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SAFE DESIGN OF COOLED TUBULAR REACTORS FOR EXOTHERMIC, MULTIPLE REACTIONS; PARALLEL REACTIONS—I

DEVELOPMENT OF CRITERIA

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Abstract—Previously reported design criteria for cooled tubular reactors are based on the prevention of reactor temperature runaway and were developed for single reactions only. In this paper it is argued that such criteria should be based on the reactor selectivity, from which eventually a maximum allowable temperature can be derived. To this end and for the pseudo-homogeneous, one dimensional model of a cooled tubular reactor in which two parallel, irreversible first order exothermic reactions are carried out, two criteria are developed for the safe design and operation of the reactor. The criteria enable us to choose tube diameters and operating conditions, which are safe in view of the derived selectivity and of possible runaway as well. The method outlined can be used in the initial design stage and requires kinetic information on both the desired and the undesired reaction.

INTRODUCTION

At designing a cooled (catalytic) tubular reactor for exothermic reactions much care is required to avoid excessive reactor temperatures with respect to reactor temperature runaway. To this end in the past several authors developed criteria for the safe design and operation of cooled tubular reactors. All these criteria are based on *single reactions* and on the phenomenon of *parametric sensitivity*. In a certain range of the values of the relevant design and operating parameters, such as the tube diameter d_t, the cooling medium temperature T_c, the reactor inlet temperature T_0 or the concentration C_{A0} of the reactant in the reactor feed, the tubular reactor has been proven to be extremely sensitive to the value of one of these parameters: after a small change of a parameter in the critical region the reactor suddenly starts to operate at a much higher temperature level.

All criteria developed up to now have been based on the conception that this should be avoided and that the reactor should operate outside of the region of high parametric sensitivity.

Moreover, the available criteria have been based on a single reaction taking place and on a specified maximum allowable temperature T_{ma}, which must not be surpassed. The criteria developed up to now are then based on determining the process conditions at which the reactor for the specified T_{ma} is at the boundary of the regions of high and low parametric sensitivity, so that the process conditions can be chosen such that runaway is prevented. The available criteria exhibit some imperfections. First because if really only one single reaction takes place, it does not matter that the reactor temperature gets very high; the higher the temperature the shorter the reactor can be, provided the construction materials remain strong enough and the catalyst remains active. Secondly because specifying a T_{ma} in itself can be rather arbitrary, although usually it is based on small scale laboratory experiments, which, of course, does give strong indications for industrial reactors despite the scale-up problems. A maximum allowable temperature can be specified for various reasons, e.g. such as catalyst life, reactor selectivity, strength of construction materials, temperature runaway or explosion limits. Here we will discuss *multiple reactions* and limit ourselves to runaway and selectivity aspects. We first will derive criteria for maintaining a required reactor selectivity and later we will demonstrate that temperature runaway will not occur, if the derived selectivity criteria are adhered to. We will restrict ourselves to exothermic parallel first order reactions in a pseudo-homogeneous, cooled tubular reactor.

LITERATURE SURVEY

Bilous and Amundson[1] were the first to describe the phenomenon of parametric sensitivity in cooled tubular reactors. This parametric sensitivity was used by Barkelew[2] to develop design criteria for cooled tubular reactors in which first order, second order and product-inhibited reactions take place. He presented diagrams from which for a certain tube diameter d_t the required combination of C_{A0} and T_c can be derived to avoid runaway or vise versa. Later van Welsenaere and Froment[3] did the same for first order reactions, but they also used the inflexion points in the reactor temperature T vs relative conversion X_A trajectories, which describe the course of the reaction in the tubular reactor. With these trajectories they derived a less conservative criterion. Morbidelli and Varma[4] recently devised a method for single order reactions based on the isoclines in a temperature-conversion plot as proposed by Oroskar and Stern[5]. Agnew and Potter[6] did the same as Barkelew for heterogeneous catalytic reactors and presented design diagrams to prevent runaway, including also the parameter of the ratio of the tube to the catalyst particle diameter d_t/d_p. Burghardt and Warmuzinski[7] considered multiple reactions and also took the heat

effect of the secondary reaction into account, however, they did not study the selectivities achieved in the reactor.

Multiple steady states in catalyst particles have been studied by McGreavy and Adderley[8] and by Rajadhyaksha *et al.*[9] and they presented criteria to avoid this multiplicity. However, it has been shown[10, 11] that multiplicity arising from interparticle gradients are not very likely under industrial operating conditions. Other criteria to avoid runaway were developed by Dente and Collina[12] and Hlavácek *et al.*[13]. Emig *et al.*[14] proved experimentally that the criteria of Barkelew, of Agnew and Potter and of McGreavy and Adderley all predict runaway remarkedly well for a single first order reaction in a cooled catalytic tubular reactor.

Only Westerterp[15] up to now also took the required selectivity into account in a reactor stability study, but only for tank reactors. We will use his study as a starting point and extend it to multiple reactions in a cooled tubular reactor. We will use the homogeneous tubular reactor model, which is also representative for tubular reactors filled with catalyst particles provided that $d_t/d_p \leq 8$[11].

THE MATHEMATICAL MODEL FOR THE PLUG FLOW REACTOR WITH PARALLEL REACTIONS

We consider a tubular reactor in which two parallel reactions occur:

$$\begin{array}{l} \quad\quad P \\ A \nearrow \\ A \searrow \\ \quad\quad X. \end{array} \qquad (1)$$

In these reactions A is the reactant, P is the desired and X the undesired product. Both reactions are irreversible, exothermic and of the first order and conversion rates are given by:

$$R_{wP} = k_P C_A \qquad (2)$$

$$R_{wX} = k_X C_A. \qquad (3)$$

Here R_w is expressed as kmoles convert per unit of time and per unit of mass of catalyst.

The pseudo-homogeneous one-dimensional model of the cooled, tubular reactor used by us is based on the following assumptions:

—the concentration and temperature gradients only occur in the axial direction;

—the only transport mechanism operating in the axial direction is the overall flow itself, which is supposed to be the plug flow;

—the physical and chemical data ρ_g, ρ_B, c_P, $\Delta H, U$ are assumed to be independent of temperature;

—the temperature of the cooling medium T_c is constant.

The mass and heat balances for this reactor model are:

$$u\frac{dC_P}{dz} = R_{wP}\rho_B \qquad (4)$$

$$u\frac{dC_X}{dz} = R_{wX}\rho_B \qquad (5)$$

$$u\frac{dT}{dz} = -(\Delta H_P R_{wP} + \Delta H_X R_{wX})\frac{\rho_B}{\rho_g c_p} - \frac{4U}{d_t \rho_g c_p}(T - T_c). \qquad (6)$$

In order to compare the two competing reactions we use the reference temperature T_R introduced by Westerterp[15]. This is the temperature at which the reaction velocity constants k_p and k_x are equal and have the value of k_R. From this condition follows:

$$k_R \equiv k_{p|T_R} = K_{X|T_R} = A_P\, e^{(-E_P/RT_R)} = A_X\, e^{(-E_X/RT_R)}. \qquad (7)$$

We now can derive the value of the reference temperature T_R and also a reference reaction velocity constant k_R:

$$T_R = \frac{E_P(p-1)}{R \ln\left(\frac{A_X}{A_P}\right)} \text{ and } k_R = \left(\frac{A_P^{\,p}}{A_X}\right)^{1/(p-1)} \qquad (8)$$

in which $p = E_X/E_P$. With T_R and k_R the following dimensionless variables can be introduced: $\mathbf{T} = T/T_R$, the dimensionless temperature; $\kappa = k_p/k_R$, the dimensionless reaction velocity constant of the desired reaction and $\kappa^p = k_X/k_R$, the dimensionless reaction velocity constant of the undesired reaction. Now κ depends on the dimensionless temperature according to:

$$\kappa = e^{\gamma_P(1-(1/\mathbf{T}))} \text{ with } \gamma_P = E_P/RT_R. \qquad (9)$$

The reaction velocity constants of both reactions are now defined by the set of dimensionless parameters: k_R, T_R, γ_p and p instead of by A_P, A_X, E_P and E_X. The ratio of the activation energies p is a measure for the temperature sensitivity of the selectivity of the reacting system. If $p > 1$ the selectivity increases with decreasing temperatures. In this case the reactor has to be operated at a temperature level below the reference temperature in order to obtain high selectivities. For $p < 1$ the reactor should operate at the highest possible temperatures; this case is not of interest for this study.

Equations (4)–(6) can be made dimensionless after introducing the dimensionless quantities X_P, X_X, Z, H, Da, $\Delta\mathbf{T}_{ad}$ and U^* (see the list of symbols for their definitions). The transformed equations are:

$$\frac{dX_P}{dZ} = Da\,\kappa(1 - X_P - X_X) \qquad (10)$$

$$\frac{dX_X}{dZ} = Da\,\kappa^p(1 - X_P - X_X) \qquad (11)$$

$$\frac{d\mathbf{T}}{dZ} = Da\,\Delta\mathbf{T}_{ad}(\kappa + H\kappa^p)(1 - X_P - X_X) - Da\,U^*(\mathbf{T} - \mathbf{T}_c). \qquad (12)$$

This set of equations describes the behaviour of parallel reactions in a tubular reactor using the relative conversion to desired product X_P and to undesired product X_X, the dimensionless temperature T and the dimensionless reactor length Z. The reaction system is characterized by the ratio of the reaction heats H in addition to k_R, T_R, γ_p and p. The operating and design conditions are determined by: $\mathbf{T}_c$, the dimensionless cooling medium temperature; Da, the dimensionless residence time in the reactor; U^*, the dimensionless cooling capacity per unit of reactor volume and $\Delta\mathbf{T}_{ad}$, the dimensionless adiabatic temperature rise for the desired reaction, which of course depends on the initial concentration of the reactant A.

If only the temperature behaviour of the reactor has to be studied and not the individual conversions to the products P and X, the system of the three equations (10)–(12) can be reduced to two simultaneous differential equations after introducing the total conversion of the reactant A, X_A:

$$\frac{dX_A}{dZ} = Da(\kappa + \kappa^p)(1 - X_A) \tag{13}$$

$$\frac{d\mathbf{T}}{dZ} = Da\Delta\mathbf{T}_{ad}(\kappa + H\kappa^p)(1 - X_A) - Da\,U^*(\mathbf{T} - \mathbf{T}_c) \tag{14}$$

in which

$$X_A = X_P + X_X. \tag{15}$$

The reactor temperature as related to the conversion X_A can be found after dividing eqns (14) by (13), from:

$$\frac{d\mathbf{T}}{dX_A} = \Delta\mathbf{T}_{ad}\frac{1 + H\kappa^{p-1}}{1 + \kappa^{p-1}} - U^*\frac{\mathbf{T} - \mathbf{T}_c}{(\kappa + \kappa^p)(1 - X_A)}. \tag{16}$$

If the reactor feed does not contain any product P or X, the reactor yield of desired product is given by $\theta_P = C_{PL}/C_{A0} = X_{PL}$ the selectivity of the reactor by $S_P = C_{PL}/(C_{A0} - C_{AL}) = X_{PL}/X_{AL}$ and the local or differential selectivity at any place in the reactor by $S'_P = -dC_P/dC_A = +dX_P/dX_A$. The selectivity ratio is $S_{PX} = X_P/X_X$, the reciprocal selectivity ratio $S_{XP} = X_X/X_P$ and the differential reciprocal selectivity ratio $S'_{XP} = dX_X/dX_P$. The reactor selectivity now is:

$$S_P = \frac{X_P}{X_A} = \frac{1}{1 + S_{XP}} \tag{17}$$

The differential reciprocal selectivity ratio is found by dividing eqns (11) by (10):

$$S'_{XP} = \kappa^{p-1} \tag{18}$$

and the reactor reciprocal selectivity ratio by integrating S'_{XP} along the reactor:

$$S_{XP} = \frac{X_A}{\int_0^{X_A}\frac{1}{1 + S'_{XP}}\,dX_A} - 1 \tag{19}$$

THE BEHAVIOUR OF THE $\mathbf{T}(X_A)$ FUNCTIONS

The behaviour of the $\mathbf{T}(X_A)$ functions can be analysed in the same way as Barkelew[2] did. For parallel reactions there is a great similarity in behaviour as for single reactions. The trajectories $\mathbf{T}(X_A)$ can be obtained by numerical integration of eqn (16); some are shown in Fig. 1. The trajectories have a characteristic maximum temperature $\mathbf{T}_m$ in the hot spot of the reactor; for trajectory c in Fig. 1 conditions are such that $\mathbf{T}_m$ has an extremely high value, so that here we have runaway conditions. The relation between the hot spot temperature $\mathbf{T}_m$ and the conversion X_A can easily be determined, because in the hot spot $d\mathbf{T}/dX_A$ is equal to zero in eqn (16) which gives:

$$(X_A) = 1 - \frac{U^*}{\Delta\mathbf{T}_{ad}^*\dfrac{\mathbf{T}_m - \mathbf{T}_c}{\kappa_m + H\kappa_m{}^p}} \tag{20}$$

The curve of this locus of maxima is also shown in Fig. 1. To the left of this locus curve the derivative $d\mathbf{T}/dX_A$ of a trajectory is always positive, reactor temperatures increase with increasing conversion and reactor length; to the right of the locus curve $d\mathbf{T}/dX_A$ is always negative and there the reactor temperatures always decrease. The maximum of the trajectory is found on the locus curve. The locus curve also reaches an extremum at a lowest value of X_A, below which no hot spot temperatures can be found. The temperature $(\mathbf{T}_m)_M$ corresponding to that extremum can be found by setting $d(X_A)_m/d\mathbf{T}_m$ equal to zero in (20):

$$\frac{(\mathbf{T}_m)_M^2[1 + H(\kappa_m)_M{}^{p-1}]}{\gamma_p[1 + pH(\kappa_m)_M{}^{p-1}]} - (\mathbf{T}_m)_M = \mathbf{T}_c. \tag{21}$$

The locus curve also exhibits another extremum for $T \gg 1$ far beyond the range of practical interest. For higher values of X_A two hot spot temperatures are possible: one above and one below the value of $(\mathbf{T}_m)_M$. The hot spot temperature under runaway conditions lies above $(\mathbf{T}_m)_M$, of course.

The locus of maxima curve is controlled by the reaction parameters γ_p, p and H and two design and operating variables $\mathbf{T}_c$ and $U^*/\Delta\mathbf{T}_{ad}$, whereas the temperature $(\mathbf{T}_m)_M$ by the same reaction parameters and $\mathbf{T}_c$ only. Figure 2 shows that upon increasing the ratio $U^*/\Delta\mathbf{T}_{ad}$ the locus curve can intersect the $X_A = 0$ axis at two points, below and above the temperature $(\mathbf{T}_m)_M$. The locus curves for several values of $\mathbf{T}_c$ are shown in Fig. 3. We see that upon increasing the cooling area of the reactor or decreasing the reactant concentration in the feed, that is increasing the value of $U^*/\Delta\mathbf{T}_{ad}$, and upon decreasing the coolant temperature $\mathbf{T}_c$, the dangerous region where $d\mathbf{T}/dX_A > 0$, decreases.

MAXIMUM ALLOWABLE TEMPERATURES BASED ON SELECTIVITY CRITERIA

We will now investigate how the selectivity depends on the trajectories in the reactor in order to develop design and operating criteria. To this end we use the

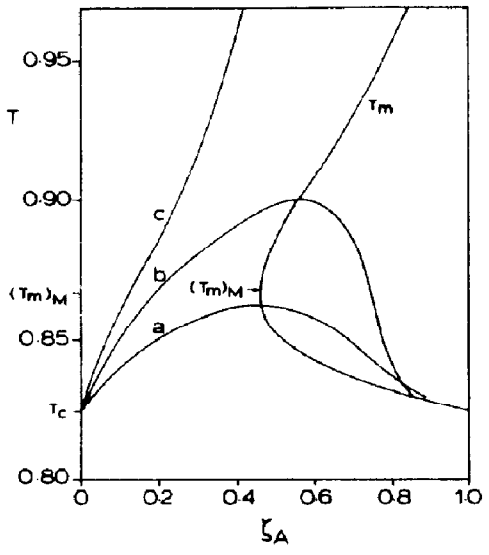

Fig. 1. Temperature profiles in the reactor and locus of maxima curve $\mathbf{T}_m$; $p = 2$, $H = 2$, $\gamma_p = 15$, $U^*/\Delta\mathbf{T}_{ad} = 1.5$, $\Delta\mathbf{T}_{ad} = 0.2 - a$; $0.4 - b$; $0.6 - c$.

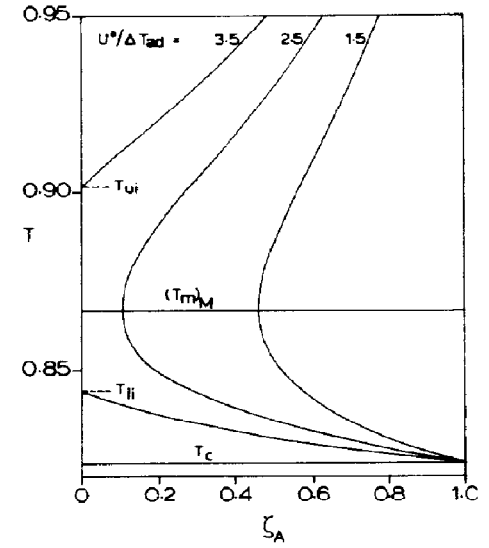

Fig. 2. Locus of maxima curves for a few values of the ratio $U^*/\Delta\mathbf{T}_{ad}$; $p = 2$, $H = 2$, $\gamma_p = 15$.

differential reciprocal selectivity ratio

$$\frac{dX_X}{dX_P} = S'_{XP} = \kappa^{p-1} = e^{\gamma_p(p-1)(1-(1/T))} \tag{18}$$

which is a measure of the extent of the local coproduction of the undesired product X with respect to the local production of the desired product P. According to eqn (18) S'_{XP} depends on the temperature only for a given

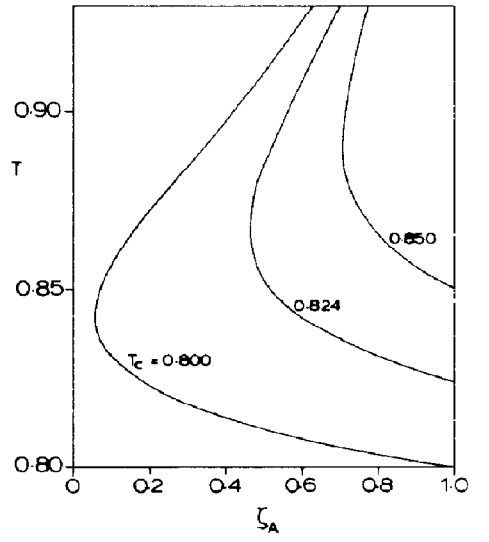

Fig. 3. Locus of maxima curves for a few coolant temperatures; $p = 2$, $H = 2$, $\gamma_p = 15$, $U^*/\Delta\mathbf{T}_{ad} = 1.5$.

reaction system and increases with temperature for $p > 1$. Only values of p larger than one are of interest as has been said. The maximum value of S'_{XP} is then reached at the highest temperature in the reactor, that is in the hot spot. At all other points of the relevant trajectory S'_{XP} is lower than in the hot spot. As a consequence the integral reciprocal selectivity ratio S_{XP} for any outlet conversion X_{AL} must be lower than S'_{XP} in the hot spot. We therefore start to specify a maximum allowable value of $(S'_{XP})_{ma}$, which later on will be compared with the integral S_{XP} of the reactor. The value of $(S'_{XP})_{ma}$ is related to the maximum allowable temperature $\mathbf{T}_{ma}$:

$$(S'_{XP})_{ma} = \kappa_{ma}^{p-1} = e^{\gamma_p(p-1)(1-(1/\mathbf{T}_{ma}))}. \tag{22}$$

This relation defines the maximum allowable temperature in the reactor:

$$\mathbf{T}_{ma} = \frac{\gamma_p(p-1)}{\gamma_p(p-1) - \ln(S'_{XP})_{ma}} \tag{23}$$

which it is not allowed to surpass. The definition of this maximum allowable temperature is now based on the properties of the reaction system γ_p, p and the selectivity limit $(S'_{XP})_{ma}$ only and not on an arbitrary temperature limit. The higher the required reactor selectivity, the lower the value of $\mathbf{T}_{ma}$.

DEVELOPMENT OF SELECTIVITY CRITERIA

We now can derive criteria for the selection of design and operating conditions. The criteria proposed depend on the shape of the locus curve, which either crosses the $X_A = 0$ axis or does not touch it, depending on the values of $U^*/\Delta\mathbf{T}_{ad}$ and $\mathbf{T}_c$, see Figs. 2 and 3.

The first criterion is based on a locus intersecting the $X_A = 0$ axis. As shown in Fig. 2 there are two points of

intersection T_{ui} and T_{li}, the upper and lower intersection temperatures. For all reactor inlet temperatures T_0 in the range $T_{li} < T_0 < T_{ui}$ the reactor temperatures will decrease over the entire reactor length; for $T_0 \leq T_{li}$, the reactor temperature initially increases but never can get higher than T_{li}, see Fig. 4. The values of T_{li} and T_{ui} can be found by solving:

$$H\kappa_m^{\,p} + \kappa_m = \frac{U^*}{\Delta T_{ad}}(T_m - T_c) \tag{24}$$

which relation is obtained after putting $(X_A)_m$ in eqn (20) equal to zero. It now depends on the value of T_{ma} what conditions in the reactor have to be chosen so that T_{ma} will not be surpassed. Vice versa we also can choose the values of $U^*/\Delta T_{ad}$ and T_c in such a way that T_{ma} and either T_{ui} or T_{li} coincide, so that for any value of $T_0 \leq T_{ma} = T_{ui}$ or T_{li} the reactor temperatures always remain below T_{ma}. After introducing the maximum allowable differential reciprocal selectivity ratio $(S'_{XP})_{ma}$ given by eqn (22) into eqn (24) we find:

$$(S'_{XP})_{ma}^{1/(p-1)}[1 + H(S'_{XP})_{ma}] = \frac{U^*}{\Delta T_{ad}}(T_{ma} - T_c) \tag{25}$$

Moreover, for values of $U^*/\Delta T_{ad}$ also higher than those given by eqn (25), the required T_{ma} value will not be surpassed. Therefore we now can formulate our first criterion as:

$$\left(\frac{U^*}{\Delta T_{ad}}\right)(T_{ma} - T_c) \geq (S'_{XP})_{ma}^{1/(p-1)}[1 + H(S'_{XP})_{ma}] \tag{26}$$

whereas T_{ma} is defined by (23).

The second criterion for the maximum allowable temperature is derived from the locus curves which do not intersect the $X_A = 0$ axis. The criterion is based on the property of the trajectories, that they start at the inlet point T_0, $X_A = 0$ for $T_0 \geq T_c$ with their maximum slope and that beyond this point the slope decreases due to the heat exchange with the cooling medium provided runaway does not occur. If now, as is shown in Fig. 5, the tangent to the trajectory at the reactor inlet passes through the point T_{ma}, $(X_A)_{ma}$ on the locus curve, then the reactor temperature never can reach this T_{ma} value because of the decreasing slopes of the trajectory, provided there is no inflexion point in the trajectory. This will be checked later on. Hence, our second criterion is based on the condition:

$$\left(\frac{dT}{dX_A}\right)_{X_A=0} \leq \frac{T_{ma} - T_0}{(X_A)_{ma}}. \tag{27}$$

This criterion is equivalent to the first criterion of van Welsenaere and Froment[3]. On substituting $dT/dX_A)_{X_A=0}$ by (16) and eliminating $(X_A)_{ma}$ by using (20), the criterion (27) after some rearrangement becomes:

$$\Delta T_{ad} \leq \frac{T_{ma} - T_0}{1 - \dfrac{U^*}{\Delta T_{ad}} \dfrac{T_{ma} - T_c}{\kappa_{ma}(1 + H\kappa_{ma}^{p-1})}} * \frac{\kappa_0(1 + \kappa_0^{p-1})}{\kappa_0(1 + H\kappa_0^{p-1}) - \dfrac{U^*}{\Delta T_{ad}}(T_0 - T_c)}. \tag{28}$$

Often in practice the inlet temperature T_0 equals the coolant temperature T_c. For this case this second criterion after introducing $(S'_{XP})_{ma}$ by (22) becomes:

$$\left(\frac{U^*}{\Delta T_{ad}}\right)(T_{ma} - T_c) \geq (S'_{XP})_{ma}^{1/(p-1)}[1 + H(S'_{XP})_{ma}]\left[1 - \frac{T_{ma} - T_c}{\Delta T_{ad}} \frac{1 + \kappa_c^{p-1}}{1 + H\kappa_c^{p-1}}\right] \tag{29}$$

for $T_0 = T_c$. This second criterion can be considered as a more strict version of the first one because it differs in the term

$$\left[1 - \frac{(T_{ma} - T_c)}{\Delta T_{ad}} * \frac{1 + \kappa_c^{p-1}}{1 + H\kappa_c^{p-1}}\right]$$

only and this term is always < 1.

The practical significance of both criteria can easily be evaluated by substituting the definitions of U^* and ΔT_{ad} into (26) and (29):

$$\frac{U(T_{ma} - T_c)}{d_t \cdot C_{A0}} \geq -\frac{k_R \rho_B \Delta H_P}{4} * (S'_{XP})_{ma}^{1/(p-1)}[1 + H(S'_{XP})_{ma}] * P_{1,2} \tag{30}$$

in which P is for the first criterion $P_1 = 1$ and for the second criterion with $T_0 = T_c$:

$$P_2 = 1 - \frac{(T_{ma} - T_c)}{\Delta T_{ad}} * \frac{1 + \kappa_c^{p-1}}{1 + H\kappa_c^{p-1}}. \tag{31}$$

So for the design of a reactor to reach a certain selectivity the group $U(T_{ma} - T_c)/d_t C_{A0}$ must be kept constant

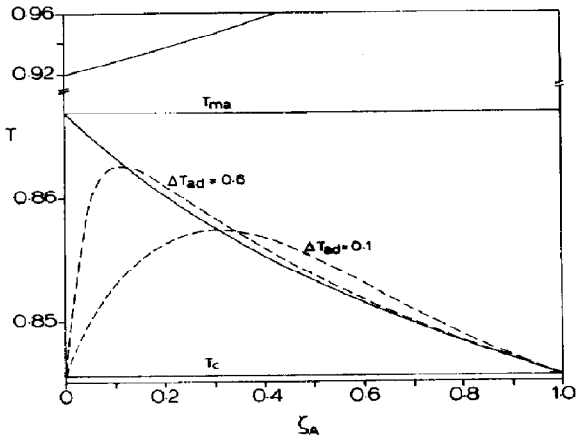

Fig. 4. Temperature profiles according to the first criterion; $p = 2$, $H = 2$, $\gamma_p = 15$, $(S'_{XP})_{ma} = 0.1$, $Da_c/Da_{min} = 1.6$

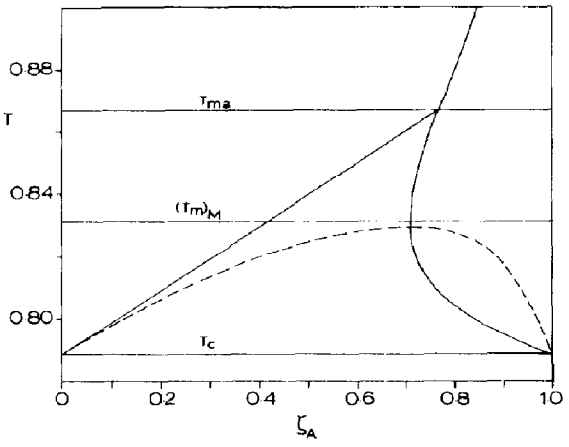

Fig. 5. Temperature profile according to the second criterion; $p = 2$, $H = 2$, $\gamma_p = 15$, $(S'_{XP})_{ma} = 0.1$, $\Delta T_{ad} = 0.1$, $Da_c/Da_{min} = 6.0$.

at a certain value. Once the reactor has been constructed and installed (which means that d_t can not be varied anymore) at varying reactor loads (influencing the value of U) or varying feed concentrations C_{A0} the group $U(T_{ma} - T_c)/C_{A0}$ must be kept constant in order to maintain the reactor selectivity. Calculation of the maximum safe tube diameter using either one of the two criteria is quite straightforward for a particular set of the operating conditions of T_c and C_{A0}. The second criterion (29) which has been derived for the more general case leads to more accurate results. The first criterion (26) gives more conservative results but it is simpler to use. How the criteria work out is demonstrated in Fig. 6. In this figure for the first criterion are shown the locus of maxima curves for a fixed value of $U^*(T_{ma} - T_c)/\Delta T_{ad}) = 0.120$. At low values of $T_{ma} - T_c$ the value of $U^*/\Delta T_{ad}$ is large, in this case the lower intersection point T_{li} of the locus of maxima curve with the T_c axis coincides with T_{ma}. With increasing values of $T_{ma} - T_c$ they remain coinciding up till at a certain point also the lower and upper intersection points T_{li} and T_{ui} coincide: now the locus of maxima curve just touches the T axis. At increasing $T_{ma} - T_c$ even more, T_{ma} now will coincide with T_{ui} instead of T_{li}. We see that a whole collection of locus of maxima curves satisfies the criterion. We have to realise that at increasing $T_{ma} - T_c$ the reactor tube lengths necessarily become longer, because T_c and therefore also the average temperature level in the reactor decrease.

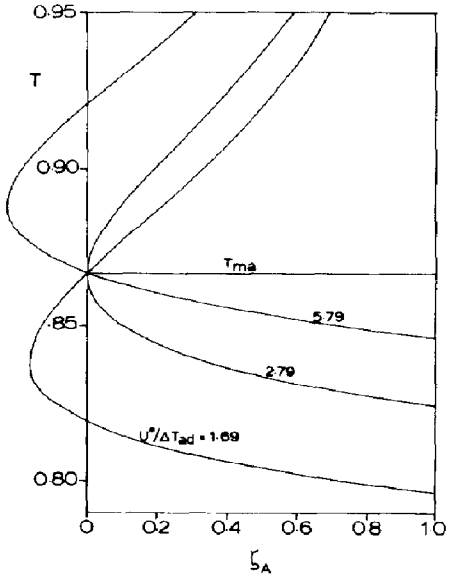

Fig. 6. Locus of maxima curves according to the first criterion $p = 2$, $H = 2$, $\gamma_p = 15$, $(S'_{XP})_{ma} = 0.1$.

SELECTION OF PRACTICAL VALUES FOR THE COOLING MEDIUM TEMPERATURE

We still have to evaluate a practical range of values for the cooling medium temperature, because at too low values of T_c the reactor becomes excessively long and therefore too expensive.

The lowest value of T_c for which a reactor still has an industrially acceptable length can be called the minimum allowable coolant temperature $(T_c)_{min}$. In order to determine $(T_c)_{min}$ the relation between reactor length and coolant temperature should be established by numerical integration of eqns (13) and (14). This relation also can be obtained in a simpler approach. For isothermal operation at T_{ma} the lowest possible reactor length and the minimum Damköhler number for the required selectivity $(S'_{XP})_{ma}$ and for a certain conversion X_{AL} is obtained. For a constant temperature eqn (13) can be integrated between the limits $Z = 0$, $X_{A0} = 0$ and $Z = 1$, X_{AL} leading to:

$$Da_{min} = \frac{-\ln(1 - X_{AL})}{\kappa_{ma}(1 + \kappa_{ma}^{p-1})}. \tag{32}$$

On the other hand isothermal operation at T_c results in the highest possible reactor length and the maximum Damköhler number Da_c for the same conversion X_{AL}:

$$Da_c = \frac{-\ln(1 - X_{AL})}{\kappa_c(1 + \kappa_c^{p-1})}. \tag{33}$$

Then the ratio Da_c/Da_{min} is a measure of the increase of the reactor length due to the value chosen for T_c and for given values of T_{ma} or $(S'_{XP})_{ma}$. After eliminating T_{ma} from (32) by (22) we find:

$$\frac{Da_c}{Da_{min}} = \frac{(S'_{XP})_{ma}^{1/(p-1)}[1 + (S'_{XP})_{ma}]}{\kappa_c(1 + \kappa_c^{p-1})}. \tag{34}$$

Calculation of the ratio Da_c/Da_{min} as a function of the temperature difference $(T_{ma} - T_c)$ for varying parameters values of γ_p, p and (S'_{XP}) reveals that above some value of $(T_{ma} - T_c)$ the ratio Da_c/Da_{min} becomes very sensitive to the coolant temperature. The boundary of this sensitivity is in the range of Da_c/Da_{min} from 3 to 5.

Therefore we will use for the minimum allowable value of $(T_c)_{min}$ the value at which the ratio Da_c/Da_{min} equals 5 for cheap reactors or 3 for expensive reactors. For these values of Da_c/Da_{min}, the corresponding value of $(T_c)_{min}$ can be calculated from eqn (34) by trial and error calculations. However, the practical values of $(S'_{XP})_{ma}$ are much lower than unity, so that the term κ_c^{p-1} in eqn (34) can be neglected since $\kappa_c^{p-1} \ll 1$ and we find:

$$(T_c)_{min} = \frac{\gamma_p}{\gamma_p - \ln \dfrac{(S'_{XP})_{ma}^{1/(p-1)}[1 + (S'_{XP})_{ma}]}{Da_c/Da_{min}}} \quad (35)$$

in which a value of 3 to 5 has to be substituted for Da_c/Da_{min}. This gives us a practical range for the cooling medium temperatures $(T_c)_{min} \leq T_c < T_{ma}$.

THE RELATION BETWEEN THE INTEGRAL AND DIFFERENTIAL SELECTIVITIES

Both criteria for achieving the desired selectivity in a cooled tubular reactor were based on the differential selectivity ratio S'_{XP}. However, plant economics are controlled by the integral selectivity ratio S_{XP} of the entire reactor. We therefore calculated numerically the values of S_{XP} for a wide range of reaction parameters p, γ_p, H and operating variables Da_c/Da_{min}, ΔT_{ad} and $(S'_{XP})_{ma}$. We assumed $T_0 = T_c$ and $X_{AL} = 0.99$.

A typical relation between S_{XP} and $(S'_{XP})_{ma}$ is shown in Fig. 7. From this figure it can be seen that the ratio Da_c/Da_{min} and the reaction parameter p have a significant influence on the difference between S_{XP} and $(S'_{XP})_{ma}$. Further ΔT_{ad} has only a slight effect and the results for the reactions parameters γ_p and H showed that the influence of either γ_p or H is rather small. Now after determining the desired value of S_{XP} we can derive from Fig. 7 the value of S'_{XP} which has to be substituted into the criteria. We recommend to neglect the influence of γ_p, H and ΔT_{ad} on $S_{XP}/(S'_{XP})_{ma}$.

CHECK FOR PARAMETRIC SENSITIVITY

We still have to check whether both criteria do not lead us into the region of high parametric sensitivity resulting in a runaway of the reactor temperatures. The first criterion is inherently parametrically stable, because it was based on the region below the upper branch of the locus curve. For the second criterion the situation is more complicated and has to be analysed more in detail, as is done in the appendix. An investigation of the region of practical values of the parameters disclosed that no temperature runaway occurs, if the second selectivity criterion is adhered to. Therefore the same conclusion as for the first criterion can be drawn: trajectories calculated according to the second criterion still fall in the region of low parametric sensitivity.

PROCEDURE FOR SAFE DESIGN OF COOLED TUBULAR REACTORS FOR PARALLEL FIRST ORDER REACTIONS

Now that we feel sure that a reactor designed according to either one of the criteria developed, will operate outside of the danger area of reactor runaways we can base a reactor design on them. In order to design a reactor the following procedure can be followed:

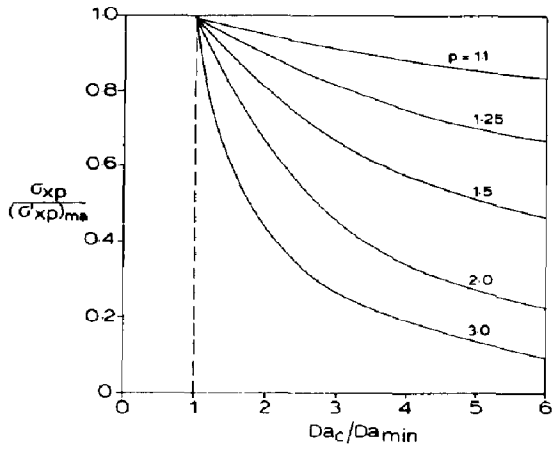

Fig. 7. Effect of p on the relationship between $(S_{XP})/(S'_{XP})_{ma}$ and Da_c/Da_{min} for the first criterion; $H = 2$, $\gamma_p = 15$, $\Delta T_{ad} = 0.6$, $(S'_{XP})_{ma} = 0.01 \div 0.30$.

(1) Determine from the laboratory data, whether the reactions under consideration can be described by a system of parallel reactions.

(2) Fit the data obtained in the laboratory by first order rate expressions of the type $R_{wP} = k_P C_A$ and $R_{wX} = k_X C_A$ in the temperature range of interest. Check whether the use of first order kinetics is allowed.

(3) Calculate the reaction parameters k_R, T_R, γ_p and p

(4) Choose on economic grounds, especially on raw materials costs and product value, a value of the maximum allowable reciprocal selectivity ratio $(S_{XP})_{ma}$.

(5) Choose a value of Da_c/Da_{min} in agreement with the investment costs of the reactor and determine a minimum value for the cooling medium temperature.

(6) Determine with Fig. 7 the maximum allowable differential reciprocal selectivity ratio $(S'_{XP})_{ma}$ assuming complete conversion of the reactants.

(7) Calculate with the criteria eqns (30, 31) the minimum value of $U(T_{ma} - T_c)/d_t C_{A0}$ and choose practical values for d_t and C_{A0}.

(8) If d_t is larger than required for the process, either a higher selectivity towards desired product or a shorter reactor can be chosen by increasing the coolant temperature. If d_t is too small, lower selectivities and/or lower coolant temperatures have to be accepted.

We should warn that the method has been developed for first order reactions; for reactions of different order and especially for reactions with Langmuir–Hinshelwood or Eley Rideal kinetics the method will not work. Although the data given in Fig. 7 refer to a total conversion of $X_A = 0.99$, our criteria are also valid for lower conversions and will always result in a situation, where the reactor operates in the region of low parametric sensitivity. The use of Fig. 7, of course, is restricted to complete conversion of the reactant.

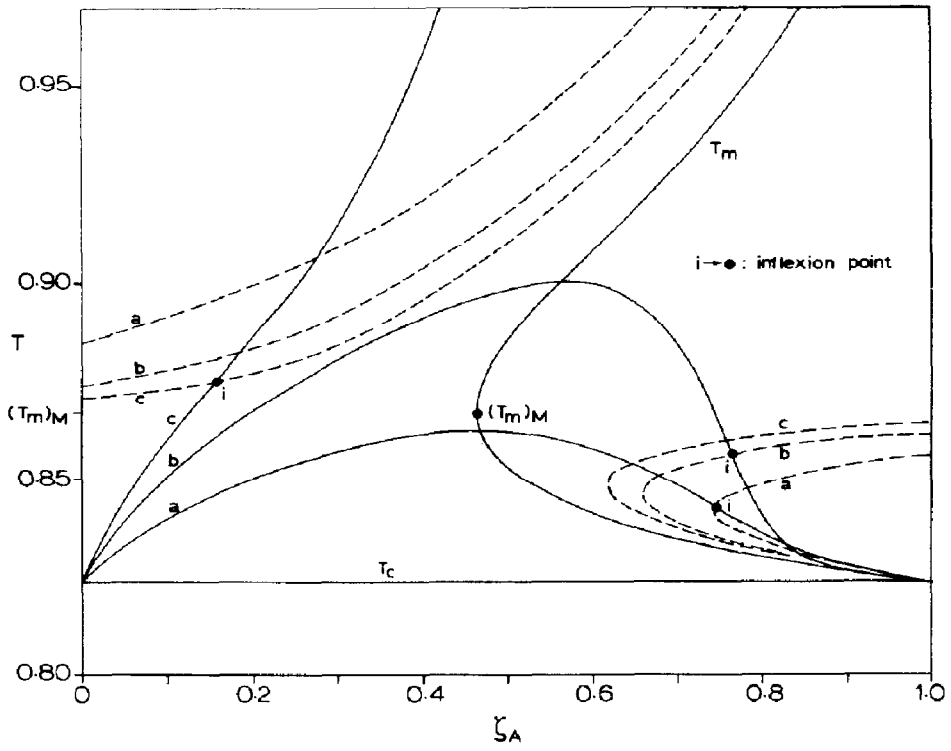

Fig. 8. Temperatures profiles in the reactor and loci of inflexion points curves (the dotted ones); $p = 2$, $H = 2$, $\gamma_p = 15$, $U^*/\Delta T_{ad} = 1.5$, $\Delta T_{ad} = 0.2 - a$; $0.4 - b$; $0.6 - c$.

CONCLUSIONS

Based on the model presented for two parallel, first order reactions in a cooled pseudohomogeneous reactor we may conclude that:

—the use of the maximum $(T_m)_M$ in the locus of maxima curve for the design of reactors is not justified for multiple reactions;

—the prescription of one maximum allowable temperature as determined in the laboratory and the design of a reactor on the basis of the kinetics of the desired reaction alone, can lead to erroneous results and considerable deviations in the integral selectivity found in the laboratory and on a large scale;

—the method outlined here requires kinetic information on both the desired and the undesired reaction;

—criteria for maintaining reactor selectivity require more stringent design and operating conditions than the criteria for the prevention of a runaway; the proposed criterion of keeping $U(T_{ma} - T_c)/d_t C_{A0}$ constant at a desired value enables us to select a practical set of reactor design parameters and to select new values for operating parameters at changing operating conditions. Simultaneously the reactor operates in the region of low parametric sensitivity, so that there is no danger of runaway.

—the use of the parameters T_R and also k_R, γ_p and p, which are characteristic for the set of reactions involved, leads to a generally valid set of dimensionless equations, which can be more easily manipulated than e.g. the coolant temperature. In the studies e.g. by Barkelew and Froment, the relevant dimensionless groups are very sensitive towards the values chosen for T_c and T_{ma}.

NOTATION

A	pre-exponential factor in Arrhenius equations, $m^3/kg\,s$
$A,B,C,$	constants defined in the Appendix
C	concentration of species, $kmol/m^3$
c_p	specific heat of reaction mixture, J/kgK
d_P	catalyst particle size, m
d_t	tube diameter, m
E	activation energy, J/kmol
H	$\Delta H_X/\Delta H_P$
ΔH	heat of reaction, J/kmol (exothermic)
k	reaction velocity constant, $m^3 kg\,s$
k_R	reference reaction velocity constant, $m^3/kg\,s$
L	reactor length, m
p	E_X/E_P
P	parameter defined in the text [eqns (30), (31)]
R	gas constant, 8.314 kJ/kmol K
R_w	rate of production of species per unit mass of catalyst, kmol/kg s
S_P	reactor selectivity
S_{XP}	X_X/X_P, reciprocal selectivity ratio
$S_{\bar{X}P}$	dX_X/dX_P, differential reciprocal selectivity ratio
T	temperature, K or °C
T_c	coolant temperature, K or °C

T_{li} temperature corresponding to the lower intersection point of locus of maxima curve and $X_A = 0$ axis
T_{ui} temperature corresponding to the upper intersection point of locus of maxima curve and $X_A = 0$ axis
T_m maximum reactor temperature (in the hot spot)
$(T_m)_M$ temperature corresponding to maximum of locus of maxima curve
T_{ma} maximum allowable reactor temperature, K
T_R reference temperature, K
u superficial gas velocity, m/s
U total heat transfer coefficient, W/m^2K
U^* $4U/k_R\rho_B\rho_g c_p d_t$
X relative degree of conversion
z coordinate in the direction of flow, m
Z z/L, dimensionless reactor length
Da $k_R\rho_B L/u$

Greek symbols

γ_p E_P/RT_R, dimensionless activation energy
θ_P reactor yield
κ k_P/k_R, dimensionless reaction velocity constant for the desired reaction
ρ_B bulk catalyst density, kg/m^3
ρ_g density of reaction mixture, kg/m^3
$\mathbf{T}$ T/T_R, dimensionless temperature
$\Delta\mathbf{T}_{ad}$ $\Delta H_P C_{A0}/T_R\rho_g c_p$, dimensionless adiabatic temperature rise of the desired reaction

Subscripts

A reactant
c coolant
i inflexion point
m maximum temperature or hot spot temperature
M maximum of locus of maxima curve
ma maximum allowable
P desired product
X undesired product
0 inlet conditions
L outlet conditions
ui upper intersection point with $X_A = 0$ axis
li lower intersection point $X_A = 0$ axis

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APPENDIX

An inspection of the temperature trajectories of Fig. 8 shows that a temperature runaway is inevitable if an inflexion point occurs before the hot spot temperature as e.g. in trajectory c. This was also observed for single reactions by van Welsenaere and Froment[3]. Therefore the condition for safe operation to avoid temperature runaway can be stated as:

$$\frac{d^2\mathbf{T}}{dX_A^2} < 0 \text{ for } \frac{d\mathbf{T}}{dx_A} > 0. \tag{a}$$

Differentiating (16) with respect to X_A leads to the following expression for the second derivative:

$$\frac{d^2\mathbf{T}}{dX_A^2} = \frac{\Delta\mathbf{T}_{ad}^2}{\kappa^2(1+\kappa^{p-1})\mathbf{T}^2(1-X_A)^2}[A(1-X_A)^2 + B(1-X_A) + C] \tag{b}$$

in which

$$A = \gamma_p(p-1)(H-1)\kappa^{p+1}(1+H\kappa^{p-1})$$

$$B = -\left(\frac{U^*}{\Delta\mathbf{T}_{ad}}\right)\kappa\{\gamma_p(p-1)(H-1)\kappa^{p-1}(\mathbf{T}-\mathbf{T}_c) + (1+H\kappa^{p-1}) \times [(1+\kappa^{p-1})\mathbf{T}^2 - \gamma(1+p\kappa^{p-1})(\mathbf{T}-\mathbf{T}_c)]\}$$

$$C = \left(\frac{U^*}{\Delta\mathbf{T}_{ad}}\right)(\mathbf{T}-\mathbf{T}_c)\{\left(\frac{U^*}{\Delta\mathbf{T}_{ad}}\right) \times [(1+\kappa^{p-1})\mathbf{T}^2 - \gamma_p(1+p\kappa^{p-1}) \times (\mathbf{T}-\mathbf{T}_c)] - \frac{1}{\Delta\mathbf{T}_{ad}}\kappa(1+\kappa^{p-1})^2\mathbf{T}^2\}.$$

Expression (b) is too complicated to represent the condition (a) in a simple form. However, equating (b) to zero leads to the relation between $\mathbf{T}_i$ and $(X_A)_i$ at the inflexion point:

$$A_i(1-X_{Ai})^2 + B_i(1-X_{Ai}) + C_i = 0. \tag{c}$$

The solution of this quadratic equation gives the expression for the locus of inflexion:

$$(X_{Ai})_{1,2} = 1 + \frac{B_i \mp \sqrt{(B_i^2 - 4A_iC_i)}}{2A_i} \tag{d}$$

with $-$ for $(X_{Ai})_1$ and $+$ for $(X_{Ai})_2$. According to (d) the locus of inflexion is determined by the reaction parameters γ_p, p and H and the operating variables $\mathbf{T}_c$, $\Delta\mathbf{T}_{ad}$ and U^*. Each locus of inflexion curve, as shown by the dotted lines in Fig. 8, has two branches. The branch $(X_{Ai})_1$ corresponds to the inflexion point before the hot spot, whereas the branch $(X_{Ai})_2$ corresponds to the inflexion point beyond the hot spot. The trajectories a and b do not intersect their locus of inflexion branch $(X_{Ai})_1$ whereas the trajectory c does. The trajectories which have no inflexion points before the hot spot can be considered as safe with respect to runaway.

In the case of the second criterion for low values of $\mathbf{T}_c$ the temperature $(\mathbf{T}_m)_M$ can be lower than $\mathbf{T}_{ma}$ and the trajectory can intersect the locus of maxima curve above $(\mathbf{T}_m)_M$. But runaway still will not occur provided the trajectory does not intersect its corresponding locus of inflexion branch $(X_{Ai})_1$ given by (d). This requires a numerical computation of the locus of inflexion branch $(X_{Ai})_1$ and the trajectory. As an approximation also a possible intersection of the locus of inflexion branch $(X_{Ai})_1$ and the tangent to the trajectory at the reactor inlet conditions ($T_0 = T_c$,

$X_{Ao} = 0$) can be considered. This requirement is more severe than the former one, as was discussed. The equation of the tangent to the trajectory at the inlet conditions given by (27) can be written as:

$$(X_A)_t = \frac{1 + \kappa_c^{p-1}}{\Delta T_{ad}(1 + H\kappa_c^{p-1})}(T - T_c). \qquad \text{(e)}$$

Equations (d) and (e) were solved numerically for many combinations of critical parameter values derived from the second criterion. The following ranges of parameter values were investigated: $1.1 < p < 4.0$; $5 < \gamma_p < 90$; $1.1 < H < 5.0$; $0.01 < \Delta T_{ad} < 1.0$; $3 < Da_c/Da_{min} < 9$ and $0.01 < (S'_{XP})_{ma} < 0.30$. Within this wide range of variation of each parameter no intersection between (d) and (e) was found: the locus of inflexion branch was always situated above the tangent to the critical trajectory.