

SAFE DESIGN OF COOLED TUBULAR REACTORS FOR EXOTHERMIC MULTIPLE REACTIONS: MULTIPLE-REACTION NETWORKS

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Abstract—The model of the pseudo-homogeneous, one-dimensional cooled tubular reactor is applied to a multiple-reaction network. It is demonstrated for a network which consists of two parallel and two consecutive reactions. Three criteria are developed to obtain an integral yield which does not deviate more than a chosen fraction from the maximum yield that can be obtained in an isothermal reactor. The criteria enable us to choose relevant design and operating conditions for the safe execution of a reaction network in a tubular reactor. The method is illustrated for the production of maleic anhydride by air oxidation of benzene.

1. INTRODUCTION

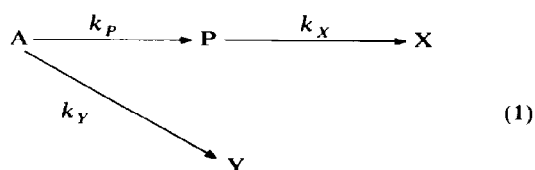
Westerterp, Ptasinaky and Overtoom (Westerterp and Ptasinaky, 1984a, b; Westerterp *et al.*, 1984a; Westerterp and Overtoom, 1985) discussed the design of cooled tubular reactors in which either two parallel or two consecutive reactions are carried out. An extensive literature survey is given by Westerterp and Ptasinaky (1984a). They demonstrated that, with a set of dimensionless groups exclusively characterizing either the reaction system or the design and operating conditions of the tubular reactor itself, criteria can be derived which relate uniquely the values of operating and design parameters with the required selectivity or integral yield and the reaction system parameters. Moreover they demonstrated that these criteria are much more strict than runaway criteria, so that the reactor always operates safely as long as the criteria are adhered to. These criteria were of the following form:

$$U^*(\Theta_{ma} - \Theta_c)/\Theta_{ad} \geq f(p, j_p, H, S_p \text{ or } X_p).$$

The dimensionless group $U^*(\Theta_{ma} - \Theta_c)/\Theta_{ad}$ is representative for the ratio of the heat withdrawal rate and the maximum heat production rate; it only depends on the reactor design and operating variables. The other dimensionless group describing the reactor performance is Da , a dimensionless residence time in the reactor. At the right-hand side only properties of the reaction system (and not of the reactor) and the desired yield or selectivity appear. Θ_{ma} as a maximum allowable temperature is a constraint which is governed by the desired yield or selectivity. The dimensionless groups describing the reaction system are K , p , H and j_p .

Since the method works in the case of parallel as well as consecutive reactions, more complex systems combining both reaction types can be studied as well. In this study we will discuss the design and operation of a cooled tubular reactor for a combination of such reactions. To this end we have chosen the following network of first-order exothermic reactions, where P is the desired product and the rate constants are of the

Arrhenius type:



Since this reaction system consists of parallel and consecutive reactions it will behave like systems with either parallel or consecutive reactions, e.g. because of the consecutive reaction there will always be an optimal residence time and, because of the parallel reaction, the differential selectivity will always be less than one. In case only exothermic reactions are carried out the temperature will initially increase along the reactor tube, reach a maximum in the hot spot and afterwards decrease due to the heat exchange with the cooling medium. The optimal residence time or reactor length at a given reactor load depends on the shape of the temperature profile.

Westerterp and Westerink (1988) discussed the reaction system according to scheme (1) in case the reactions were carried out in a tank reactor. They discussed the relevant kinetic parameters and showed that the ratios of the activation energies, E_X/E_P and E_Y/E_P , and of the pre-exponential factors, A_X/A_P and A_Y/A_P , are of major importance. We will restrict ourselves to systems where $A_X < A_P < A_Y$ and $E_X < E_P < E_Y$ for the reasons outlined elsewhere (Westerterp and Westerink, 1988).

For the reaction system considered a possible Arrhenius plot is given in Fig. 1, where the logarithm of k is plotted vs the reciprocal temperature. In general we desire to operate as far as possible at the left-hand side of this plot, because here temperatures and consequently reaction rates are high. At the onset of reaction (no P has been formed yet) we choose a temperature where the selectivity for the reactions $A \rightarrow P$ and $A \rightarrow Y$ is high. For a certain minimum selectivity

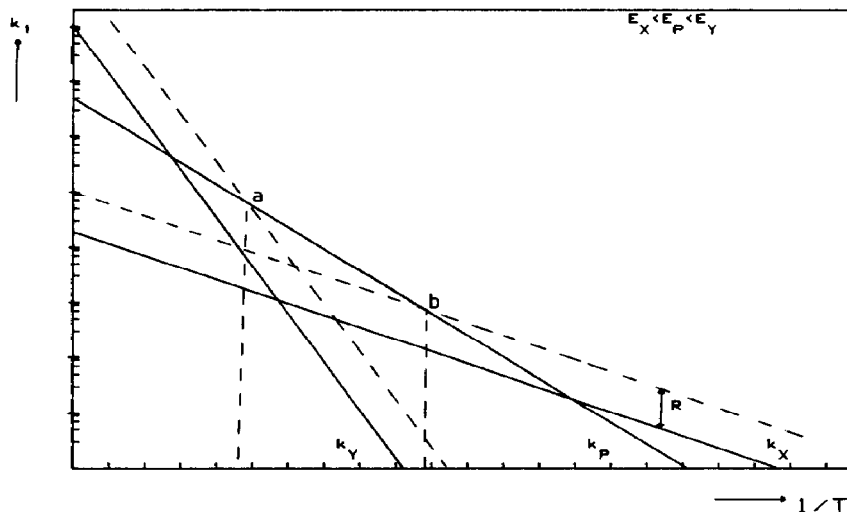


Fig. 1. General Arrhenius plot for the reaction system chosen [eq. (1)].

S'_p all reaction rates k_p to the right of point a are acceptable. As soon as some P has been formed the consecutive reaction has also to be taken into account. For a certain yield of X_p the ratio k_p/k_X has to be larger than say a factor R . This implies that the reaction rates k_p always have to be higher than indicated in Fig. 1 and that only reaction rates left of point b are acceptable. In order to achieve the desired selectivity the reactor temperature T must be in the range of $T_b < T < T_a$. We can understand that the higher our selectivity or yield requirements the smaller our allowable temperature range of $T_b - T_a$ will be.

The method of deriving the relevant dimensionless groups has been discussed by Westerterp *et al.* (Westerterp and Ptasinaky, 1984a, b; Westerterp *et al.*, 1984a; Westerterp and Overtoom, 1985; Westerterp and Westerink, 1988) and will not be repeated here. These groups are based on a reference reaction rate constant k_R taken at a reference temperature T_R . In our case we take this temperature, where both rate constants k_p and k_Y are equal; here k_R and T_R are true constants based on the particular reaction system only. The dimensionless groups p , q , B , j_p , H_X and H_Y are representative for the reaction system considered and U^* , Da , Θ_{ad} , Θ_o and Θ_c are representative for the operating and design variables. We refer to the Notation for their significance.

We must discriminate between reactor sections in which non-converted reactants can be recovered or not. In case recovery is possible the reactants are recycled to the inlet of the reactor. For our particular system in that case the reactor must operate at high selectivities and low conversions whereas the reactor design and operating conditions chosen are dominated by plant economics only. This case will not be discussed here (Westerterp and Ptasinaky, 1984a, b; Westerterp *et al.* 1984a; Westerterp and Overtoom, 1985; Westerterp and Westerink, 1988). In the case

when no recovery is possible a maximum yield should be aimed at, hence we will discuss the design of a tubular reactor in which a certain minimum required yield has to be achieved. In the next sections we will introduce the basic equations that govern the conversion and temperature profiles in a cooled tubular reactor based on the pseudo-homogeneous one-dimensional model. Next we will introduce a new type of conversion parameter that appears to be useful in case schemes with consecutive reactions are studied. Using this parameter selectivities in relation to isothermal and non-isothermal tubular reactors are discussed. Afterwards we will use the theory of isothermal reactors to formulate temperature regions for a non-isothermal tubular reactor that ensures a desired yield. Finally we will develop criteria that lead to the design of a tubular reactor in which this desired yield can be achieved. We will illustrate our method with an example.

2. BASIC EQUATIONS

In our tubular reactor the reactions of scheme (1) occur. In that reaction network A is the reactant, P the desired product and X and Y are undesired by-products. All reactions are first-order and irreversible. The conversion rates are given by:

$$R_{wA} = -(k_P + k_Y)C_A$$

$$R_{wP} = k_P C_A - k_X C_P$$

$$R_{wY} = k_Y C_A$$

$$R_{wX} = k_X C_P$$

Here R_{wJ} is expressed in moles of species J converted per unit time and per unit of catalyst mass.

We will use the pseudo-homogeneous, one-dimensional model of the tubular reactor, the plug-flow reactor, which has no radial temperature or

concentration gradients. Moreover, we assume the temperature of the cooling medium to be constant along the tube length and the physical and chemical data ρ_a , ρ_b , C_{pg} and $-\Delta H$ to be independent of temperature. These assumptions lead to the following heat and mass balances for this type of reactor:

$$u \frac{dC_A}{dz} = R_{wA} \rho_b \quad (2)$$

$$u \frac{dC_P}{dz} = R_{wP} \rho_b \quad (3)$$

$$u \frac{dC_Y}{dz} = R_{wY} \rho_b \quad (4)$$

$$u \frac{dC_X}{dz} = R_{wX} \rho_b \quad (5)$$

$$\rho_g C_{pg} u \frac{dT}{dz} = [k_P C_A (-\Delta H)_P + k_Y C_A (-\Delta H)_Y + k_X C_P (-\Delta H)_X] \rho_b - \frac{4U}{d_i} (T - T_c) \quad (6)$$

The reactor feed does not contain any P, X and Y, so that $C_{Po} = C_{Xo} = C_{Yo} = 0$. We transform the species concentrations to conversions according to

$$\frac{C_{Ao} - C_A}{C_{Ao}} = \frac{C_P}{C_{Ao}} + \frac{C_X}{C_{Ao}} + \frac{C_Y}{C_{Ao}} = X_A = X_P + X_X + X_Y \quad (7)$$

and make the equations dimensionless by multiplying by $L/C_{Ao}u$ or $L/T_R u$ and introducing the dimensionless kinetic rate constants $K = k_P/k_R$, $K^P = k_Y/k_R$ and $BK^q = k_X/k_R$:

$$\frac{dX_A}{dZ} = Da(K + K^P)(1 - X_A) \quad (8)$$

$$\frac{dX_P}{dZ} = Da[K(1 - X_A) - BK^q X_P] \quad (9)$$

$$\frac{dX_X}{dZ} = Da BK^q X_P \quad (10)$$

$$\frac{dX_Y}{dZ} = Da K^P (1 - X_A) \quad (11)$$

$$\frac{d\Theta}{dZ} = Da \Theta_{ad} [(K + H_Y K^P)(1 - X_A) + H_X BK^q X_P] - Da U^* (\Theta - \Theta_c) \quad (12)$$

Here the following dimensionless groups or variables are used:

$$U^* = \frac{4U}{k_R d_i C_{pg} \rho_b \rho_g} \quad Da = k_R \rho_b L/u$$

$$\Theta_{ad} = \frac{(-\Delta H)_P C_{Ao}}{T_R \rho_g C_{pg}} \quad Z = z/L.$$

Because of eq. (7) relations (8)–(12) are interrelated and this set of five can be reduced to a set of four equations

by dividing each equation by dX_A/dZ :

$$\frac{dX_P}{dX_A} = \frac{K}{K + K^P} - \frac{BK^q X_P}{(K + K^P)(1 - X_A)} \quad (13)$$

$$\frac{dX_X}{dX_A} = \frac{BK^q X_P}{(K + K^P)(1 - X_A)} \quad (14)$$

$$\frac{dX_Y}{dX_A} = \frac{K}{K + K^P} \quad (15)$$

$$\frac{d\Theta}{dX_A} = \Theta_{ad} \left[\frac{K + H_Y K^P}{K + K^P} + \frac{H_X BK^q X_P}{(K + K^P)(1 - X_A)} \right] - \frac{U^*(\Theta - \Theta_c)}{(K + K^P)(1 - X_A)} \quad (16)$$

Because of the non-linearity of K with respect to Θ being $K = \exp[j_P(1 - 1/\Theta)]$ these differential equations cannot be solved analytically. Further the boundary conditions are:

$$\begin{aligned} Z = 0 \quad T = T_o \\ X_A = 0 \\ X_P = 0 \\ X_X = 0 \\ X_Y = 0. \end{aligned}$$

3. CHOICE OF A CONVENIENT CONVERSION PARAMETER

The term $X_P/(1 - X_A)$ appears in the mass balances for P and X as well as in the differential equation describing the reactor temperature profiles. Later on we will discuss the differential selectivity in both isothermal and non-isothermal reactors. Since the differential selectivity $S'_P = dX_P/dX_A$ is given by eq. (13) it is convenient to use the term $X_P/(1 - X_A)$ instead of X_A . Since X_A increases along the reactor length, the term $X_P/(1 - X_A)$ must increase along the reactor length to be a suitable replacement for X_A , so that

$$\frac{d[X_P/(1 - X_A)]}{dZ} > 0.$$

Since also $dX_A/dZ > 0$, the following criterion holds too:

$$\frac{d[X_P/(1 - X_A)]}{dX_A} > 0.$$

Working out the left-hand side of this equation leads with $dX_P/dX_A = S'_P$ to

$$\frac{d[X_P/(1 - X_A)]}{dX_A} = [S'_P + X_P/(1 - X_A)]/(1 - X_A) \quad (17)$$

We have to realize that in view of the consecutive character of the reaction $A \rightarrow P \rightarrow X$ we have to stop the reaction as soon as $dX_P/dX_A = S'_P = 0$, otherwise we pass the point of the maximum yield of P. In our region of interest of $S'_P > 0$ the right-hand side of eq.

(17) is positive, so that $X_P/(1 - X_A)$ increases continuously. The term $X_P/(1 - X_A)$ can be used as long as it increases with increasing X_A . Beyond the maximum of X_P the value of S'_P is negative because there is a net consumption of P. Still eq. (17) can be used up till $-S'_P$ has become equal to $X_P/(1 - X_A)$.

4. CURVES OF CONSTANT DIFFERENTIAL SELECTIVITY

The differential selectivity S'_P as described by eq. (13) can be studied in a two-dimensional plot of Θ vs $X_P/(1 - X_A)$ with S'_P as a parameter. Equation (13) can be rewritten as

$$X_P/(1 - X_A) = \frac{K - (K + K^p)S'_P}{BK^q} \quad (18)$$

Differential isoselectivity curves of Θ vs $X_P/(1 - X_A)$ are plotted in Fig. 2 for several values of S'_P . Apparently for each $S'_P (> 0)$ value a maximum value of $X_P/(1 - X_A)$ exists. In the previous paragraph we showed that $X_P/(1 - X_A)$ increases with increasing X_A as long as $S'_P > 0$, so at the maximum value of $X_P/(1 - X_A)$ the conversion X_A has also reached its highest value for a constant value of S'_P . The yield of P is related to the conversion of A by multiplying the latter by the integral selectivity or in the case of constant differential selectivity by the differential selectivity S'_P . Hence for a given differential selectivity the maximum yield is achieved at the maximum of $X_P/(1 - X_A)$. Using these maxima it is possible to derive an optimal temperature profile. Starting at low temperatures and high selectivities the profile passes through the maxima: this profile will lead to the absolute maximum yield since for each differential selectivity the maximum contribution to the integral yield is obtained. As can be concluded from this optimal profile it is not possible to achieve a yield arbitrarily close to 100% as was possible in case of either only parallel or only

consecutive reactions (Westerterp and Ptasinsky, 1984a, b; Westerterp *et al.*, 1984a; Westerterp and Overtoom, 1985). Also this optimal temperature profile cannot be achieved in practice since in that case the optimum reactor temperature increases from 0 K up to infinity. We have to realize that in Fig. 2 the vertical scale covers a range of $0.4 T_R - 1.6 T_R$, whereas T_R usually has values of 400–1000 K. In this plot $T_R = 848$ K. Even a part of this optimum profile is hard to approach because also runaway has to be prevented. In practice because of the prevention of runaway the reactor will operate in a rather narrow temperature range, almost isothermally. Hence, instead of optimal temperature profiles optimal isothermal reactors should be studied.

If the inlet temperature Θ_0 equals the temperature of the cooling medium Θ_c and the highest temperature Θ_{hs} is reached in the hot spot, the reactor will operate in between the isotherms Θ_c and Θ_{hs} .

5. THE BEHAVIOUR OF ISOTHERMAL REACTORS

The behaviour of isothermal reactors is described by eqs (13)–(15). In practice we are interested in the desired product P only, so that solving eq. (13) for a constant value of K gives us

$$X_{Piso} = \frac{(1 - X_{Aiso})^{BK^q/(K + K^p)} - (1 - X_{Aiso})}{1 + K^{p-1} - BK^{q-1}} \quad (19)$$

With increasing conversions X_{Aiso} the yield X_{Piso} will initially increase, reach a maximum at X_{Pmax} and beyond this maximum the yield will decrease. This is shown in Fig. 3, where X_{Piso} is plotted vs X_{Aiso} for a given set of kinetic parameters and for several temperatures. The maximum yield is reached when the differential selectivity has just become zero. Hence, using

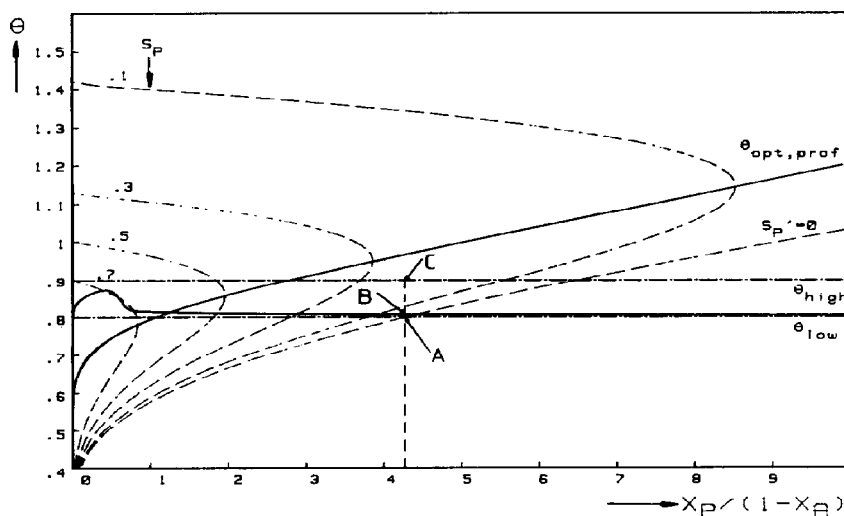


Fig. 2. Lines of constant differential selectivity and the optimal temperature profile. Data are $p = 1.5$, $q = 0.8$, $B = 0.11$, $j_p = 15$.

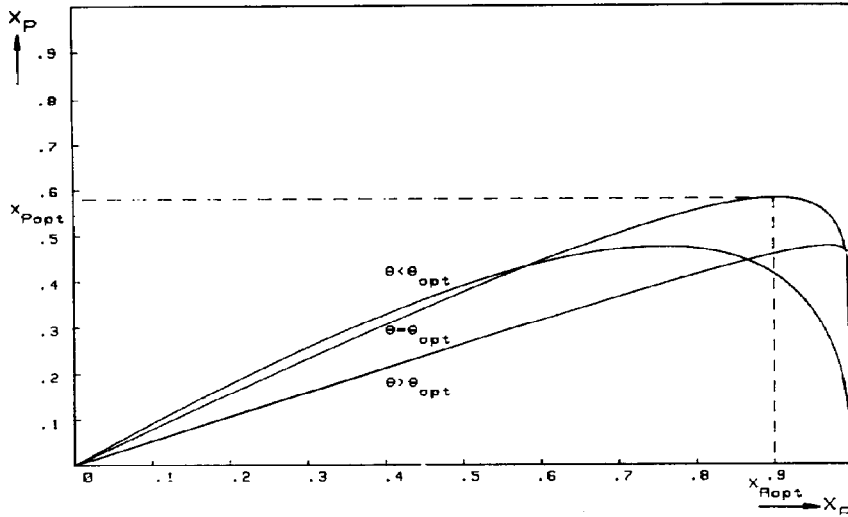


Fig. 3. Yield vs conversion in an isothermally operating reactor, at optimal isothermal conditions and at a temperature above and below Θ_{opt} .

eq. (13):

$$(1 - X_{Amax}) = BK^{q-1} X_{Pmax} \quad (20)$$

Substitution into eq. (19) leads to

$$X_{Pmax} = \frac{K}{BK^q} \left(\frac{K + K^p}{BK^q} \right)^{\frac{1}{K+K^p-1}} \quad (21)$$

and

$$X_{Amax} = 1 - \left(\frac{K + K^p}{BK^q} \right)^{\frac{1}{K+K^p-1}} \quad (22)$$

The maximum yield X_{Pmax} still depends on the temperature. Setting the derivative of eq. (21) with respect to Θ equal to zero gives the following implicit equation to determine the optimal temperature at which the highest maximum yield X_{Popt} of all maximum yields X_{Pmax} is achieved in an isothermally operating reactor:

$$\left(1 - \frac{K + K^p}{BK^q} \right)^2 + \left[1 - \frac{K + K^p}{BK^q} + \ln \left(\frac{K + K^p}{BK^q} \right) \right] \times \left(\frac{K}{BK^q} + \frac{p-q}{1-q} \frac{K^p}{BK^q} \right) = 0. \quad (23)$$

In Fig. 3 the isotherm with $\Theta = \Theta_{opt}$ gives the highest maximum yield that can be achieved in an isothermally operating reactor. Figure 4 is a cross-plot of Fig. 3.

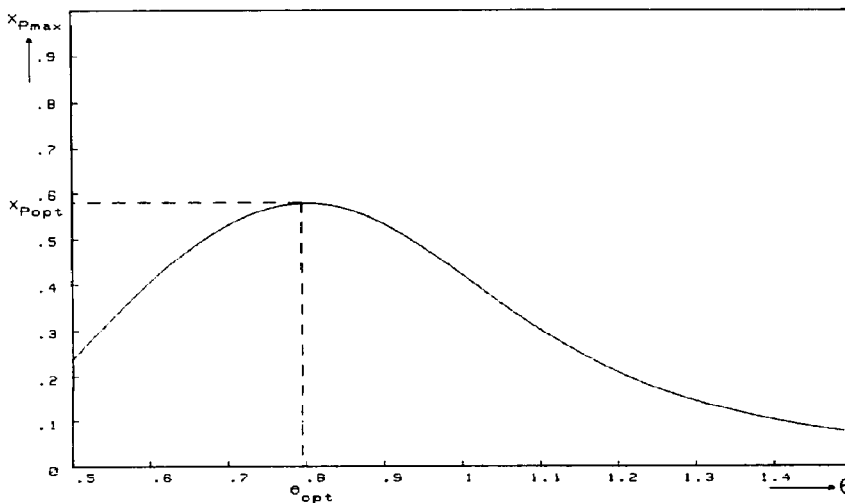


Fig. 4. Maximum and optimal yield in an isothermally operating reactor as a function of the reactor temperature. Same data as for Fig. 2.

Here the maximum achievable yield $X_{P_{\max}}$ under isothermal conditions is given as a function of Θ , the maximum in this curve is the optimal yield $X_{P_{\text{opt}}}$.

For a given temperature the required residence time Da_{\max} to reach the conversion $X_{A_{\max}}$ is given by eq. (8), which after integration gives

$$Da_{\max} = \frac{-\ln(1 - X_{A_{\max}})}{K + K^P} \quad (24)$$

At this residence time the reaction has to be stopped because otherwise there would be a net consumption of the desired product P.

6. THE BEHAVIOUR OF NON-ISOTHERMAL REACTORS

The trajectory in a non-isothermal reactor is given by eqs (13) and (16). In case exothermic reactions are carried out the temperature will increase until the hot spot is reached, afterwards the temperature will gradually decrease. For multiple reactions one may expect more than one hot spot. In case of two consecutive reactions a first hot spot may occur due to the first reaction $A \rightarrow P$, a second may occur due to the consecutive reaction $P \rightarrow X$. In the Appendix it is proven that no multiple hot spots will occur in our case. Hence the trajectory has only one maximum.

The temperature in the hot spot is found by setting eq. (16) equal to zero:

$$\Theta_{\text{ad}} [K + H_Y K^P + H_X B K^q X_P / (1 - X_A)] - U^*(\Theta - \Theta_c) / (1 - X_A) = 0 \quad (25)$$

Using the relation $X_P = S_{P_{\text{hs}}} X_A$, we find that

$$X_{A_{\text{hs}}} = \frac{1 - \frac{U^*(\Theta_{\text{hs}} - \Theta_c)}{\Theta_{\text{ad}}(K_{\text{hs}} + H_Y K_{\text{hs}}^P)}}{1 - \frac{H_X B K_{\text{hs}}^q S_{P_{\text{hs}}}}{K_{\text{hs}} + H_Y K_{\text{hs}}^P}} \quad (26)$$

or also

$$\frac{X_P / (1 - X_A)_{\text{hs}}}{U^*(\Theta_{\text{hs}} - \Theta_c) / \Theta_{\text{ad}} - K_{\text{hs}} - H_Y K_{\text{hs}}^P} = \frac{H_X B K_{\text{hs}}^q - \frac{U^*(\Theta_{\text{hs}} - \Theta_c)}{\Theta_{\text{ad}} S_{P_{\text{hs}}}}}{\Theta_{\text{ad}} S_{P_{\text{hs}}}} \quad (27)$$

In these equations $S_{P_{\text{hs}}}$ is the integral selectivity as achieved up to the hot spot. The integral selectivity will be a mean value of the achieved differential selectivities at the reactor inlet ($X_A = 0$) and at the hot spot ($X_A = X_{A_{\text{hs}}}$). The differential selectivity is given by eq. (13); this relation will be used to estimate the integral selectivity in the hot spot. We will discuss several possibilities to estimate $S_{P_{\text{hs}}}$. *Firstly* we may substitute the differential selectivity at inlet conditions ($X_A = 0$, $\Theta = \Theta_o$), which is, according to eq. (13):

$$S_{P_1} = \frac{1}{1 + K_o^P} \quad (28)$$

The differential selectivity will always decrease in the first part of the reactor because of the increasing

temperature and of the conversion of P. Hence, the integral selectivity in the first part of the reactor will be lower than $S'_{P_1}(X_A = 0)$, so that the influence of the undesired reactions is underestimated. In case of strongly exothermic undesired reactions ($H_X, H_Y > 1$) using $S'_{P_1}(X_A = 0)$ will lead to a too low value for the hot spot temperature.

Secondly we can substitute the differential selectivity at the hot spot conditions:

$$S_{P_2} = \frac{K_{\text{hs}}}{K_{\text{hs}} + K_{\text{hs}}^P} - \frac{B K_{\text{hs}}^q}{K_{\text{hs}} + K_{\text{hs}}^P} \frac{X_{P_{\text{hs}}}}{1 - X_{A_{\text{hs}}}} \quad (29)$$

In the hot spot both conversion and temperature are at their maximum values in the interval $0 < X_A < X_{A_{\text{hs}}}$, hence the differential selectivity is at a minimum value. Consequently we overestimate the heat production by the undesired reactions. Using S_{P_2} in the case when H_X or $H_Y > 1$ leads to values for Θ_{hs} that are far too high.

As a *third* alternative, giving values of $S_{P_{\text{hs}}}$ between $S'_{P_1}(X_A = 0)$ and $S'_{P_1}(X_A = X_{A_{\text{hs}}})$, we studied

$$S_{P_3} = \frac{1}{1 + K_{\text{hs}}^{P-1}} \quad (30)$$

We can easily verify that $S_{P_2} < S_{P_3} < S_{P_1}$.

There remains the question of which value of S_P to use in eq. (26). In general we are only interested in reaction networks that give a high yield. In that case the consecutive reaction is still largely suppressed in the first part of the reactor tube (Westerterp and Overtoom, 1985), hence before the hot spot almost no undesired product X is formed. Consequently the conditions in the hot spot are mainly dominated by the heat effects of the desired and the undesired parallel reactions only. In previous articles (Westerterp and Ptasinsky, 1984a, b; Westerterp *et al.*, 1984a; Westerterp and Overtoom, 1985; Westerterp and Westerink, 1988) we demonstrated that a certain maximum allowable temperature should not be exceeded in order to achieve a desired yield or selectivity. We will apply the same method so a too high estimate for the hot spot temperature should be selected which means that the initial heat production should be overestimated in order to be on the safe side. Consequently it depends on the heat of reaction of the undesired parallel reaction whether we must over- or underestimate the selectivity.

From numerical evaluation it appeared that S_{P_3} gave the most accurate predictions. The conversion due to the parallel reaction was slightly overestimated, hence S_{P_3} will be used only in the case when $H_Y > 1$. By doing so we are sure that we are on the safe side and that reactor temperatures will be lower than assumed. S_{P_1} will be used in case $H_Y < 1$. Using S_{P_2} leads to far too high values of the hot spot temperature in the case when $H_Y > 1$. This leads to the instructions:

— use S_{P_1} if $H_Y < 1$

— use S_{P_3} if $H_Y > 1$.

Substituting either S_{P_1} or S_{P_3} for $S_{P_{\text{hs}}}$ into eq. (26) or

(27) enables us to calculate the locus of maxima curves in a $\Theta_{hs} - X_{Ahs}$ or a $\Theta_{hs} - X_{Phs}/(1 - X_{Ahs})$ plot. Several locus curves are shown in Fig. 5, in which also some trajectories are plotted for several values of U^* , Θ_c and Θ_{ad} . As can be seen, the slope of the trajectory outside the locus of maxima curve is positive while the slope is negative in the area enveloped by the locus of maxima curve.

The locus of maxima curve is influenced by the reaction parameters j_p , p , q , H_X , H_Y and B , and by two design and operating parameters, Θ_c and U^*/Θ_{ad} . Figure 5(a) and (b) demonstrate that at increasing ratio U^*/Θ_{ad} or at decreasing Θ_c the locus curves shift to the left. At certain combinations of values of Θ_c and

U^*/Θ_{ad} , the locus curves start to intersect the $X_A = 0$ axis, as was the case for two parallel or two consecutive reactions. Two points of intersection are possible, the corresponding temperatures Θ_{iu} and Θ_{iu} are indicated. In the case when the reactor is operated at an inlet temperature Θ_o which is lower than Θ_{iu} , the reactor temperature will initially increase until the maximum temperature is reached on the lower branch of the locus curve; afterwards the temperature will decrease and eventually approach Θ_c . In case the inlet temperature is chosen between Θ_{iu} and Θ_{iu} the reactor temperature will decrease along the entire length of the reactor tube. As long as $\Theta_o < \Theta_{iu}$ no runaway will occur.

In the case when the locus of maxima curve does not

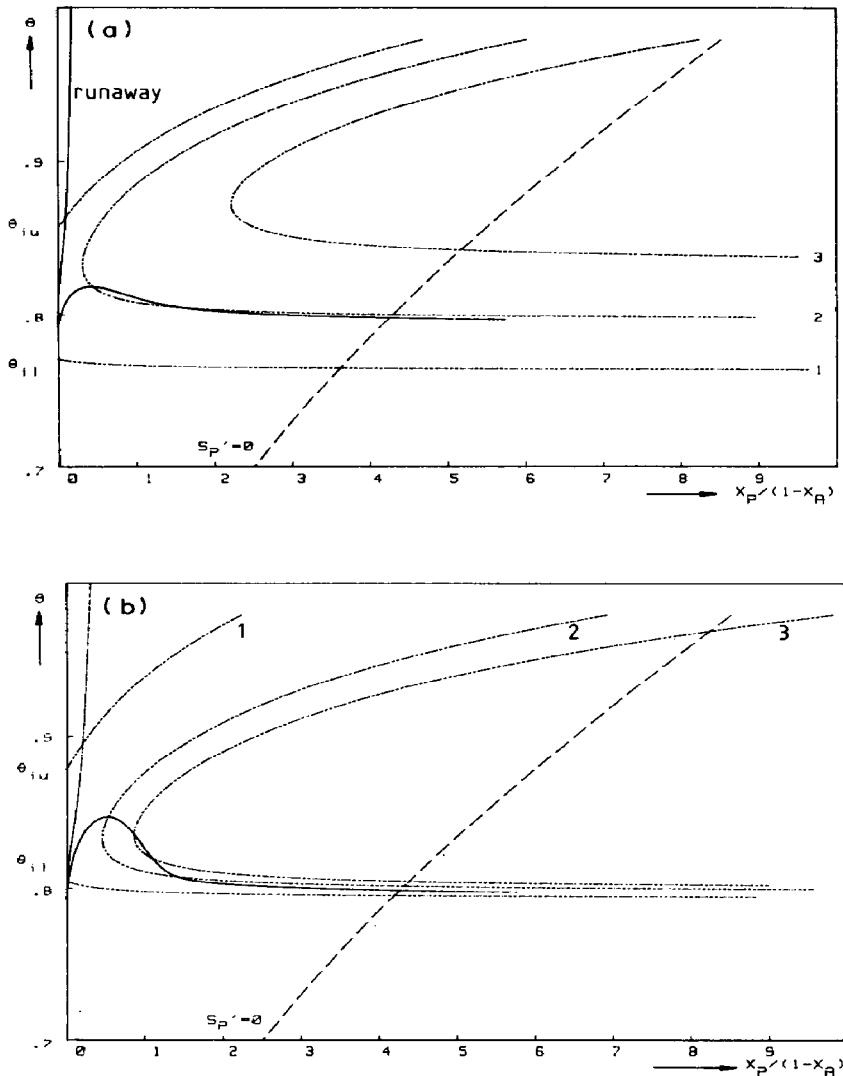


Fig. 5. Locus of maxima curves. In (a) Θ_c is varied (0.76, 0.79 and 0.82), and in (b) U^* is varied (0.60, 0.30 and 0.25). Two temperature trajectories are plotted in both figures, one under runaway conditions (trajectory b, $\Theta_{ad} = 1.2$) and one under stable conditions (trajectory a, $\Theta_{ad} = 0.6$). Data are $p = 1.5$, $q = 0.8$, $B = 0.11$, $j_p = 15$, $H_X = H_Y = 2$, $U^*/\Theta_{ad} = 1.3$ [(a)] and $\Theta_c = 0.79$ [(b)]. The trajectories refer to the locus curve with $\Theta_c = 0.79$ and $U^* = 0.30$, respectively.

intersect the $X_A = 0$ axis runaway is possible for any value of Θ_o : whether runaway occurs or not depends on the values of U^* and Θ_{ad} . This is demonstrated in Fig. 5.

7. A CRITERION WHICH GUARANTEES A DESIRED YIELD

Until now we studied the possible yield in isothermal reactors and the temperature behaviour of non-isothermal reactors. Furthermore in the Appendix we proved that only one hot spot occurs in the case of our system of multiple exothermic reactions.

From Fig. 4 we can see that there is only one isothermal reactor temperature Θ_{opt} at which the maximum of the maximum yield is achieved. We called this the optimum yield X_{Popt} ; for yields in isothermal reactors, lower than the optimum, two isotherms are possible to achieve equal maximum yield, one at a temperature higher and one at a temperature lower than Θ_{opt} .

In practice a reactor will not operate isothermally, so that the maximum isothermal yield cannot be obtained. The selectivity achieved is worse than the selectivity achieved under isothermal conditions due to the temperature profile in the non-isothermal reactor. In the case when the non-isothermal reactor operates in a temperature range below Θ_{opt} the optimal conversion, where the reaction has to be stopped and achieved at $S'_p = 0$, is lower than X_{Aopt} ; on the other hand at a temperature above Θ_{opt} the optimal conversion is higher than X_{Aopt} , as can be seen in Fig. 2.

We will now compare a non-isothermal reactor with two isothermal reactors. We assume that one isothermal reactor operates at Θ_{low} and the other one at Θ_{high} ; furthermore we assume that the non-isothermal reactor operates above $\Theta_{low} = \Theta_c = \Theta_o$ and that for the hot spot temperature holds $\Theta_{hs} = < \Theta_{high}$. In the non-isothermal reactor the temperature will initially

increase and if U^* is sufficiently high the hot spot temperature Θ_{hs} will remain below Θ_{high} . Beyond the hot spot the temperature decreases and, for long reactors, will become almost equal to Θ_{low} at the outlet of the reactor. In both the non-isothermal reactor and the isothermal one the reaction has to be stopped as soon as $S'_p = 0$. For the isothermal reactor the reaction has to be stopped at point A in Fig. 2. At point A $X_{Piso}/(1 - X_{Aiso})$ for the isothermal reactor is equal to $X_p/(1 - X_A)$ at point B, which corresponds to the non-isothermal reactor. For the non-isothermal reactor the conversion X_A at point B will be higher because of the higher average temperature level. As a consequence $X_{Pnon-iso} < X_{Piso}$ for $X_p/(1 - X_A) = X_{Piso}/(1 - X_{Aiso})$. Therefore we may conclude that a non-isothermal reactor that operates as indicated in Fig. 2 between two temperatures Θ_{low} and Θ_{high} will not necessarily have a yield that is higher than $X_{Pmax}(\Theta_{low})$, not even if $\Theta_{high} = \Theta_{opt}$. This is a very important phenomenon which will be accounted for in the determination of our design criteria.

Now assume that we aim for a certain yield X_{Pd} . This yield is defined as the yield which does not deviate more than a chosen fraction d from the maximum obtainable yield X_{Popt} . Hence

$$X_{Pd} \geq (1 - d)X_{Popt} \quad (31)$$

We state that there are two temperatures Θ_{mi} , being the lowest required temperature, and Θ_{ma} , being the maximum allowable temperature, between which the reactor should operate in order to achieve a desired yield X_{Pd} . In the ultimate situation Θ_{mi} will equal Θ_{ma} and the reactor has to be operated isothermally in order to achieve the desired yield.

We will use Figs 2 and 6 to define the lower (Θ_{mi}) and upper (Θ_{ma}) temperature limit in our tubular reactor. In order to operate at a high temperature level we assume that the minimum temperature Θ_{mi} is equal to

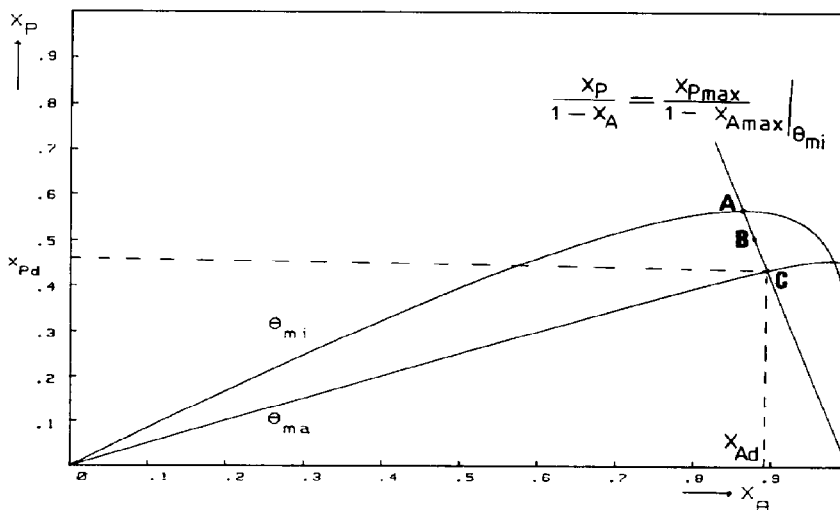


Fig. 6. Determination of the maximum allowable temperature Θ_{ma} and the minimum required temperature Θ_{mi} .

or higher than the optimal temperature Θ_{opt} ; meanwhile Θ_{mi} should be chosen in such a way that $X_{Pmax}(\Theta_{mi})$ is higher or equal to the desired yield X_{Pd} since the yield achieved under non-isothermal conditions is always lower than the yield achieved under isothermal conditions. From Fig. 2 we can understand that for a constant value of $X_P/(1-X_A)$ the yield achieved at point *B* will be lower than the yield achieved at point *A* because of the higher conversion of *A* at point *B*, where point *A* is the conversion $X_P/(1-X_A)$ at which the lower isotherm reaches its maximum yield $X_{Pmax}(\Theta_{mi})$. In Fig. 6 both isotherms Θ_{mi} and Θ_{ma} are plotted as well as the line for a constant value of $X_P/(1-X_A)$ equal to $X_{Piso}/(1-X_{Aiso})$ as given by point *A*. Therefore this line passes through the maximum of the isotherm at Θ_{mi} . The line intersects the isotherm Θ_{ma} before the isotherm Θ_{ma} has reached its maximum. We can easily see that the yield achieved in the non-isothermal reactor ($X_{Pnon-iso}$) is always higher than the yield achieved at conversion $X_A = X_{Ad}$ by the isothermal reactor. Now for each value of Θ_{mi} , with $\Theta_{opt} < \Theta_{mi} < \Theta(X_{Pd})$, a corresponding temperature Θ_{ma} can be calculated in such a way that two conditions are met simultaneously:

$$(a) X_P/(1-X_A)|_{\Theta_{mi}} = X_P/(1-X_A)|_{\Theta_{ma}}$$

and

$$(b) X_P(\Theta_{ma})|_{X_P(\Theta_{mi})/(1-X_A(\Theta_{mi}))} = X_{Pd}$$

So, as long as the reactor operates between Θ_{mi} and Θ_{ma} , the maximum yield will always be higher than X_{Pd} .

Since the reactor must operate between Θ_{mi} and Θ_{ma} the following demands can be formulated:

Since the reactor should operate above the minimum temperature Θ_{mi} the lowest temperature, being either the inlet temperature Θ_o or the coolant temperature Θ_c , should be higher than Θ_{mi} . Therefore

$$\Theta_o \text{ and } \Theta_c > \Theta_{mi}$$

The highest temperature is reached in the hot spot of the reactor, where the upper limit Θ_{ma} must not be exceeded. This leads to the following condition for the hot spot temperature:

$$\Theta_{hs} \leq \Theta_{ma}$$

These limits are calculated in the following procedure. First we calculate the optimum temperature Θ_{opt} using eq. (23) and the isotherm Θ_{max} at which the desired yield X_{Pd} would have been achieved if the reactor was operated isothermally. We use eq. (21) and solve it for the temperature: two solutions are possible the highest one is used as Θ_{max} . Now we select a minimum required temperature Θ_{mi} in such a way that

$$\Theta_{opt} < \Theta_{mi} < \Theta_{max}$$

Now we calculate the maximum isothermal yield, using eq. (21), that can be achieved in a reactor operating at $\Theta = \Theta_{mi}$. Next we calculate the conversion achieved at this point using eq. (22). Now construct the line for

constant value of $X_P/(1-X_A)$ with the yield and conversion calculated above. We intersect this line with the curve for isothermal yields in a reactor operating at Θ_{ma} using eq. (19). The following values for X_{Piso} and X_{Aiso} are used:

$$X_{Piso} = X_{Pd}$$

and

$$X_P/(1-X_A)|_{\Theta_{mi}} = X_{Piso}/(1-X_{Aiso})$$

Equation (19) is solved for Θ_{ma} , and we use this temperature for the upper limit in our temperature region.

Using these limits we will derive design criteria for the tubular reactor that guarantee a required minimum yield.

8. THE FIRST CRITERION

In the previous paragraph it was shown that the reactor must operate between Θ_{mi} and Θ_{ma} . The minimum temperature Θ_{mi} sets a lower limit to the coolant temperature Θ_c . We now will use the locus of maxima curves to formulate criteria for the design and operating variables that limit the hot spot temperature in such a way that it remains below Θ_{ma} .

The first criterion is derived from the locus curves intersecting the $X_A = 0$ [or $X_P/(1-X_A) = 0$] axis. We demonstrated that for $\Theta_o \leq \Theta_{ii}$ the reactor temperature is always below Θ_{ii} and for $\Theta_{ii} \leq \Theta_o < \Theta_{iu}$ the reactor temperature is always below Θ_o . Hence, the highest possible reactor temperature is either Θ_{ii} or Θ_{iu} . Both values are found by setting X_A equal to zero in eq. (26):

$$\frac{U^*(\Theta - \Theta_c)}{\Theta_{ad}} = K + H_Y K_P \quad (32)$$

Substitution of Θ_{ma} into this equation leads to our first criterion:

$$\frac{U^*(\Theta_{ma} - \Theta_c)}{\Theta_{ad}} = > K_{ma} + H_Y K_{P_{ma}} \quad (33)$$

As can be concluded from eq. (33) our first criterion does not depend on the integral selectivity in the hot spot.

A special case is given by the locus curve that has only one point of intersection with the $X_A = 0$ axis. For a given value of Θ_c , as can be seen in Fig. 5(a) and (b) there is one value of U^*/Θ_{ad} for which Θ_{ii} and Θ_{iu} coincide and where the locus curve just touches the $X_A = 0$ axis. Setting the derivative of eq. (25) with respect to Θ equal to zero defines the temperature Θ_i for which $\Theta_i = \Theta_{ii} = \Theta_{iu}$:

$$\frac{K_i + H_Y K_P}{K_i + p H_Y K_P} - \frac{j_P(\Theta_i - \Theta_c)}{T_i^2} = 0 \quad (34)$$

or in the case when $T_i - T_c$ is eliminated using eq. (32):

$$\frac{U^*}{\Theta_{ad}} - \frac{j_P(K_i + p H_Y K_P)}{\Theta_i^2} = 0 \quad (35)$$

From eq. (34) we can see that either Θ_c or Θ_i can be

chosen freely, so that for a given value of Θ_c the point of intersection (Θ_i) is fixed. Substitution of the maximum allowable temperature Θ_{ma} into eq. (34) or (35) leads to a criterion that gives us the required coolant temperature or the required ratio U^*/Θ_{ad} . It gives the lowest values of U^*/Θ_{ad} for which the first criterion is adhered to but it only can be applied if Θ_c according to eq. (34) is higher than Θ_{mi} because the minimum temperature in our reactor must be higher than Θ_{mi} as was stated before.

Using eq. (33) or (34) as the criterion for the design always leads to stable reactors because the temperature can never rise above the point of intersection Θ_i ($= \Theta_{ma}$). Also no estimated value of S_p in the hot spot is required.

9. THE SECOND CRITERION

The second criterion is derived from locus curves that do not intersect the $X_A = 0$ axis. The criterion is based on the property of trajectories for stable reactors that a trajectory starts at its maximum slope $d\Theta/dX_A$ at the inlet conditions: beyond the inlet the slope decreases due to the heat exchange with the cooling medium. Hence, our second criterion is based on the condition

$$\frac{d\Theta}{dX_A} \Big|_{X_A=0} <= (\Theta_{ma} - \Theta_o) / X_{Ama} \quad (36)$$

as illustrated in Fig. 7.

The slope $d\Theta/dX_A$ is given by eq. (16) and X_{Ama} by eq. (26), substituting Θ_{ma} for Θ_{hs} . The required value for S_p can be determined using S_{p1} or S_{p3} as explained before. Substitution into condition (36) leads to the following expression for the second criterion:

$$\Theta_{ad} \left(\frac{K_o + H_Y K_o^p}{K_o + K_o^p} \right) - \frac{U^*(\Theta_o - \Theta_c)}{K_o + K_o^p} <=$$

$$(\Theta_{ma} - \Theta_o) \left[\frac{1 - \frac{H_X B K_{ma}^q S_p}{K_{ma} + K_{ma}^p}}{1 - \frac{U^*(\Theta_{ma} - \Theta_c)}{\Theta_{ad}(K_{ma} + H_Y K_{ma}^p)}} \right] \quad (37)$$

In the case when Θ_o equals Θ_c our second criterion simplifies to

$$\frac{U^*}{\Theta_{ad}} (\Theta_{ma} - \Theta_c) >= (K_{ma} + H_Y K_{ma}^p) \times \left[1 - \frac{(\Theta_{ma} - \Theta_c) \left(1 - \frac{H_X B K_{ma}^q S_p}{K_{ma} + H_Y K_{ma}^p} \right)}{\Theta_{ad} \left(\frac{K_c + H_Y K_c^p}{K_c + K_c^p} \right)} \right] \quad (38)$$

It can be concluded from a comparison of the two criteria (33) and (38) that they differ in the term

$$1 - \frac{(\Theta_{ma} - \Theta_c) \left(1 - \frac{H_X B K_{ma}^q S_p}{K_{ma} + H_Y K_{ma}^p} \right)}{\Theta_{ad} \left(\frac{K_c + H_Y K_c^p}{K_c + K_c^p} \right)}$$

This term is smaller than one for high yields, so this criterion is a less stringent version of the first one. However, to apply this criterion the integral selectivity S_p has to be estimated using either S_{p1} or S_{p3} .

10. THE THIRD CRITERION

Assuming that no undesired product X has been formed and that no heat is withdrawn before the hot spot, the temperature rise in the reactor is given by

$$\begin{aligned} \Theta_{hs} - \Theta_o &= \Theta_{ad}(X_{p_{hs}} + H_Y X_{Y_{hs}}) \\ &= \Theta_{ad}[S_p + H_Y(1 - S_p)] X_{A_{hs}} \end{aligned}$$

Setting $\Theta_{hs} = \Theta_{ma}$ and calculating $(X_A)_{ma}$ with eq. (26)

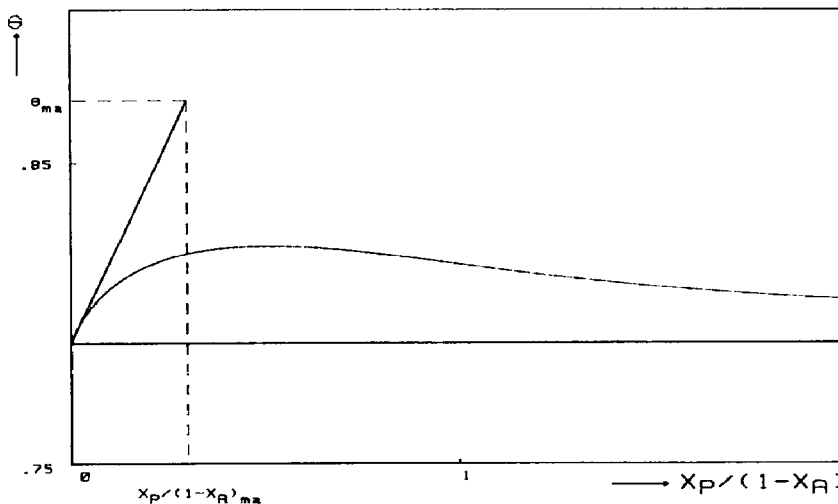


Fig. 7. Illustration of the second criterion (see text).

and in the case when Θ_o equals Θ_c , we find the following relation for the dimensionless number U^*/Θ_{ad} which is our third criterion:

$$\frac{U^*}{\Theta_{ad}} = \frac{K_{ma} + H_Y K_{ma}^p}{\Theta_{ma} - \Theta_c} - \frac{K_{ma} + H_Y K_{ma}^p - S_P H_X B K_{ma}^p}{\Theta_{ad} [S_P + H_Y (1 - S_P)]} \quad (39)$$

Intuitively it can be felt that the value U^* must have a minimum; for small values of $\Theta_{ma} - \Theta_c$ the required value of U^* , despite the low reaction rates, must be large in order to keep $\Theta_{ma} - \Theta_c$ at the required low value. On the other hand for large values of $\Theta_{ma} - \Theta_c$ the local heat production rates near the hot spot are high, so U^* should be high too. In between U^* will reach a minimum. Hence, U^* is a function of $\Theta_{ma} - \Theta_c$. Setting the derivative of U^* with respect to Θ_{ma} equal to zero leads to the formulation of the following implicit equation from which the optimum value of Θ_c can be calculated by trial and error:

$$\frac{K_{ma} + H_Y K_{ma}^p}{(\Theta_{ma} - \Theta_c)^2} - \frac{j_P (K_{ma} + p H_Y K_{ma}^p)}{(\Theta_{ma} - \Theta_c) \Theta_{ma}^2} + \frac{j_P (K_{ma} + p H_Y K_{ma}^p - S_P q H_X B K_{ma}^q)}{\Theta_{ad} \Theta_{ma}^2 [S_P + H_Y (1 - S_P)]} = 0 \quad (40)$$

For a given value of Θ_{ad} and Θ_{ma} the required value of Θ_c can be calculated; it should be checked if Θ_c lies within the region of acceptable values ($\Theta_{mi} < \Theta_c < \Theta_{ma}$). If not, then the lowest possible value of U^*/Θ_{ad} can be found by taking $\Theta_c = \Theta_{mi}$ and substituting Θ_c into eq. (39). Hence using eq. (40) the optimal value of Θ_c can be calculated which then can be substituted into eq. (39) to calculate the required value of U^*/Θ_{ad} according to the third criterion.

We must stress the fact that for the second and third criterion values of S_P are required, which are calculated using either S_{P1} or S_{P3} . These substitutions are valid only in case the heat effect of the consecutive reaction can be neglected before the hot spot is reached. If this is not the case, for instance if H_X is considerably larger than 1, only the first criterion is legitimate since for this criterion no estimates of S_P are required.

11. SELECTION OF PRACTICAL VALUES OF Θ_c

The required residence time is strongly dependent on the value of the coolant temperature. For isothermal reactors the required residence time Da is calculated from eq. (24). For a non-isothermal reactor, as can be seen in Fig. 6, the required yield X_{Pd} will be reached before X_{Ad} . The longest residence time required to reach X_{Ad} is found if the isotherm $\Theta = \Theta_{mi}$ is followed. Since we select the coolant temperature $\Theta_c = \Theta_{mi}$, the corresponding residence time Da_{lp} for the isothermal reactor operating at the coolant temperature Θ_c is

$$Da_{lp} = \frac{-1}{K_c + K_c^p} \ln(1 - X_{Ad}) \quad (41)$$

After setting a maximum for the tube length in the reactor to be built, that is a maximum allowable residence time, and with the known value of Θ_{ma} the value of Θ_c can be calculated. In practice the reactor operates at higher temperatures than Θ_c and the required yield will be reached before X_{Ad} so the actual residence time will be shorter than Da_{lp} .

The shortest residence time in an isothermal reactor to reach the required yield is found for the highest possible temperature (Θ_{ma}), which leads to

$$Da_{sp} = \frac{-1}{K_{ma} + K_{ma}^p} \ln(1 - X_{Ad}) \quad (42)$$

Equations (41) and (42) enable us to select reactor temperature regimes where reactor operation under realistic conditions is possible.

12. DESIGN PROCEDURE FOR COOLED TUBULAR REACTORS

In the previous paragraphs we discussed how a temperature region can be determined for which a tubular reactor achieves a minimum desired yield. We showed that the reactor should operate between two temperature limits, the lower limit Θ_{mi} and the upper limit Θ_{ma} . We stated that as long as $\Theta_c \geq \Theta_{mi}$ and $\Theta_{hs} \leq \Theta_{ma}$ the reactor operates within this area. We also derived criteria that ensure that the hot spot temperature Θ_{hs} remains below a preset temperature Θ_{ma} . Based on these results the following design procedure, leading to the design of a safely operating cooled tubular reactor for the execution of reaction networks, can be developed.

- (1) Make an Arrhenius plot of all reactions involved and determine whether high or low temperatures or a region of temperatures are desired to obtain high yields. In case high temperatures are required the reactor should operate at the highest possible temperature, in case low temperatures are required the reactor should operate at the lowest possible temperature. These designs are dominated by plant economics and mechanical constraints. In the case when the reactor should operate inside a regime the following procedure can be used.
- (2) For the reaction system considered determine the relevant reaction system parameters k_R , T_R , p , q , B , j_P , H_X and H_Y .
- (3) Calculate the absolute optimal temperature Θ_{opt} and the corresponding values of X_{Aopt} and X_{Popt} .
- (4) Calculate for several values of $X_{Piso} < X_{Popt}$ the isotherm Θ_{max} from eq. (21) so that $X_{Piso} = X_{Pmax}$. Also calculate the corresponding conversion X_{Amax} with eq. (22) and the residence time Da_{max} with eq. (24). Now select a design value for the yield X_{Pd} that leads to an acceptable residence time Da_{max} under isothermal conditions.
- (5) Calculate for the chosen value of X_{Pd} and for several values of Θ_{mi} , where $\Theta_{opt} < \Theta_{mi} < \Theta_{max}$, the maximum allowable temperature Θ_{ma} . Also

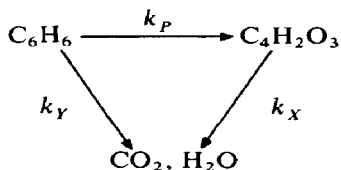
calculate the corresponding conversion X_{Ad} and the longest possible residence time Da_{1p} . Now select temperature regimes that do not lead to too long residence times and also do not demand a too narrow temperature regime (so that the reactor would have to operate almost under isothermal conditions).

- (6) Decide whether to use S_{P1} or S_{P3} and determine their values from eq. (28) or (30). Calculate for the remaining regimes as determined in step (5) the required values of U^*/Θ_{ad} using the three criteria for Θ_{ma} .
- (7) Determine, for each value of U^*/Θ_{ad} and a range of reactor loads, the maximum tube diameter and the value of the heat transfer coefficient.
- (8) Calculate the required optimal reactor length, using numerical integration techniques, for the configurations determined in step (6).
- (9) Choose an economical design based mainly upon the required tube diameters, number of tubes and tube lengths.
- (10) Check the design chosen for the effects of operational upsets, e.g. changes of the reactor load and of the feed concentration and if necessary correct the values chosen under (9).

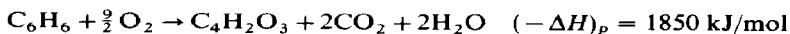
13. AN EXAMPLE

In the previous sections we derived criteria that enable us to design a reactor that achieves a required yield. We will demonstrate the method by applying it to the industrial process of the oxidation of benzene with air to maleic anhydride.

One of the synthesis routes for the production of maleic anhydride is based on the direct air oxidation of benzene with a vanadium pentoxide catalyst. An excess of air is applied, but the reactant benzene cannot be recovered economically so the reactor must operate at high yields. The main by-products are CO_2 and H_2O , which are formed according to



Kinetic data were presented by Wohlfahrt and Emig (1980) for the following system of reactions:



In practice selectivities of 50–60% and benzene conversions of 85–95% are achieved, so yields of 40–50% are realistic. The following conversion rates are given:

$$-R_{wA} = k_P[C_6H_6] + k_Y[C_6H_6]$$

$$R_{wY} = k_Y[C_6H_6]$$

$$R_{wP} = k_P[C_6H_6] - k_X[C_4H_2O_3]$$

$$R_{wX} = k_X[C_4H_2O_3].$$

Here A stands for benzene, P for the desired product maleic anhydride and X and Y are CO_2 and H_2O formed due to the consecutive and the parallel reactions, respectively. The corresponding rate constants are:

$$k_P = 4280 \exp\{-12,660/[T(K)]\} \text{ m}^3/(\text{kg cat s})$$

$$k_Y = 70,100 \exp\{-15,000/[T(K)]\} \text{ m}^3/(\text{kg cat s})$$

$$k_X = 26 \exp\{-10,800/[T(K)]\} \text{ m}^3/(\text{kg cat s}).$$

Furthermore the following physical data are available:

$$C_{pg} = 1.09 \text{ kJ}/(\text{kg K})$$

$$\rho_g = 1.01 \text{ kg}/\text{m}^3$$

$$\rho_b = 900 \text{ kg}/\text{m}^3$$

and the concentration of benzene in the feed is

$$C_{A0} = 0.83 \text{ mole \%}$$

which corresponds to a Θ_{ad} of 0.63.

With these data the following parameters are calculated:

$$T_R = 848 \text{ K} \quad k_R = 1.4 \times 10^{-3} \text{ m}^3/\text{kg s}$$

$$j_P = 14.9 \quad q = 0.85 \quad H_X = 0.77$$

$$B = 0.055 \quad p = 1.18 \quad H_Y = 1.77 \quad \Theta_{ad} = 0.63.$$

14. DETERMINATION OF THE OPERATING AND DESIGN VARIABLES

With eqs (21)–(23) the absolute optimal yield X_{Popt} and the corresponding temperature Θ_{opt} and conversion X_{Aopt} are calculated. The following results are obtained:

$$\Theta_{opt} = 0.667$$

$$X_{Popt} = 0.590$$

$$X_{Aopt} = 0.904.$$

Substituting these data into eq. (24) gives the required residence time:

$$Da_{opt} = k_R \rho_b L/u = 1950$$

which is far too high, requiring a residence time L/u of 1550 s. From these results we can conclude that a yield

lower than 59% has to be accepted in order to obtain a realistic reactor design. For several isothermal maximum yields X_{Pmax} the required temperatures Θ_{max} were calculated. The required residence time Da_{max}

is calculated with eq. (24). The results are listed in Table 1.

As can be seen from Table 1 yields close to the optimal yield $X_{Popt} = 0.59$ require extremely long residence times. We will accept residence times between 1 and 10 s and therefore aim for a yield of 48% which can be achieved in an isothermal reactor operating at a temperature $\Theta_{max} = 0.94$. In Table 2 the maximum allowable temperature T_{ma} is determined for several minimum temperatures T_{mi} . Also the maximum allowable temperature rise is given as well as the longest possible residence time $Da_{ip} = Da(X_{Ad}, T_{mi})$ to reach the yield X_{Pd} . It can be seen that in case of minimum temperatures close to the maximum allowable temperature the maximum residence times are relatively short but an almost isothermal operating reactor is required, which will lead to high values of U^* and uneconomical reactor designs. On the other hand in case of large allowable regions the minimum temperature is low and therefore the required resi-

dence time will be relatively long. Since we aim for residence times shorter than 10 s the minimum temperature should be $T = 755$ K or higher.

Using the criteria we are able to calculate values of U^*/Θ_{ad} , the results are listed in Table 3. We estimated S_p using S_{p3} , because $H_Y = 1.77 > 1$.

From Table 3 we conclude that the required cooling capacity must be $U^*/\Theta_{ad} > = 18.1$. Since U^* depends on both the reactor tube diameter and the reactor load we will calculate the maximum tube diameter for varying reactor loads. A method outlined by Westerterp *et al.* (1984b) was used. The results are listed in Table 4.

For a reactor load of $u_o/\varepsilon = 1.8$ m/s the temperature and conversion profiles of X_A and X_P were calculated. The plots are shown in Fig. 8. The optimal residence time is 7.1 s, which leads to an optimal reactor length of $L = 12.8$ m.

We checked the design for changes in the feed concentration C_{A0} . For some values of Θ_{ad} temperature trajectories and conversion profiles are shown in Fig. 9(a) and (b). As can be seen runaway occurs for $\Theta_{ad} = 0.87$ which corresponds to a concentration of 1.15 mole % benzene.

The reactor will be overheated with more than 400 K, which for sure will result in damage. Again we see that the margin between runaway conditions ($\Theta_{ad} = 0.87$) and conditions required for maintaining the correct yield ($\Theta_{ad} = 0.63$) is large. This was also demonstrated previously by Westerterp, Ptasinaky and Overtoom (Westerterp and Ptasinaky, 1984a, b; Westerterp *et al.*, 1984a; Westerterp and Overtoom, 1985), who for multiple reactions showed that a good selectivity is lost easier than runaway occurs.

Table 1. Temperatures, conversion and residence time for several yields in isothermal reactors. $j_P = 14.9$, $B = 0.055$, $p = 1.18$, $q = 0.85$

| X_P | Θ_{max} | X_{Amax} | Da_{max} | τ (s) |
|-------|----------------|------------|------------|------------|
| 0.52 | 0.862 | 0.959 | 21 | 17 |
| 0.50 | 0.903 | 0.965 | 9.8 | 7.8 |
| 0.49 | 0.923 | 0.968 | 6.7 | 5.3 |
| 0.48 | 0.943 | 0.970 | 4.69 | 3.7 |
| 0.47 | 0.963 | 0.972 | 3.35 | 2.7 |
| 0.46 | 0.983 | 0.974 | 2.41 | 1.9 |
| 0.45 | 1.004 | 0.975 | 1.75 | 1.4 |

Table 2. Determination of the maximum allowable temperature T_{ma} for a required minimum yield of 48%. $j_P = 14.9$, $B = 0.055$, $p = 1.18$, $q = 0.85$

| T_{mi} (K) | $X_{Pmax}(T_{mi})$ | $X_{Amax}(T_{mi})$ | T_{ma} (K) | $T_{ma} - T_{mi}$ (K) | Da_{ip} |
|-----------------|--------------------|--------------------|-----------------|--------------------------|-----------|
| 746 | 0.511 | 0.962 | 797 | 51 | 15.0 |
| 755 | 0.506 | 0.963 | 797 | 42 | 12.3 |
| 763 | 0.501 | 0.965 | 797 | 34 | 10.2 |
| 772 | 0.496 | 0.966 | 797 | 25 | 8.4 |
| 780 | 0.491 | 0.967 | 797 | 17 | 7.0 |
| 789 | 0.486 | 0.968 | 797 | 8.5 | 5.9 |
| 797 | 0.481 | 0.969 | 797 | 0.0 | 4.9 |

Table 3. Required values of U^*/Θ_{ad} according to the three criteria given by eqs (33), (38) and (39) in order to achieve a desired yield of at least 48% at a residence time shorter than 10 s

| Θ_{ma} | Θ_c | Θ_{ad} | U^*/Θ_{ad} according to | | |
|---------------|------------|---------------|--------------------------------|---------------|---------------|
| | | | Equation (33) | Equation (38) | Equation (39) |
| 0.946 | 0.892 | 0.63 | 19.3 | 18.1 | 18.2 |

15. CONCLUSIONS

Based on the model presented here for multiple-reaction networks in a cooled tubular reactor we may conclude that the criteria derived enable us to select

Table 4. Maximum tube diameter and heat transfer coefficient for several reactor loads which satisfy the criteria given by Table 3

| u_0/ε (m/s) | U (W/m ² K) | $d_{t,max}$ (m) |
|----------------------------|-----------------------------|----------------------|
| 0.6 | 82 | 2.0×10^{-2} |
| 1.2 | 115 | 2.8×10^{-2} |
| 1.8 | 146 | 3.5×10^{-2} |
| 2.4 | 175 | 4.2×10^{-2} |

practical values of the design and operating variables in order to achieve a desired yield. It should be mentioned that the method presented requires kinetic information about both undesired reactions and the desired reaction, and the required tube length, can be obtained by numerical integration only and that the method will work in case of first-order reactions only.

Also it was shown that for the scheme discussed in this paper it is not possible to design a safely operating reactor in which a network of reactions is carried out where 100% yield can be approached at will.

NOTATION

- A pre-exponential factor, m³/(kg s)
 B dimensionless kinetic factor,
 $= (A_X/A_P) \exp [j_P(1 - q)]$

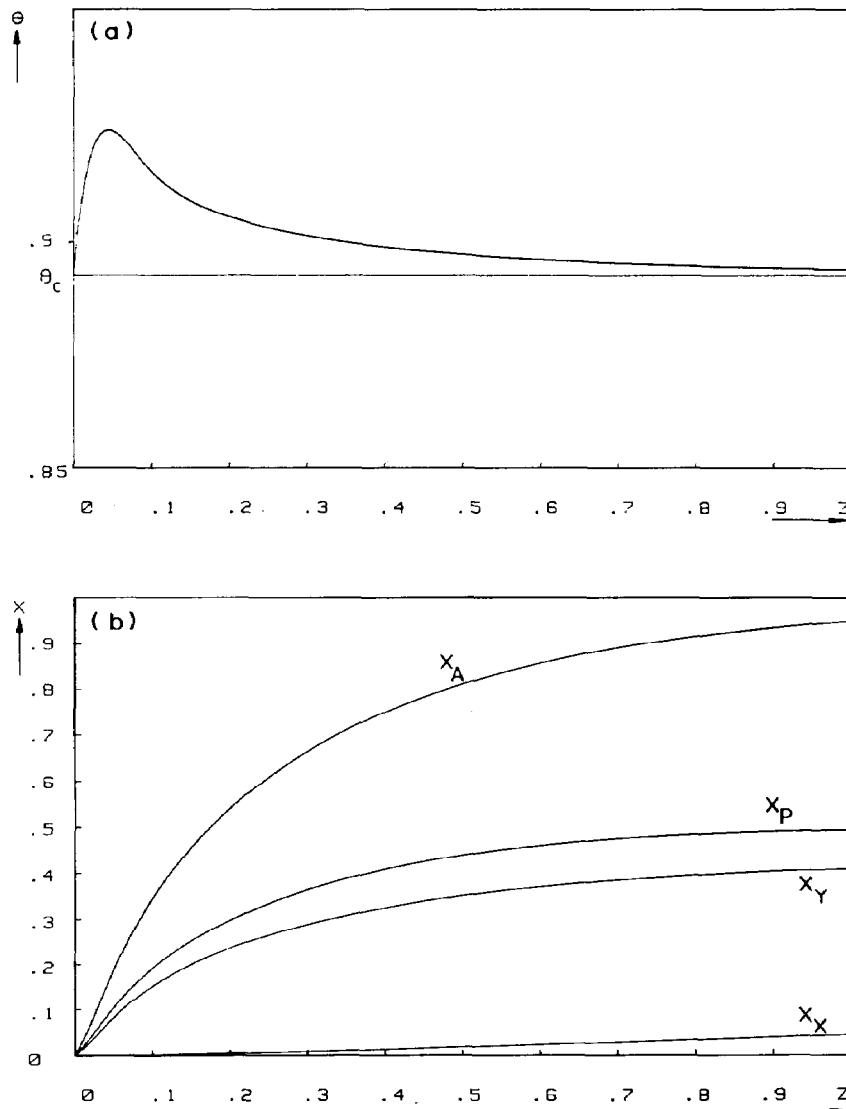


Fig. 8. Profiles for the temperature (a) and the conversion (b) for the design presented in the example. The oxidation of benzene to maleic anhydride.

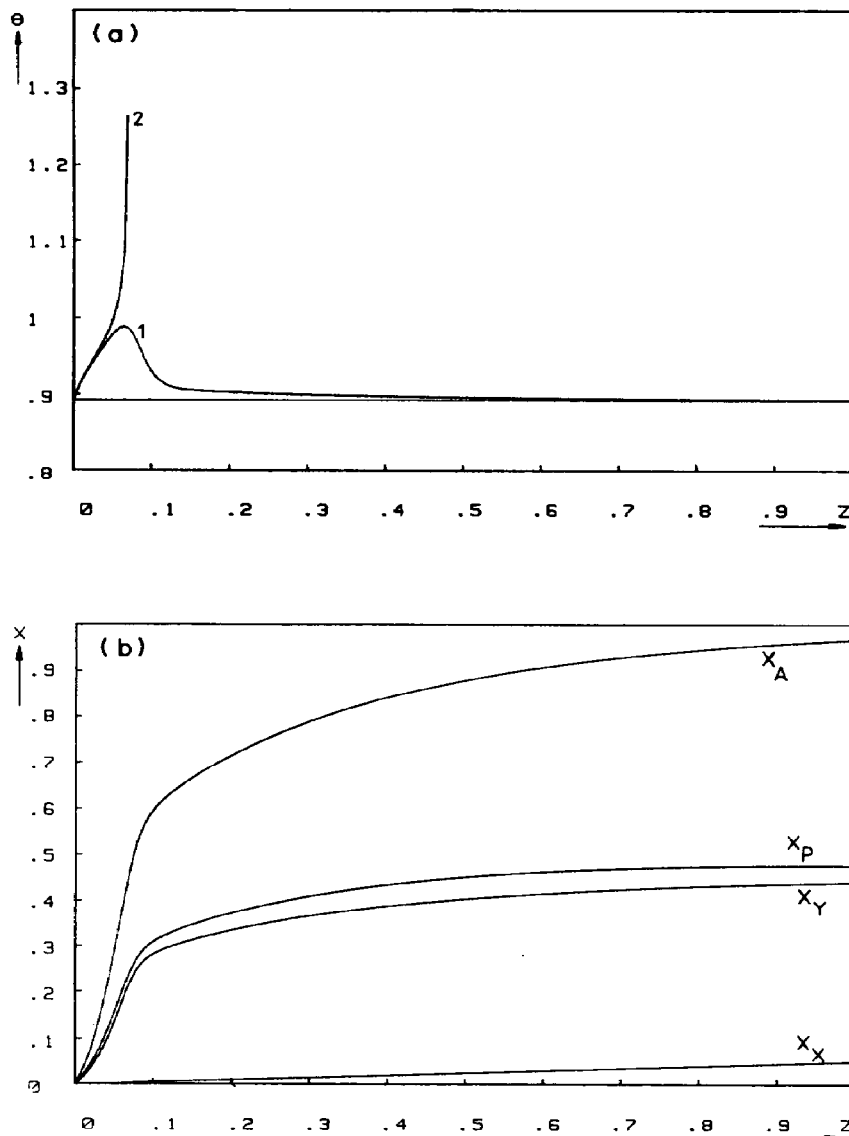


Fig. 9. Temperature (a) and conversion profiles (b) for changes in the feed concentration of the reactor designed in the example. For profile 1 in (a) and for the conversions in (b) the feed concentration is 1.12 mole % benzene. For trajectory 2 in (a) the concentration is 1.15 mole % benzene.

| | | | |
|----------------|---|----------|---|
| C | concentration of species, mol/m ³ | L | reactor length, m |
| C_{pg} | specific heat of reaction mixture, J/(kg K) | p | E_Y/E_P |
| d_t | tube diameter, m | q | E_X/E_P |
| Da | $k_R \rho_b L / u$, dimensionless residence time | R_{wJ} | rate of production of species J , mol/(kg cat s) |
| E_i | activation energy for the reaction i , J/mol | S_P | integral selectivity achieved in the hot spot, $= X_P / X_A$ |
| H_i | $\Delta H_i / \Delta H_P$, ratio of reaction heats | S'_P | differential selectivity, $= dX_P / dX_A$ |
| $(\Delta H)_P$ | heat of reaction for the production of P J/mol | T | temperature, K |
| j_P | dimensionless activation temperature, $= E_P / (RT_R)$ | T_R | reference temperature, K |
| k | reaction rate constant, m ³ /(kg s) | u_o | superficial gas velocity based on empty cross-section, m/s |
| K | k_p / k_R , dimensionless rate constant | U | total heat transfer coefficient, W/(m ² K) |
| k_R | reference reaction rate constant, m ³ /(kg s) | U^* | $4U / k_R \rho_b \rho_g C_{pg} d_t$ |

| | |
|-----|--------------------------------------|
| X | relative degree of conversion |
| z | coordinate in direction of flow, m |
| Z | z/L , dimensionless reactor length |

Greek letters

| | |
|---------------|---|
| ε | bed porosity |
| ρ_b | bulk catalyst density per unit of reactor volume, kg/m^3 |
| ρ_g | density of the reaction mixture, kg/m^3 |
| Θ | T/T_R , dimensionless temperature |
| Θ_{ad} | $-\Delta H_p C_{A0} / T_R \rho_g C_{pg}$, dimensionless adiabatic temperature rise |

Subscripts

| | |
|-----|--|
| A | reactant |
| c | coolant |
| hs | hot spot |
| il | lower point of intersection |
| iu | upper point of intersection |
| lp | longest possible |
| ma | maximum allowable |
| max | optimum under isothermal conditions |
| mi | minimum required |
| o | inlet conditions |
| opt | absolute optimum |
| P | product |
| sp | shortest possible |
| X | undesired product formed by the consecutive reaction |
| Y | undesired product formed by the parallel reaction |

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APPENDIX

Introduction to multiple hot spots

In previous studies criteria were developed that were based on the assumption that only one hot spot occurs. These criteria ensure that this hot spot temperature is not surpassed at any point in the reactor.

In the case when multiple reactions occur one may expect the possibility of more than one hot spot. For example two hot spots may occur in the case when two exothermic consecutive reactions are carried out: the first hot spot will be caused by the first reaction, and the second one will occur due to the second reaction.

The number and location of all hot spots that could possibly occur in the case when multiple reactions are carried out should be studied. We will use the reaction scheme presented as scheme (1) and discuss also the systems with either parallel or consecutive reactions, only putting the appropriate terms equal to zero.

Features of multiple hot spots

For the case that two hot spots occur, some possible trajectories are given in Figs A1 and A2. We can easily see that between two hot spots a minimum must occur. In this minimum, of course, $d\Theta/dZ = 0$ as was the case for the maxima. So we cannot discriminate between maxima and minima by the first derivative only. The extremum can be characterized by the second derivative of the temperature Θ with respect to the reactor length coordinate Z . For $d^2\Theta/dZ^2 > 0$ the extremum is a minimum, for $d^2\Theta/dZ^2 < 0$

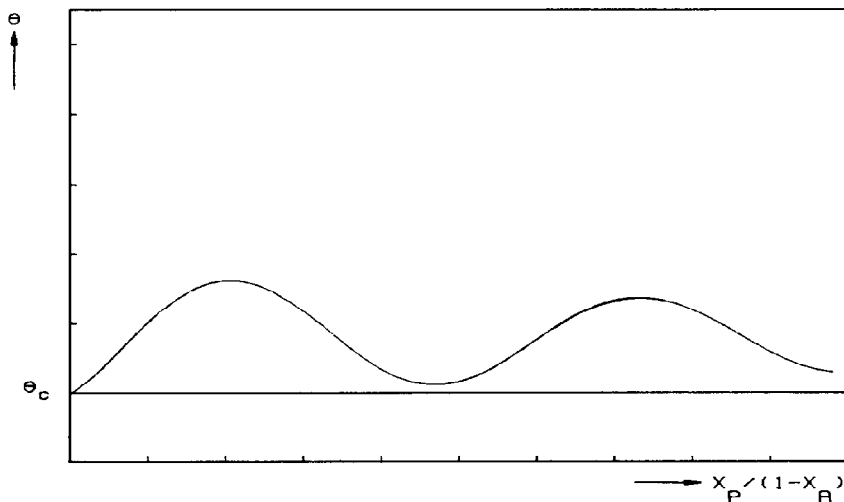


Fig. A1. A temperature trajectory with two hot spots along the reactor tube.

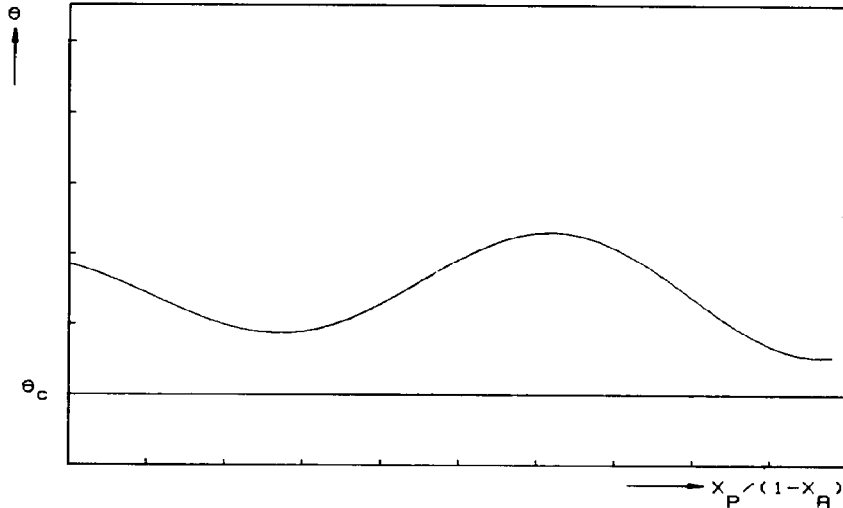


Fig. A2. A temperature trajectory with two hot spots of which the first one is located at the inlet.

it is a maximum. We will use the second derivative to define the border between regions where maxima and minima occur.

Model equations

In a tubular reactor which can be described by the pseudo-homogeneous one-dimensional model, the temperature trajectories are fully determined by the following set of differential equations for the reaction system under consideration:

$$\frac{dX_A}{dZ} = Da(K + K^p)(1 - X_A) \tag{a}$$

$$\frac{dX_P}{dZ} = Da[K(1 - X_A) - BK^q X_P] \tag{b}$$

$$\frac{d\Theta}{dZ} = Da\Theta_{ad}[(K + H_Y K^p)(1 - X_A) + H_X BK^q X_P] - Da U^*(\Theta - \Theta_c) \tag{c}$$

The locus of extrema, defined by $d\Theta/dZ = 0$ is given by

$$K_{ex} + H_Y K_{ex}^p + H_X BK_{ex}^q \left(\frac{X_P}{1 - X_A} \right) - \frac{U^*(\Theta_{ex} - \Theta_c)}{\Theta_{ad}(1 - X_A)} = 0 \tag{d}$$

Instead of studying this locus curve in a three-parameter space (Θ, X_A, X_P) we will consider the conversion X_A in terms of $X_P/(1 - X_A)$ and study the relation in a $X_P/(1 - X_A), \Theta$ plane. The term $X_P/(1 - X_A)$ was chosen because this term also occurs in the relation used to characterize the extrema. It was demonstrated already before that the conversion X_A may be replaced by the term $X_P/(1 - X_A)$ within a certain range of differential selectivities.

The locus of extrema

We will use the isothermal reactor operating at the temperature in the extremum Θ_{ex} in order to obtain estimates of the values of X_A in the extremum. The isothermal reactor is described by

$$\frac{X_P}{1 - X_A} = \frac{K}{K + K^p - BK^q} [(1 - X_A)^{\frac{BK^q}{K + K^p} - 1} - (1 - X_A)]$$

After division by $1 - X_A$ and some rearrangements this leads to

$$\left(\frac{X_P}{1 - X_A} \cdot \frac{K + K^p - BK^q}{K} + 1 \right)^{\frac{1}{\frac{BK^q}{K + K^p} - 1}} = 1 - X_A \tag{e}$$

Substitution of the value of $1 - X_A$ of eq. (e) into eq. (d) leads to a relation for the temperature in the extremum:

$$K + H_Y K^p + H_X BK^q \frac{X_P}{1 - X_A} = \frac{U^*}{\Theta_{ad}} (\Theta - \Theta_c) \times \left[1 + \frac{X_P}{1 - X_A} \left(\frac{K + K^p - BK^q}{K} \right) \right]^{1 - \frac{BK^q}{K + K^p}}$$

or after rearranging:

$$\left[\frac{K + H_Y K^p + H_X BK^q \left(\frac{X_P}{1 - X_A} \right)}{\frac{U^*}{\Theta_{ad}} (\Theta - \Theta_c)} \right]^{1 - \frac{BK^q}{K + K^p}} = 1 + \left(\frac{X_P}{1 - X_A} \right) \left(\frac{K + K^p - BK^q}{K} \right) \tag{f}$$

For known values of U^*/Θ_{ad} and Θ_c , eq. (f) gives us the relation between Θ and $X_P/(1 - X_A)$ in the extrema, both for the minima and the maxima. Some of these extrema curves are plotted in Figs A3 and A4 (curves c, c_r and c_l). Inside the extrema curve the derivative $d\Theta/dZ$ is negative so the trajectories decrease, while outside the curve the derivative is positive; hence there the trajectories will increase. We can see that for diminishing values of U^*/Θ_{ad} the curve of extrema separates into two branches (Fig. A4, curves c_1 and c_r). Inside these branches $d\Theta/dZ$ is still negative so the trajectories will decrease in the inside region. In Figs A3 and A4 two trajectories are plotted for some values of U^* and Θ_{ad} keeping the ratio U^*/Θ_{ad} constant in each figure. In Fig. A4 the danger of more than one hot spot is clearly illustrated by trajectory a, where the temperature decreases at the onset of the reaction, but eventually a runaway occurs. For even smaller values of U^*/Θ_{ad} the left branch completely disappears.

Characterization of all points on the locus of extrema

The second derivative of Θ with respect to Z will be used to characterize the extrema defined by relation (f). The second

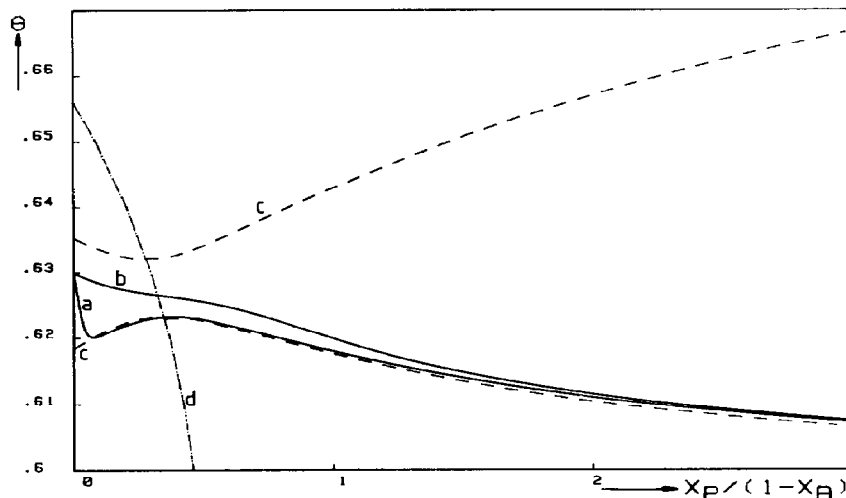


Fig. A3. Two branches of a locus of extrema curve (c), the curve (d) that marks the border between maxima and minima, and two trajectories (a) and (b). Data are $p = 1.5$, $q = 0.8$, $B = 0.11$, $j_P = 15$, $H_X = H_Y = 2$, $\Theta_c = 0.6$, $\Theta_o = 0.63$ and $U^*/\Theta_{ad} = 0.0053$. Trajectory (a) $\Theta_{ad} = 5$, $U^* = 0.0265$; (b) $\Theta_{ad} = 0.5$, $U^* = 0.00265$.

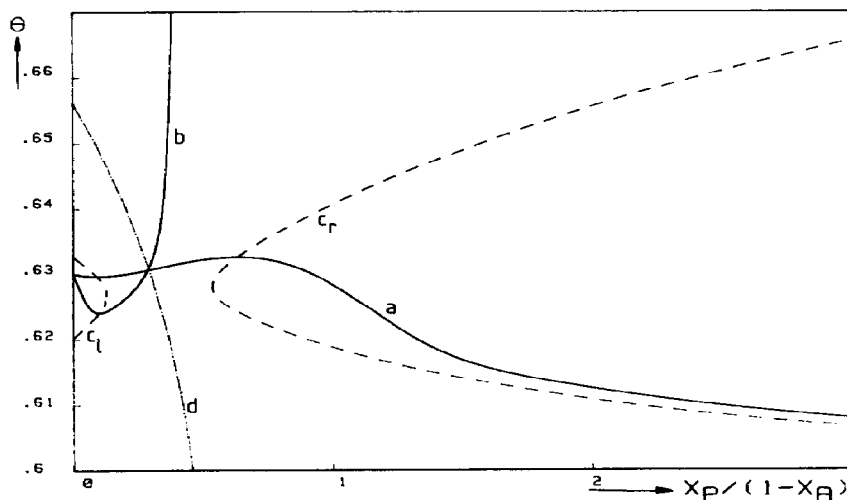


Fig. A4. The locus of extrema curve with two branches (c_r and c_l), the border curve (d) and two trajectories (a) and (b). Same data as for Fig. A3, except now $U^*/\Theta_{ad} = 0.00518$. Trajectory (a) $\Theta_{ad} = 0.5$, $U^* = 0.00259$; (b) $\Theta_{ad} = 5$, $U^* = 0.0259$.

derivative as derived from eq. (c) is

$$\begin{aligned} \frac{1}{Da} \cdot \frac{d^2\Theta}{dZ^2} = & \Theta_{ad} \left[\left(1 + p H_Y K^{p-1} \right) (1 - X_A) \right. \\ & + q H_X B K^{q-1} \left. \right] \left(\frac{dK}{d\Theta} \right) \left(\frac{d\Theta}{dZ} \right) \\ & + \Theta_{ad} \left[- \left(K + H_Y K^p \right) \left(\frac{dX_A}{dZ} \right) \right. \\ & \left. + H_X B K^q \left(\frac{dX_P}{dZ} \right) \right] - U^* \left(\frac{d\Theta}{dZ} \right). \end{aligned}$$

Since only the sign of the second derivative in the extremum is of interest and furthermore in the extremum $d\Theta/dZ = 0$ holds this relation can be rearranged to

$$\begin{aligned} \frac{1}{Da} \cdot \frac{d^2\Theta}{dZ^2} \Big|_{Z_{ex}} = & \Theta_{ad} \left[- \left(K + H_Y K^p \right) \left(\frac{dX_A}{dZ} \right) \right. \\ & \left. + H_X B K^q \left(\frac{dX_P}{dZ} \right) \right]. \end{aligned} \quad (g)$$

From this equation we can easily see that for parallel reactions with $BK^q = 0$ we have only maxima since $d^2\Theta/dZ^2$ is always negative. As no minimum occurs there can be one hot spot only for parallel reactions.

Substitution of eqs (a) and (b) into eq. (g) leads to

$$\frac{-1 \left(\frac{d^2 \Theta}{dZ^2} \right)}{Da^2 \Theta_{ad} (1 - X_A)} = (K + H_Y K^p)(K + K^p) - H_X BK^q \left(K - BK^q \frac{X_P}{1 - X_A} \right). \quad (h)$$

The right-hand side of this equation gives a relation that can be used to characterize the extrema: if the right-hand side of relation (h) is negative the extremum is a minimum, and vice versa. The borderlines between regions where minima and maxima occur is obtained if the right-hand side of eq. (h) is set equal to zero, so that

$$(K + H_Y K^p)(K + K^p) - H_X BK^q \left[K - BK^q \left(\frac{X_P}{1 - X_A} \right) \right] = 0$$

which leads to the following expression for the borderline curve:

$$\left(\frac{X_P}{1 - X_A} \right) = \frac{K}{BK^q} - \frac{(K + H_Y K^p)(K + K^p)}{H_X B^2 K^{2q}}. \quad (i)$$

Typical plots of relation (i) are given in Figs A3 and A4 as curves d. The second derivative is positive at the left of the curve d so that the extrema on the locus of extrema curve are minima while on the right-hand side of the curve the extrema are maxima. In Fig. A3 the area enclosed by curve c is still continuous but already exhibits a constriction. At still lower values of U^*/Θ_{ad} it falls apart in two separate areas, whereas curve d now lies between these areas.

The existence of minima in temperature trajectories

The locus of extrema and the regions of minima and maxima can be used to investigate the existence of temperature minima. To reach a minimum the temperature must decrease. For a trajectory to decrease it must be situated inside the region indicated by the locus of extrema curve. After the minimum has been passed the temperature should rise again. From the plots in Figs A3 and A4 where the horizontal axis equals Θ_c we can easily see that only for the inlet condition $\Theta_o > \Theta_c$ can we have a trajectory that decreases at the onset of the reaction, as shown in Fig. A2. It is not possible to obtain trajectories as presented in Fig. A1 since in that case the temperature should rise inside the locus of extrema branch.

Discussion and conclusions

Apparently it is possible to obtain more than one hot spot in the case of a multiple-reaction system like the one presented. We can easily understand that systems with parallel reactions only can have only one hot spot since in that case the reactant has to make a choice between either one of the reactions. In the case of consecutive reactions intrinsically the reactant fed can produce heat twice: first in the reaction $A \rightarrow P$ and afterwards again in $P \rightarrow X$. As the reaction proceeds the concentration of A diminishes continuously. So from the concentration point of view the first reaction cannot be ignited again. However the concentration of P continuously increases. This also increases the reaction rate of $P \rightarrow X$ and if the combined conditions of concentration and temperature are favourable a second ignition can occur.

The reasoning given above holds too for the reaction system consisting of both parallel and consecutive reactions. Based upon the discussions above we may conclude that more than one hot spot may occur in the case of a reaction system like the one presented in a tubular reactor.

We can understand that no multiple hot spot can occur in case the inlet temperature Θ_o and the cooling temperature Θ_c are higher than the point of intersection of the borderline (d) with the $X_P/(1 - X_A) = 0$ axis. The point of intersection between curve d and the $X_P/(1 - X_A) = 0$ axis is given by

$$\frac{X_P}{1 - X_A} = \frac{K}{BK^q} - \frac{(K + H_Y K^p)(K + K^p)}{H_X B^2 K^{2q}} = 0. \quad (j)$$

For the inlet conditions $\Theta_o = \Theta_c$ to be above the point of intersection the following criterion must be satisfied:

$$\frac{K}{BK^q} - \frac{(K + H_Y K^p)(K + K^p)}{H_X B^2 K^{2q}} < 0 \text{ at } \Theta = \Theta_c$$

or after some rearrangements:

$$\frac{H_X BK_c^{q+1}}{(K_c + H_Y K_c^p)(K_c + K_c^p)} < 1.$$

In the case of our example the critical value of Θ_c for which multiple hot spots may occur is found by setting eq. (j) equal to zero and solving it for $\Theta_{c,crit}$. This leads to

$$\Theta_{c,crit} = 0.40$$

which corresponds to a value of 66°C. Due to the low value of this temperature which would lead to very long residence times we may conclude that under practical conditions no multiple hot spots will occur in the reactor of our example.