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Optimal operation of exothermic consecutive reactions *via* maximum principle

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Abstract

A computational algorithm *via* the maximum principle has been suggested for the prediction of an optimum catalyst dilution profile under which the yield of the intermediate species in a system of exothermic consecutive reactions is maximized at the reactor outlet. A significant feature in the problem analysis is the enlargement of the Hamiltonian by including the energy conservation equation and a corresponding augmentation of the adjoint vector. The computed catalyst dilution profile therefore forces the optimal operation of a non-isothermal reactor with constant coolant temperature and as such represents a practical strategy in reactor design.

Key words : Optimum catalyst, exothermic consecutive reactions, reactor design, catalyst dilution.

The use of Pontryagin's maximum principle for the solution of certain optimal problems in chemical engineering is of recent origin. A most comprehensive treatise dealing with a study of complex systems optimization *via* this technique has been published by Fan[1]. An earlier version called the 'discrete maximum principle' dealt with an optimal study of staged processes[2]. Fan has investigated a large number of interesting cases in chemical reaction engineering of which the problem of consecutive reaction has found a prominent place. Thomas and Wood[3] have studied the problem of a consecutive reaction *via* the maximum principle for the prediction of an optimum catalyst composition profile for a bi-functional catalyst system. Rosenbrock[4] has discussed at length the applicability of the maximum principle. A close look at the problems investigated from the point of view of prediction of optimum temperature profiles reveals the conspicuous omission of the energy conservation equation in the formulation of the Hamiltonian, owing to the assumption concerning the absence of heat effects other than the temperature dependence of rate constants. What has been achieved is the use of computational algorithm in the analysis of industrial process systems for the prediction of a temperature profile which maximizes a stated objective function. If an answer to the more important question as to how such a temperature profile could be actually realized in a reactor where significant heat effects due to exothermic chemical reactions intervene is forthcoming this would indeed represent a significant advance in the application of the maximum principle in process design.

For highly exothermic gas-solid catalytic reactions, catalyst dilution has been suggested as a logical and expedient method for the control of the severity of axial temperature profile in a packed bed reactor[5]. This strategy is often used to effect isothermal kinetic measurements. A stochastic model for describing quantitatively the influence of catalyst dilution on conversion has been proposed by van Den Bleek[6]. Recently Narsimhan[7] has shown how it is possible to predict a catalyst dilution profile which will force an optimal temperature profile in either a plug flow reactor or a system of well mixed fluid bed reactors where a simple reveroible exothermic reaction takes place. The work reported in this paper represents an attempt to extend the strategy of prediction of catalyst dilution profile in forcing the optimal operation in a nonisothermal reactor where irreversible consecutive reactions of exothermic nature take place. As a preliminary communication only a computational algorithm will be developed. Fan[1] has dealt with the problem of predicting an optimum temperature profile for a consecutive reaction scheme of negligible heat of reaction effect, whereby the yield of the intermediate species is maximized at the reactor exit. In this paper the problem is extended to the consideration of a non-isothermal system in a packed bed reactor cooled at the wall by a coolant of constant temperature.

Analysis

Consider the following consecutive exothermic reaction scheme ;

$$A \xrightarrow[-\triangle H_1]{k_1} \quad B \xrightarrow[-\triangle H_2]{k_2} C \tag{1}$$

taking place in a plug flow reactor with a specified holding time of T secs. The temperature policy $x_3(\theta)$ which maximises the yield of the intermediate species B can be obtained readily in a manner indicated by Fan[1]. This optimal policy $x_3^+(\theta)$ would be still valid even when the reactions are exothermic as indicated in eqn. (1). However, since the reactor operation would involve jacket cooling at temperature x_c, $x_c(\theta)$ could be used as a decision variable so that the optimal temperature policy is automatically realised. $x_c(\theta)$ is obtained from the following equality (Fig. 1)

$$\frac{dX_3^+}{d\theta} = (j_1k_1x_1 + j_2k_2x_2) - \left[\frac{St \cdot v}{r_m}(x_3^+ - x_c)\right] \tag{2}$$

or

$$x_c(\theta) = x_3^+(\theta) - \left[(j_1k_1x_1 + j_2k_2x_2) - \frac{dx_3^+(\theta)}{d\theta}\right]\frac{r_m}{St. v} \quad , \tag{2A}$$

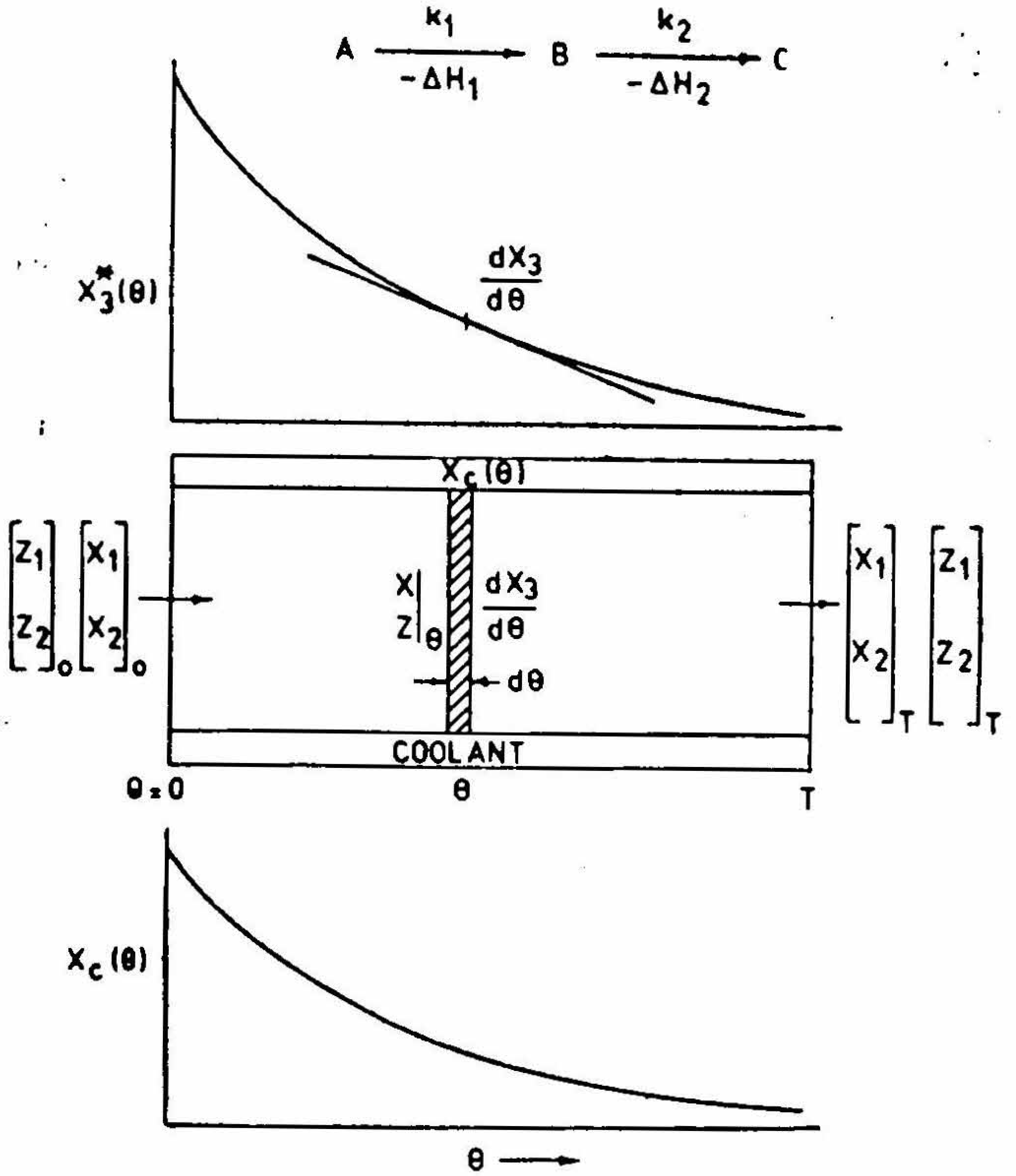

FIG. 1. Strategy of coolant temperature profile $X_c(\theta)$ for optimal operation of a PFR

where

$$j_1 = \frac{-\Delta H_1}{c_p} \; ; \quad j_2 = \frac{-\Delta H_2}{c_p}$$

St = Stanton Number, $h/v\, c_p$;

r_w = wall heat transfer area per unit reactor volume

v = average fluid velocity in the reactor

c_p = heat capacity per unit volume.

Since $x_3^+(\theta)$ information is based on the knowledge of the state and adjoint vectors at any time θ obtained by the integration of the state and adjoint equations, using eqn. (2A) there exists a possibility of assigning a discrete but rough coolant temperature policy by partitioning the jacket and allowing the coolant to boil under predetermined pressures. Evidently the cost of implementing such an experimenal scheme would far outweigh the benefit of higher yield of B owing to the attendant optimal policy. It is therefore desirable to consider catalyst dilution as a strategy which would force the optimal operation on the system. The catalyst dilution profile could be obtained by the application of the Maximum Principle operating on the augmented state and adjoint equations. As a preliminary exercise it would be necessary to obtain an acceptable form for the modified volume based rate constant which would involve the catalyst dilution factor α. If α is defined as the fraction of active catalyst in unit volume of the bed, then the modified rate constant may be related to the true constant by the following expression :

$$\bar{k}_i = \phi_i'(\alpha) \cdot k_i \tag{3}$$

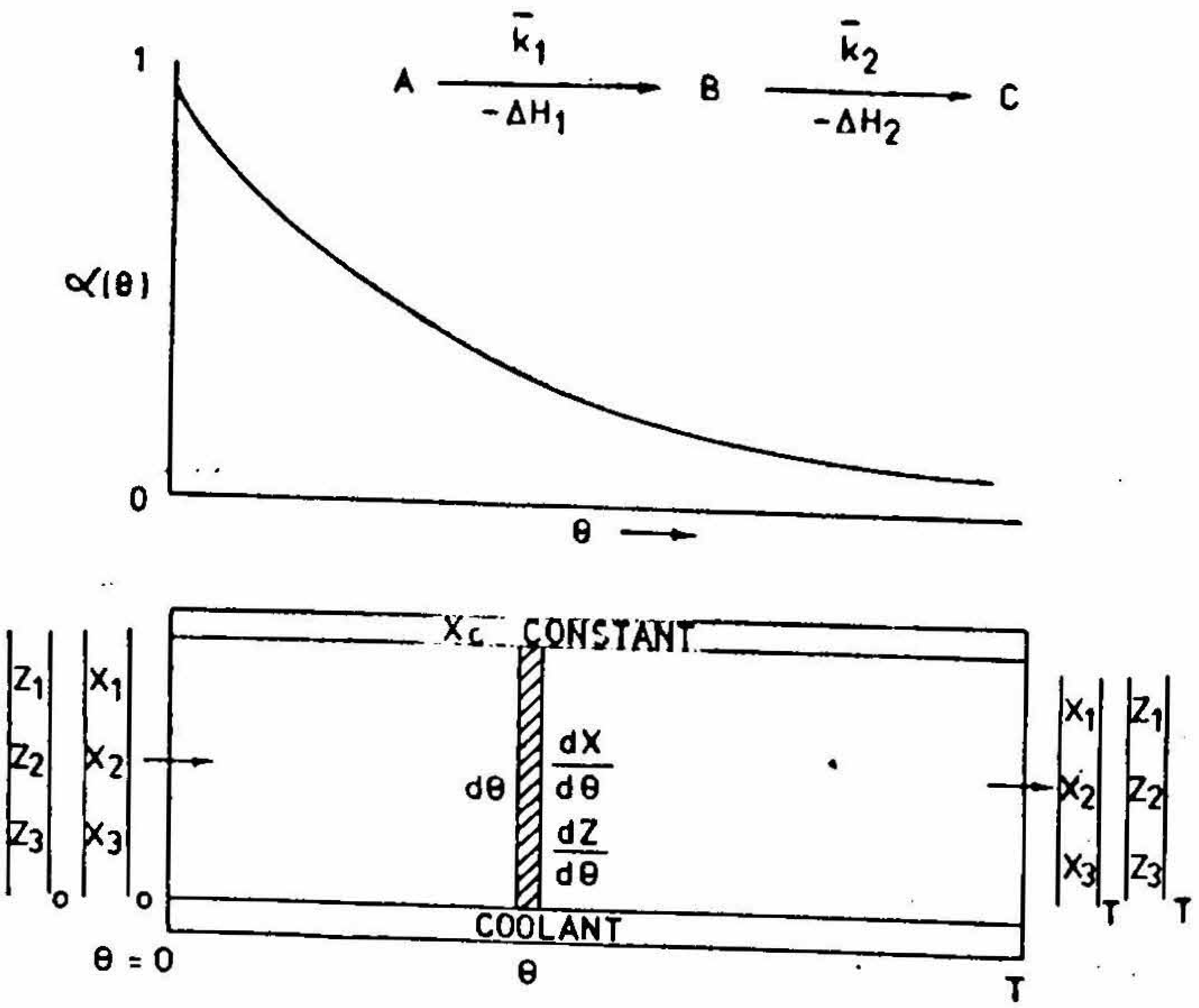

FIG. 2. Strategy of catalyst dilution profile $\alpha(\theta)$ for optimal operation of a PFR.

where $\phi(\alpha)$ is a function which represents the effect of dilution on the average catalytic activity. Since the average catalytic activity is a distributed property, certain probability considerations must underlie the manner in which α should appear in the expression for the modified rate constant. van Den Bleck has analysed three models of catalyst dilution of which the one involving stochastic considerations *via* Monte-Carlo technique is probably the best. For the present case however a simple exponential probability distribution would be used to represent the relative average activity of the catalyst system. This takes the form

$$\phi(\alpha) = \exp - \left(\frac{1-\alpha}{\alpha}\right) \tag{4}$$

The functional form of eqn. (4) has the appropriate limits when α tends to unity or zero, namely $\phi(1) = 1$; and $\phi(0) = 0$. Therefore the expression for the modified rate constant may be rewritten as

$$\bar{k}_i = \phi(\alpha) \,.\, k_{i0} \exp - (E_i/RT) \tag{5}$$

With the modification suggested through eqn. (5), the state equations may be given by

$$\frac{dx_1}{d\theta} = -\bar{k}_1 x_1 = f_1 \tag{6}$$

$$\frac{dx_2}{d\theta} = \bar{k}_1 x_1 - \bar{k}_2 x_3 = f_2 \tag{7}$$

$$\frac{dx_3}{d\theta} = (j\bar{k}_1 x_1 + j_2\bar{k}_2 x_2) - \left[\frac{St \cdot v}{r_m}(x_3 - x_c)\right] = f_3 \tag{8}$$

The Hamiltonian H may be given by

$$H(X, Z;\ \alpha) = (Z_1 f_1 + Z_2 f_2 + Z_3 f_3) \tag{9}$$

where the Z's are the adjoint variables. The adjoint equations may be given by

$$-\frac{dZ_1}{d\theta} = \bar{k}_1 (Z_1 - Z_2 - jZ_3) \tag{10}$$

$$\frac{dZ_2}{d\theta} = \bar{k}_2 (Z_2 - j_2 Z_3) \tag{11}$$

$$\frac{dZ_3}{d\theta} = \frac{\bar{k}_1 E_1}{\alpha R X_3^2}[x_1(Z_1 - Z_2 - j_1 Z_3)] + \frac{\bar{k}_2 E_2}{\alpha R X_3^2}[x_2(Z_2 - j_2 Z_3] + Z_3 \overline{St} \tag{12}$$

where $\overline{St} = St \cdot v/r_m$.

The boundary conditions on the state and adjoint equations at $\theta = O$ and $\theta = T$ are.

$$\begin{aligned} &\underline{\theta = O} \quad X = X(O), \text{ known} \\ &\qquad\quad\ Z = Z(O), \text{ not known} \\ &\underline{\theta = T} \quad X = X(T), \text{ not known} \\ &\qquad\quad\ Z = Z(T), \text{ known, equal to} \end{aligned} \tag{13}$$

$(d_1\ d_2\ d_3)$, based on the objective function S

$$S = d_1 X_1(T) + d_2 X_2(T) + d_3 X_3(T). \tag{13A}$$

The catalyst dilution profile $\alpha(\theta)$ which renders the exit concentration of B maximum at $\theta = T$ is obtained by setting the derivative $\partial H/\partial\alpha = 0$.
$\alpha(\theta)$ is then obtained as

$$\alpha(\theta) = \frac{(E_2 - E_1)/RX_3}{\ln\left[\dfrac{E_2\ k_2 O}{E_1\ \ k_{10}}\right] + \ln\left[\dfrac{X_1}{X_2} \dfrac{(Z_2 - j_2 Z_3}{(Z_2 - Z_1 + j_1 Z_3)}\right]} \tag{14}$$

The solution of the two point boundary value problem consists in the integration of the state equations 6, 7 and 8 and the adjoint equations 10, 11 and 12. The computational algorithm is given below :

1. Assign an initial value for adjoint vector $Z(O)$.
2. With known initial value for $X(O)$, compute $\alpha(O)$ from eqn. (14).
3. Divide the O-T interval into n small segments. At the end of the first interval assume a value of $\alpha = \alpha_1(1)$.
4. Connect $\alpha(O)$ and $\alpha_1(1)$ by a straight line and integrate the state and adjoint equations along the line. Obtain then the first estimate of the state and adjoint vector at the end of the first interval, namely $X_1(1)$ and $Z_1(1)$.
5. Using the first estimates, obtain a better value of α from eqn. (14). Join $\alpha(O)$ and the new value $\alpha_2(1)$ by a straight line and integrate the state and adjoint equations along the new line. Obtain a refined estimate $\alpha_3(1)$ and continue till $\alpha_\infty(1)$ becomes constant.
6. Assume a catalyst dilution at the end of the second interval $\alpha_1(2)$ and repeat 4, 5 and 6 as indicated above.
7. Proceed till the end of the nth interval until the value obtained for Z matches $Z(T)$. If it does not, go back to 1 and choose a new value for $Z(O)$.

The computational algorithm indicated above provides a catalyst dilution profile $\alpha = \alpha(\theta)$ under which the yield of B at the reactor outlet is maximised. The procedure has to work under the normal constraint on α being in the interval 0–1. On this information the reactor may be filled with catalyst and inert material to give the stipulated profile. In the present analysis, the system is considered to be pseudo-homogeneous with catalyst effectiveness factor being unity.

Nomenclature

A, B, C	Species
C_p	Heat capacity
d	Coefficients in eqn. 13 A
E	Activation energy
f	Conservation equation
H	Hamiltonian defined by eqn. 9
	Parameter defined by eqn. 2A
k	Homogeneous rate constant
r_w	Heat transfer area per unit reactor volume
St	Stanton number
S	Objective function
T	Total reactor holding time
v	Average fluid velocity in reactor
X	State Vector
x	State variable
Z	Adjoint Vector
α	Catalyst dilution
ΔH	Heat of reaction
θ	Holding time
ϕ	Function of α

Subscript

1, 2	Species A, B; iteration; reaction 1, 2
3	Temperature
c	Coolant
o	Pre-exponential factor

Superscript

+	Optimal
−	Modified

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