
ESTIMATION OF THE CATALYST PELLET ACTIVITY DISTRIBUTION FROM KINETIC DATAAlena BRUNOVSKÁ^a and Josef HORÁK^b^a *Department of Organic Technology,
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The possibility of estimating the activity distribution inside an industrial catalyst pellet from measurements of the composition of the outlet stream of a laboratory stirred tank reactor vs volumetric flow rate is discussed. It is assumed that the form of the reaction rate expression for the chosen testing reaction is known and the value of the corresponding reaction rate constant can be evaluated from the measurements in the kinetic region on the crushed pellet. A procedure is proposed which allows to determine whether the activity distribution estimation is feasible, and demands on the model test reaction are discussed. The estimation technique is applied to simulated (both precise and noisy) data.

The estimation of the activity distribution inside an industrial catalyst pellet can be useful for several reasons. Pellets with non-uniform active catalyst distribution are produced purposely to increase effectiveness factor, selectivity, or resistance to deactivation. Then the estimation of the active catalyst distribution is needed in order to control the impregnation procedure for preparing the pellet with desired activity profile. Non-uniform activity distribution can also be caused by deactivation. Then the estimation of the activity distribution can yield information about the mechanism and course of deactivation.

The catalyst pellet can be nonhomogeneous owing to either catalytic activity or diffusional properties. To estimate both nonhomogeneities from kinetic data is not feasible, so we assume that the pellet is diffusionally homogeneous, *i.e.*, that the value of the effective diffusion coefficient is uniform throughout the pellet. The aim of the estimation technique proposed is to obtain information about the activity inside the pellet.

THEORETICAL

To estimate the distribution, a test reaction is used. It is assumed that the form of its reaction rate expression is known, and the value of the reaction rate constant can

be evaluated from measurements in the kinetic region on the crushed pellet. Further, the values of the effective diffusion coefficients have to be estimated by a different method. The proposed method, in principle, allows to estimate their values simultaneously but with a certain inaccuracy and uncertainty.

The activity (or the "rate constant density function") is defined as the ratio of the local rate constant $k(r)$ and its volume averaged value k_m (see refs^{1,2})

$$\Phi(r) = \frac{k(r)}{k_m}, \quad (1)$$

where

$$k_m = \frac{1}{V_p} \int_{V_p} k(r) dV_p. \quad (2)$$

The rate constant density function has to satisfy the condition

$$\frac{1}{V_p} \int_{V_p} \Phi(r) dV_p = 1. \quad (3)$$

To estimate the activity distribution, the dependence of the composition of the outlet stream from the laboratory continuous stirred tank reactor on volumetric flow rate under steady state conditions and constant inlet stream composition has to be measured.

The goal of the method is to estimate the activity distribution inside the pellet to obtain the best fit of the measured and computed (for given activity distribution) reactor outlet concentrations. As the objective function,

$$F[\Phi(r)] = \sum_{i=1}^I \sum_{j=1}^J (C_{ji} - C_{ji,exp})^2 \quad (4)$$

has been used, where C_{ji} is the concentration corresponding to the distribution $\Phi(r)$, J is the number of analysed components and I the number of measurements.

The estimation has two levels. At the first stage we find out whether the test reaction and reaction conditions are properly chosen, in the second one the optimization procedure is carried out.

Analysis of the Method and Diffusion Coefficient Estimation Feasibility

To determine in general, whether the method is feasible or not, is not easy. Whether a reliable estimate of the activity distribution from kinetic data is possible at all, depends on the form of the reaction rate equation. For some rate equations the test

is not sensitive. The test sensitivity further depends on the fact how far is the considered region from the kinetic one. In the kinetic region, the reaction proceeds in the whole pellet and the mean reaction rate does not depend on the activity distribution. Deep inside the diffusion region, the mean reaction rate is a function of activity distribution, but on the other hand, the reactants penetrate only into a part of the pellet near the active zone border. Therefore the kinetic measurements can reflect only the state of the penetrated zone of the pellet. In the practical realization, it is necessary to take into account also the uncertainty due to experimental noise.

As the preliminary analysis, a heuristic procedure is suggested consisting in the pellet behaviour simulation for a given kinetic equation.

Preliminary Analysis

We choose several different activity distributions satisfying Eq. (3), and compute the reactor outlet gas phase concentration for the whole volumetric flow interval investigated. Three different cases can be distinguished:

- a) The simulated dependences are equal; the method is then principally unapplicable.
- b) The differences between individual dependences are smaller than the dispersion of experimental data; then the method is not feasible because of limited accuracy.
- c) The dependences are significantly different, then we can estimate the activity distribution.

As different activity distributions we can choose, for example, the uniform, increasing and decreasing distributions towards the pellet center. Another possibility is to assume activity in a narrow region (at one point) and alter its position.

This heuristic approach is more feasible from the practical point of view than a general analysis of the form of functions and results. It is obvious that an analogical analysis can be made before we start the kinetic tests to find out whether the rate equation form is reasonable for the estimation method and how deep in the diffusion region the region of the chosen reaction conditions is located.

To estimate the diffusion coefficient along with the activity distribution appears to be an ill-posed problem (flat extreme). A possibility to circumvent this difficulty is to employ a two-level optimization: By using a one-parameter optimization procedure, to look for the value of the diffusion coefficient and for each value to estimate the activity distribution which minimizes objective function (4). However, since the minimum of the objective function with respect to the diffusion coefficient is flat, this method can fail for data with experimental error. Then we need more information about activity, for example, which part of the pellet is active, or whether the distribution has increasing or decreasing tendency, *etc.*

Application of Optimization Techniques

Providing the preliminary analysis exhibits the feasibility of the method, we can employ some optimization techniques to find the activity distribution minimizing objective function (4) for a given value of the diffusion coefficient.

Since Φ is unlikely to be linear, we cannot expect to be able to express it in a closed form. Two different approaches have been employed:

a) Representation in a "parametric" form – the step function (Fig. 1) has been selected

$$\Phi(\varphi) = \beta X_{\langle \varphi_1, \varphi_2 \rangle}(\varphi), \quad (5)$$

where

$$X_{\omega}(\varphi) = \begin{cases} 1 & \dots \varphi \in \omega \\ 0 & \dots \varphi \notin \omega \end{cases}, \quad \beta = \frac{1}{\varphi_2^{n+1} - \varphi_1^{n+1}}, \quad (6)$$

n is the integer characteristic of the pellet geometry, and φ is the dimensionless space coordinate.

b) Representation in a "non-parametric" form, *i.e.*, by a piece-wise linear function given by the values $\Phi(\varphi_k)$ in equidistant mesh points dividing the interval $\langle 0, 1 \rangle$.

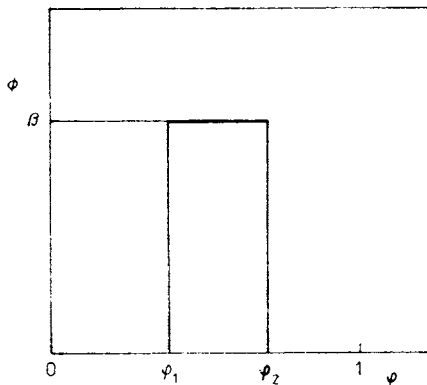


FIG. 1
Step function representation

Mathematical Model of the Pellet and Reactor

Let us consider the test reaction $A \rightarrow$ products of m -th order, isothermal conditions, and negligible external diffusion. Then the model equations in the dimensionless form are as follow:

$$\nabla^2 Y_A = Th_A^2 R \quad (7)$$

(mass balance of the pellet)

$$\varphi = 0 : dY_A/d\varphi = 0 \quad (8)$$

$$\varphi = 1 : Y_A = Y_A(1)$$

(Dirichlet boundary conditions)

$$1 - Y_A(1) = Z_R \bar{R} \quad (9)$$

(mass balance of the reactor)

$$R = \Phi Y_A^m \quad (10)$$

(reaction rate equation)

$$\bar{R} = (n + 1) \int_0^1 \varphi^n R d\varphi \quad (11)$$

(relation for the mean reaction rate).

From Eqs (7), (8), (9), and (11) we obtain the boundary condition

$$\varphi = 1 : dY_A/d\varphi = \frac{Th_A^2}{Z_R(n + 1)} [1 - Y_A(1)]. \quad (12)$$

In case of the step function representation we can take into account that the reaction does not take place outside the interval $\langle \varphi_1, \varphi_2 \rangle$ where we obtain solution of the Eq. (7) in the closed form

$$\varphi \in \langle 0, \varphi_1 \rangle : Y_A = Y_{A1} \quad (13)$$

$$\varphi = \varphi_1 : Y_A = Y_{A1}, dY_A/d\varphi = 0 \quad (14)$$

$$\varphi \in \langle \varphi_1, \varphi_2 \rangle : \nabla^2 Y_A = Th_A^2 R \quad (15)$$

$$\varphi = \varphi_2 : Y_A = Y_{A2} = Y_A(1) + \frac{\bar{R}Th_A^2}{n + 1} \frac{\psi_n(\varphi_2)}{\varphi_2^n} \frac{1}{d\psi_n/d\varphi} \quad (16)$$

$$\varphi \in (\varphi_2, 1) : Y_A = Y_A(1) - [Y_A(1) - Y_{A2}] \psi_n(\varphi)/\psi_n(\varphi_2) \quad (17)$$

where $\psi_n(\varphi) = \varphi - 1$ for $n = 0$ (slab), $\psi_n(\varphi) = \ln \varphi$ for $n = 1$ (infinite cylinder), and $\psi_n(\varphi) = 1 - 1/\varphi$ for $n = 2$ (sphere).

Optimization Technique

For a simple reaction with one reactant, the objective function in the dimensionless

form becomes

$$F[\Phi(\varphi)] = \sum_{i=1}^I (Y_{A_i}(1) - Y_{As_i})^2, \quad (18)$$

where Y_{As} is the measured and $Y_A(1)$ the computed dimensionless concentration on the pellet surface (and in the gas phase of the reactor as well).

For the step function representation, the objective function has two parameters φ_1 and φ_2 , both from the interval $\langle 0, 1 \rangle$ and $\varphi_1 < \varphi_2$. The minimum of the objective function has been estimated by the sectioning method³.

In case of nonparametric representation, the objective function has K parameters $\Phi(\varphi_1), \Phi(\varphi_2), \dots, \Phi(\varphi_K)$. The constraint is relation (3) which in the dimensionless form becomes

$$(n + 1) \int_0^1 \Phi(\varphi) \varphi^n d\varphi = 1 \quad (19)$$

and the non-negativity of $\Phi(\varphi_k)$. To find the minimum of function (18) a gradient type method has been employed^{4,5}. The gradient is the vector with components (cf. Appendix)

$$\frac{\partial F}{\partial \Phi_k} = \sum_{i=1}^I \left\{ - (n + 1) Th_A^2 \int_{\varphi_k - \Delta\varphi/2}^{\varphi_k + \Delta\varphi/2} \varphi^n p_i Y_{A_i}^m d\varphi \right\} \quad k = 1, \dots, K \quad (20)$$

and p is the solution of the adjoint equation

$$\nabla^2 p - Th_A^2 \Phi^m Y_A^{m-1} = 0 \quad (21)$$

with boundary conditions

$$\varphi = 0 : dp/d\varphi = 0$$

$$\varphi = 1 : dp/d\varphi = \left[Y_A(1) - Y_{As_i} - p(1) \frac{Th_A^2}{Z_R} \right] \frac{1}{(n + 1)}. \quad (22)$$

Due to the constraints (relation (19) and non-negativity of Φ) the projected gradient method has been applied. The $(l + 1)$ -th iteration is computed from the l -th one by the scheme

$$\Phi_k^{l+1} = \Phi_k^l - \lambda^l \gamma_k^l, \quad (23)$$

where

$$\gamma_k = s_k - q$$

and

$$s_k = \begin{cases} \partial F / \partial \Phi_k & \text{for } \Phi_k > \varepsilon \text{ or } \Phi_k \leq \varepsilon \text{ and } \partial F / \partial \Phi_k \leq 0 \\ 0 & \text{for } \Phi_k \leq \varepsilon \text{ and } \partial F / \partial \Phi_k > 0 \end{cases}$$

$$q = (n + 1) \int_0^1 s \varphi^n d\varphi.$$

The step length λ^1 has been determined by a one-parameter optimization method in the gradient direction (as in the method of steepest descent).

The system of model equations as well as the relation for the gradient components has been solved numerically. For the reaction-diffusion equation the finite difference scheme has been employed to obtain a system of nonlinear algebraic equations which has been solved by the Newton-Raphson procedure with adjustable step length. As the first iteration the solution for the first-order reaction has been chosen. Using the finite difference scheme for the adjoint equation we obtain a system of linear algebraic equations.

RESULTS AND DISCUSSION

As the testing reaction a second-order one has been chosen. We assume that the value of the effective diffusion coefficient as well as the volume-averaged reaction rate constant are known. To find out whether the problem is solvable or not and which reaction conditions are suitable, the preliminary analysis described in the theoretical part has been employed. The uniform activity distribution and the model of the pellet with one point activity distributions² have been considered. For the second-order reaction it follows

$$Y_A(1) = 1 - Y_{A1}^2 Z_R \quad (24)$$

$$Y_{A1}^2 = - \frac{(n + 1)(Y_A(1) - Y_{A1})}{Th_A^2 \ln \varphi_1} \quad (25)$$

where Y_{A1} is the concentration at the active point φ_1 .

The simulated outlet reactor concentration *vs* volumetric flow rate are illustrated in Figs 2, 3, and 4 for several different values of the Thiele modulus. In Fig. 5 several concentration profiles in the pellet with uniform activity distribution are compared for the given values of the Thiele moduli. This shows how deep the regime in the diffusion region is located. It is obvious, that with increasing the Thiele modulus the pellet response is more sensitive to the activity distribution. On the other hand, it decreases the concentration in the region near the pellet center so that the test can be insensitive to the activity distribution in this zone.

In the preliminary analysis described, the change of the Thiele modulus has been realized by changing the reaction rate constant. The value of the Thiele modulus can be adjusted by the inlet concentration, too.

On the basis of this preliminary analysis, the data for $Th_A^2 = 10$ ($k_m = 1 \text{ m}^3 \cdot \text{kmol}^{-1} \text{ s}^{-1}$, $Z_{RO} = 1.5 \cdot 10^{-5} \text{ kmol}$), cylindrical geometry, and chosen activity

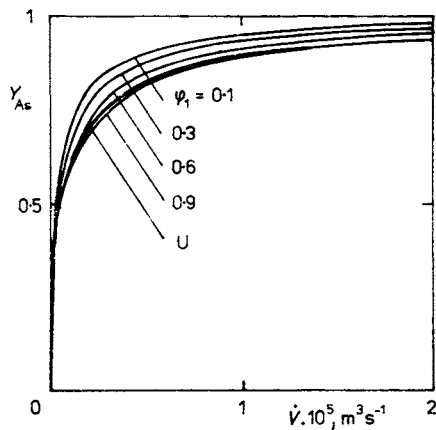


FIG. 2

Gas phase concentration vs volumetric flow rate ($Th_A^2 = 1$, $k_m = 0.1 \text{ m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$, $Z_{RO} = 1.5 \cdot 10^{-5} \text{ kmol}$, $n = 1$). U uniform activity distribution. Activity at point $\varphi_1 = 0.1; 0.3; 0.6; 0.9$

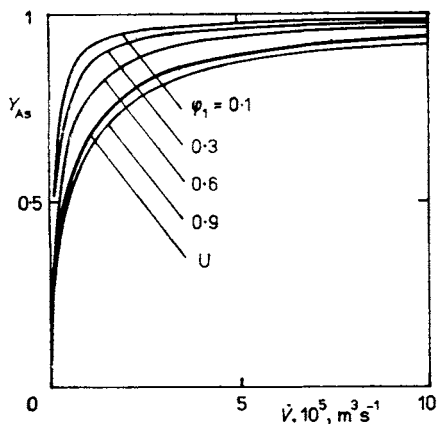


FIG. 3

Gas phase concentration vs volumetric flow rate ($Th_A^2 = 10$, $k_m = 1 \text{ m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$, $Z_{RO} = 1.5 \cdot 10^{-5} \text{ kmol}$, $n = 1$). U uniform activity distribution. Activity at point $\varphi_1 = 0.1; 0.3; 0.6; 0.9$

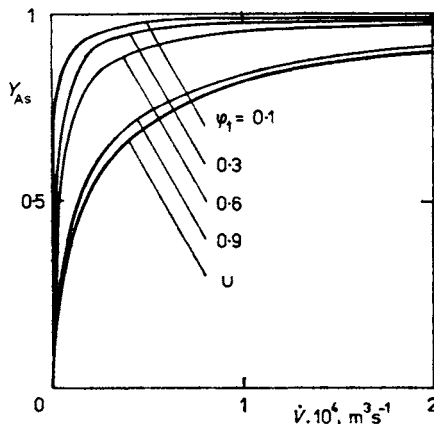


FIG. 4

Gas phase concentration vs volumetric flow rate ($Th_A^2 = 100$, $k_m = 10 \text{ m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$, $Z_{RO} = 1.5 \cdot 10^{-5} \text{ kmol}$, $n = 1$). U uniform activity distribution. Activity at point $\varphi_1 = 0.1; 0.3; 0.6; 0.9$

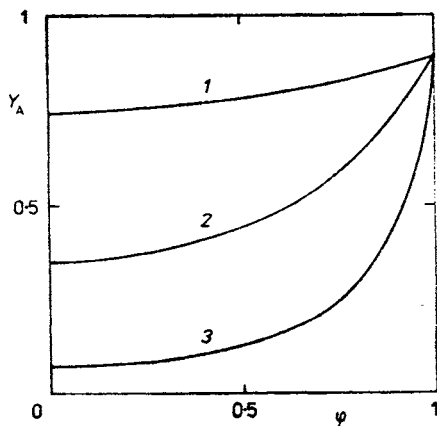


FIG. 5

Concentration profile in the pellet with uniform activity distribution ($n = 1$, $Z_{RO} = 1.5 \cdot 10^{-5}$ kmol). 1 $Th_A^2 = 1$, $\dot{V} = 1 \cdot 10^{-5} \text{ m}^3 \text{ s}^{-1}$; 2 $Th_A^2 = 10$, $\dot{V} = 5 \cdot 10^{-5} \text{ m}^3 \text{ s}^{-1}$; 3 $Th_A^2 = 100$, $\dot{V} = 1 \cdot 10^{-4} \text{ m}^3 \text{ s}^{-1}$

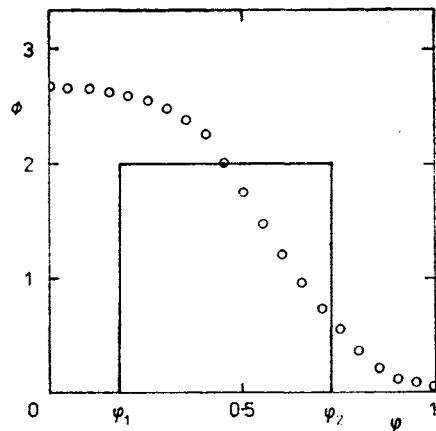


FIG. 6

Step function representation. Example 1

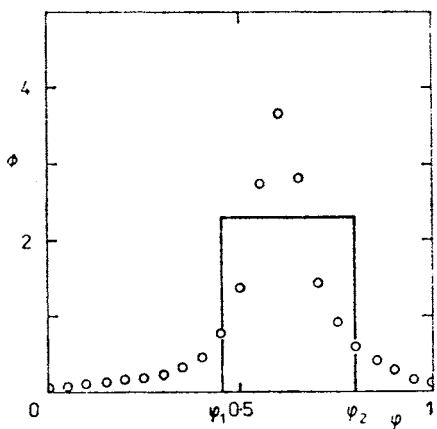


FIG. 7

Step function representation. Example 2

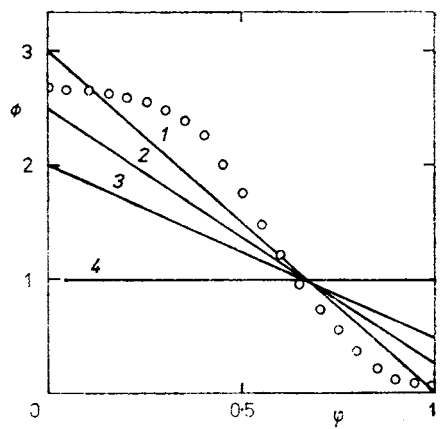


FIG. 8

Selection of the first iteration for the gradient method. Example 1. 1 $F = 0.0023$; 2 $F = 0.0102$; 3 $F = 0.0216$; 4 $F = 0.0494$

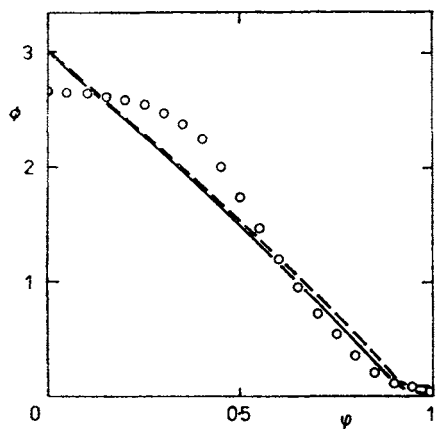


FIG. 9

Non-parametric activity distribution representation. Example 1. Full line — precise data; dashed line — data with accidental error $\pm 5\%$

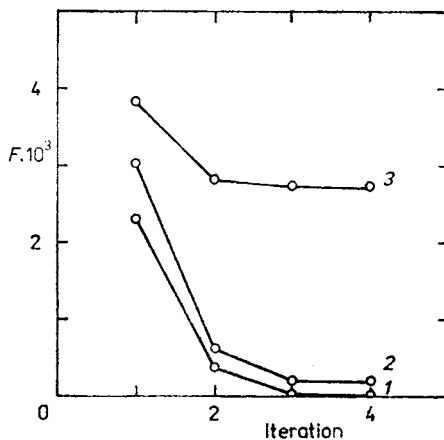


FIG. 10

Decrease of the objective function by the gradient method. Example 1. 1 Precise data; 2 data with accidental error $\pm 0.5\%$; 3 data with accidental error $\pm 5\%$

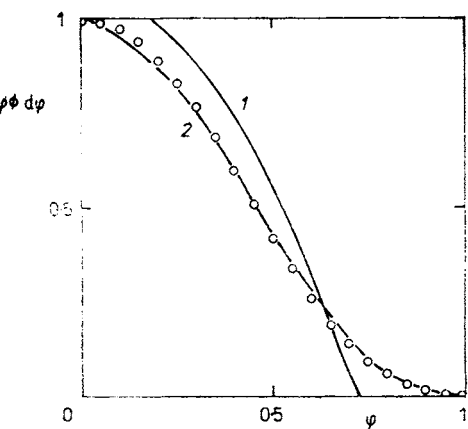


FIG. 11

Comparison of integral (26) for estimated and simulated data. Example 1. 1 Step function representation; 2 non-parametric representation

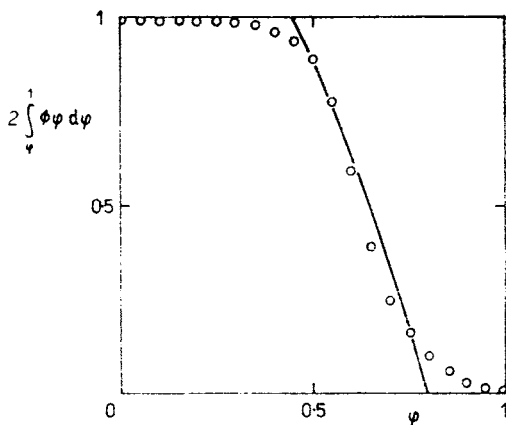


FIG. 12

Comparison of integral (26) for estimated and simulated data. Example 2. Step function representation

distribution have been simulated. For the activity distribution, two examples have been considered: the partially deactivated pellet (example one) and non-uniformly impregnated pellet (example two), satisfying constraint (19).

The resulting activity distributions for the step function representations are in Figs 6 and 7. This representation is adequate in case of example two where the activity is restricted to a narrow region. For example one it is necessary to use the non-parametric form representation. In this case, as the first iteration the linear function satisfying condition (19) has been chosen. A reasonable linear function has been selected from several ones by comparing the values of the objective function. This procedure is illustrated in Fig. 8. After having found a first iteration, the activity profile has been computed iteratively by the proposed gradient-type method. In Fig. 9 the last iteration is exhibited, the decrease of the objective function by this gradient method procedure is in Fig. 10. These figures contain also the solution for the data with simulated noise.

The method is not sensitive enough to the activity near the pellet center due to cylindrical geometry. This is why we introduce the dependence of the integral variable

$$(n + 1) \int_{\varphi}^1 \varphi^n \Phi \, d\varphi \quad (26)$$

on the dimensionless space coordinate φ (both examples, Figs 11 and 12).

The results obtained indicate that the suggested activity distribution estimation technique works also for noisy data. The representation of the activity distribution in a non-parametric form appears to be suitable for estimation in case of partially deactivated pellet while the step function representation can be used in case of impregnation control.

APPENDIX

In this Appendix we derive formula (20) for the radiant and adjoint Eq. (21).

The objective function (18) can, be rewritten

$$F = 2 \sum_{i=1}^I \mathcal{J}_i, \quad (A1)$$

where

$$\mathcal{J}_i = \frac{1}{2} [Y_{A_i}(1) - Y_{A_{s,i}}]^2 \quad (A2)$$

and the gradient components are

$$\frac{\partial F}{\partial \Phi_k} = \sum_{i=1}^I \delta \mathcal{J}_i, \quad (A3)$$

where

$$\delta \mathcal{J}_i = [Y_{A_i}(1) - Y_{A_{s_i}}] \delta Y_{A_i}(1). \quad (A4)$$

By linearizing Eqs (7) and (12) we obtain

$$\nabla^2 \delta Y_A = Th_A^2 Y_A^m \delta \Phi + Th_A^2 \Phi m Y_A^{m-1} \delta Y_A \quad (A5)$$

$$\delta Y'_A(1) = - \frac{Th_A^2}{Z_R(n+1)} \delta Y_A(1). \quad (A6)$$

After multiplying (A5) by $(n+1) \varphi^n p_i$, integrating over $\langle 0, 1 \rangle$, interchanging sides, and adding to (A4), we obtain

$$\begin{aligned} \delta \mathcal{J}_i &= [Y_{A_i}(1) - Y_{A_{s_i}}] \delta Y_A(1) + \\ &+ (n+1) \int_0^1 \varphi^n p_i [\nabla^2 \delta Y_A - Th_A^2 Y_A^m \delta \Phi - Th_A^2 \Phi m Y_A^{m-1} \delta Y_A] d\varphi. \end{aligned} \quad (A7)$$

Integrating by parts we have

$$\begin{aligned} \delta \mathcal{J}_i &= [Y_{A_i}(1) - Y_{A_{s_i}}] \delta Y_A(1) + (n+1) \int_0^1 \varphi^n [\nabla^2 p_i - Th_A^2 \Phi m Y_A^{m-1} p_i] \cdot \\ &\cdot \delta Y_A d\varphi - (n+1) \left\{ \int_0^1 \varphi^n p_i Th_A^2 Y_A^m \delta \Phi d\varphi + \right. \\ &\left. + p'_i(1) \delta Y_A(1) - p_i(1) \delta Y'_A(1) \right\} \end{aligned} \quad (A8)$$

and using Eq. (A6),

$$\begin{aligned} &[Y_{A_i}(1) - Y_{A_{s_i}}] \delta Y_A(1) - [p'_i(1) \delta Y_A(1) + p_i(1) \delta Y'_A(1)] (n+1) = \\ &= \delta Y_A(1) \left[Y_{A_i}(1) - Y_{A_{s_i}} - p'_i(1) (n+1) - p_i(1) \frac{Th_A^2}{Z_R} \right]. \end{aligned} \quad (A9)$$

If p is the solution of the adjoint equation

$$\nabla^2 p - Th_A^2 \Phi m Y_A^{m-1} p = 0 \quad (A10)$$

satisfying the boundary conditions

$$p'(0) = 0$$

$$p'(1) = \left[Y_A(1) - Y_{As} - p(1) \frac{Th_A^2}{Z_R} \right] \frac{1}{(n+1)}, \quad (A11)$$

then by substituting Eq. (A9) into (A8) we obtain

$$\delta \mathcal{J}_i = -(n+1) \int_0^1 \varphi^n p_i Th_A^2 Y_{A,i}^m \delta \Phi d\varphi, \quad (A12)$$

where

$$\delta \Phi(\varphi_k) = \begin{cases} 0 & \text{for } \Phi_k = \Phi_j \quad (j \neq k) \\ 1 & \text{for } \Phi_k = \Phi_j \quad (j = k). \end{cases} \quad (A13)$$

Then,

$$\delta \mathcal{J}_i = -(n+1) \int_{\varphi_k - \Delta\varphi/2}^{\varphi_k + \Delta\varphi/2} \varphi^n p_i Y_{A,i}^m Th_A^2 d\varphi. \quad (A14)$$

The gradient components are

$$\frac{\partial F}{\partial \Phi_k} = \sum_{i=1}^I \delta \mathcal{J}_i = \sum_{i=1}^I \left\{ -(n+1) \int_{\varphi_k - \Delta\varphi/2}^{\varphi_k + \Delta\varphi/2} \varphi^n p_i Y_{A,i}^m Th_A^2 d\varphi \right\}. \quad (A15)$$

LIST OF SYMBOLS

a	characteristic dimension of catalyst pellet
C	concentration
C_{ref}	reference inlet concentration
D	effective diffusion coefficient
F	objective function
I	number of measurements
J	number of analysed components
k	reaction rate constant
k_m	volume-averaged reaction rate constant
K	number of mesh points
m	reaction order
n	integer characteristic of pellet geometry
p	adjoint variable
r	space coordinate
R	dimensionless reaction rate
Th	Thiele modulus, $Th_A^2 = a^2 k_m C_{A,ref}^{m-1} / D_A$
\dot{V}	volumetric flow rate
V_p	volume of pellet
W	mass of pellet
Y	dimensionless concentration, $Y_A = C_A / C_{A,ref}$
Z_R	dimensionless parameter, $Z_R = k_m W C_{A,ref}^{m-1} / (q \dot{V}) = Z_{RO} k_m / \dot{V}$
ρ	pellet density

φ	dimensionless space coordinate, $\varphi = r/a$
Φ	activity
ω	active region

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