OPTIMAL CATALYST PELLET ACTIVITY DISTRIBUTIONS FOR DEACTIVATING SYSTEMS

ALENA BRUNOVSKÁ[†]

Department of Organic Technology, Slovak Institute of Technology, Radlinského 9, 812 37 Bratislava, Czechoslovakia

MASSIMO MORBIDELLI

Department of Chemical Engineering and Materials Science, University of Cagliari, Piazza d'Armi, 09123 Cagliari, Italy

and

PAVOL BRUNOVSKÝ

Institute of Applied Mathematics, Comenius University, Mlynská dolina, 842 15 Bratislava, Czechoslovakia

Abstract—The optimal activity distribution in catalyst pellets for reacting systems which undergo deactivation is analysed. A general optimality criterion is developed, which allows one to conclude that, under quite general conditions, the optimal activity distribution is of the Dirac-delta type.

INTRODUCTION

As an important component of catalyst design, optimal active catalyst distribution in the porous structure of the inert support has received considerable attention in the literature. The main results have been recently reviewed by Dougherty and Verykios (1987). Most previous works have been devoted to the problem of increasing the effectiveness factor or selectivity in some specific reacting systems. Only a few papers dealt with catalytic systems undergoing deactivation, again considering specific cases (De Lancey, 1973; Corbett and Luss, 1974; Becker and Wei, 1977a, b). For example, De Lancey (1973) estimated the optimal activity distribution for an isothermal first-order reaction and homogeneous poisoning using Pontrjagin's maximum principle.

In this paper the problem of catalyst design for systems which undergo deactivation is analysed. In particular, we refer to noble-metal catalysts dispersed within a particle of inert support. These systems are widely used in industry for hydrogenation and oxidation reactions, which constitute intermediate steps in the production of a variety of chemical products. In most cases the catalyst undergoes deactivation. Its

replacement or, when possible, its regeneration, constitutes a significant part of the production cost.

The aim of the present paper is to optimize the catalyst pellet performance by suitably locating the active element within the particle support. To this

aim, a general optimality condition is derived which allows to solve the optimization problem under quite general conditions including any rate expression for both the main reaction and the poisoning process under non-isothermal conditions.

THE OPTIMIZATION PROBLEM

The catalyst which is progressively poisoned with operating time has to be periodically replaced or regenerated, depending upon whether the poisoning is irreversible or reversible. The duration of the operating time and the values of the effectiveness factor as a function of time depend upon the active-catalyst distribution within the support. In general, by locating the active catalyst inside the pellet it is possible to increase the resistance against deactivation, i.e. to increase the duration of the operating time. On the other hand, at least for positive-order reactions, the maximum value of the effectiveness factor is obtained when the active catalyst is located at the external surface (Morbidelli *et al.*, 1985; Chemburkar *et al.*, 1987). Thus, an economic criterion is needed to define the optimal active catalyst distribution. A reasonable one is profit per time:

$$\text{profit per time} = \frac{\text{price of the product} - \text{cost of the catalyst}}{\text{operating time}} = \frac{\alpha_1 \int_0^{\tau^*} \eta \, d\tau - \alpha_2}{\tau^*} \quad (1)$$

where α_1 and α_2 are weighting coefficients proportional to the price of the product and to the cost of the catalyst, respectively, τ^* is the operating time, and η is the effectiveness factor.

The aim of this work is to determine the initial pellet activity distribution $a(\varphi, 0)$ and the operating time τ^* for which the maximum value of the following objective function, proportional to the profit per time,

[†]Author to whom correspondence should be addressed.

defined above:

$$\mathscr{I}[a(\varphi, 0), \tau^*] = \frac{\gamma \displaystyle\int_0^{\tau^*} \eta \, d\tau - 1}{\tau^*} \qquad (2)$$

($\gamma = \alpha_1/\alpha_2$) is obtained. We optimize over the class of all possible distributions of the same amount of active catalyst. Note that we admit also distributions concentrating the active catalyst into isolated points which are represented by Dirac-delta functions.

THE BASIC EQUATIONS

Let us consider a catalyst pellet in which an irreversible reaction is taking place together with irreversible adsorption of catalyst poison. Since the rate of the poison adsorption is usually considerably lower than that of the catalytic reaction (the form of which may otherwise be arbitrary) the quasi-steady-state approximation can be safely adopted. In addition, we assume negligible external resistances to mass and heat transport. The catalyst activity distribution is a function of location and time, and is defined as the ratio between the local concentration of available catalytically active sites and its volume-averaged initial value:

$$a(\varphi, \tau) = \sigma(\varphi, \tau)/\bar{\sigma} \qquad (3)$$

where

$$\bar{\sigma} = (n + 1) \int_0^1 \sigma(\varphi, 0) \varphi^n \, d\varphi. \qquad (4)$$

Under these conditions, the model equations in dimensionless form are as follows:

Mass balance of the reactant

$$\nabla^2 Y = \Phi^2 R \qquad (5)$$

Mass balance of the poison

$$\nabla^2 Y_p = \Phi_p^2 R_p \qquad (6)$$

Energy balance

$$\nabla^2 \upsilon = - \beta \Phi^2 R \qquad (7)$$

with boundary conditions

$$\varphi = 0: \partial Y/\partial\varphi = \partial Y_p/\partial\varphi = \partial\upsilon/\partial\varphi = 0$$
$$\varphi = 1: Y = Y_p = \upsilon = 1. \qquad (8)$$

The deactivation reaction is accounted for by a balance of the active sites, which in terms of the activity distribution function reduces to

$$\frac{\partial a}{\partial \tau} = - R_p \qquad (9)$$

with initial condition

$$a = a(\varphi, 0) \quad \text{at } \tau = 0 \qquad (10)$$

where the initial activity distribution has to satisfy the following constraint arising from its definition (3) and eq. (4):

$$(n + 1) \int_0^1 a(\varphi, 0) \varphi^n \, d\varphi = 1. \qquad (11)$$

Note that no restrictions are imposed on the expressions of the rates of the reaction and the poisoning processes, for which the following general form is assumed:

$$R = R(Y, Y_p, a, \upsilon); \ R_p = R_p(Y, Y_p, a, \upsilon). \qquad (12)$$

The effectiveness factor η is normalized with respect to the initial value of the reaction rate computed at surface conditions and to the initial activity distribution:

$$\eta = \int_0^1 \varphi^n R \, d\varphi \Big/ \int_0^1 a(\varphi, 0) \varphi^n \, d\varphi$$

$$= (n + 1) \int_0^1 \varphi^n R \, d\varphi = \bar{R} \qquad (13)$$

thus representing the mean reaction rate as a function of time.

GENERAL CONDITION FOR OPTIMAL ACTIVITY DISTRIBUTION

Consider the general deactivation process described above [eqs (5)–(7) and (9)] in a symmetric domain with boundary conditions (8) and initial condition (10). The goal is to find the initial distribution $\hat{a}(\varphi, 0)$ subject to the constraints

$$(n + 1) \int_0^1 \varphi^n \hat{a}(\varphi, 0) \, d\varphi = 1 \text{ and } \hat{a}(\varphi, 0) \geqslant 0 \quad (14)$$

and the time $\hat{\tau} > 0$, such that for $\tau^* = \hat{\tau}$ and $a(\varphi, 0) = \hat{a}(\varphi, 0)$ the objective function (2) is maximized. In the Appendix the following necessary condition for optimality is developed:

If $\hat{a}(\varphi, 0)$ is optimal, then, for any given initial distribution $a(\varphi, 0)$, one has

$$\int_0^1 \varphi^n \Psi(\varphi, 0) \hat{a}(\varphi, 0) \, d\varphi \geqslant \int_0^1 \varphi^n \Psi(\varphi, 0) a(\varphi, 0) \, d\varphi \qquad (15)$$

where $\Psi(\varphi, \tau)$ is obtained as a solution of the system of adjoint equations given in the Appendix with coefficients depending on $\hat{a}(\varphi, 0)$, whose detailed form is in fact irrelevant at this stage.

In order to satisfy condition (15), $\hat{a}(\varphi, 0)$ can be "substantially" non-zero solely at points φ_o at which $\Psi(\varphi, 0)$ attains its maximum over [0, 1]. By "substantially non-zero" we mean

$$\int_{\varphi_o - \varepsilon}^{\varphi_o + \varepsilon} \hat{a}(\varphi, 0) \varphi^n \, d\varphi \neq 0 \qquad (16)$$

for arbitrarily small $\varepsilon > 0$.

Indeed, suppose this is not true, i.e. that eq. (16) holds while

$$\Psi(\varphi_o', 0) > \Psi(\varphi_o, 0) \qquad (17)$$

for some $\varphi_o' \neq \varphi_o$. We show that in such a case it is possible to construct another distribution $a(\varphi, 0)$ satisfying the constraints (11) which violates the optimality criterion (15).

From eq. (17) and the continuity of Ψ it follows that, for sufficiently small $\varepsilon > 0$, all the values of $\Psi(\varphi, 0)$ in the interval $\varphi_o - \varepsilon \leqslant \varphi \leqslant \varphi_o + \varepsilon$ are smaller than any of its value in the interval $\varphi'_o - \varepsilon \leqslant \varphi' \leqslant \varphi'_o + \varepsilon$. Define

$$a(\varphi, 0) = \begin{cases} \hat{a}(\varphi, 0) + (\varphi - \varphi'_o + \varphi_o)^n \hat{a}(\varphi - \varphi'_o + \varphi_o, 0)/\varphi^n & \text{for } \varphi'_o - \varepsilon \leqslant \varphi \leqslant \varphi'_o + \varepsilon \\ 0 & \text{for } \varphi_o - \varepsilon \leqslant \varphi \leqslant \varphi_o + \varepsilon \quad (18) \\ \hat{a}(\varphi, 0) & \text{otherwise.} \end{cases}$$

Then, we have $a(\varphi, 0) \geqslant 0$ and

$$\int_0^1 \varphi^n a(\varphi, 0) \mathrm{d}\varphi = \int_{\varphi'_o - \varepsilon}^{\varphi'_o + \varepsilon} \varphi^n \left[\hat{a}(\varphi, 0) \right.$$

$$+ \left. \frac{(\varphi - \varphi'_o + \varphi_o)^n}{\varphi^n} \hat{a}(\varphi - \varphi'_o + \varphi_o, 0) \right] \mathrm{d}\varphi$$

$$+ \int_{\langle 0,1 \rangle \setminus (\langle \varphi_o - \varepsilon, \varphi_o + \varepsilon \rangle \cup \langle \varphi'_o - \varepsilon, \varphi'_o + \varepsilon \rangle)} \varphi^n \hat{a}(\varphi, 0) \mathrm{d}\varphi$$

$$= \int_{\langle 0,1 \rangle \setminus \langle \varphi_o - \varepsilon, \varphi_o + \varepsilon \rangle} \varphi^n \hat{a}(\varphi, 0) \mathrm{d}\varphi$$

$$+ \int_{\varphi'_o - \varepsilon}^{\varphi'_o + \varepsilon} (\varphi - \varphi'_o + \varphi_o)^n \hat{a}(\varphi - \varphi'_o + \varphi_o) \mathrm{d}\varphi$$

$$= \int_{\langle 0,1 \rangle \setminus \langle \varphi_o - \varepsilon, \varphi_o + \varepsilon \rangle} \varphi^n \hat{a}(\varphi, 0) \mathrm{d}\varphi$$

$$+ \int_{\varphi_o - \varepsilon}^{\varphi_o + \varepsilon} \varphi^n \hat{a}(\varphi, 0) \mathrm{d}\varphi = \int_0^1 \varphi^n \hat{a}(\varphi, 0) \mathrm{d}\varphi = 1. \quad (19)$$

Hence $a(\varphi, 0)$ satisfies constraints (11).

Since from eq. (17) it follows that $\Psi(\varphi - \varphi_o + \varphi'_o, 0) > \Psi(\varphi, 0)$ for all $\varphi_o - \varepsilon \leqslant \varphi \leqslant \varphi_o + \varepsilon$, through similar manipulations we obtain

$$\int_0^1 \varphi^n \Psi(\varphi, 0) a(\varphi, 0) \mathrm{d}\varphi$$

$$= \int_{\langle 0,1 \rangle \setminus \langle \varphi_o - \varepsilon, \varphi_o + \varepsilon \rangle} \varphi^n \Psi(\varphi, 0) \hat{a}(\varphi, 0) \mathrm{d}\varphi$$

$$+ \int_{\varphi_o - \varepsilon}^{\varphi_o + \varepsilon} \Psi(\varphi - \varphi_o + \varphi'_o, 0) \hat{a}(\varphi, 0) \mathrm{d}\varphi$$

$$> \int_{\langle 0,1 \rangle \setminus \langle \varphi_o - \varepsilon, \varphi_o + \varepsilon \rangle} \varphi^n \Psi(\varphi, 0) \hat{a}(\varphi, 0) \mathrm{d}\varphi$$

$$+ \int_{\varphi_o - \varepsilon}^{\varphi_o + \varepsilon} \varphi^n \Psi(\varphi, 0) \hat{a}(\varphi, 0) \mathrm{d}\varphi$$

$$= \int_0^1 \varphi^n \Psi(\varphi, 0) \hat{a}(\varphi, 0) \mathrm{d}\varphi \quad (20)$$

which contradicts the necessary condition for optimality (15).

As a conclusion, it can be observed that the optimality criterion (15) practically excludes any initial distribution $a(\varphi, 0)$ which is not of the Dirac-delta type. Indeed, it is highly unlikely that $\Psi(\varphi, 0)$ would attain its maximum simultaneously at more than one point at which $a(\varphi, 0)$ is substantially non-zero and

therefore it is not meaningful to consider this possibility any further. Consequently, having found the optimal distribution in the class of all one-peak Dirac-delta ones we do not expect any other distribution to improve the objective functional any further.

In fact, for any given distribution, we have shown through eq. (15) that it is possible to construct a suitable Dirac delta distribution which improves the objective functional (2). Of course, the mathematical proof presented above is not completely rigorous and we are not very optimistic about the change for it to be found since $\Psi(\varphi, 0)$ is obtained as a result of solving a system of partial differential equations, the coefficients of which depend on $\hat{a}(\varphi, 0)$ itself. However, since $\Psi(\varphi, 0)$ is the result of an integration process, it certainly has some continuity and well-behaving properties. For this reason, condition (15) can be regarded as a fully satisfactory mathematical justification to consider one-peak Dirac-delta function initial distributions as the only candidates for optimal ones.

In addition, as we will see below, criterion (15) may exclude some delta distributions as well and indicate in which direction to move the activity location point to find the optimal one.

APPLICATION TO THE CASE OF INDEPENDENT POISONING WITH FIRST-ORDER ISOTHERMAL REACTIONS

Once it has been established that the optimal activity distribution is of the Dirac-delta type, the optimization problem reduces to the selection, among all possible Dirac-delta distributions, of the optimal one depending upon the particular reacting system and operating conditions under consideration. For illustrative purposes, let us consider the case of an isothermal first-order reaction with dimensionless rate equation

$$R = aY \quad (21)$$

which occurs together with independent chemisorption of catalyst poison, leading to the following rate expression for the deactivation process:

$$R_p = aY_p. \quad (22)$$

First, we consider a Dirac-delta activity distribution located at the point φ_1. The initial condition, in coincidence with eq. (11), is

$$a(\varphi, 0) = \frac{\delta(\varphi - \varphi_1)}{(n + 1)\varphi_1^n} \quad \text{at } \tau = 0. \quad (23)$$

For $\tau > 0$ it is convenient to express the activity as a product of the initial activity distribution and

a time-dependent variable $\mu(\tau)$, i.e.

$$a(\varphi, \tau) = a(\varphi, 0)\, \mu(\tau) \qquad (24)$$

where $\mu(0) = 1$.

The solution of the model eqs (5), (6) with the rate expressions (21) and (22) and with boundary conditions (8) can be written in the following closed form:

$$\varphi \in \langle 0, \varphi_1 \rangle: \quad Y = Y_1, \; Y_p = Y_{p1} \qquad (25)$$

$$\varphi = \varphi_1: \quad Y = Y_1 = (n + 1)/(n + 1 + x\mu) \qquad (26)$$

$$Y_p = Y_{p1} = (n + 1)/(n + 1 + \alpha x\mu) \qquad (27)$$

$$\varphi \in (\varphi_1, 1\rangle: \quad Y = 1 - (1 - Y_1)\zeta_n(\varphi)/\zeta_n(\varphi_1) \qquad (28)$$

$$Y_p = 1 - (1 - Y_{p1})\zeta_n(\varphi)/\zeta_n(\varphi_1) \qquad (29)$$

where $\quad \zeta_n(\varphi) = 1 - \varphi \qquad \text{for } n = 0$

$$= \ln(1/\varphi) \qquad \text{for } n = 1 \qquad (30)$$

$$= (1 - \varphi)/\varphi \qquad \text{for } n = 2$$

and $x = \Phi^2 \zeta_n(\varphi_1)$, and $\alpha = \Phi_p^2/\Phi^2$. Substituting eqs (23), (24), (27) and the deactivation rate expression (22) reduces eq. (9) to

$$\frac{\partial a}{\partial \tau} = -\frac{\delta(\varphi - \varphi_1)}{(n + 1)\varphi_1^n}\mu\frac{n + 1}{n + 1 + \alpha x\mu}$$

$$= \frac{\delta(\varphi - \varphi_1)}{(n + 1)\varphi_1^n}\frac{\mathrm{d}\mu}{\mathrm{d}\tau} \qquad (31)$$

which leads to

$$\frac{\mathrm{d}\mu}{\mathrm{d}\tau} = -\mu\frac{n + 1}{n + 1 + \alpha x\mu}. \qquad (32)$$

Integrating from $\tau = 0$ to τ and $\mu = 1$ to μ we obtain

$$\tau = \frac{\alpha x}{n + 1}(1 - \mu) - \ln \mu. \qquad (33)$$

When using the Dirac-delta activity distribution (23), the objective functional (2) becomes a function of two parameters: the active point location φ_1 and the operating time τ^*. Equation (33) relating τ and μ allows us to express the objective function (2) in a closed form as a function of the active point location φ_1 and the relative activity μ^* at time τ^*:

Note that if for some μ^* the value of $\mathscr{J}$ is negative for $x = 0$ then it remains negative for all $x \geqslant 0$. Such values of μ^* are uninteresting since for them the catalytic process cannot be profitable no matter where the active catalyst is placed.

To find the optimal value of μ^* we have to maximize the function $z(\mu^*) = \mathscr{J}|_{x=0}$ in the subinterval of $\langle 0, 1 \rangle$, in which z is non-negative.

Using de l'Hospital's rule we obtain a formula for z which is independent of α:

$$z(\mu^*) = [(\mu^* - 1)\gamma + 1]/\ln \mu^*. \qquad (35)$$

In order to have $z(\mu^*) \geqslant 0$ for some $0 \leqslant \mu^* \leqslant 1$ one needs $\gamma \geqslant 1/(1 - \mu^*)$: for such γ, $z(\mu^*) \geqslant 0$ for $0 \leqslant \mu^* \leqslant 1 - 1/\gamma$. Note that from the expression for the right boundary of this interval γ can be expressed as

$$\gamma = 1/(1 - \mu^*). \qquad (36)$$

To maximize $z(\mu^*)$ we first find its local extrema. Those are the solutions of the equation $z'(\mu^*) = 0$ which is

$$\gamma \ln \mu^* + \gamma(1 - \mu^*)/\mu^* - 1/\mu^* = 0. \qquad (37)$$

From this equation we can express γ as a function of μ^*:

$$\gamma = 1/(\mu^* \ln \mu^* + 1 - \mu^*). \qquad (38)$$

Since $\ln \mu^* < 0$ and $\mu^* \ln \mu^* + 1 - \mu^* > 0$ for all $0 \leqslant \mu^* \leqslant 1$ from eq. (37) it follows that
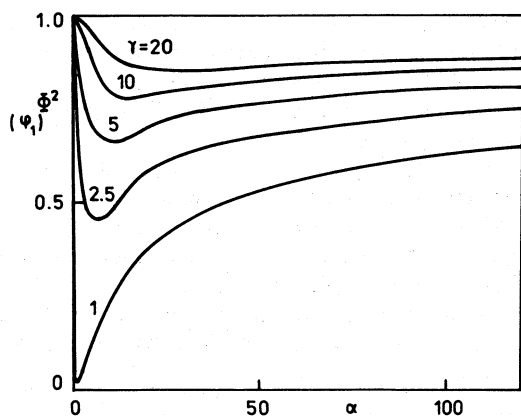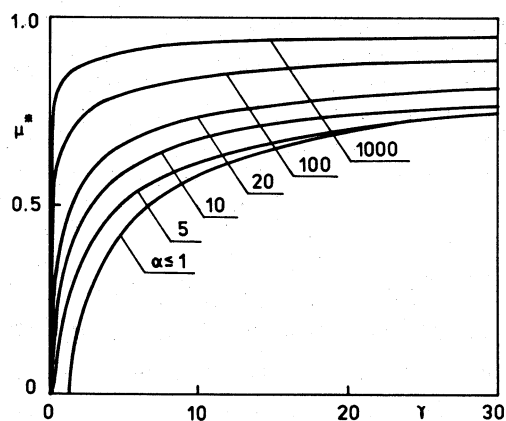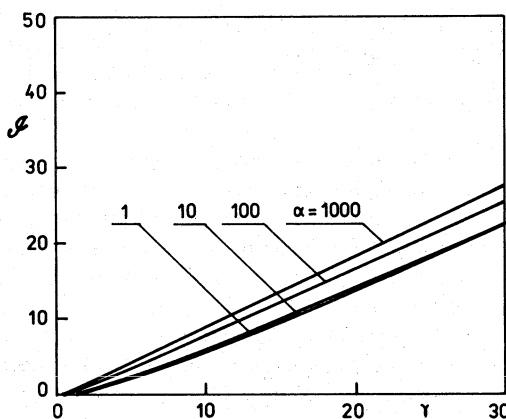
$$\gamma \geqslant 1/(1 - \mu^*). \qquad (39)$$

Comparing eqs (36) and (39) we see that for all $\gamma > 1/(1 - \mu^*)$ there is a unique root of eq. (37) in the interval $\langle 0, 1 - 1/\gamma \rangle$: this root is the optimal value of μ^*.

We can summarize our analysis as follows. For each $0 < \alpha \leqslant 1$ there is a positive threshold value of γ below which the process cannot be profitable for any choice of τ^* and φ_1. For γ above this threshold value the optimal location of the active catalyst is always at the boundary of the pellet and the optimal operating time moves monotonically from infinity to zero for

$$\mathscr{J}(\varphi_1, \mu^*) = \frac{\gamma \alpha (n + 1)\left(\dfrac{n + 1}{x}\dfrac{\alpha - 1}{\alpha}\ln\dfrac{n + 1 + x\mu^*}{n + 1 + x} + 1 - \mu^*\right) - (n + 1)}{\alpha x (1 - \mu^*) - (n + 1)\ln \mu^*} \qquad (34)$$

For $0 < \alpha \leqslant 1$ it readily appears that for $x \geqslant 0$ the denominator of eq. (34) is increasing while the numerator is decreasing. It follows that, for fixed μ^*, in those intervals of x on which $\mathscr{J}$ is positive, it decreases with x. Consequently, for those values of μ^* for which $\mathscr{J}$ is positive for $x = 0$ it attains its maximum with respect to $x \geqslant 0$ at this point. Since $x = 0$ corresponds to $\varphi_1 = 1$ this means that all the active catalyst should be located at the external pellet surface. This is because in this case $\Phi > \Phi_p$, i.e. the intraparticle transport resistance is larger for the main reactant than for the poison.

the parameter γ moving from the threshold value to infinity.

Since for $\alpha > 1$ both the numerator and the denominator of eq. (34) increase with x the optimal location of the active catalyst can be somewhere inside the pellet. Its precise location depends upon the parameter γ, the reaction kinetic parameters and the pellet geometry. In this case the maximum of function (34) with respect to x (i.e. φ_1) and μ^* have to be found numerically, using any of the standard optimization techniques available in the literature. As an example,

Fig. 1. $(\varphi_1)^{\Phi^2}$ vs α for various values of γ ($n = 1$).

Fig. 2. $(\varphi_1)^{\Phi^2}$ vs γ for various values of α ($n = 1$).
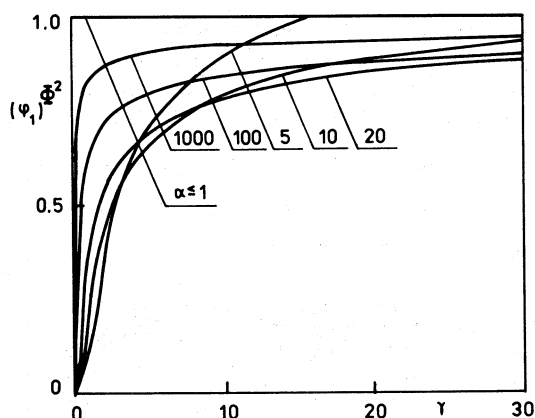
Fig. 3. Optimal operation time, τ^* vs γ, for various values of α ($n = 1$).

Fig. 4. Optimal residual activity, μ^* vs γ, for various values of α ($n = 1$).

Fig. 5. Objective function, $\mathscr{I}$ vs γ, for various values of α ($n = 1$).

the effect of the parameters γ and α on the optimal active catalyst location for a cylindrical pellet ($n = 1$) is shown in Figs 1 and 2, respectively. The corresponding values of the optimal operating time, optimal residual activity and optimal objective function are shown in Figs 3–5. From the results shown in Figs 1 and 3 it appears that, for fixed γ and increasing

values of the ratio $\alpha = \Phi_p^2/\Phi^2$, the optimal location first moves towards the pellet interior but then comes back towards the pellet external surface, while the optimal operation time increases monotonically. On the other hand, from Figs 2 and 3 it appears that, for fixed α, decreasing values of the catalyst replacement cost (i.e. increasing values of γ) lead to optimal catalyst locations closer to the pellet external surface and to lower optimal operating times, τ^*. However, as expected, from the results shown in Fig. 5 it appears that better performance is achieved when the intraparticle diffusion resistance of the poison is larger than that of the main reactant.

In order to further support the results of the theoretical analysis reported above, and to investigate the possibility of their transfer into practical applications, let us consider the following step distribution function

$$\varphi \in \langle 0, \varphi_1) \text{ and } \varphi \in (\varphi_2, 1\rangle: a(\varphi, \tau) = 0$$
$$\varphi \in \langle \varphi_1, \varphi_2 \rangle: a(\varphi, 0) = 1/(\varphi_2^{n+1} - \varphi_1^{n+1}) \tag{40}$$

which is such as to satisfy constraint (11). By recalling that the reaction does not take place outside the interval $\langle \varphi_1, \varphi_2 \rangle$ the pellet mass balances can be
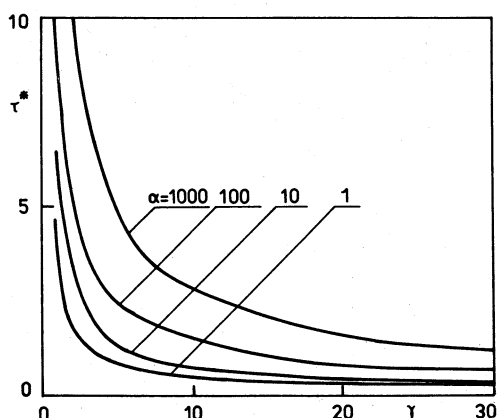
recast in the following form:

$$\varphi \in \langle 0, \varphi_1 \rangle: \quad Y = Y_1, \, Y_p = Y_{p1} \qquad (41)$$

$$\varphi = \varphi_1: \quad Y = Y_1, \, Y_p = Y_{p1}$$

$$\partial Y/\partial \varphi = \partial Y_p/\partial \varphi = 0 \qquad (42)$$

$$\varphi \in \langle \varphi_1, \varphi_2 \rangle: \quad \nabla^2 Y = \Phi^2 R, \, \nabla^2 Y_p = \Phi_p^2 R_p \qquad (43)$$

$$\varphi = \varphi_2: \quad Y = Y_2, \, Y_p = Y_{p2}$$

$$\partial Y/\partial \varphi = -(1 - Y_2)(d\zeta_n/d\varphi)_{\varphi = \varphi_2}/\zeta_n(\varphi_2)$$

$$\partial Y_p/\partial \varphi = -(1 - Y_{p2})(d\zeta_n/d\varphi)_{\varphi = \varphi_2}/\zeta_n(\varphi_2) \qquad (44)$$

$$\varphi \in (\varphi_2, 1\rangle: \quad Y = 1 - (1 - Y_2)\zeta_n(\varphi)/\zeta_n(\varphi_2)$$

$$Y_p = 1 - (1 - Y_{p2})\zeta_n(\varphi)/\zeta_n(\varphi_2). \qquad (45)$$

The system of eqs (41)–(45) has been solved numerically, by discretizing the space coordinate φ by a standard finite-difference scheme. The activity value at each position inside the pellet has been computed as a function of time by integrating eq. (9) by a marching technique. The values of the objective function (2) and of the effectiveness factor (13) have been computed through suitable quadrature formulae.

In the case of step activity distribution, the objective function (2) is a function of three parameters, φ_1, φ_2 and τ^*. In all the performed optimization runs the optimal initial activity distribution has been given by the narrowest possible step distribution of the adopted discretization procedure (i.e. $\varphi_2 - \varphi_1 =$ step size in the finite-difference scheme) centered at the optimal location predicted by the ideal Dirac-delta distribution. A typical example is shown in Fig. 6, where the curves represent step distributions (i.e. values of φ_1 and φ_2 with optimized operating time, τ^*) which exhibit the same value of the objective function $\mathscr{J}$ (2). It clearly appears that the best performance corresponds to a Dirac-delta activity distribution, i.e. $\varphi_1 = \varphi_2 = 0.67$. It is also worth noting that the performance of such a Dirac-delta distribution is actually quite closely approached by step distribution of relatively small width and centered at the
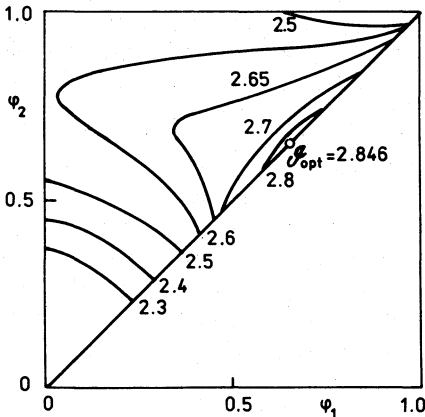
same point. This result is of great importance with respect to the actual preparation of such optimally distributed catalyst pellets, as it has been previously discussed in the context of non-deactivating reacting systems (Morbidelli *et al.*, 1982).

Finally, in order to further illustrate the general condition for optimality (15) the adjoint variable profiles $\Psi(\varphi, 0)$ for the reacting systems under examination, are shown in Fig. 7(a) and (b) for step and Dirac-delta activity distributions, respectively. These have been obtained by solving numerically the system of the adjoint equations which in the case under examination reduces to

$$\nabla^2 p + a(1 - p\Phi^2) = 0 \qquad (46)$$

$$\nabla^2 q - q\Phi_p^2 a - \Psi a = 0 \qquad (47)$$

$$\partial \Psi/\partial \tau + Y(1 - p\Phi^2) - q\Phi_p^2 Y_p - \Psi Y_p = 0 \qquad (48)$$

with boundary and terminal conditions

$$\tau = \hat{\tau}: \quad \Psi(\varphi, \tau) = 0 \qquad (49)$$

$$\tau \in \langle 0, \hat{\tau}\rangle; \quad \varphi = 0: \quad \partial p/\partial \varphi = \partial q/\partial \varphi = \partial \Psi/\partial \varphi = 0 \qquad (50)$$

$$\varphi = 1: \quad p = q = 0. \qquad (51)$$
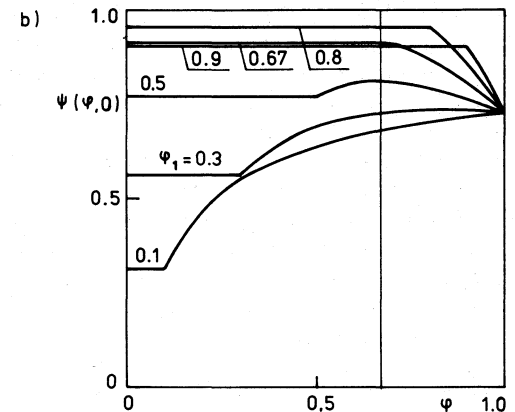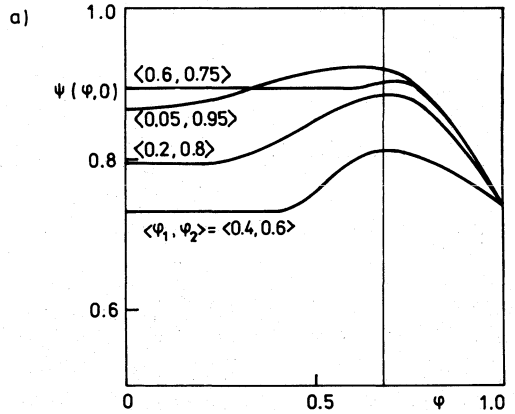
Fig. 7. Adjoint variable $\Psi(\varphi, 0)$ profiles. The vertical solid line indicates location of the optimal Dirac-delta distribution (parameter values: $\alpha = 10$, $\gamma = 5$, $\Phi^2 = 1$, $n = 1$). (a) Step function activity distributions. (b) Dirac-delta activity distributions.

Fig. 6. Level lines of the objective function $\mathscr{J}$ for various step activity distributions (parameter values: $\alpha = 10$, $\gamma = 5$, $\Phi^2 = 1$, $n = 1$).

Since the system parameters adopted in Figs 6 and 7 are the same, it can be noted that also in the latter case is the optimal Dirac-delta distribution located at $\varphi_1 = 0.67$ [as indicated by the solid vertical line in Fig. 7(a) and (b)]. It is rather surprising that for all step-size distributions considered, even the widest one $\langle 0.05, 0.95 \rangle$, the maximum of the $\Psi(\varphi, 0)$ curves is very close to the location of the optimal Dirac-delta distribution. This provides a useful initial information for the optimum search. In Fig. 7(b) the adjoint profiles $\Psi(\varphi, 0)$ are shown relative to Dirac-delta distributions centered at various locations φ_1. It appears that using criterion (15) it is possible to exclude the locations $\varphi_1 = 0.1, 0.3$ and 0.5, since the corresponding adjoint functions exhibit their maximum values at other locations. In addition, the function $\Psi(\varphi, 0)$ indicates in all cases that the optimal location should be to the right (i.e. larger values of φ_1) since the value of the integral in the right-hand side of condition (15) increases when moving the Dirac-delta location in this direction. On the other hand, criterion (15) is not fine enough to exclude the location points to the right of the optimal one (i.e. 0.8 and 0.9). The only way to exclude such points is in fact by comparing the corresponding values of the objective function, as has been done in the numerical optimization procedure described above.

CONCLUDING REMARKS

A method for determining the optimal activity distribution in catalyst pellets for reacting systems undergoing deactivation has been developed. As the objective function, profit per time taking into account the price of the product and the cost of catalyst replacement or regeneration has been considered. A general condition for optimality has been developed which allows one to conclude that Dirac-delta activity distributions are the only candidates for optimal ones. It is remarkable that such a conclusion is of quite general validity, since it applies to any kind of kinetic expression for the main reaction as well as for the poisoning process and any pellet geometry. Even though not reported here in detail for brevity reasons, it is worth mentioning that the same conclusion can be reached when accounting for external mass and heat transfer resistances as well as for other types of objective functions. In such cases the derivation follows closely the arguments reported in the recent paper by Wu et al. (1990) referring to the case of non-isothermal reacting systems of a fully general nature in the absence of deactivation. Also in this case it has been found that the optimal activity distribution is of the Dirac delta type.

As an illustrative example the case of an isothermal first-order reaction with independent poisoning has been investigated. The effect of the kinetic parameters and operating conditions on the optimal location of the Dirac-delta distribution, as well as on the optimal operating time, has been discussed in detail. In particular, it has been found that for values of the ratio

between the poison and the main-reactant Thiele moduli smaller than one the optimal location of the active catalyst is at the external pellet surface. For values of this parameter larger than one the optimal location moves towards the pellet interior to an extent which depends upon the specific operating conditions under examination. Finally, in order to establish the possibility of transferring the results of this work to practical applications, the performance of step activity distributions has been investigated. Such distributions have in fact been investigated experimentally in the context of optimal catalyst design for non-deactivating systems [cf. Wu et al. (1990)].

NOTATION

a	activity
a	characteristic dimension of catalyst pellet
a_p	equilibrium poison adsorbed amount
C	concentration
D	diffusion coefficient
$(-\Delta H)$	heat of reaction
$\mathscr{J}$	objective function
k	reaction rate constant
n	integer characteristic of pellet geometry ($n = 0$, slab; $n = 1$, cylinder; $n = 2$, sphere)
p	adjoint variable
q	adjoint variable
r	reaction rate
R	dimensionless main reaction rate
R_p	dimensionless poisoning rate
s	adjoint variable
t	time
T	temperature
t^o	characteristic deactivation time
x	$= \Phi^2 \zeta_n(\varphi_1)$, dimensionless parameter
Y	$= C_A/C_{Ao}$, dimensionless reactant concentration
Y_p	$= C_p/C_{po}$, dimensionless poison concentration

Greek letters

α	$= \Phi_p^2/\Phi^2$, ratio of Thiele moduli
α_1	price of product
α_2	cost of catalyst
β	$= (-\Delta H)D_A C_{Ao}/(\lambda T_o)$, dimensionless reaction heat
γ	$= \alpha_1/\alpha_2$, dimensionless parameter
η	effectiveness factor
λ	thermal conductivity
μ	relative activity defined by eq. (24)
σ	concentration of available catalytically active sites
τ	$= t/t^o$, dimensionless time
υ	$= T/T_o$, dimensionless temperature
φ	dimensionless space coordinate
Φ	$= a[r_o/(D_A C_{Ao})]^{1/2}$, reaction Thiele modulus
Φ_p	$= a[a_p/(D_p C_{po} t^o)]^{1/2}$, poison Thiele modulus
Ψ	adjoint variable

Subscripts

*	terminal conditions
o	surface conditions
p	poison
1, 2	activity location

REFERENCES

Becker, E. and Wei, J., 1977a, Nonuniform distribution of catalysts on supports. I. Bimolecular Langmuir reactions. *J. Catal.* **46**, 365–371.

Becker, E. and Wei, J., 1977b, Nonuniform distribution of catalysts on supports. II. First order reactions with poisoning. *J. Catal.* **46**, 372–381.

Chemburkar, R. M., Morbidelli, M. and Varma, A., 1987, Optimal catalyst activity profiles in pellets—VII. The case of arbitrary reaction kinetics with finite external heat and mass transport resistances. *Chem. Engng Sci.* **42**, 2621–2632.

Corbett, W. E. and Luss, D., 1974, The influence of nonuniform catalytic activity on the performance of a single spherical pellet. *Chem. Engng Sci.* **29**, 1473–1483.

De Lancey, G. B., 1973, An optimal catalyst activation policy for poisoning problems. *Chem. Engng Sci.* **28**, 105–118.

Dougherty, R. C. and Verykios, X. E., 1987, Nonuniformly activated catalysts. *Catal. Rev. Sci. Engng* **29**, 101–150.

Morbidelli, M., Servida, A. and Varma, A., 1982, Optimal catalyst activity profiles in pellets—I. The case of negligible external mass transfer resistance. *Ind. Engng Chem. Fundam.* **21**, 278–284.

Morbidelli, M., Servida, A., Carrà, S. and Varma, A., 1985, Optimal activity profiles in pellets—III. *Ind. Engng Chem. Fundam.* **24**, 116–118.

Wu, H., Brunovská, A., Morbidelli, M. and Varma, A., 1990, Optimal catalyst activity profiles in pellets—IX. General nonisothermal reacting systems with arbitrary kinetics. *Chem. Engng Sci.* (in press).

APPENDIX: DEVELOPMENT OF THE OPTIMALITY CONDITION (15)

Let $\hat{\tau}$ be the optimal time and let $\hat{a}(\varphi, 0)$ be the optimal initial activity distribution. Then, it follows that

$$I(\hat{a}) = \int_0^{\hat{\tau}} \eta \, d\tau = (n + 1) \int_0^{\hat{\tau}} \int_0^1 \varphi^n R \, d\varphi \, d\tau \quad (A1)$$

is maximum over all $\hat{a}$s subject to the constraints (14). In particular, if we take any $a(\varphi, 0)$ satisfying eq. (14), then

$$a_\varepsilon(\varphi, 0) = \hat{a}(\varphi, 0) + \varepsilon[a(\varphi, 0) - \hat{a}(\varphi, 0)] \quad (A2)$$

will satisfy eq. (14) for all $0 \leqslant \varepsilon \leqslant 1$. Thus, in order to satisfy eq. (A1) we must have

$$\frac{d}{d\varepsilon} I(a_\varepsilon)|_{\varepsilon = 0} \leqslant 0. \quad (A3)$$

Let us denote $\delta X = dX/d\varepsilon$. By differentiating eqs (5)–(7), (9), the boundary condition (8) and eq. (A2) with respect to ε at $\varepsilon = 0$ we obtain

$$\nabla^2 \delta Y = \Phi^2 \left(\frac{\partial R}{\partial Y} \partial Y + \frac{\partial R}{\partial Y_p} \delta Y_p + \frac{\partial R}{\partial \upsilon} \delta \upsilon + \frac{\partial R}{\partial a} \partial a \right) \quad (A4)$$

$$\nabla^2 \delta Y_p = \Phi_p^2 \left(\frac{\partial R_p}{\partial Y} \delta Y + \frac{\partial R_p}{\partial Y_p} \delta Y_p + \frac{\partial R_p}{\partial \upsilon} \delta \upsilon + \frac{\partial R_p}{\partial a} \delta a \right) \quad (A5)$$

$$\nabla^2 \delta \upsilon = -\beta \Phi^2 \left(\frac{\partial R}{\partial Y} \partial Y + \frac{\partial R}{\partial Y_p} \delta Y_p + \frac{\partial R}{\partial \upsilon} \delta \upsilon + \frac{\partial R}{\partial a} \partial a \right) \quad (A6)$$

$$-\frac{\partial \delta a}{\partial \tau} = \frac{\partial R_p}{\partial Y} \delta Y + \frac{\partial R_p}{\partial Y_p} \delta Y_p + \frac{\partial R_p}{\partial \upsilon} \delta \upsilon + \frac{\partial R_p}{\partial a} \delta a \quad (A7)$$

$$\varphi = 1: \delta Y(1, \tau) = \delta Y_p(1, \tau) = \delta \upsilon(1, \tau) = 0 \quad (A8)$$

$$\tau = 0: \delta a(\varphi, 0) = a(\varphi, 0) - \hat{a}(\varphi, 0). \quad (A9)$$

Thus using eqs (A4)–(A6), eq. (A1) reduces to

$$\begin{aligned}
\delta I = (n + 1) &\int_0^{\hat{\tau}} \int_0^1 \varphi^n \left(\frac{\partial R}{\partial Y} \delta Y + \frac{\partial R}{\partial Y_p} \delta Y_p \right. \\
&\left. + \frac{\partial R}{\partial \upsilon} \delta \upsilon + \frac{\partial R}{\partial a} \delta a \right) d\varphi \, d\tau \\
+ (n + 1) &\int_0^{\hat{\tau}} \int_0^1 \varphi^n p \left[\nabla^2 \delta Y - \Phi^2 \left(\frac{\partial R}{\partial Y} \delta Y \right. \right. \\
&\left. \left. + \frac{\partial R}{\partial Y_p} \delta Y_p + \frac{\partial R}{\partial \upsilon} \delta \upsilon + \frac{\partial R}{\partial a} \delta a \right) \right] d\varphi \, d\tau \\
+ (n + 1) &\int_0^{\hat{\tau}} \int_0^1 \varphi^n q \left[\nabla^2 \delta Y_p - \Phi_p^2 \left(\frac{\partial R_p}{\partial Y} \delta Y \right. \right. \\
&\left. \left. + \frac{\partial R_p}{\partial Y_p} \delta Y_p + \frac{\partial R_p}{\partial \upsilon} \delta \upsilon + \frac{\partial R_p}{\partial a} \delta a \right) \right] d\varphi \, d\tau \\
+ (n + 1) &\int_0^{\hat{\tau}} \int_0^1 \varphi^n s \left[\nabla^2 \delta \upsilon + \beta \Phi^2 \left(\frac{\delta R}{\partial Y} \delta Y \right. \right. \\
&\left. \left. + \frac{\partial R}{\partial Y_p} \delta Y_p + \frac{\partial R}{\partial \upsilon} \delta \upsilon + \frac{\partial R}{\partial a} \delta a \right) \right] d\varphi \, d\tau \\
+ (n + 1) &\int_0^{\hat{\tau}} \int_0^1 \varphi^n \frac{\partial}{\partial \tau} (\Psi \delta a) \, d\varphi \, d\tau \\
+ (n + 1) &\int_0^1 \varphi^n \Psi(\varphi, 0) \, \delta a(\varphi, 0) \, d\varphi \quad (A10)
\end{aligned}$$

where $p(\varphi, \tau)$, $q(\varphi, \tau)$, $s(\varphi, \tau)$ and $\Psi(\varphi, \tau)$ are adjoint variables (corresponding to Lagrangian multipliers) and the following relationships have been used:

$$\Psi(\varphi, \hat{\tau}) = 0 \quad (A11)$$

$$\begin{aligned}
(n + 1) &\int_0^{\hat{\tau}} \int_0^1 \varphi^n \frac{\partial}{\partial \tau} (\Psi \delta a) \, d\varphi \, d\tau \\
= (n + 1) &\int_0^{\hat{\tau}} \int_0^1 \varphi^n \left[\frac{\partial \Psi}{\partial \tau} \delta a + \Psi \frac{\partial \delta a}{\partial \tau} \right] d\varphi \, d\tau \\
= (n + 1) &\int_0^{\hat{\tau}} \int_0^1 \varphi^n \left[\frac{\partial \Psi}{\partial \tau} \delta a - \Psi \left(\frac{\partial R_p}{\partial Y} \delta Y + \frac{\partial R_p}{\partial Y_p} \delta Y_p \right. \right. \\
&\left. \left. + \frac{\partial R_p}{\partial \upsilon} \delta \upsilon + \frac{\partial R_p}{\partial a} \delta a \right) \right] d\varphi \, d\tau \quad (A12)
\end{aligned}$$

By selecting p, q and s so as to satisfy the boundary conditions

$$\varphi = 1: p(1, \tau) = q(1, \tau) = s(1, \tau) = 0 \quad (A13)$$

and integrating by parts twice one obtains

$$\int_0^1 \varphi^n p \, \nabla^2 \delta Y \, d\varphi = \int_0^1 \varphi^n \delta Y \, \nabla^2 p \, d\varphi \quad (A14)$$

$$\int_0^1 \varphi^n q \, \nabla^2 \delta Y_p \, d\varphi = \int_0^1 \varphi^n \delta Y_p \, \nabla^2 q \, d\varphi \quad (A15)$$

$$\int_0^1 \varphi^n s \, \nabla^2 \delta \upsilon \, d\varphi = \int_0^1 \varphi^n \delta \upsilon \, \nabla^2 s \, d\varphi. \quad (A16)$$

Substituting eqs (A12) and (A14)–(A16) into eq. (A10) and grouping terms multiplied by δY, δY_p, $\delta \upsilon$ and δa into separate integrals one obtains

$$\begin{aligned}
\delta I = (n + 1) \int_0^{\hat{\tau}} \int_0^1 \varphi^n \delta Y &\left(\frac{\partial R}{\partial Y} + \nabla^2 p - p \Phi^2 \frac{\partial R}{\partial Y} \right. \\
&\left. - q \Phi_p^2 \frac{\partial R_p}{\partial Y} + s \beta \Phi^2 \frac{\partial R}{\partial Y} - \Psi \frac{\partial R_p}{\partial Y} \right) d\varphi \, d\tau
\end{aligned}$$

$$+ (n + 1) \int_0^{\tilde\tau} \int_0^1 \varphi^n \delta Y_p \left(\frac{\partial R}{\partial Y_p} - p\Phi^2 \frac{\partial R}{\partial Y_p} + \nabla^2 q \right.$$

$$\left. - q\Phi_p^2 \frac{\partial R_p}{\partial Y_p} + s\beta\Phi^2 \frac{\partial R}{\partial Y_p} - \Psi \frac{\partial R_p}{\partial Y_p} \right) d\varphi \, d\tau$$

$$+ (n + 1) \int_0^{\tilde\tau} \int_0^1 \varphi^n \delta\upsilon \left(\frac{\partial R}{\partial \upsilon} - p\Phi^2 \frac{\partial R}{\partial \upsilon} - q\Phi_p^2 \frac{\partial R_p}{\partial \upsilon} \right.$$

$$\left. + \nabla^2 s + s\beta\Phi^2 \frac{\partial R}{\partial \upsilon} - \Psi \frac{\partial R_p}{\partial \upsilon} \right) d\varphi \, d\tau$$

$$+ (n + 1) \int_0^{\tilde\tau} \int_0^1 \varphi^n \delta a \left(\frac{\partial R}{\partial a} - p\Phi^2 \frac{\partial R}{\partial a} - q\Phi_p^2 \frac{\partial R_p}{\partial a} \right.$$

$$\left. + s\beta\Phi^2 \frac{\partial R}{\partial a} - \Psi \frac{\partial R_p}{\partial a} + \frac{\partial \Psi}{\partial \tau} \right) d\varphi \, d\tau$$

$$+ (n + 1) \int_0^1 \varphi^n \Psi(\varphi, 0) \, \delta a(\varphi, 0) \, d\varphi. \qquad (A17)$$

By selecting p, q, s and Ψ so as to satisfy the following system of adjoint equations:

$$\nabla^2 p + \frac{\partial R}{\partial Y}(1 - p\Phi^2 + s\beta\Phi^2) - \frac{\partial R_p}{\partial Y}(q\Phi_p^2 + \Psi) = 0 \qquad (A18)$$

$$\nabla^2 q + \frac{\partial R}{\partial Y_p}(1 - p\Phi^2 + s\beta\Phi^2) - \frac{\partial R_p}{\partial Y_p}(q\Phi_p^2 + \Psi) = 0 \qquad (A19)$$

$$\nabla^2 s + \frac{\partial R}{\partial \upsilon}(1 - p\Phi^2 + s\beta\Phi^2) - \frac{\partial R_p}{\partial \upsilon}(q\Phi_p^2 + \Psi) = 0 \qquad (A20)$$

$$\frac{\partial \Psi}{\partial \tau} + \frac{\partial R}{\partial a}(1 - p\Phi^2 + s\beta\Phi^2) - \frac{\partial R_p}{\partial a}(q\Phi_p^2 + \Psi) = 0 \qquad (A21)$$

eq. (A17) reduces to

$$\delta I = (n + 1) \int_0^1 \varphi^n \Psi(\varphi, 0) \, \delta a(\varphi, 0) \, d\varphi = \frac{dI}{d\varepsilon}. \qquad (A22)$$

Finally, using eq. (A9), eq. (A22) leads to

$$\delta I = (n + 1) \int_0^1 \varphi^n \Psi(\varphi, 0) \left[a(\varphi, 0) - \hat{a}(\varphi, 0) \right] d\varphi \qquad (A23)$$

which substituted into eq. (A3) leads to the general condition for optimality

$$\int_0^1 \varphi^n \Psi(\varphi, 0) \, \hat{a}(\varphi, 0) \, d\varphi \geq \int_0^1 \varphi^n \psi(\varphi, 0) \, a(\varphi, 0) \, d\varphi. \qquad (A24)$$