

SAFE DESIGN AND OPERATION OF TANK REACTORS FOR MULTIPLE REACTIONS: UNIQUENESS AND MULTIPLICITY

K. R. WESTERTERP and E. JANSMA

Chemical Reaction Engineering Laboratories, Department of Chemical Engineering, Twente University of
Technology, P.O. Box 217, 7500 AE Enschede, Netherlands

(Received 2 February 1984; accepted in revised form 13 November 1984)

Abstract—A method is developed to design a tank reactor for unique operation and for two simultaneous or consecutive reactions of the first order. Dimensionless groups are introduced which are either exclusively representative for the properties of the reaction system or exclusively for the design and operating variables. In a plot of the dimensionless slopes of the heat withdrawal line versus the dimensionless residence time in the reactor the region is indicated, where operation under conditions of uniqueness is feasible. The method is illustrated with two industrial examples; the oxidation of naphthalene and of ethylene. Whereas under conditions of uniqueness the naphthalene oxidation is shown to be feasible in a tank reactor, the ethylene oxidation cannot be executed economically in a tank reactor.

INTRODUCTION

With the theory of the autothermal reactors van Heerden [1, 2] has demonstrated how for a single, first order reaction at most two stable and one unstable steady states exist in which a tank reactor may operate at definite conditions of heat withdrawal rate HWR and chemical heat production rate HPR. Westerterp [3] showed that for two simultaneous or consecutive reactions even five steady states are possible, three stable and two unstable ones. The design engineer and the operator in general desire to avoid this situation of multiple steady states (multiplicity) and aim at an operation with only one, stable steady state (uniqueness).

Uppal *et al.* [4, 5] studied the dynamic behaviour of a tank reactor for a single first order reaction, classified types of dynamic behaviour such as limit cycles, extinction and ignition, and defined regions of multiplicity and uniqueness. Aris [6] developed criteria for uniqueness for a single first order reaction. Balakotaiah and Luss in pioneering papers [7, 8, 9, 10] solved this problem for multiple reactions and defined uniqueness criteria in tank reactors for both two reaction and multireaction systems as well. Their criteria are difficult to handle, because the kinetic rate constants they use in the relevant dimensionless groups are based on the operating and design conditions of the reactor, such as T_o , T_c , C_{A_o} , U and Da , and therefore are no true constants. We therefore in this study will use a different set of dimensionless groups, which are either representative for the reaction system alone or exclusively for the design and operating conditions. In this study we will determine under what design and operating conditions a tank reactor—for a particular reaction system—can be operated safely in a state of uniqueness. We will restrict ourselves to a reaction system of two first order parallel or consecutive reactions and to systems for which $E_X/E_P = p > 1$ for the reasons outlined elsewhere [3].

The method of deriving the relevant dimensionless groups has been discussed by Westerterp *et al.* [3, 11, 12, 13, 14] and will not be repeated here. They are based on the reference kinetic rate constant k_R taken at the reference temperature T_R , where both kinetic rate constants k_P and k_X are equal. Here k_R and T_R are true constants, which are representative for the reaction system under study. The dimensionless groups p , γ_P and H are representative for the reaction system and U^* , Da , ΔT_{ad} , T_o and T_c for the operating and design conditions, see the notation for their significance.

BASIC EQUATIONS FOR A TANK REACTOR

We consider simultaneous reactions (SR) of the type $A \xrightarrow{k_P} P$ and $A \xrightarrow{k_X} X$ or consecutive reactions (CR) of

the type $A \xrightarrow{k_P} P \xrightarrow{k_X} X$, all of the first order and with P as the desired product. For constant physical and thermochemical properties, constant coolant and reactor inlet temperatures and a reactor feed containing only reactant A , the operating points for the tank reactor are found for $HWR = HPR$. In dimensionless form—see the notation—the well-known expressions for the tank reactor are:

for the heat withdrawal rate:

$$HWR = \frac{(1 + U^*Da)}{\Delta T_{ad}} \left[T - \frac{T_o \times U^*DaT_c}{1 + U^*Da} \right] \quad (1)$$

and for the heat production rate for SR:

$$HPR_{SR} = \left[\frac{\kappa Da + H\kappa^p Da}{1 + \kappa Da + \kappa^p Da} \right] \quad (2)$$

or for CR:

$$HPR_{CR} = \frac{\kappa Da}{1 + \kappa Da} \left[1 + H \frac{\kappa^p Da}{1 + \kappa^p Da} \right] \quad (3)$$

The maximum values of the heat production rates are H and $1 + H$ respectively. To abbreviate we can also

introduce an apparent feed inlet temperature T_M :

$$T_M = \frac{T_o + U^*DaT_c}{1 + U^*Da} = T_o \frac{1 + U^*DaT_c/T_o}{1 + U^*Da} \quad (4)$$

We should realize that T_M is not a constant, but strongly dependent on the operating and design conditions τ , U , A , T_o and T_c .

DETERMINATION OF THE DESIRED REACTION TEMPERATURE

The yield of a tank reactor is given by $\theta_P = S_P X_A$. For cases, where non-converted reactant A can be recovered from the reactor product and recycled to the reactor a maximum selectivity S_P should be aimed at [15], otherwise the yield should be at its maximum. These requirements can be deviated from only on economic grounds. The selectivity of a tank reactor is for simultaneous reactions:

$$S_{P,SR} = [1 + \kappa^p]^{-1} \quad (5)$$

and for consecutive reactions:

$$S_{P,CR} = [1 + \kappa^p Da]^{-1} \quad (6)$$

For $p > 1$ the selectivity increases with decreasing reactor temperatures, so with recycle of non-converted reactant the reactor should be operated at the lowest possible reactor temperature in as far as selectivity is concerned. With $\kappa = \exp[\gamma_p(1 - 1/T)]$ eq. (5) directly sets the required reactor temperature for SR for a preset value of $S_{P,SR}$; for CR the required reactor temperature for a fixed value of $S_{P,CR}$ still depends on the residence time Da in the reactor.

The recycle ratio R , defined as the total reactor load divided by the fresh feed, is given by $R_{CR} = 1/X_A = 1 + (\kappa Da)^{-1}$. There are practical economic limits to the value of R , further at no recycle $R = 1$. In Fig. 1 an

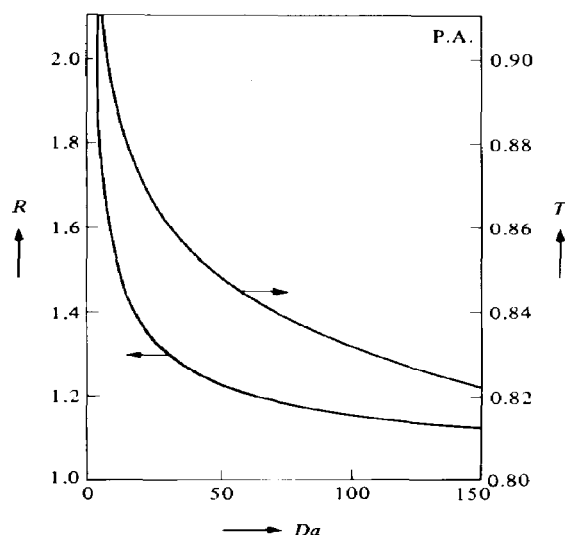


Fig. 1. Recycle ratio and optimum temperature for consecutive reactions as a function of the residence time in the reactor and for $S_{P,CR} = 0.80$. For data see Fig. 4.

illustration is given of the corresponding values of T and R as a function of Da for a desired value of $S_{P,CR}$. For SRs the recycle ratio is given by $R = 1 + S_{P,SR}/\kappa Da$. R as a function of Da can be determined, because at a desired value of $S_{P,SR}$ the value of κ and of T is known from eq. (5) for a given set of reactions with known p and γ_p . Vice versa, for practical values of R and Da the range of values $S_{P,SR}$, that can be obtained in practice, can be determined: this is shown in Fig. 2.

In case non-converted reactant cannot be recycled the maximum attainable yield has to be aimed at. In a tank reactor the yield is given for simultaneous reactions by:

$$\theta_{P,SR} = \frac{\kappa Da}{1 + \kappa Da + \kappa^p Da} \quad (7)$$

and for consecutive reactions by:

$$\theta_{P,CR} = \frac{\kappa Da}{(1 + \kappa Da)(1 + \kappa^p Da)} \quad (8)$$

The optimum reactor temperature T_{opt} , giving the highest yield at a given reactor residence time, is found with the condition $\partial\theta_P/\partial T|_{Da} = 0$ [3]. This leads to the conditions for SR:

$$1 + (1 - p)\kappa^p Da = 0 \quad (9)$$

and for CR:

$$p\kappa^p Da(1 + \kappa Da) - (1 + \kappa^p Da) = 0 \quad (10)$$

For CRs from eq. (10) T_{opt} can be found with a trial and error procedure; for SRs an explicit expression can be found. The optimum temperature is

$$T_{SR,opt} = \left[1 + \frac{1}{p\gamma_p} \ln(p-1)Da \right]^{-1} \quad (11)$$

Introducing the value of $T_{SR,opt}$ into eq. (7) gives the value of the optimum yield for SRs:

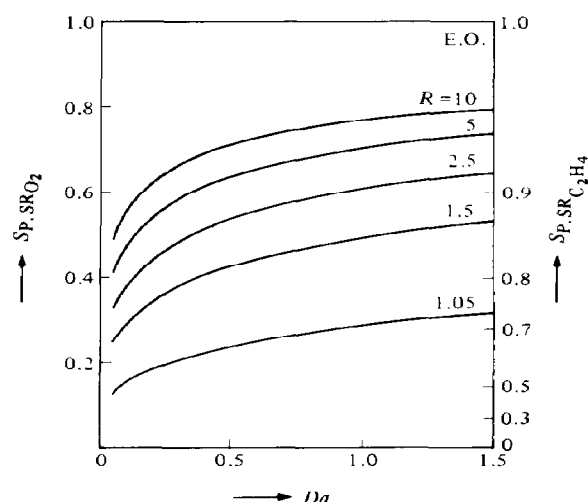


Fig. 2. Selectivity as a function of the recycle ratio and the reactor residence time for simultaneous reactions. For data see Fig. 8.

$$\theta_{P,SR,opt} = \frac{[(p-1)Da]^{(p-1)/p}}{p + [(p-1)Da]^{(p-1)/p}} \quad (12)$$

We see that for SRs the optimum yield is only determined by the reactor residence time Da and p , the ratio of the activation energies of the two reactions. For practical values of Da the obtainable yields for SRs can now be determined with eq. (12) and for CRs by solving eq. (10) for T_{opt} and introducing this value into eq. (8). This is shown in Fig. 3 for a particular case of CR's. For SR's similar curves are obtained. In the following section we will explore whether unique steady state operation can be achieved in practice for the desired values of S_p or θ_p .

CONSTRAINTS TO THE OPERATING AND DESIGN CONDITIONS

The conditions in a tank reactor cannot be chosen at will. Besides the requirement of uniqueness, there are also practical limits to the reactor lay-out and its operation. The various constraints will be discussed now and illustrated in Fig. 4, where the dimensionless group $(1 + U^*Da)/\Delta T_{ad}$ is plotted as a function of Da . The dimensionless group $(1 + U^*Da)/\Delta T_{ad}$ is representative for the slope of the dimensionless HWR expression (1) in a HWR T plot.

Constraints on the residence time

There are certain limits to the residence time, mainly determined by the reactor volume that can be installed and well mixed and by the time required for reaching steady conditions after start-up or operational changes. For liquid phase reactions in a tank reactor e.g. τ is usually between 500 and 10000 s and for gas-solid reactions in fluidized beds between 1 and 10 s. These limits, which are not sharp, are given in Fig. 4 by lines 1 and 2; between these lines reactor operation is feasible.

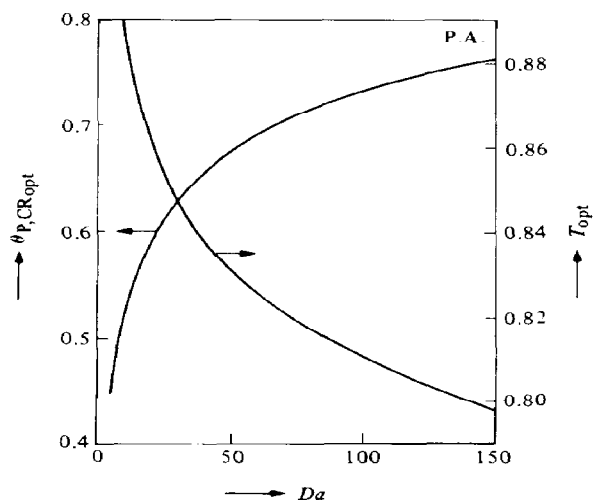


Fig. 3. Optimum yield and optimum temperature as a function of the reactor residence time for consecutive reactions. For data see Fig. 4.

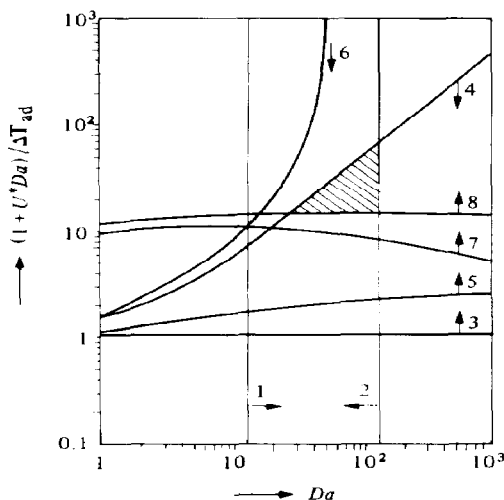


Fig. 4. Constraints for the design and operation of a tank reactor. The shaded area contains the region of possible operation. The oxidation of naphthalene. Data are $k_R \rho_B = 13$ s, $T_R = 770$ K, $p = 2.19$, $H = 1.75$, $\gamma_P = 13.5$, $\Delta T_{ad} = 0.96$, $U^*_{max} = 0.46$, $\theta_p = 0.80$, $T_o = 0.47$ and no recycle.

Constraints on the cooling area

The cooling capacity is represented by the number $U^* = UA/k_R \rho c_p V_R$. For the adiabatic reactor $U^* = 0$, so that the horizontal line 3 at $1/\Delta T_{ad}$ gives a lower limit. The maximum amount of cooling area—in the reactor or an external cooler—sets an upper limit U^*_{max} to U^* , which results in line 4 in Fig. 4 for a given value of $\Delta T_{ad} \cdot U^*_{max}$ is determined by the overall heat transfer coefficient and by the maximum cooling area, that can be installed per unit of reactor volume. Reactor operation is feasible between lines 3 and 4. Both lines are also influenced by $\Delta T_{ad} = \Delta H_A C_{A0}/\rho c_p T_R$, that is by the reactant concentration in the feed—and move downward with increasing reactant concentrations. The maximum value of UA/V_R depends on the construction possibilities (internal and/or external cooling, tube diameters, coils or jacket cooling, etc.) and on the energy consumption for mixing in the reactor and for pumping of the coolant.

Constraints on the reactor feed and coolant temperatures

Constraints on T_o and T_c have to be studied in conjunction, because T_M is the determining factor. T_o usually is not lower than the temperature of the surroundings and normally taken at the temperature at which the reactor feed is available in the plant. The value of T_c depends on the choice of the coolant, e.g. cooling water, but is much higher if steam is produced (180–320°C), or oils (200–400°C) or molten salts (150–500°C) are used. These ranges together with T_o and U^*Da give a range of possible values for T_M . For a reactor, where T_{opt} , as a function of Da if necessary, has been determined with eqs (5), (6), (9) and (10), this leads to two conditions

for the $T_{M \min}$:

$$\frac{1 + U^*Da}{\Delta T_{ad}} \geq \frac{HPR(T_{opt})}{(T_{opt} - T_{M \min})} \quad (13)$$

and for the $T_{M \max}$:

$$\frac{1 + U^*Da}{\Delta T_{ad}} \leq \frac{HPR(T_{opt})}{(T_{opt} - T_{M \max})} \quad (14)$$

The last condition is only realistic if $T_c < T_{opt}$. These two conditions are shown as lines 5 and 6 in Fig. 4; between these lines reactor operation is feasible. In Fig. 5 is shown how these lines vary between $T_{M \min}$ and $T_{M \max}$ for varying values of T_c/T_o .

The stability requirement for the operating point

For an operating point to be stable the slope of the HWR line must be higher than the slope of the HPR curve at T_{opt} . After partial differentiation at constant Da we can find the conditions for SRs:

$$\frac{1 + U^*Da}{\Delta T_{ad}} > \frac{\gamma_p}{T_{opt}^2} \times \left\{ \frac{\kappa Da + H p \kappa^p Da + (H - 1)(p - 1) \kappa Da \kappa^p Da}{(1 + \kappa Da + \kappa^p Da)^2} \right\}_{T = T_{opt}} \quad (15)$$

and for CRs:

$$\frac{1 + U^*Da}{\Delta T_{ad}} > \frac{\gamma_p}{T_{opt}^2} \left\{ H p \frac{\kappa Da \kappa^p Da}{(1 + \kappa Da)(1 + \kappa^p Da)^2} + \frac{\kappa Da}{(1 + \kappa Da)^2} + H \frac{\kappa Da \kappa^p Da}{(1 + \kappa Da)^2(1 + \kappa^p Da)} \right\}_{T = T_{opt}} \quad (16)$$

This condition leads to line 7 in Fig. 4, above this line reactor operation is feasible.

The uniqueness requirement

There is no multiplicity if $HWR(T_{opt}) = HPR(T_{opt})$ is the only solution; this means that in Fig. 6a the

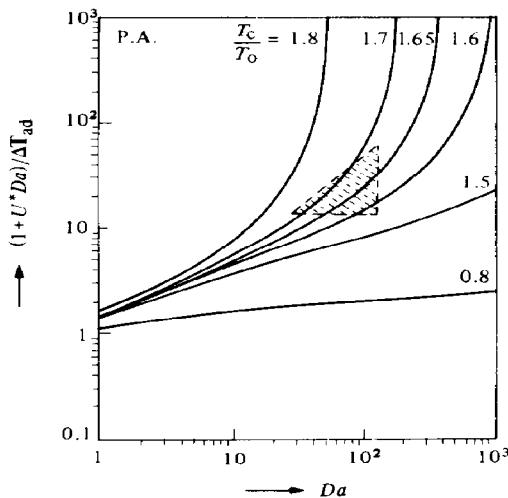


Fig. 5. Lines of constant cooling temperatures in a HWR slope- Da plot. Same data as for Fig. 4.

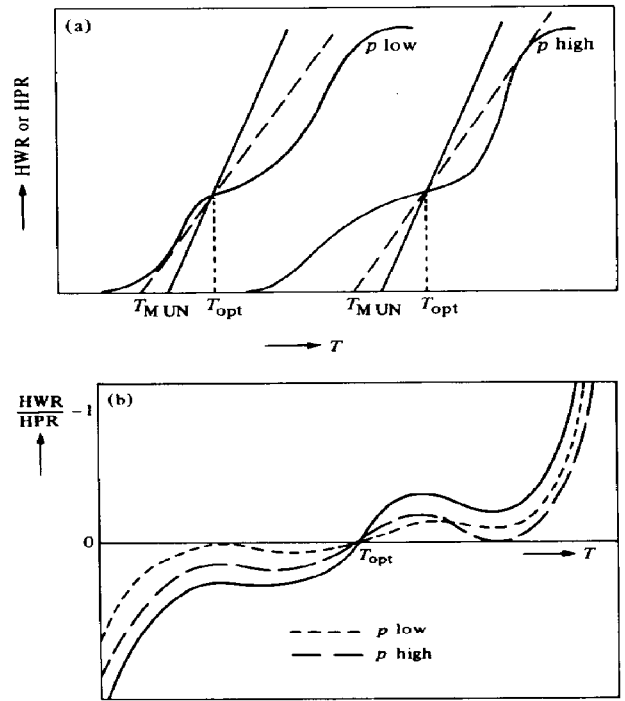


Fig. 6. Plot of (a) HWR and HPR and (b) $HWR/HPR - 1$ vs the reactor temperature for two consecutive or simultaneous reactions.

HWR-line only at $T = T_{opt}$ has a point of intersection with the HPR-curve. This is again illustrated in Fig. 6b, where $F = HWR/HPR - 1$ is plotted vs T . Now if in Fig. 6a the slope of the HWR-line passing through the point $HPR(T_{opt}), T_{opt}$ is diminished, eventually a value of the slope is reached where the HWR line touches the HPR-curve—either in the lower or upper branch of the HPR-curve, see the interrupted lines in Fig. 6a—and two possible operating points are obtained; in this case T_M reaches the value T_{MUN} . Therefore, as long as the slope of the HWR-line $(1 + U^*Da)/\Delta T_{ad}$ is higher than this critical slope, we have conditions of uniqueness. This leads to the requirement

$$\frac{1 + U^*Da}{\Delta T_{ad}} > \frac{HPR(T_{opt})}{T_{opt} - T_{MUN}} \quad (17)$$

This condition is plotted as line 8 in Fig. 4; above this line reactor operation is feasible under conditions of uniqueness. From left to right along line 8 the value of T_{MUN} decreases, see Fig. 5. Line 8 in Fig. 4 is independent of the reactant concentration in the feed. We see that line 8 is almost horizontal, which means that the minimum slope of the HWR line for uniqueness is almost constant; e.g. with increasing Da both T_{opt} —determined with eqs (9) or (10)—and T_{MUN} decrease, but the difference $T_{opt} - T_{MUN}$ remains almost constant. The value of T_{MUN} can easily be found with a search routine, in which a starting value of T_M is changed until $HWR/HPR - 1 = 0$ for a certain value of $T \neq T_{opt}$. For the lower branch of the HPR-curve where $T < T_{opt}$, only the temperature region

from $T_{opt} - \Delta T_{ad} \text{HPR}(T_{opt})/(1 + U^*Da)$ to T_{opt} has to be searched; for all values of $T_M > T_{MUN}$ we find $[\text{HWR}(T)/\text{HPR}(T)] - 1 < 0$. As soon as for a certain value of $T \neq T_{opt}$ in the temperature range mentioned we obtain $\text{HWR}(T)/\text{HPR}(T) - 1 = 0$, we have found T_{MUN1} , the minimum value of T_M to maintain conditions of uniqueness in the lower branch of the HPR-curve. For the upper branch of the HPR curve where $T > T_{opt}$, only the temperature region from T_{opt} up till $T_{opt} + \Delta T_{ad} [m - \text{HPR}(T_{opt})]/(1 + U^*Da)$ has to be searched. Here $m = 1 + H$ for CR's, $m = H$ for SR's with $H > 1$ and $m = 1$ for SR's with $H \leq 1$. For the upper branch we have $\text{HWR}/\text{HPR} - 1 > 0$ as long as $T_M > T_{MUNu}$. Finally for T_{MUN} the highest value of T_{MUN1} or T_{MUNu} is taken as the minimum value T_{MUN} , at which conditions of uniqueness are obtained for given values of T_{opt} , U^* and Da and a given reaction system.

Possible region of operation

All the constraints and requirements mentioned leave the shaded area in Fig. 4 as the allowable region of operation, where all conditions are fulfilled. We studied the influence of the various constraints but almost always the feasibility region is bounded by the lines 4, 8, 1 and 2 provided the choice of the cooling medium and T_o has been correct. In Fig. 7 a feasibility diagram has been given. Now assume that we want to operate the reactor at a certain residence time Da . For this value of Da point A gives the minimum value of $(1 + U^*Da)/\Delta T_{ad}$ for which a unique operation is feasible. By substituting U_{max}^* in this value, ΔT_{admax} or the maximum allowable reactant concentration in the feed is found. Vice versa, for a chosen design value of ΔT_{adD} , in point A the minimum value of the cooling area U_{min}^* will be found. With these boundaries we choose design values U_D^* and ΔT_{adD} , for which U_{min}^*

$< U_D^* < U_{max}^*$ and $\Delta T_{adD} < \Delta T_{admax}$, which correspond to point D. The flexibility of the reactor is now given by line 4 with $(1 + U_D^*Da)/\Delta T_{ad}$, where in the points B and C the minimum and maximum allowable values of Da are found. For values of ΔT_{ad} lower than ΔT_{adD} line 4 moves upward, for higher values downward till the limit for uniqueness is reached in point A of the intersection of lines 4 and 8. This leads to a design procedure.

DESIGN PROCEDURES FOR UNIQUE CONDITIONS IN A TANK REACTOR

We will first discuss a design procedure, where a certain yield has to be achieved. A possible procedure—see Fig. 7—could go along the following lines:

1. Determine for the reaction system under consideration the values of k_R , T_R , p , γ_P and H .
2. Determine from practical considerations the allowable values of the reactor residence time V_R/Q and the corresponding values of Da_{min} and Da_{max} .
3. Determine $\theta_{P,opt}$ as a function of Da with eqs (9) or (10). If the values of $\theta_{P,opt}$ are too low in the allowable Da -range, the reaction cannot be executed economically in a tank reactor without recycle of non-converted reactant.
4. With equation (17) determine the boundary line for uniqueness. Below this line either blow-out or runaway of the reactor can occur.
5. Choose a design value of Da_D and determine for point A in Fig. 7 the values of U_{min}^* and ΔT_{admax} . If ΔT_{admax} is much lower than the ΔT_{admax} , which can be handled in a cooled tubular reactor [11–14], the reaction without recycle cannot be carried out in a tank reactor, because feed dilution is very costly.
6. Now choose design values for U_D^* and ΔT_{adD} (point D).
7. Determine the values of T_M obtained in points B and E in Fig. 7. With the values T_{MB} and T_{ME} and with U_D^* determine with equation (4) the values of T_o and $(T_c/T_o)_{max}$ and $(T_c/T_o)_{min}$ for the cooling system. If the range of T_{cmax} to T_{cmin} is not practical, choose a different coolant or change T_o till a suitable range of T_c is obtained for the Da range under consideration. Check the coolant temperature increase with:

$$\frac{\Delta T_c}{\Delta T_{ad}} = \text{HPR} \frac{\tau_c (\rho c_p)_R V_c}{\tau (\rho c_p)_c V_R}$$

and see whether it is acceptable. τ_c is the residence time of the coolant in the cooling tubes; V_c the volume of the cooling tubes and V_R the net reaction volume. $(\rho c_p)_R/(\rho c_p)_c$ is the ratio of the heat capacities of the reaction mixture and the coolant in J/m^3K .

8. Now that the design values for U_D^* , Da_D , ΔT_{adD} and T_{MD} (or T_{cD} or T_{oD}) have been fixed, the optimum cooling temperatures for the range of allowable Da values can be determined by solving the implicit

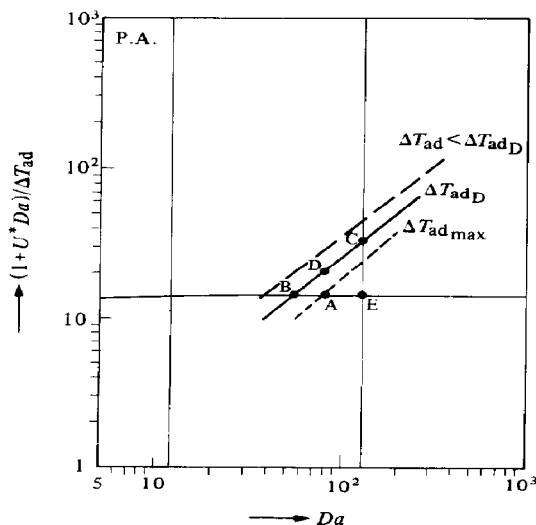


Fig. 7. The design procedure for a tank reactor for multiple reactions and a unique operation. Same data as for Fig. 4.

equation:

$$\frac{1 + U_D^* Da}{\Delta T_{adD}} = \left\{ \text{HPR}_{\text{opt}} \left[\frac{T_{\text{opt}} - T_o}{1 + U_D^* Da T_c / T_o} \right] \right\}$$

for T_c . Now also the required range of T_c values is known and also the cooling system can be further elaborated for the design.

9. Check whether the other constraints (lines 3, 5, 6 and 7) can be neglected.

The design of a reactor, where a certain *selectivity* has to be achieved, goes along similar lines. In this case T_{opt} , as a function of Da if necessary, is determined with eq. (5) or (6) and the boundary line (17) is determined with the corresponding values of T_{opt} . We will now discuss two examples.

TWO EXAMPLES

We will demonstrate the usefulness of the method outlined for two examples, of which the first one is carried out in practice in fluid bed reactors and the second one is not. We, however, here will discuss their feasibility in a tank reactor.

The data used to construct Figs 1, 3, 4, 5 and 7 all are based on the reaction system of the *air oxidation of naphthalene* for the production of phthalic anhydride. This reaction, which consists of two *CR*'s of the first order, is carried out in a fluid bed, which is assumed to behave as a tank reactor. The reaction system and the relevant parameters have been amply discussed elsewhere by Westerterp [3] and by Westerterp and Overtoom [14]. The design is based on the following data: $(UA/V_R)_{\text{max}} = 8000 \text{ W/m}^3\text{K}$, $C_{A0} = 0.8 \text{ mol}\%$ and $T_o = 90^\circ\text{C}$ to avoid naphthalene deposits in the reactor feed lines. In this case $k_R \rho_B = 13 \text{ s}^{-1}$, so that we take $Da_{\text{min}} = 13$ and $Da_{\text{max}} = 130$. From Fig. 3 we read that in this range of Da values a yield of 0.54 to 0.76 can be obtained at optimum reactor temperatures. For the design we take $Da_D = 80$, which leaves us still sufficient margin to underload the reactor. On the boundary line for uniqueness we find for point A in Fig. 7, that $(1 + U^* Da) / \Delta T_{ad} \geq 14.4$. For $C_{A0} = 0.8 \text{ mol}\%$ we have $\Delta T_{ad} = 0.96$, so that $U_{\text{min}}^* = 0.16$; this corresponds to $UA/V_R = 2800 \text{ W/m}^3\text{K}$ or to $A = 7 \text{ m}^2/\text{m}^3$ reactor volume for $U = 400 \text{ W/m}^2\text{K}$. If we would install the maximum cooling area then $U_{\text{max}}^* = 0.46$, which gives $\Delta T_{ad \text{ max}} = 2.60$ or $C_{A0} = 2.17 \text{ mol}\%$.

We now choose $U_D^* = 0.23$ and $Da_D = 80$, which leaves us sufficient operating flexibility to cope with plant upsets and enables us to work under unique conditions for $C_{A0} = 0.8 \text{ mol}\%$. From Fig. 3 we see that $\theta_{P,D} = 0.72$ at $T_{\text{opt},D} = 0.87$ (397°C), from Fig. 5 for $T_o = 0.47$ we read that T_c ranges from 0.74 to 0.81 ($297\text{--}351^\circ\text{C}$). At the design point $T_c = 0.78$ (324°C). We have to use oil or molten salt cooling. The temperature increase of the coolant, which depends on the design of the cooling coils, can easily be kept within a few degrees. The reactor can handle feed concen-

trations up to $C_{A0} < 1.7 \text{ mol}\%$ and residence times between $4 < \tau < 10 \text{ s}$ for $C_{A0} = 0.8 \text{ mol}\%$, still maintaining unique conditions.

The data in Fig. 2 and 8 refer to the *oxidation of ethylene with oxygen*. The reaction system consists of two *SR*'s of the first order and has been discussed by Westerterp and Ptasiński [12], for the relevant data see that paper. This reaction is carried out in practice in cooled tubular reactors with $R \approx 2.5$ and a selectivity towards ethylene of 0.75, which corresponds with $S_{P,PR} = 0.33$ towards oxygen. The tubular reactors are run with $C_{A0} \approx 6 \text{ mol}\%$; this is a limit to avoid explosive mixtures.

For our study we take $(UA/V_R)_{\text{max}} = 8000 \text{ W/m}^3\text{K}$ and $T_o = 50^\circ\text{C}$. For this reaction system $k_R \rho_B = 0.12 \text{ s}^{-1}$, so that $Da_{\text{min}} = 0.12$ and $Da_{\text{max}} = 1.2$. From Fig. 2 we can read, that for $R = 2.5$ a range of selectivities towards ethylene can be achieved from 0.80 to 0.91. However, for these high selectivities reactor temperatures are so low that unique operation in a tank reactor is impossible. We therefore will aim at a selectivity of 0.75, to which corresponds a range of recycle ratios of 1.07 to 1.69 according to Fig. 2.

Figure 8 gives the design plot for the ethylene oxide reactor for a selectivity of 0.75 towards ethylene. The region of feasibility is extremely small. With $U_{\text{max}}^* = 9.43$ and $\Delta T_{ad} = 1.21$ (6 mol% oxygen) the allowable Da range is 0.75–1.20, which we consider too narrow. This means that no sufficient cooling area can be built into a tank reactor—at the available temperature difference between the fluid bed and the coolant—in order to cope with the high heat evolution with $C_{A0} = 6 \text{ mol}\%$. The value of R is low (≈ 1.15), which means that the oxygen is nearly consumed ($X_A \approx 0.87$). We can further derive that sufficient flexibility is obtained for feed concentrations of around 3 mol% oxygen, but we have to realize that a reduction of the oxygen concentration to a half, doubles the recirculation of hydrocarbons and inert. This is most probably not an economic proposition.

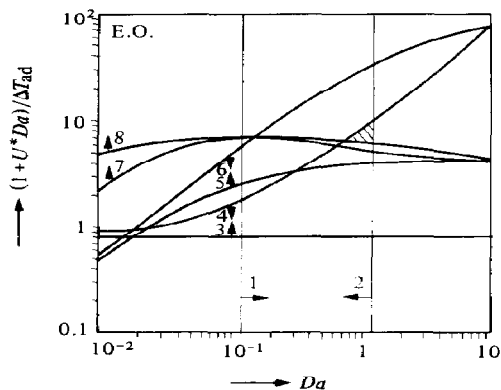


Fig. 8. The design diagram for the ethylene oxidation (simultaneous reactions, recycle of non-converted reactant). Data are $k_R \rho_B = 0.12 \text{ s}^{-1}$, $T_R = 549 \text{ K}$, $p = 1.50$, $H = 2.25$, $\gamma_P = 13.1$, $\Delta T_{ad} = 1.22$, $U_{\text{max}}^* = 9.43$ and $T_o = 0.59$.

DISCUSSION AND CONCLUSIONS

The method outlined of plotting all the design and operation constraints in a diagram of the dimensionless slope of the HWR-line vs the dimensionless residence time in the reactor gives us a practical means to the study of the feasibility of two simultaneous or consecutive reactions of the first order in a tank reactor and gives useful results for the reactor design and unique operation. The method of choosing our dimensionless groups is based on the properties k_R and T_R of the reaction system under study. For the reactor design and operation we have five dimensionless groups, which are truly and exclusively representative for the residence time in the reactor Da , the overall heat transfer coefficient and cooling area per unit of reactor volume U^* , the reactant concentration in the feed ΔT_{ad} , the coolant temperature T_c or the reactor feed inlet temperature T_o .

The method of choosing dimensionless groups used in other studies and which is based on the temperature $T_M = (T_o + GT_c)/(1 + G)$ with $G = UA/\rho c_p Q$ as a reference temperature and on $Da' = k_{TM} V_R/Q$ leads to ever changing values of T_M and of Da' , as soon as T_o , T_c , A , V_R or Q is changed. Further for one specific reactor G itself is not a constant, but also a function of Da' , because $UA/\rho c_p Q = UA/k_{TM} \rho c_p V_R^* Da'$. As k is a strongly temperature dependent function, Da' varies rapidly at changing T_o or T_c even for reactors with a constant residence time. Moreover, for each individual reaction in the reaction system a different, temperature dependent Damköhler number is found, which leads to multidimensional spaces to explore regions of uniqueness, which seriously hampers the understanding and their use for design purposes.

Our method can easily be extended to reactions of different orders and to multireaction networks. In the latter case we have to derive k_R and T_R from the kinetic rate constants of the desired and the main undesired reaction. For each additional reaction, e.g. the formation of Y , we can introduce $k_{RY} = \alpha k_R$, $k_Y = \beta k^q$ with $E_Y/E_P = q$ and $H' = \Delta H_Y/\Delta H_P$. We now have additional dimensionless groups to describe the properties of the reaction system, but still have the same five dimensionless numbers to describe the reactor design and operation variables, so that we still can study the design of a tank reactor in one, two-dimensional plot. This will be treated in a following paper.

NOTATION

A	pre-exponential factor, $m^3/kg s$
A	total cooling area in reactor, m^2
C	concentration, $kmol/m^3$
c_p	specific heat of reaction mixture, $J/kg K$
Da	$k_R \rho_B \tau$; dimensionless residence time, Damköhler number
E	activation energy, $J/kmol$
H	$\Delta H_X/\Delta H_P$; ratio of reaction heats
ΔH	heat of reaction (exothermic), $J/kmol$
HPR	(dimensionless) heat production rate

HWR	(dimensionless) heat withdrawal rate
k	reaction rate constant, $m^3/kg s$
P	E_X/E_P ; ratio of activation energies
Q	volumetric flow rate, m^3/s
R	gas constant, $J/kmol K$
R	recycle ratio, reactor load/fresh feed
S_P	selectivity, $C_P/(C_{A0} - C_A)$
T	temperature, K or $^{\circ}C$
T_M	$(T_o + U^* Da T_c)/(1 + U^* Da)$
T_{MUN}	minimum value of T_M at which conditions of uniqueness can be obtained, K or $^{\circ}C$
T_R	reference temperature, K
U	total heat transfer coefficient, $W/m^2 K$
U^*	$(UA/k_R \rho_p c_p V_R)$
V_R	total reaction volume, m^3
X	conversion
γ_P	E_P/RT_R ; dimensionless activation energy
θ_P	yield, C_P/C_{A0}
κ	k_P/k_R ; dimensionless reaction rate constant for the desired reaction
ρ_B	bulk catalyst density, $kg cat/m^3$ reactor volume
ρ	density of the reaction mixture kg/m^3
T	T/T_R ; dimensionless temperature
ΔT_{ad}	$(\Delta H_P C_{A0}/\rho c_p T_R)$; dimensionless adiabatic temperature rise of the desired reaction
τ	V_R/Q , residence time in the reactor, s

Subscripts

A	reactant
c	coolant
CR	consecutive reactions
D	design
max	maximum
min	minimum
o	inlet conditions
opt	optimum
P	desired product
SR	parallel reactions
X	undesired product X
Y	undesired product Y

REFERENCES

- [1] Van Heerden C., Autothermic processes, *Ind. Engng. Chem.* 1953, **45** 1242.
- [2] Van Heerden C., The character of the stationary state of exothermic processes, *Chem. Eng. Sci.* 1958 **8** 133.
- [3] Westerterp K. R., Maximum allowable temperatures in chemical reactors, *Chem. Engng. Sci.* 1962 **17** 423.
- [4] Uppal A., Ray W. H. and Poore A. B., On the dynamic behaviour of continuous stirred tank reactors, *Chem. Engng. Sci.* 1974 **29** 967.
- [5] Uppal A., Ray W. H. and Poore A. B., The classification of the dynamic behaviour of continuous stirred tank reactors—influence of reactor residence time, *Chem. Engng. Sci.* 1976 **31** 205.
- [6] Aris R., On stability criteria of chemical reaction engineering, *Chem. Engng. Sci.* 1969 **24** 149.
- [7] Balakotaiah V. and Luss D., Multiplicity features of reacting systems, *Chem. Engng. Sci.* 1983 **38** 1709.
- [8] Balakotaiah, V. and Luss D., Exact steady-state multiplicity criteria for two consecutive or parallel reactions in

- lumped-parameter systems, *Chem. Engng Sci.* 1982 **37** 433.
- [9] Balakotaiah V. and Luss D., Structure of the steady-state solutions of lumped-parameter chemically reacting systems, *Chem. Engng Sci.* 1982 **37** 1611.
- [10] Balakotaiah V. and Luss D., Multiplicity criteria for multireaction and networks, *A.I.Ch.E. J.* 1983 **29** 552.
- [11] Westerterp K. R. and Ptasincky K. J., Safe design of cooled tubular reactors for exothermic, multiple reactions. Parallel reactions. Development of criteria, *Chem. Engng Sci.* 1984 **39** 235.
- [12] Westerterp K. R. and Ptasincky K. J., The design and operation of an ethylene oxide reactor, *Chem. Engng Sci.* 1984 **39** 245.
- [13] Westerterp K. R. and Overtoom R. R. M., Safe design of cooled tubular reactors for exothermic, multiple reactions. Consecutive reactions, *Chem. Engng Sci.* 1985 **40** 155.
- [14] Westerterp K. R. and Overtoom R. R. M., The design and operation of a naphthalene oxidation reactor, accepted by *Chem. Engng Sci.*
- [15] Westerterp K. R., van Swaaij W. P. M. and Beenackers A. A. C. M., *Chemical Reactor Design and Operation*, 1984, Wiley, New York.