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Optimization of the reactor–regenerator system with catalytic parallel–consecutive reactions

Zbigniew Szwast*, Stanislaw Sieniutycz

Chemical and Process Engineering Department, Warsaw University of Technology, ul. Waryńskiego 1, 00-645 Warsaw, Poland

Abstract

The system with moving deactivating catalyst, composed of a cocurrent tubular reactor and a catalyst regenerator with an additional flux of a fresh catalyst, has been investigated. For the temperature dependent catalyst deactivation, the optimization problem has been formulated in which a maximum of a process profit flux is achieved by a best choice of temperature profile along tubular reactor, best catalyst recycle ratio and best catalyst activity after regeneration. The set of parallel–consecutive reactions, A+B→R and R+B→S, with desired product R has been taken into account. A relatively unknown, powerful discrete algorithm in which a suitably defined Hamiltonian is constant along the optimal path, has been applied for optimization. The optimal solutions have been discussed. In particular, it has been shown that an increase of the unit cost of catalyst regeneration or an increase of the catalyst recycle ratio causes such optimal temperatures in reactor which save the catalyst, as the optimal temperature profiles are then shifted towards lower temperatures. Finally these profiles reach isothermal shape at the level of minimum allowable temperature and then there is no further possibility to control the reactor process by the temperature profile. Thus the catalyst activity after regeneration, as well as an average catalyst activity in the reactor do decrease when the unit catalyst regeneration cost increases. This is a new form of catalyst saving, as the catalyst deactivation rate becomes reduced when an average catalyst activity is allowed to decrease. It is important that this form of catalyst saving appears in the region where any saving of the catalyst by an optimal choice of temperature profile is impossible. It has been also shown that for small values of the catalyst recycle ratio, the catalyst regenerator should be removed from the system. In such a case, the renewal of catalyst takes place due to a fresh catalyst input, exclusively.

Keywords: Catalyst deactivation; Catalyst regeneration; Catalyst regulation; Optimization; Hamiltonian algorithms

1. Introduction

The system investigated consists of a cocurrent tubular reactor with moving deactivating catalyst and a catalyst regenerator. Fig. 1 illustrates the process principle and basic designations, where L – reactants mass flux in reactor, $c[0]$ and $c[t_k]$ – reagent concentrations in the inlet and outlet reactants flux, respectively, t_k – common residence time of reactants and catalyst in reactor, S – catalyst mass flux in reactor, S_f – fresh catalyst mass flux, S_r – recycled catalyst mass flux, a_f – fresh catalyst activity, $a[0]$ and $a[t_k]$ – inlet and outlet catalyst activity, respectively, and a_R – catalyst activity after regeneration.

Catalyst mass flux in the reactor, S, constitutes the sum of mass fluxes S_f and S_r

$$S = S_r + S_f = \mathrm{const}, \tag{1}$$

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*Corresponding author.

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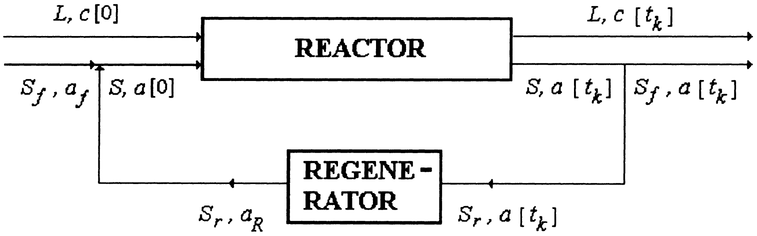

Fig. 1. System of cocurrent tubular reactor–catalyst regenerator.

whereas the catalyst recycle ratio, R, is defined by Eq. (2), then Eqs. (3) and (4):

$$R = S_r/S_f, \tag{2}$$

$$S_f = \frac{S}{R+1}, \tag{3}$$

$$S_R = \frac{RS}{R+1}. \tag{4}$$

Catalyst represented by the recycled flux S_r is regenerated in catalyst regenerator to an optimal activity a_R, $a_R \leq a_f$, starting with $a[t_k]$. Activity of catalyst entering the reactor, $a[0]$, results from mixing of catalyst fluxes: S_f with activity $a_f=1$ and S_r with activity a_R. As far as the definition of catalyst activity of Szepe and Levenspiel [1] definition of catalyst activity and their mathematical model of catalyst deactivation can be applied, for the case of first-order catalyst deactivation, the catalyst activity $a[0]$ can be computed as [2]:

$$a[0] = \frac{S_f a_f + S_r a_R}{S_f + S_r} = \frac{a_f + R a_R}{1+R} = \frac{1 + R a_R}{1+R}. \tag{5}$$

The process controls are: a temperature profile along the reactor $T[t]$, a catalyst recycle ratio R and catalyst activity after regeneration a_R. All these controls should be chosen in a best way via an optimization, meaning that they should maximize the process profit flux P.

The results reported here are restricted to the problem with fixed residence time of reagents (the same as the residence time of catalyst particles) in the tubular reactor, t_k. However, although the results of optimization calculation presented in this paper are restricted to the problem with fixed residence time of reagents, the optimization algorithm derived here can be applied for both variants of the process: the variant with the fixed time t_k, and the variant with the free time t_k.

The optimal temperatures have to lie in an allowable range defined as

$$T_* \leq T[t] \leq T^*, \tag{6}$$

where T and T^* describe minimum and maximum allowable temperatures, respectively.

The investigations are focused on the set of parallel–consecutive reactions, A+B→R and R+B→S, with R being the desired product. This is the same set of reactions for which Burghardt and Skrzypek [3] and Skrzypek [4] were evaluating their optimal temperature profiles along the tubular reactor, in their investigations of optimal temperature strategies of reactions without catalyst deactivation.

The authors of the present paper were also searching for an optimal residence time of reagents in the tubular reactor in both the cases, when a slip between catalyst particles and continuous phase is taken into account or ignored. Moreover, an optimal concentration of catalyst in reagents mixture was also considered. But these problems are omitted in this paper.

The basic purpose of this work is to formulate an optimization problem for the system of (tubular) reactor and regenerator and to derive an efficient algorithm for optimization of this complex system. Next, based on the computational results, we are determining the effect of catalyst recycle on optimal temperature strategies and optimal extent of catalyst reactivation in the regenerator. We also investigate the effect of the catalyst regeneration cost on the temperature policies and the optimal regeneration extent of the catalyst. These investigations, of basic nature, while not linked here with particular chemical examples, can nonetheless be applied to a large number of industrial catalytic schemes which work with parallel–consecutive reactions such as: gasification and oxidation of coal, sulphur oxidation, benzene chlorination, etc. With this in mind, both the catalyst deactivation model and ranges of numerical data (e.g. those describing activation energies for reaction and deactivation processes) are taken realistic. They conform with Szepe [5] numerical data of deactivation kinetics in various industrial reactions and with Skrzypek [4] numerical data for optimization tests in which the catalyst decay was neglected.

2. Mathematical model of catalyst deactivation

According to the model of Szepe and Levenspiel [1], catalyst activity a is defined as the ratio of reaction rate in the presence of current catalyst and the rate in the presence of fresh catalyst.

For a temperature dependent and concentration independent catalyst deactivation, deactivation rate can be written in the following form:

$$\frac{\mathrm{d}a}{\mathrm{d}t} = -k_{\mathrm{d}o} \exp(-E_{\mathrm{d}}/RT[t])a, \tag{7}$$

valid for $0 \le t \le t_k$, where E_{d} – activation energy of catalyst deactivation and R – gas constant.

3. Mathematical model of chemical reactions

Mathematical analysis and computer calculations refer to the following set of parallel–consecutive reactions, with desired product R:

$$\mathrm{A} + \mathrm{B} \overset{E_1,k_{10}}{\rightarrow} \mathrm{R}, \tag{8}$$

$$\mathrm{R} + \mathrm{B} \overset{E_2,k_{20}}{\rightarrow} \mathrm{S}. \tag{9}$$

The catalytic reactions (8) and (9) are described by the following equations:

$$\frac{\mathrm{d}c_{\mathrm{A}}[t]}{\mathrm{d}t} = -k_1 a c_{\mathrm{A}} c_{\mathrm{B}}, \tag{10}$$

$$\frac{\mathrm{d}c_{\mathrm{B}}[t]}{\mathrm{d}t} = -k_1 a c_{\mathrm{A}} c_{\mathrm{B}} - k_2 a c_{\mathrm{B}} c_{\mathrm{R}}, \tag{11}$$

$$\frac{\mathrm{d}c_{\mathrm{R}}[t]}{\mathrm{d}t} = k_1 a c_{\mathrm{A}} c_{\mathrm{B}} - k_2 a c_{\mathrm{B}} c_{\mathrm{R}}, \tag{12}$$

$$\frac{\mathrm{d}c_{\mathrm{S}}[t]}{\mathrm{d}t} = k_2 a c_{\mathrm{B}} c_{\mathrm{R}}, \tag{13}$$

valid for $0 \le t \le t_k$. The reaction rate constants k_1 and k_2 satisfy the following equation:

$$k_i = k_{i0} \exp(-E_i/RT[t]), \tag{14}$$

valid for i=1,2, where E_i – activation energy of reaction i, for i=1,2.

An instantaneous concentration of the desired reagent R satisfies the following stechiometric relationship:

$$c_{\mathrm{R}}[t] = c_{\mathrm{B}}[t] - 2c_{\mathrm{A}}[t] + 2c_{\mathrm{A}}[0] - c_{\mathrm{B}}[0], \tag{15}$$

valid for $0 \le t \le t_k$. Moreover, dimensionless concentration $x_i[t]$ for i=A,B,R and $0 \le t \le t_k$ defined by Eq. (16), as well as constant M defined by Eq. (17), can be introduced.

$$x_i[t] c_i[t]/c_{\mathrm{B}}[0], \tag{16}$$

$$M = c_{\mathrm{A}}[0]/c_{\mathrm{B}}[0]. \tag{17}$$

Applying Eqs. (15)–(17) in Eqs. (10)–(12) yields

$$\frac{\mathrm{d}x_{\mathrm{A}}[t]}{\mathrm{d}t} = -k_1 a x_{\mathrm{A}} x_{\mathrm{B}}, \tag{18}$$

$$\frac{\mathrm{d}x_{\mathrm{B}}[t]}{\mathrm{d}t} = -k_1 a x_{\mathrm{A}} x_{\mathrm{B}} - k_2 a x_{\mathrm{B}}(x_{\mathrm{B}} - 2x_{\mathrm{A}} + 2M - 1), \tag{19}$$

$$\frac{\mathrm{d}x_{\mathrm{R}}[t]}{\mathrm{d}t} = k_1 a x_{\mathrm{A}} x_{\mathrm{B}} - k_2 a x_{\mathrm{B}}(x_{\mathrm{B}} - 2x_{\mathrm{A}} + 2M - 1), \tag{20}$$

for $0 \le t \le t_k$, where (cf. Eqs. (15)–(17))

$$x_{\mathrm{R}}[t] = x_{\mathrm{B}}[t] - 2x_{\mathrm{A}}[t] + 2M - 1. \tag{21}$$

Note that Eq. (13) is dependent with respect to Eqs. (10)–(12). Moreover, in the problem considered, the final concentration of reagent S, $c_{\mathrm{S}}[t_k]$, is free. Thus Eq. (13) can be neglected in further analysis.

4. Process profit flux

The maximization problem for optimization of the process profit flux is considered. The process profit flux, P, is defined as a difference between the flux of the desired reagent value and the flux of the total process cost. It is described by the following equation:

$$P = \frac{L}{\rho} c_{\mathrm{R}}[t_k] M_{\mathrm{R}} \mu_{\mathrm{R}} - S_{\mathrm{f}} \mu_{\mathrm{f}} - S_{\mathrm{r}} K_{\mathrm{r}}[a[t_k], a_{\mathrm{R}}] - K_{\mathrm{c}}. \tag{22}$$

The first term on the right-hand side of Eq. (22) describes the flux of desired reagent value, the second term describes the flux of fresh catalyst cost, the third term – flux of catalyst regeneration cost and the last one – flux of fixed cost K_{c}. As in virtually all contemporary works on optimization, we assume that the costs of the optimal control (here temperature control) are the same as the control costs of process in general. Thus we assume that the heating costs can be included to the fixed costs of the process, and hence they do not affect the optimization solution. There are techniques (e.g. autotransformer heating of fluids to achieve a required profile $T(t)$) which realize this concept with a considerable precision.

The following symbols are applied: ρ – reagents mixture density, M_{R} – molar mass of desired reagent R, μ_{R} – unit price of desired reagent R, μ_{f} – unit price of fresh catalyst, $K_{\mathrm{r}}[a[t_k], a_{\mathrm{R}}]$ – cost of catalyst regeneration from activity $a[t_k]$ to a_{R} (cf. [6,7] for example).

A simplest and explicit form of function $K_{\mathrm{r}}[a[t_k], a_{\mathrm{R}}]$ is taken into account. It reads as follows:

$$K_{\mathrm{r}}[a[t_k], a_{\mathrm{R}}] = \mu_{\mathrm{r}}(a_{\mathrm{R}} - a[t_k]), \tag{23}$$

where μ_{r} – unit cost of catalyst regeneration per unit catalyst activity.

Applying Eq. (23) in Eq. (22) yields

$$P = \frac{L}{\rho} c_{\mathrm{R}}[t_k] M_{\mathrm{R}} \mu_{\mathrm{R}} - S_{\mathrm{f}} \mu_{\mathrm{f}} - S_{\mathrm{r}} \mu_{\mathrm{r}}(a_{\mathrm{R}} - a[t_k]) - K_{\mathrm{c}}, \tag{24}$$

which can be transformed into following dimensionless form:

$$F = x_{\mathrm{R}}[t_k] - S_{\mathrm{f}} \lambda - S_{\mathrm{r}} A (a_{\mathrm{R}} - a[t_k]) - k_{\mathrm{c}}, \tag{25}$$

where F – dimensionless profit flux defined by Eq. (26), λ – dimensionless unit price of fresh catalyst defined by Eq. (27), A – dimensionless unit cost of catalyst regeneration per unit catalyst activity defined by Eq. (28) and k_{c} – dimensionless flux of constant cost defined by Eq. (29).

$$F = \frac{P}{(L/\rho) M_{\mathrm{R}} \mu_{\mathrm{R}} c_{\mathrm{B}}[0]}, \tag{26}$$

$$\lambda = \frac{\mu_{\mathrm{f}}}{(L/\rho) M_{\mathrm{R}} \mu_{\mathrm{R}} c_{\mathrm{B}}[0]}, \tag{27}$$

$$A = \frac{\mu_{\mathrm{r}}}{(L/\rho) M_{\mathrm{R}} \mu_{\mathrm{R}} c_{\mathrm{B}}[0]}, \tag{28}$$

$$k_{\mathrm{c}} = \frac{K_{\mathrm{c}}}{(L/\rho) M_{\mathrm{R}} \mu_{\mathrm{R}} c_{\mathrm{B}}[0]}. \tag{29}$$

Moreover, applying Eq. (20), one can write the following relationship:

$$x_{\mathrm{R}}[t_k] = \int_0^{t_k} (\mathrm{d}x_{\mathrm{R}}/\mathrm{d}t)\mathrm{d}t = \int_0^{t_k} (k_1 a x_{\mathrm{A}} x_{\mathrm{B}} - k_2 a x_{\mathrm{B}}(x_{\mathrm{B}} - 2x_{\mathrm{A}} + 2M - 1))\mathrm{d}t, \tag{30}$$

which is valid when the desired reagent R does not appear in the fresh reagents mixture.

The dimensionless process profit flux, Eq. (25), constitutes the performance index for the optimization problem considered below. With Eqs. (3), (4) and (30), Eq. (25) can be transformed to the following final form:

$$F = \int_0^{t_k} (k_1 a x_{\mathrm{A}} x_{\mathrm{B}} - k_2 a x_{\mathrm{B}}(x_{\mathrm{B}} - 2x_{\mathrm{A}} + 2M - 1))\mathrm{d}t - \frac{S\lambda}{R+1} - \frac{SRA(a_{\mathrm{R}} - a[t_k])}{R+1} - k_{\mathrm{c}}. \tag{31}$$

5. Optimization problem and algorithm applied

The dimensionless process profit flux, Eq. (31), has to be maximized by an optimal choice of temperature profile along tubular reactor, catalyst recycle ratio and catalyst activity after regeneration. It has to be maximized when temperature controls are in an allowable region defined by inequality (6), the state (dynamic) Eqs. (7), (18) and (19), as well as catalyst mixing function (5) are satisfied and the residence time of reagents and catalyst in the tubular reactor, t_k, is fixed. (Note that the concentration of reagent R does not appear on the right-hand side of the state Eqs. (18), (19) and (7), thus, Eq. (20) can be excluded from the set of state equations.)

As a discrete algorithm is being applied to solve the optimization problem, the procedure starts with the replacement of the continuous model of tubular reactor by a corresponding discrete model of the N-stage cascade of reactors with ideal mixing, n=1,. . ., N. The performance index (31), state Eqs. (18), (19) and (7), as well as Eqs. (21), (14) and (5) take the form of Eqs. (32)–(38)), respectively,

$$F = \sum_{n=1}^{N} (k_1^n a^n x_{\mathrm{A}}^n x_{\mathrm{B}}^n - k_2^n a x_{\mathrm{B}}^n (x_{\mathrm{B}}^n - 2x_{\mathrm{A}}^n + 2M - 1))\theta^n - \frac{S\lambda}{R+1} - \frac{SRA(a_{\mathrm{R}} - a^N)}{R+1} - k_{\mathrm{c}}, \tag{32}$$

$$\frac{x_{\mathrm{A}}^n - x_{\mathrm{A}}^{n-1}}{\theta^n} = -k_1^n a^n x_{\mathrm{A}}^n x_{\mathrm{B}}^n, \tag{33}$$

$$\frac{x_{\mathrm{B}}^n - x_{\mathrm{B}}^{n-1}}{\theta^n} = -k_1^n a^n x_{\mathrm{A}}^n x_{\mathrm{B}}^n - k_2^n a^n x_{\mathrm{B}}^n (x_{\mathrm{B}}^n - 2x_{\mathrm{A}}^n + 2M - 1), \tag{34}$$

$$\frac{a^n - a^{n-1}}{\theta^n} = -k_{\mathrm{d}}^n a^n, \tag{35}$$

$$x_{\mathrm{R}}^n = x_{\mathrm{B}}^n - 2x_{\mathrm{A}}^n + 2M - 1, \tag{36}$$

$$k_i^n = k_{i0} \exp(-E_i/RT^n), \tag{37}$$

$$a^0 = \frac{S_{\mathrm{f}} a_{\mathrm{f}} + S_{\mathrm{r}} a_{\mathrm{R}}}{S_{\mathrm{f}} + S_{\mathrm{r}}} = \frac{a_{\mathrm{f}} + R a_{\mathrm{R}}}{1+R} = \frac{1 + R a_{\mathrm{R}}}{1+R}, \tag{38}$$

which are valid for n=1,. . ., N. The symbols with superscript n refer to reagent concentration or catalyst activity at the stage n (or after this stage), as well as to temperature at the stage n. The variable describing residence time at the stage θ^n is defined by the following equation:

$$\theta^n = t^n - t^{n-1}, \tag{39}$$

valid for n=1,. . ., N, where t^n – total residence time at the first n stages of the cascade.

Eqs. (32)–(39) constitute the complete set of equations describing optimization problem considered in this paper.

The optimization problem is solved at two optimization levels. At the lower level, optimal discrete temperature profiles and catalyst activities after regeneration, for various fixed values of catalyst recycle ratio, have to be found, whereas, at the higher level, an optimal value of catalyst recycle ratio has to be found.

Note that constant term k_{c} can always be neglected when optimizing the performance index, Eq. (32). For optimization calculation at the lower level of optimization the second term on the right-hand side of Eq. (32) can be also neglected as connected with fixed value of R.

For optimization calculations at the lower level of optimization, the discrete optimization algorithm with a constant Hamiltonian [2,8,9] worked out by the authors of this paper, is applied. The algorithm applies a discrete Hamiltonian H^{n-1} defined for n=1,. . ., N by Eq. (40))

$$\begin{aligned} H^{n-1}[x_{\mathrm{A}}^n, x_{\mathrm{B}}^n, a^n, z_1^{n-1}, z_1^{n-1}, z_1^{n-1}, T^n] &= k_1^n a^n x_{\mathrm{A}}^n x_{\mathrm{B}}^n - k_2^n a x_{\mathrm{B}}^n (x_{\mathrm{B}}^n - 2x_{\mathrm{A}}^n + 2M - 1) \\ &\quad - z_1^{n-1} k_1^n a^n x_{\mathrm{A}}^n x_{\mathrm{B}}^n - z_2^{n-1} (k_1^n a^n x_{\mathrm{A}}^n x_{\mathrm{B}}^n \\ &\quad + k_2^n a^n x_B^n (x_{\mathrm{B}}^n - 2x_{\mathrm{A}}^n + 2M - 1)) - z_3^{n-1} k_{\mathrm{d}}^n a^n. \end{aligned} \tag{40}$$

Necessary optimality conditions for this algorithm are described by the following equations:

$$\frac{z_1^n - z_1^{n-1}}{\theta^n} = -\frac{\partial H^{n-1}}{\partial x_{\mathrm{A}}^n}, \tag{41}$$

$$\frac{z_2^n - z_2^{n-1}}{\theta^n} = -\frac{\partial H^{n-1}}{\partial x_{\mathrm{B}}^n}, \tag{42}$$

$$\frac{z_3^n - z_3^{n-1}}{\theta^n} = -\frac{\partial H^{n-1}}{\partial a^n}, \tag{43}$$

$$\frac{H^n - H^{n-1}}{\theta^n} = \frac{\partial H^{n-1}}{\partial t^n}, \tag{44}$$

$$\begin{aligned} \hat{H}^{n-1}[\hat{x}_{\mathrm{A}}^n, \hat{x}_{\mathrm{B}}^n, \hat{a}^n, \hat{z}_1^{n-1}, \hat{z}_1^{n-1}, \hat{z}_1^{n-1}, \hat{T}^n] &= \max_{T_* \le T^n \le T^*} [\hat{x}_{\mathrm{A}}^n, \hat{x}_{\mathrm{B}}^n, \hat{a}^n, \hat{z}_1^{n-1}, \hat{z}_1^{n-1}, \hat{z}_1^{n-1}, T^n], \end{aligned} \tag{45}$$

where z^n – adjoint vector, whose dimension equals to the dimension of the state vector. Here the three-dimensional state vector with components x_{A}^n, x_{B}^n and a^n, respectively, is considered. The symbol with dash refers to optimal value of some variable.

Boundary conditions for adjoint Eqs. (41) and (42) are described by Eq. (46). Note that the form of Eq. (46) results from the fact that the final concentrations of reagents A and B are free. On the other hand, boundary conditions for adjoint Eq. (43), which take catalyst recirculation into account, are described by Eqs. (47) and (48).

$$z_1^N = z_2^N = 0, \tag{46}$$

$$z_3^0 = SA, \tag{47}$$

$$z_3^N = \frac{RSA}{R+1}. \tag{48}$$

The optimization problem formulated above (maximization of the dimensionless process profit flux) is related to the variant with fixed value of the residence time of reagents and catalyst in the tubular reactor, t_k. Also, our results of optimization calculations, presented below, are related to this variant only. However, it should be underlined that the optimization procedure presented above, Eqs. (40)–(48)), is valid for both variants: that with fixed t_k, and that with free t_k. This is the only difference that affects the form of boundary condition applied for Eq. (44). For the variant with fixed value of t_k, the value of H^N is undetermined, whereas for the variant with free t_k, the value of H^N has to satisfy the following equation:

$$H^N = 0. \tag{49}$$

When the variant with fixed t_k is computed, the optimal value of the Hamiltonian has to be found. This is a particular value of the Hamiltonian for which t_k assumes a given fixed value. In the opposite variant, when t_k is free, the optimal value of t_k has to be found, whereas the optimal value of the Hamiltonian equals zero.

In order to solve Eqs. (40)–(48), state Eqs. (33)–(35), and additional Eqs. (37)–(39), a computer program was written and then a numerical solution of the optimization problem was obtained. The results were obtained for N=12 – stage cascade of reactors with ideal mixing. Our numerical experiments for various N have shown that the value N=12 was sufficient to secure a good approximation of the tubular reactor by the cascade. Thus, the obtained results are applicable to the tubular reactor.

6. Results

The results were obtained for the following data: L=100 kg min^{-1}, ρ=1 kg l^{-1}, S=10 kg min^{-1}, t_k= 2 min, E_1=67 kJ mol^{-1}, E_2=125 kJ mol^{-1}, E_d=105 kJ mol^{-1}, $k_{10}=5\times10^3$ l (mol min)$^{-1}$, $k_{20}=3\times10^{10}$ l (mol min)$^{-1}$, $k_{d0}=4\times10^{15}$ min^{-1}, T_*=335 K, T^*= 355 K, $c_A[0]=c_B[0]$=1 mol l^{-1}, M=1, and $c_R[0]=c_S[0]$=0. The data describing kinetics of reactions are the same as those applied in the paper by Burghardt and Skrzypek [3], devoted to optimal temperature profiles for the set of parallel–consecutive reactions (8) and (9) undergoing without catalyst deactivation. Also the range of allowable temperatures is the same as that in the paper [3]. The data describing kinetics of catalyst deactivation were chosen from the range of realistic values evaluated by Wanke and Flynn and cited by Butt and Petersen [10]. The selected results are presented in Figs. 2–5.

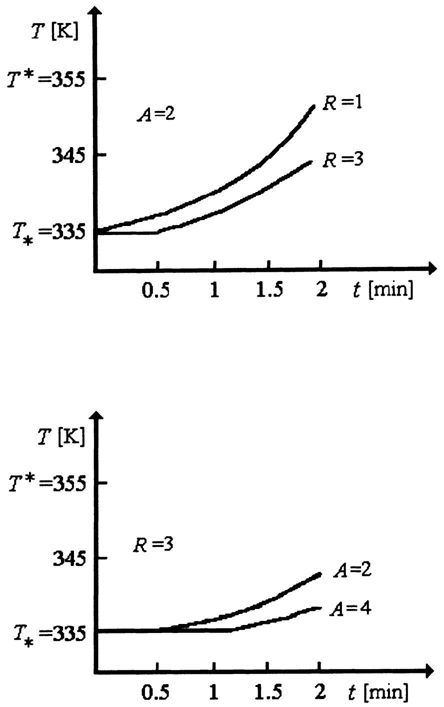

Fig. 2. Optimal temperature profile for various values of catalyst recycle ratio R and unit regeneration cost A.

Fig. 2 shows that when for A=const catalyst recycle ratio R increases (a mean number of catalyst particles residing in the reactor increases) or for R=const A increases (catalyst regeneration cost increases) the optimal temperatures save the catalyst as the optimal temperature profile is shifted towards lower temperatures.

Fig. 3 shows that, for small values of catalyst recycle ratio R, the catalyst regenerator should be removed from the system – see that the curve $a_R[R]$ starts from R>1 and that a critical value of R, R_{cr}, exists which increases with A. This means that the range of values of catalyst recycle ratio R, for which the system without catalyst regenerator is optimal one, increases with the unit cost of catalyst regeneration A. For R>R_{cr} the function $a_R[R]$ is increasing one, reaching max-

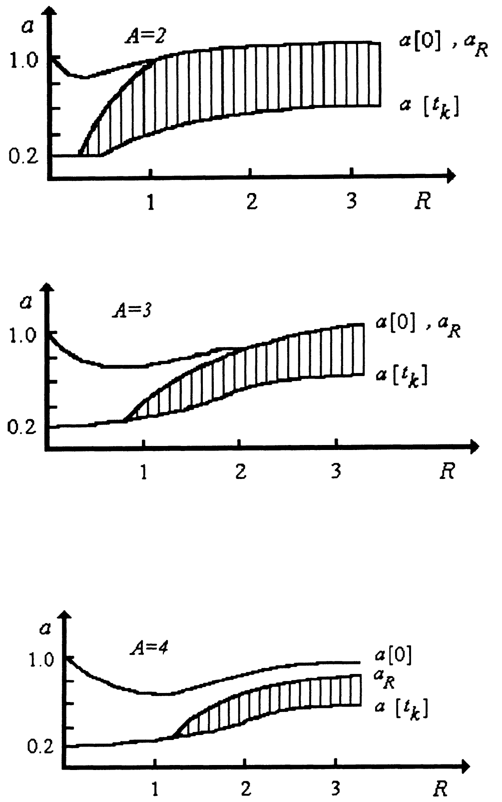

Fig. 3. Optimal catalyst activities in inlet $a[0]$ and outlet $a[t_k]$ fluxes of the reactor and after regeneration a_R versus recycle ratio R.

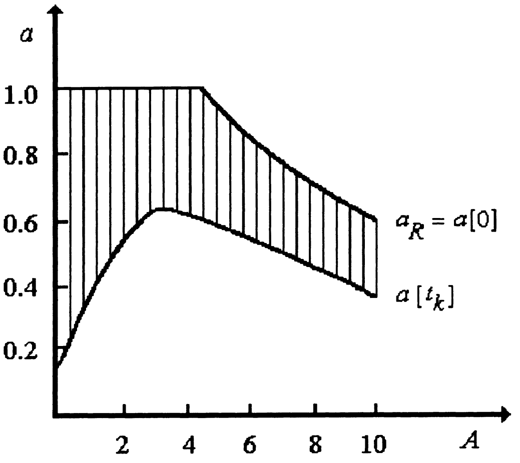

Fig. 4. Optimal catalyst activities in inlet and outlet fluxes of the reactor versus A for a process without stream S_f.

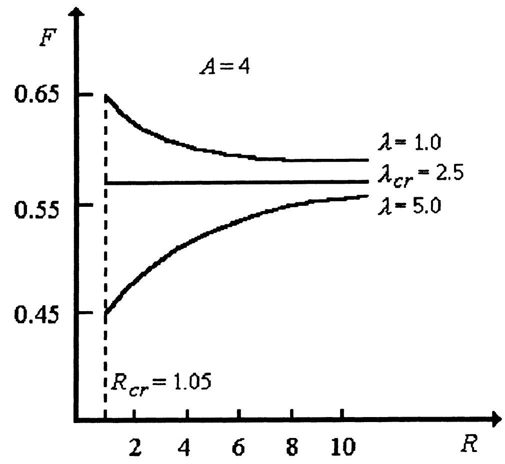

Fig. 5. Performance index F versus catalyst recycle ratio R for A=4 and various prices of fresh catalyst λ.

imal catalyst activity after regenerator, the property which can be observed for every cases presented in Fig. 3, i.e. A=2, A=3, A=4. It is important that when the catalyst recycle ratio R reaches values larger than presented in Fig. 3, the function $a_\mathrm{R}[R]$ becomes a decreasing one. This phenomenon is explained in the text connected with Fig. 4.

Fig. 4 is valid for the case when whole catalyst flux leaving reactor is regenerated, i.e. there is no fresh catalyst flux, S_f=0. It shows that, for small values of unit cost of catalyst regeneration A, the catalyst is regenerated to maximum possible value, a_R=1, whereas the activity of catalyst leaving reactor $a[t_k]$ increases with A. This results from the fact that, in this range of A, the optimal temperature profile is shifted in direction of lower temperatures when A increases. For larger values of A, an isothermal profile of temperature at the level of minimum allowable temperature T_* is an optimal one; in such a case there is no possibility to control reactor process by temperature profile. Thus the catalyst activity after regeneration a_R and the activity of catalyst leaving reactor $a[t_k]$, as well as the average catalyst activity in reactor do decrease when the unit catalyst regeneration cost A increases. This is a new form of catalyst saving, as the catalyst deactivation rate becomes reduced when an average catalyst activity is allowed to decrease. It is important that this form of catalyst saving appears in the region where any saving of the catalyst by an optimal choice of temperature profile is impossible.

Fig. 5 shows the optimal values of the performance index F versus catalyst recycle ratio R for the system reactor–catalyst regenerator, for various values of dimensionless unit price of fresh catalyst λ. It was underlined in the text describing Fig. 3 that the system reactor–catalyst regenerator is an optimal one for $R>R_{\mathrm{cr}}$. For $A=4$ critical value $R_{\mathrm{cr}}=1.05$, cf. Fig. 3. Thus the curves presented in Fig. 5 are related to $R>R_{\mathrm{cr}}=1.05$. One can observe that for critical value of λ, $\lambda_{\mathrm{cr}}=2.5$ (for $A=4$), the optimal value of performance index F (dimensionless process profit flux) does not depend on catalyst recycle ratio R. For $\lambda<\lambda_{\mathrm{cr}}$ the function $F[R]$ is a decreasing one. It means that for $\lambda<\lambda_{\mathrm{cr}}$ the system reactor–catalyst regenerator is not an optimal one, thus the regenerator should be removed from the system. In this case the fresh catalyst is cheap enough to take the total responsibility for catalyst renewal in the reactor. Reverse situation is observed for the case of $\lambda>\lambda_{\mathrm{cr}}$. The function $F[R]$ is increasing one in such a case. The optimal value of catalyst recycle ratio R approaches infinity. The fresh catalyst is too expensive to be supplied to the system. Because of relatively low unit cost of catalyst regeneration, catalyst regenerator should take the total responsibility for catalyst renewal in the reactor. Concluding one can confirm that there is no optimal solution for simultaneous renewal of catalyst, by input of the fresh catalyst flux and regeneration. But, in fact, the system reactor–regenerator has always to work with additional flux of fresh catalyst as the catalyst losses from the system always exist. Thus the scheme of the industrial system reactor–regenerator is exactly like that presented in Fig. 1. However, the catalyst recycle ratio is not a process control variable; it is a parameter, whose value results from the knowledge of the magnitude of the catalyst loss from the system. Thus, the industrial optimization problem can be formulated as follows. Find the optimal temperature profile along tubular reactor and catalyst activity after regeneration for fixed value of catalyst recycle ratio. This is exactly the same optimization problem as the one solved in this paper.

7. Conclusions

The following general conclusions can be formulated.

When the catalyst recycle ratio R increases (a mean number of catalyst particles residing in the reactor increases), the optimal temperatures save the catalyst (working time is longer and longer), because the optimal temperature profile is shifted towards lower temperatures.

When the catalyst regeneration cost (measured by dimensionless variable A) increases, the optimal temperatures save the catalyst (regeneration is more and more expensive), again, because the optimal temperature profile is shifted towards lower temperatures.

For small values of the catalyst recycle ratio R, the catalyst regenerator should be removed from the system of reactor and regenerator (no sense to regenerate a small recycled catalyst flux). The range $[0, R]$ of those values of R for which the system without catalyst regenerator is an optimal system increases with the unit cost of catalyst regeneration, A.

For the case when whole catalyst flux leaving reactor is regenerated (there is no fresh catalyst flux, $S_{\mathrm{f}}=0$) one can confirm the validity of the following statement. For small values of unit cost of catalyst regeneration A the catalyst is regenerated to maximum possible value, $a_{\mathrm{R}}=1$, whereas the activity of catalyst leaving reactor $a[t_k]$ increases with A. This statement results from the fact that, in this range of A, the optimal temperature profile is shifted in direction of lower temperatures when A increases. For larger values of A, an isothermal profile of temperature at the level of minimum allowable temperature T_* is an optimal one; in such a case there is no possibility to control the reactor process by a temperature profile. This is associated with the decrease of value for a number of quantities (catalyst activity after regeneration, a_{R}, the activity of catalyst leaving the reactor, $a[t_k]$, and the average catalyst activity) when the unit regeneration cost A increases. This is a new form of catalyst saving, because the catalyst deactivation rate becomes reduced when an average catalyst activity is allowed to decrease. It is important that this form of catalyst saving appears in the region where any saving of the catalyst by an optimal choice of temperature profile is impossible.

There is no optimal stationary solution for simultaneous renewal of catalyst, by input of the fresh catalyst flux and regeneration. But, in fact, the reactor–regenerator system has always to work with additional flux of fresh catalyst, because the catalyst losses from the system always do exist. Thus the scheme of an industrial reactor–regenerator system is exactly like that presented in Fig. 1. However, the catalyst recycle ratio is not a control variable; it is rather a parameter, whose value results from the knowledge of the magnitude of catalyst loss from the system. Thus, the industrial optimization problem can be formulated as follows. Find the optimal temperature profile along tubular reactor and catalyst activity after regeneration for a fixed value of catalyst recycle ratio. This is exactly the same optimization problem as the one which was solved at the lower level of the optimization described in this paper.

Closing our communication we would like to stress that the Hamiltonian method of optimization applied in this paper to reacting processes with catalyst decay has proved to be an effective and powerful tool for optimization of diverse systems such as heat exchangers, separation systems and non-catalytic chemical reactors. The implementation of this method to catalytic processes in multiphase reactors extends its realm of applications considerably, thus making possible optimization of many new catalytic systems currently investigated.

8. List of symbols

A	dimensionless unit cost of catalyst regeneration per unit activity, Eq. (28)
a	catalyst activity defined as the ratio of reaction rate in presence of current catalyst and the rate in presence of fresh catalyst (dimensionless)
a_f	fresh catalyst activity
a_R	catalyst activity after regeneration
a^n	catalyst activity at and after stage n of the cascade of reactors with ideal mixing
c_i	concentration of reagent i (mol l^{-1})
E_d	activation energy of catalyst deactivation (J mol^{-1})
E_i	activation energy of reaction i (J mol^{-1})
F	dimensionless process profit flux, Eqs. (25) and (26)
H^n	Hamiltonian (in optimization algorithm)
K_c	flux of fixed cost (\$ min^{-1})
K_r	cost of catalyst regeneration from activity $a[t_k]$ to a_R (\$ kg^{-1})
k_c	dimensionless flux of fixed cost defined by Eq. (29)
k_d	catalyst deactivation rate constant (min^{-1})
k_i	reaction rate constant (l (mol min)$^{-1}$)
$k_{\mathrm{d}0}$	frequency factor in Arrhenius expression for k_d (min^{-1})
$k_{\mathrm{i}0}$	frequency factor in Arrhenius expression for k_i (l (mol min)$^{-1}$)
k_i^n	reaction rate constant for reaction undergoing in the cascade (l (mol min)$^{-1}$)
L	reactants mass flux in reactor (kg min^{-1})
M	constant defined by Eq. (17)
M_R	molar mass of desired reagent R (kg mol^{-1})
n, N	current and total number of stages in the cascade, respectively
P	process profit flux (\$ min^{-1})
R	gas constant or catalyst recycle ratio (kg kg^{-1})
S	catalyst mass flux in reactor (kg min^{-1})
S_f	fresh catalyst mass flux (kg min^{-1})
S_r	recycled catalyst mass flux (kg min^{-1})
T	temperature (K)
T_*, T^*	minimum and maximum allowable temperature, respectively (K)
t	time (min)
t_k	residence time of reactants and catalyst in reactor (min)
t^n	total residence time in the first n stage of the cascade (min)
x_i	dimensionless concentration of reagent i defined by Eq. (16)
x^n	dimensionless concentration at and after stage n of the cascade of reactors
z^n	adjoint vector (in optimization algorithm)
λ	dimensionless unit price of fresh catalyst, Eq. (27)
μ_f	unit price of fresh catalyst (\$ kg^{-1})
μ_R	unit price of desired reagent R (\$ kg^{-1})
μ_r	unit cost of catalyst regeneration per unit catalyst activity and unit mass (\$ kg^{-1})
ρ	reagents mixture density (kg l^{-1})
θ^n	residence time at the stage n of the cascade, Eq. (39) (min)

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