$

$$\bar{D}_i = \bar{D}(\theta_i); \quad \tau \in \langle 0, \tau^* \rangle; \quad \varrho \in \langle 0, 1 \rangle$$

(the equation of diffusion in one particle),

$$c_i(\tau, 1) = C_i(\tau) = F(\phi_i, \theta_i) \quad (4)$$

(equilibrium at the particle surface – boundary condition for Eq. (3)).

The initial conditions for Eqs (1) and (3) follow from the way the organization of the cascade is changed at the switching time (the  $i$ -th adsorber becomes to be the  $(i - 1)$ th one for  $i = 2, \dots, n$ , the first one is removed and a fresh one is added to the end) and the requirement that the process be periodic:

$$\begin{aligned} c_1(0, \varrho) &= c_2(\tau^*, \varrho) \\ c_2(0, \varrho) &= c_3(\tau^*, \varrho) \\ &\vdots \\ c_{n-1}(0, \varrho) &= c_n(\tau^*, \varrho) \end{aligned} \quad (5)$$

$$\begin{aligned} c_n(0, \varrho) &= 0 \\ \phi_1(0) &= \phi_2(\tau^*) \theta_2 / \theta_1 \\ &\vdots \\ \phi_{n-1}(0) &= \phi_n(\tau^*) \theta_n / \theta_{n-1} \\ \phi_n(0) &= 0. \end{aligned} \quad (6)$$

The adequacy of this model has been tested in<sup>4</sup> for an experimental stirred adsorber, which is described in<sup>5</sup>.

Our goal consists in finding such values of  $\theta_1, \dots, \theta_n$  within given bounds which allow the maximal value of the period  $\tau^*$  for which the outlet concentration  $\phi_n(\tau)$  does not exceed the given concentration level  $\phi^*$  for  $0 \leq \tau \leq \tau^*$ .

#### *Solution of the Equations (1)–(6)*

In order to solve our optimization problem, we have first to solve the system of Eqs (1)–(6) modelling the periodic steady state of the cascade. This system is a coupled system of partial and ordinary differential equations. The coupling of the equations for the  $i$ -th member with those of the  $(i - 1)$ th member of the cascade goes in two directions. While for the solution of the Eq. (1) for the  $i$ -th member the knowledge of  $\phi_{i-1}$  is needed, to solve Eqs (1), (2) for the  $(i - 1)$ th member one needs the initial values  $c_{i-1}(0, \varrho)$  and  $\phi_{i-1}(0)$  which are determined according to (5), (6) by  $c_i(\tau^*, \varrho)$  and  $\phi_i(\tau^*)$ . This is why the system of Eqs (1)–(6) has to be solved iteratively.

The iterative method we have used simulates the transient behaviour of the system.

One chooses the initial iteration of the outlet concentration of the particular adsorbers  $\phi_1^0(\tau)$ ,  $\phi_2^0(\tau)$ ,  $\dots$ ,  $\phi_{n-1}^0(\tau)$ . The following iteration  $\phi_1(\tau)$ ,  $\phi_2(\tau)$ ,  $\dots$ ,  $\phi_n(\tau)$  is obtained by solving the system of Eqs (2)–(6) and

$$\delta(d\phi_i/d\tau) = \theta_{i-1}\phi_{i-1}^0 - \theta_i\phi_i - dq_i/d\tau. \quad (7)$$

This iteration step is repeated until the successive two iterations match each other up to a prescribed degree of accuracy. In each iteration step the Eqs (2)–(7) for the  $i$ -th member do not depend on the solution of the equations of the member 1 to  $(i - 1)$ , but they depend on the solution of the system of equations for the  $(i + 1)$ th member through the initial conditions (5), (6). Therefore we have to solve the system of equations for decreasing  $i$  starting from the equations for the  $n$ -th member.

The solution of the system of Eqs (2)–(7) for the  $i$ -th member requires another iteration procedure. It is based on the series expressions

$$q_i(\tau) = \frac{6}{\pi^2} \left( C_i(\tau) \sum_{m=1}^{\infty} \frac{1}{m^2} - C_i(0) \alpha_i(\tau) - \int_0^{\tau} \alpha_i(\tau - \lambda) \frac{dC_i(\lambda)}{d\lambda} d\lambda \right) - \frac{6}{\pi} \sum_{m=1}^{\infty} \frac{(-1)^m}{m} \exp(-\bar{D}_i m^2 \pi^2 \tau) \int_0^1 \varrho C_i(0, \varrho) \sin(m \pi \varrho) d\varrho \quad (8)$$

where

$$\alpha_i(\tau) = \sum_{m=1}^{\infty} \frac{1}{m^2} \exp(-\bar{D}_i m^2 \pi^2 \tau) \quad (9)$$

and

$$C_i(0, \varrho) = C_{i+1}(\tau^*, \varrho) = -\frac{2\bar{D}_{i+1}}{\varrho} \sum_{m=1}^{\infty} (-1)^m m \pi \sin(m \pi \varrho) \cdot \int_0^{\tau^*} \exp(\bar{D}_{i+1} m^2 \pi^2 (\tau - \tau^*)) C_{i+1}(\tau) d\tau + \frac{2}{\varrho} \sum_{m=1}^{\infty} \sin(m \pi \varrho) \exp(-\bar{D}_{i+1} m^2 \pi^2 \tau^*) \int_0^1 \varrho C_{i+1}(0, \varrho) \sin(m \pi \varrho) d\varrho \quad (10)$$

and on the implicit Euler difference scheme for the Eq. (7). We compute successively the values  $\phi(\tau_j)$ ,  $C(\tau_j)$ ,  $q(\tau_j)$  for a chosen sequence of points  $\tau_0 = 0$ ,  $\tau_1, \dots, \tau_n = \tau^*$  by the following iterative procedure: given  $\phi(\tau_{j-1})$ ,  $C(\tau_{j-1})$ ,  $q(\tau_{j-1})$  choose  $\phi(\tau_j)$ , compute  $C(\tau_j)$  from (4), then  $q(\tau_j)$  from (8) and check whether the implicit formula (7) is satisfied. If not, readjust  $\phi(\tau_j)$  until satisfactory coincidence is achieved.

### Solution of the Optimization Problem

Similarly as in<sup>1</sup>, in order to solve our optimization problem we introduce an auxiliary cost functional

$$Y(\theta_1, \dots, \theta_n) = \int_0^{\tau^*} [\phi_n(\tau) \theta_n - \phi^*]^+ d\tau, \quad (11)$$

where

$$\xi^+ = \begin{cases} \xi & \text{if } \xi \geq 0 \\ 0 & \text{if } \xi < 0. \end{cases} \quad (12)$$

The concentration of the adsorbate in the outflowing stream can be kept below  $\phi^*$  on  $\langle 0, \tau^* \rangle$  for a given  $\tau^*$  if and only if  $\min Y(\theta_1, \dots, \theta_n) = 0$  for this  $\tau^*$ . Thus, we compute  $\min Y(\theta_1, \dots, \theta_n)$  and then increase or decrease  $\tau^*$  according to whether  $\min Y(\theta_1, \dots, \theta_n)$  is zero or not, until sufficient accuracy of  $\tau^*$  is achieved.

In order to minimize  $Y$  we have used the simple gradient method. For the case the bounds of the temperature would be reached we have modified the method as the projected gradient one. This, however, never happened in our computations. The components  $\partial Y / \partial \theta_i$  of the gradient can be expressed by the formulas

$$\begin{aligned} \frac{\partial Y}{\partial \theta_n} = \int_0^{\tau^*} & \left[ j(\theta_n, \phi_n(\tau)) \phi_n(\tau) + 4\bar{D}_n \pi \frac{\partial F}{\partial \theta_n} \frac{\partial p_n(\tau, 1)}{\partial \varrho} + \frac{1}{\varrho} \phi_n(\tau) \psi_n(\tau) + \right. \\ & \left. + 4\pi \frac{d\bar{D}}{d\theta_n} \int_0^1 \varrho^2 \frac{\partial c_n}{\partial \varrho} \frac{\partial p_n}{\partial \varrho} d\varrho \right] d\tau - \frac{\psi_{n-1}(0)}{\theta_{n-1}} \phi_n(\tau^*), \end{aligned} \quad (13)$$

$$\begin{aligned} \frac{\partial Y}{\partial \theta_i} = \int_0^{\tau^*} & \left[ 4\bar{D}_i \pi \frac{\partial F}{\partial \theta_i} \frac{\partial p_i(\tau, 1)}{\partial \varrho} + \frac{\phi_i(\tau)}{\delta} \psi_i(\tau) + 4\pi \frac{d\bar{D}}{d\theta_i} \int_0^1 \varrho^2 \frac{\partial c_i}{\partial \varrho} \frac{\partial p_i}{\partial \varrho} d\varrho - \right. \\ & \left. - \frac{1}{\delta} \phi_i(\tau) \psi_{i+1}(\tau) \right] d\tau + \frac{\psi_i(0)}{\theta_i} \phi_i(0) - \frac{\psi_{i-1}(0)}{\theta_{i-1}} \phi_i(\tau^*) \quad \text{for } i < n, \end{aligned} \quad (14)$$

where  $\psi_i$  and  $p_i$  solve the adjoint system of equations

$$\frac{\partial p_i}{\partial \tau} + \bar{D}_i \nabla^2 p_i = 0, \quad (15)$$

$$\frac{d\psi_i}{d\tau} - \frac{\psi_i \theta_i}{\delta} + \frac{\partial F}{\partial \phi_i} \frac{4\pi}{3} \frac{d p_i(\tau)}{d\tau} + \frac{\theta_i \psi_{i+1}}{\delta} = \begin{cases} j(\theta_i \phi_i(\tau)) \theta_i & \text{for } i = n, \\ 0 & \text{for } i < n, \end{cases} \quad (16)$$

$$p_1(\tau^*, 1) = 0, \quad \psi_1(\tau^*) = 0;$$

$$p_i(0, \varrho) = p_{i+1}(\tau^*, \varrho) \quad \text{for } \varrho \in \langle 0, 1 \rangle, \quad \psi_i(0) = \psi_{i+1}(\tau^*) \theta_i / \theta_{i+1},$$

$$i = 1, \dots, n-1; \quad (17)$$

$$p_i(\tau, 1) = \psi_i(\tau) / \delta, \quad i = 1, \dots, n, \quad \text{for } \tau \in \langle 0, \tau^* \rangle;$$

$$\psi_{n+1}(\tau) = 0 \quad \text{for } \tau \in \langle 0, \tau^* \rangle,$$

where

$$P_i(\tau) = 3 \int_0^1 \varrho^2 p_i(\tau, \varrho) d\varrho, \quad (18)$$

$$j(\theta_i, \phi_i(\tau)) = \begin{cases} 0 & \text{if } \phi_i \theta_i \leq \phi^* \\ 1 & \text{if } \phi_i \theta_i > \phi^* \end{cases} \quad (19)$$

The computations leading to this expression of the gradient are rather tedious. Their idea is the same as in the paper<sup>1</sup> (Appendix).

The structure of the system of the adjoint equations is entirely similar to that of the system of model equations, provided we reverse time and the numbering of the equations. Therefore in order to solve the adjoint system we can adopt the same iterative procedure as for the system of model equations (of course, with time and the numbering of equations reversed), the series expansion (8) for  $q_i$  and (10) for  $c_i(0, \varrho)$  replaced by the series expansions

$$P_i(s) = \frac{6}{\pi^2 \delta} \left( \psi_i(s) \sum_{m=1}^{\infty} \frac{1}{m^2} - \psi_i(0) \alpha_i(s) - \int_0^s \alpha_i(s-\lambda) \frac{d\psi_i(s)}{ds} d\lambda \right) - \frac{6}{\pi} \sum_{m=1}^{\infty} \frac{(-1)^m}{m} \exp(-\tilde{D}_i m^2 \pi^2 s) \int_0^1 \varrho p_i(0, \varrho) \sin(m \pi \varrho) d\varrho, \quad (20)$$

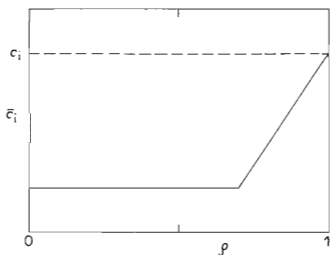


FIG. 2

Piecewise linear approximation of  $c$  inside the particle

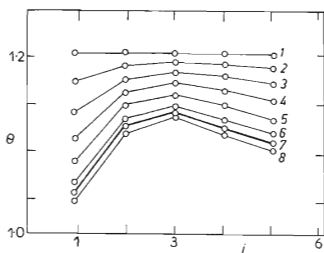


FIG. 3

Temperatures in the particular members of the cascade (numbering of curves corresponding to the order of approximation)

$$\begin{aligned}
 p_i(0, \varrho) = p_{i+1}(\tau^*, \varrho) = & -\frac{2\bar{D}_{i+1}}{\varrho} \sum_{m=1}^{\infty} (-1)^m m \pi \sin(m \pi \varrho) \cdot \\
 & \int_0^{\tau^*} \exp(\bar{D}_{i+1} m^2 \pi^2 (s - \tau^*)) \frac{\psi_{i+1}(s)}{\delta} ds + \frac{2}{\varrho} \sum_{m=1}^{\infty} \sin(m \pi \varrho) \cdot \\
 & \cdot \exp(-\bar{D}_{i+1} m^2 \pi^2 \tau^*) \int_0^1 \varrho p_{i+1}(0, \varrho) \sin(m \pi \varrho) d\varrho, \quad (21)
 \end{aligned}$$

respectively.

Let us note, that by this procedure we obtain the adsorbed amount  $q_i$  and the corresponding adjoint function  $P_i$  without having to compute the entire functions  $c_i$  and  $p_i$ . However, the expressions (13) and (14) for the gradient of  $Y$  involve the derivatives of these functions. Rather than compute  $c_i$  and  $p_i$  by solving the partial differential equations (3) and (15) we approximate these functions for every fixed  $\tau$  by piecewise linear functions  $\bar{c}_i(\tau, \varrho)$  and  $\bar{p}_i(\tau, \varrho)$  such that the equalities

$$3 \int_0^1 \varrho^2 \bar{c}_i(\tau, \varrho) d\varrho = q_i(\tau), \quad (22)$$

$$\frac{\partial \bar{c}_i(\tau, 1)}{\partial \varrho} = \frac{1}{3\bar{D}_i} \frac{dq_i(\tau)}{d\tau}, \quad (23)$$

$$\bar{c}_i(\tau, 1) = C_i(\tau) \quad (24)$$

and the corresponding equalities for  $\bar{p}_i(\tau, \varrho)$  and  $P_i(\tau)$  are satisfied (Fig. 2).

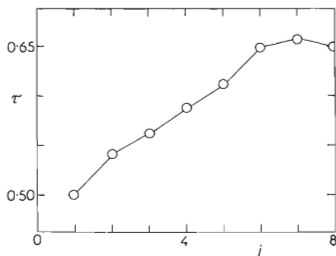


FIG. 4

Length of the interval in which the outlet concentration is below  $\phi^*$  for the  $j$ -th approximation. The percentual increase is 26%

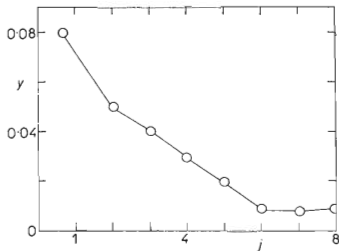


FIG. 5

Cost functional vs approximation step

Each step of the gradient method requires a solution of the system of model Eqs (1)–(6) (to obtain the value of the minimized cost functional  $Y$ ) and then the solution of the system of adjoint Eqs (15)–(19) to obtain the partial derivatives of  $Y$  with respect to the temperatures  $\theta_1, \dots, \theta_n$ .

## RESULTS

We have tested our method on a cascade of five adsorbers with following parameters, which correspond to the system of n-heptane and molecular sieve Calsit 5A:  $n = 5$ ,  $\varphi_0 = 0.5 \times 10^{-4}$  g/cm<sup>3</sup>,  $T_0 = 393$  K,  $T_{\min} = 323$  K,  $T_{\max} = 473$  K,  $V/\dot{V} = 0.36$  min,  $N/V = 0.167$  particle/cm<sup>3</sup>,  $t' = 61.58$  min,  $R = 0.5$  cm,  $a^*(\varphi_0, T_0) = 0.0983$  g/cm<sup>3</sup>,  $D = 2.8787 \times 10^{-3} \exp(-2994/T)$  cm<sup>2</sup>/s,  $M = (20.14 - 0.02772T) \times 0.1151 \times 10^{-3} \exp(1966/T) \cdot P / (1 + 0.1151 \times 10^{-3} \exp(1966/T) \cdot P)$ ,  $M$  in g/100 g,  $P$  in Pa.

Dimensionless parameters:  $\delta = 5.85 \times 10^{-3}$ ,  $\theta_{\min} = 0.822$ ,  $\theta_{\max} = 1.204$ ,  $\phi^* = 0.1$ .

The results of our computations are represented on Figs 3–5. These figures illustrate the convergence of the gradient method for a fixed  $\tau^*$  close to the optimal one. The initial temperature was chosen to be  $\theta_i = \theta_{\max}$  for  $i = 1, \dots, 5$ .

As we have pointed out in<sup>1</sup>, while the increase of temperature influence the adsorption rate positively ( $\bar{D}$  is an increasing function of  $\theta$ ), it influences the equilibrium adsorbed amount negatively (the adsorption isotherm is a decreasing function of  $\theta$ ). This leads one to expect that temperature should be high when internal diffusion is decisive for the process and low when the adsorbent becomes saturated. As seen from Fig. 3 the results of our computations are in accordance with this intuitive idea: the temperature decreases considerably when passing from adsorber 3 to 1 (note that the adsorbed amount increases with decreasing number of the adsorber). Also, the optimal temperature profile of Fig. 3 resembles partly the optimal temperature control of<sup>1</sup> (cf.<sup>1</sup> Fig. 8 – note that here adsorbed amount increases from left to right). However, there is one significant difference: unlike in the case of one adsorber the adsorption process turns out to be very sensitive to the starting temperatures.

## LIST OF SYMBOLS

$a$	concentration of the adsorbate in the particle
$a^*$	equilibrium adsorbate concentration in the particle
$C = a^*(\varphi, T)/a^*(\varphi_0, T_0)$	dimensionless equilibrium adsorbate concentration in the particle
$c = a/a^*(\varphi_0, T_0)$	dimensionless adsorbate concentration in the particle
$D$	diffusion coefficient
$\bar{D} = Dt'/R^2$	dimensionless parameter in Eq. (3)
$F$	adsorption isotherm
$M$	equilibrium adsorbed amount
$N$	number of adsorbent particles in the adsorber
$n$	number of adsorbers in the cascade



$j$	iteration step number
$P$	partial pressure of adsorbate
$P$	variable given by Eq. (18)
$p$	adjoint variable
$q$	dimensionless adsorbed amount
$R$	radius of particle
$r$	spherical coordinate
$T$	temperature in the adsorber
$T_0$	temperature of inlet flow
$T_{\min}, T_{\max}$	temperature limits
$t$	time
$t' = (4\pi NR^3 a^*(\varphi_0, T_0))/3\dot{V}\varphi_0$	time in which the amount of adsorbate corresponding to the equilibrium amount in one adsorber at temperature $T_0$ is introduced into the system
$V$	volume of the gaseous phase of the adsorber
$\dot{V}$	volumetric flow rate at temperature $T_0$
$\psi$	adjoint variable
$\delta = V/(\dot{V}t')$	dimensionless parameter in Eq. (1)
$\varrho = r/R$	dimensionless spherical coordinate
$\tau = t/t'$	dimensionless time
$\tau^*$	duration of one period
$\varphi$	gas phase concentration at temperature $T$
$\varphi_0$	gas phase concentration in the inlet flow at temperature $T_0$
$\phi = \varphi/\varphi_0$	dimensionless gas phase concentration
$\theta = T/T_0$	dimensionless temperature

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