INCORPORATION OF STATISTICAL DISTRIBUTIONS OF PARTICLE PROPERTIES IN CHEMICAL REACTOR DESIGN AND OPERATION: THE COOLED TUBULAR REACTOR

R. J. WIJNGAARDEN[†] and K. R. WESTERTERP[‡]

Chemical Reaction Engineering Laboratories, Department of Chemical Engineering, Twente University,
PO Box 217, 7500 AE Enschede, The Netherlands

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Abstract—Pellet heat and mass transfer coefficients inside packed beds do not have definite deterministic values, but are stochastic quantities with a certain distribution. Here, a method is presented to incorporate the stochastic distribution of pellet properties in reactor design and operation models. The theory presented is illustrated with a number of examples. It is shown that pellet-scale statistics have an impact on cooled tubular reactor design and operation. Cooled tubular reactor design is determined to a large extent by the objective that run away inside the reactor tubes be avoided. We obtain the highest conversion if conditions in the tubes are such that the pellet and reactor run-away mechanisms are in balance. This determines an optimum amount of particles on a diameter inside a cooled tubular reactor. This optimum is influenced by the distribution of transport coefficients over the pellets. Because of the pellet-scale statistical behaviour, a certain percentage of the tubes will always suffer run away if we operate close to the run-away region. If we have certain fluctuations in the coolant temperature, reactor pressure or load, any of these can damage a certain amount of tubes. As these fluctuations occur often, the performance of the cooled tubular reactor will deteriorate with time. The effects, as shown in this study, may cause an increase in inherent reactor instability. Therefore, if these effects are taken into account, a more conservative reactor design emerges.

1. INTRODUCTION

In packed-bed reactors, particles are not distributed completely evenly. Therefore, pellet-scale properties such as the pellet heat and mass transfer coefficients are statistically distributed. This statistical character is significant for packed-bed operation. Kirillov *et al.* (1972) studied the flow in packed beds and found that two zones exist (see Fig. 1): first, a flow-through zone in the free volume of the bed, in which gas flows along tortuous paths in the form of blending and separating streams; and second, a non-flow zone, formed by the detachment of the boundary layer located in the vicinity of the particle contact points. A sharp separation boundary, due to the existence of a free boundary layer, is formed between the zones. This boundary is constantly being deformed by rotating and pulsating vortices in the non-flow zone. Hence, flow inside packed beds is very random and chaotic.

In packed beds, transport coefficients (such as the particle heat transfer coefficient) may vary locally in two ways:

- (1) Since different parts of the surface of one particle are subjected to quite different flow regimes (see Fig. 1), coefficients may differ considerably from one point of the surface to the next. This is also true for single spheres, e.g. for heat transfer [see Denton (1951)].

- (2) Because there is certain distribution of voidage in the packed bed, the average coefficients measured for different particles may be different. It should be observed that the voidage distribution may have two origins: a stochastic distribution caused by the randomness of packing, and a systematic distribution which is caused by the "wall effect", which is important if the ratio of tube-to-particle diameters is smaller than, say, 30. The randomness of packing will also have the effect that, for some particles, larger parts of the surface will be in contact with "non-flow zones" than for others.

This study is concerned with the second effect. This effect has been illustrated by Fedoseev and Shanin (1986) and was confirmed by Wijngaarden (1988). Fedoseev and Shanin (1986) measured values of the mass transfer coefficient for individual pellets inside a packed bed. A range of values of the individual pellet coefficients up to a factor of five was reported. Wijngaarden (1988) reported a range up to a factor of 10 for pellet heat transfer coefficients.

This statistical behaviour influences the run-away behaviour of both the individual pellets and of the reactor as a whole. Liu and Amundson (1962, 1963) and Liu *et al.* (1963) introduced the concept of infinite multiplicity: pellets inside a packed bed can operate in the lower or higher stable operating point individually, and therefore there is a large number of operating points for the bed because of the large number of pellets. Eigenberger (1972) pointed out that infinite multiplicity cannot occur in practice because

[†]Present address: Koninklijke/Shell-Laboratorium, Amsterdam, PO Box 3003, 1003 AA Amsterdam, The Netherlands.

[‡]Author to whom correspondence should be addressed.

Fig. 1. A flow-through and a non-flow zone near the pellet contact points in a packed bed.

of axial dispersion of heat via the catalyst pellet contact spot areas. Another explanation would be the following. If a *pellet run away* occurs for a certain pellet in the packed bed, this pellet immediately heats up the gas surrounding it. This increase in gas temperature will result in run away for the neighbouring pellets. So, if one pellet suffers run away, this run away will be passed on from one pellet to another and a run-away front will travel through the packed bed until its boundaries are reached and the run away is complete. Or, in other words, if in a reactor one pellet exhibits run away, this pellet run away will eventually ignite the entire reactor. According to both this mechanism and the one of Eigenberger (1972) there can be no infinite multiplicity.

Furthermore, when a *reactor run away* occurs, large amounts of pellets will immediately exhibit pellet run away in the high-temperature regions of the bed. Hence, the pellet run away and reactor run away are related to each other, and the final outcome is the same. Therefore, in practice it will be hard, if not impossible, to distinguish between the two run-away mechanisms. Yet, it is very important to distinguish between pellet and reactor run aways. For example, run aways caused on a pellet scale may be prevented by *decreasing* the pellet size, thus enhancing the rate of mass and heat transfer to the particle. On the other hand, to prevent a run away on reactor scale we should *increase* the pellet size, thereby increasing the effective radial heat conductivity of the tube packing. Alternatively, by decreasing or increasing the pellet size of the catalyst bed in a reactor tube and by

studying the influence on the thermal stability of this tube, we can determine which run-away mechanism is dominating. A properly designed reactor tube should have such a pellet size that the highest thermal stability is achieved and the highest conversion without a run away. This determines the optimum number of particles on a diameter inside a cooled tubular reactor.

In this study, we shall incorporate the statistical character of the pellet heat and mass transfer coefficients in deterministic reactor design models. We shall focus on cooled tubular reactors in which a heterogeneously catalysed reaction is carried out. We assume a first-order reaction and neglect the intraparticle heat and mass transfer resistances.

2. TRANSLATION OF PELLET-SCALE STATISTICS IN REACTOR-SCALE STATISTICS

Consider a small volume element, $\Delta x_i \Delta y_i \Delta z_i$, with uniform conditions in a packed bed, such that the probability of a pellet run away, p_i , is the same for all pellets in this volume element. This chance of pellet run away, p_i , is the chance that particle external transport parameters have a value, such that the pellet run away occurs. For a reactor volume, V_R , containing N_p pellets, the number, n_p , of pellets in the small volume element is given by

$$n_p = N_p \frac{\Delta x_i \Delta y_i \Delta z_i}{V_R} \quad (1)$$

The probability that no pellet run away occurs inside

the small volume element is given by

$$(1 - p_i)^{n_p} = (1 - p_i)^{(\Delta x_i \Delta y_i \Delta z_i / V_R) N_p} \quad (2)$$

since, for all the n_p pellets, the probability that a run away does not occur, $1 - p_i$, is the same. The probability that no pellet run away occurs in the entire reactor is equal to the product of the probabilities that pellet run aways do not occur in any volume element inside the reactor, i.e.

$$1 - q = \prod_{i=1}^I (1 - p_i)^{(\Delta x_i \Delta y_i \Delta z_i / V_R) N_p} \quad (3)$$

Here q is the probability that a reactor run away is ignited by a pellet run away. I is the total number of volume elements in the reactor. Taking the natural logarithm of both sides of eq. (3) we obtain

$$\ln(1 - q) = \frac{N_p}{V_R} \sum_{i=1}^I \ln(1 - p_i) \Delta x_i \Delta y_i \Delta z_i \quad (4)$$

Choosing infinitesimally small volume elements $\Delta x_i \Delta y_i \Delta z_i = \partial x \partial y \partial z = \partial V$ we find

$$\ln(1 - q) = \frac{N_p}{V_R} \iiint_{V_R} \ln(1 - p) \partial V \quad (5)$$

Or, since

$$\langle \ln(1 - p) \rangle = \frac{1}{V_R} \iiint_{V_R} \ln(1 - p) \partial V \quad (6)$$

$\langle \ln(1 - p) \rangle$ being the average value of $\ln(1 - p)$ for the entire reactor volume, i.e. the value that would be obtained if for all pellets inside the packed bed the individual values of $\ln(1 - p)$ are added up and if the sum is divided by the number of pellets in the bed,

$$\ln(1 - q) = N_p \langle \ln(1 - p) \rangle \Leftrightarrow q = 1 - e^{N_p \langle \ln(1 - p) \rangle} \quad (7)$$

If a one-dimensional model can be used then eq. (6) simplifies to

$$\langle \ln(1 - p) \rangle = \int_0^1 \ln(1 - p) \partial \omega \quad (8)$$

The significance of eq. (7) for the behaviour of a packed-bed reactor can be illustrated in many different ways. With the following illustrations we hope to give some feeling for the impact of pellet-scale statistics.

3. APPLICATION TO PACKED-BED REACTORS

3.1. A pellet run away causes reactor run away

If one single pellet inside the reactor is bound to exhibit run-away behaviour, then for this pellet $p = 1$ and $\ln(1 - p) = -\infty$. If, for one pellet, $\ln(1 - p) = -\infty$, then $\langle \ln(1 - p) \rangle = -\infty$ as well, and hence according to eq. (7), $q = 1$. Or, if a pellet run away is bound to occur, also a run away on reactor level is ignited.

3.2. Probabilities of pellet run away are mutually independent

If all pellets in the reactor have the same probability of pellet run away p , $\langle \ln(1 - p) \rangle$ simply equals $\ln(1 - p)$ and eq. (7) becomes

$$1 - q = (1 - p)^{N_p} \quad (9)$$

The interpretation of this formula is as follows: the probability that a reactor run away is not initiated equals the probability that the first pellet does not exhibit run away, times the probability that the second pellet does not, times the probability that the third pellet does not and so on until the N_p th pellet. Or, a reactor run away is not ignited only if no pellet run away occurs at all the reactor. This reflects the assumption made in this paper, that one pellet run away will ignite complete reactor run away.

3.3. Effect of number of pellets on reactor ignition

Assume that, for a reactor of a certain length, a second one of equal length is put in series additionally (see Fig. 2). The critical hot-spot region is located in the first reactor, and therefore by adding another one no extra critical region is added. If the number of pellets in the first reactor is N_p , it will be $2N_p$ for the

Fig. 2. Axial profiles in a packed bed and in a bed of twice this length.

two reactors in series. If, for the first reactor, we have an average value of $\langle \ln(1-p) \rangle$, for the lengthened reactor the average value will be $\langle \ln(1-p) \rangle/2$, because the second part will decrease the average two-fold. According to eq. (7), for the two beds the probability that a run away will be initiated is the same as for the first bed since

$$q = 1 - e^{2N_p \langle \ln(1-p) \rangle/2} = 1 - e^{N_p \langle \ln(1-p) \rangle} \quad (10)$$

This illustrates that the probability that a reactor run away is ignited is a strong function of the size of the critical region in a reactor, but does not markedly depend on the number of particles in the reactor.

3.4. The standard deviation for p in a packed bed

The mass transfer coefficient, k_g , for a catalyst pellet inside a packed bed does not have a specific deterministic value, but is a stochastic quantity with a certain distribution. In Fig. 3, a histogram is given for k_g as determined by Fedoseev and Shanin (1986) for a constant value of Re . They measured several histograms for different velocities. The average mass transfer coefficient for all pellets inside the packed bed is given by

$$\langle k_g \rangle = \frac{1}{N_p} \sum_{i=1}^{N_p} k_{gi} \quad (11)$$

with N_p being the number of pellets. $\langle k_g \rangle$ could be calculated from the relation given by Aerov *et al.*

(1979):

$$\langle Sh \rangle = \frac{\langle k_g \rangle d_p}{D_g} = 0.395 Re^{0.64} Sc^{0.33} \quad (12)$$

The relative standard deviation

$$\frac{\sigma_{k_g}}{\langle k_g \rangle} = \sqrt{\frac{1}{N_p} \sum_{i=1}^{N_p} \left(\frac{k_{gi} - \langle k_g \rangle}{\langle k_g \rangle} \right)^2} \quad (13)$$

also depends on the velocity (see Fig. 4). The results of Fedoseev and Shanin (1986) could be correlated as

$$\frac{\sigma_{k_g}}{\langle k_g \rangle} = 2.7 Re^{-0.50}, \quad \text{for } 20 < Re < 1000 \quad (14)$$

and is also given in Fig. 4. This correlation, obtained from experiments with spherical pellets and only argon as gas, is not a general one.

3.5. A possible distribution for p

In order to illustrate the effect of the pellet-scale statistical behaviour, a statistical distribution for the mass and/or heat transfer coefficient must be chosen. Because of the lack of data, this choice can only be a rather arbitrary one. We assume the logarithm of the mass and/or heat transfer coefficient to be normally distributed. Consequently, if we focus on the mass transfer coefficient, the probability for the value of k_g to become negative is zero and that to find a k_g -value, e.g. smaller than half the average value, is roughly the same as that to find a k_g -value larger than twice the average. In the case of a normally distributed

Fig. 3. A histogram of the distribution of the mass transfer coefficient, k_g , according to Fedoseev and Shanin (1986). From the histogram follows $\sigma_{k_g}/\langle k_g \rangle = 0.23$.

logarithm, we find for the density distribution of k_g

$$f_{k_g}(k_g) = \begin{cases} 0, & k_g \leq 0 \\ \frac{1}{k_g \Sigma \sqrt{2\pi}} \exp \left\{ -\frac{1}{2} \left[\frac{\ln(k_g) - \ln(\langle k_g \rangle)}{\Sigma} + \frac{\Sigma}{2} \right]^2 \right\}, & k_g > 0 \end{cases} \quad (15)$$

with

$$\Sigma = \sqrt{\ln \left[1 + \left(\frac{\sigma_{k_g}}{\langle k_g \rangle} \right)^2 \right]} \quad (16)$$

and σ_{k_g} defined by

$$\sigma_{k_g} = \sqrt{\int_0^\infty (k - \langle k_g \rangle)^2 f_{k_g}(k) \partial k} \quad (17)$$

σ_{k_g} can be approximated by eq. (14). In Fig. 5, a histogram as given by Fedoseev and Shanin (1986) and the corresponding distribution according to eq. (15) are compared for the same values of $\langle k_g \rangle$ and σ_{k_g} .

Knowing the distribution of k_g we can calculate the probability that k_g is smaller or larger than a certain value. Also, we can calculate the value of $k_{g,ra}$ below which run away of the pellet occurs [see Wijngaarden (1988) and the Appendix]:

$$\begin{aligned} \phi_{0,ra} &= \frac{2 + 2\theta_g + \theta_{ac} + \sqrt{\theta_{ac}(\theta_{ac} - 4\theta_g - 4\theta_g^2)}}{\theta_{ac} - 2\theta_g - \sqrt{\theta_{ac}(\theta_{ac} - 4\theta_g - 4\theta_g^2)}} \\ &\times \exp \left[\frac{2\theta_{ac}(1 + \theta_{ac})}{\theta_{ac} + 2\theta_g\theta_{ac} - \sqrt{\theta_{ac}(\theta_{ac} - 4\theta_g - 4\theta_g^2)}} \right] \quad (18) \\ \phi_{0,ra} &= k_{g,ra} A_p / k_0 V_p \\ \theta_{ac} &= E_a / (R \Delta T_{ad}) Le^{+2/3} \\ \theta_g &= T_g / \Delta T_{ad} Le^{+2/3} \end{aligned}$$

where $\phi_{0,ra}$ is the ratio of the mass transfer rate for which the run away occurs over the reaction rate for

an infinitely high temperature, θ_{ac} a dimensionless activation temperature and θ_g a dimensionless gas temperature.

Equation (18) was derived on the basis of a heat balance and a mass balance for a first-order reaction taking place at the outer surface of the pellet under the condition that, at the run-away pellet temperature, the slopes of the heat withdrawal line and heat production rate curve must be equal. If, in the resulting equations, the particle temperature is eliminated, a quadratic equation results one root of which is the run-away value of ϕ_0 and the second root the blow out value of ϕ_0 . It may be noted that ΔT_{ad} refers to the concentration of the surrounding gas which the particle "sees". With respect to the adiabatic temperature rise based on the reactant concentration in the reactor feed, $\Delta T_{ad,R} = (-\Delta H)C_{in}/(\rho_g C_{p,g})$, we have $\Delta T_{ad} = \Delta T_{ad,R} (1 - \zeta)$, where ζ refers to the conversion reached in the gas phase surrounding the particular pellet under study (see Appendix for further details).

The probability p that a pellet exhibits run away is equal to the probability that the value of k_g is smaller than $k_{g,ra}$ which, according to eq. (15), we can write as

$$\begin{aligned} p &= \int_0^{k_{g,ra}} \frac{1}{k_g \Sigma \sqrt{2\pi}} \\ &\times \exp \left\{ -\frac{1}{2} \left[\frac{\ln(k_g) - \ln(\langle k_g \rangle)}{\Sigma} + \frac{\Sigma}{2} \right]^2 \right\} \partial k_g \end{aligned}$$

Fig. 4. Relative standard deviation $\sigma_{k_g}/\langle k_g \rangle$ vs the particle Reynolds number. The correlation found is given by the straight line.

Fig. 5. Comparison of the histogram given in Fig. 3 with the density distribution obtained if the logarithm of k_g is assumed to be normally distributed.

or

$$p = \int_0^{k_{g,ra}/\langle k_g \rangle} \frac{1}{\xi \Sigma \sqrt{2\pi}} \exp \left\{ -\frac{1}{2} \left[\frac{\ln(\xi)}{\Sigma} + \frac{\Sigma}{2} \right]^2 \right\} \partial \xi \quad (19)$$

with Σ given by eq. (16).

3.6. Translation of pellet-scale statistics to reactor-scale statistics

For a reactor-scale deterministic model, let us assume first-order kinetics, plug flow and a one-dimensional, homogeneous packed bed. Internal and external mass and heat transfer in and to the catalyst phase are neglected. The neglect of pellet external resistances seems to contradict the occurrence of pellet run away, where the external transfer is indispensable for the multiplicity of the pellet. However, as long as k_g is sufficiently high so that no pellet run away occurs, even on the verge of run away, the maximum possible rate of external transfer is still 10–20 times higher than the rate of conversion inside the pellet. So, neglect of external transfer resistance is a reasonable assumption for reactor-scale models.

The reactor mass and heat balances can now be written as

$$\frac{\partial \zeta}{\partial \omega} = NRU \exp \left(\frac{\psi \Theta}{1 + \Theta} \right) (1 - \zeta) \quad (20)$$

$$\frac{\partial \Theta}{\partial \omega} = NRU \Delta \Theta_{ad} \exp \left(\frac{\psi \Theta}{1 + \Theta} \right) (1 - \zeta) - NTU \Theta \quad (21)$$

to be solved subject to the initial conditions

$$\omega = 0 \Rightarrow \zeta = 0 \wedge \Theta = 0. \quad (22)$$

The above set of equations can be solved numerically to yield plots of ζ and Θ vs ω (see Fig. 6), where the dimensionless adiabatic temperature rise $\Delta \Theta_{ad}$ is increased for the given values of NRU , NTU and ψ . For $\Delta \Theta_{ad} \approx 9.7$ a reactor run away occurs. For every point inside the reactor, the probability p that a pellet exhibits run away can now be calculated as follows.

(1) For each point inside the reactor we have

$$\theta_g = \frac{1 + \Theta}{\Delta \Theta_{ad}(1 - \zeta)} Le^{+2/3} \quad (23)$$

$$\theta_{ac} = \frac{\psi}{\Delta \Theta_{ad}(1 - \zeta)} Le^{+2/3}. \quad (24)$$

Thus, for every point, $\phi_{0,ra}$ can be calculated from eq. (18).

Fig. 6. The dimensionless reactor-bed temperature Θ and the conversion ζ vs the reactor length ω for several values of the adiabatic temperature rise $\Delta\Theta_{ad}$.

- (2) The mass transfer coefficient, k_g , is distributed and so is ϕ_0 . Unlike the value of $\phi_{0,ra}$, this distribution of ϕ_0 generally does not depend on the location in the reactor tube. We estimate the average value of ϕ_0 and its relative deviation from the correlations (12) and (14):

$$\langle \phi_0 \rangle = 2.4 \frac{D_g}{k_0 d_p^2} Re^{+0.64} Sc^{+0.33} \quad (25)$$

$$\frac{\sigma_{\phi_0}}{\langle \phi_0 \rangle} = 2.7 Re^{-0.50}. \quad (26)$$

The distribution of ϕ_0 is assumed to be [see also eq. (15)]

$$f_{\phi_0}(\phi_0) = \begin{cases} 0, & \phi_0 \leq 0 \\ \frac{1}{\phi_0 \Sigma \sqrt{2\pi}} \exp \left\{ -\frac{1}{2} \left[\frac{\ln(\phi_0) - \ln(\langle \phi_0 \rangle)}{\Sigma} + \frac{\Sigma}{2} \right]^2 \right\}, & \phi_0 > 0 \end{cases} \quad (27)$$

$$\Sigma = \sqrt{\ln \left[1 + \left(\frac{\sigma_{\phi_0}}{\langle \phi_0 \rangle} \right)^2 \right]}. \quad (28)$$

- (3) With the value $\phi_{0,ra}$ and the distribution of ϕ_0 , we calculate for every location inside the reactor the probability p that a pellet exhibits run away:

$$p = \int_0^{\phi_{0,ra}/\langle \phi_0 \rangle} \frac{1}{\xi \Sigma \sqrt{2\pi}} \times \exp \left\{ -\frac{1}{2} \left[\frac{\ln(\xi)}{\Sigma} + \frac{\Sigma}{2} \right]^2 \right\} \partial \xi. \quad (29)$$

An example is shown in Fig. 7. We have chosen rather arbitrarily $\langle \phi_0 \rangle = 0.05$ and $\sigma_{\phi_0}/\langle \phi_0 \rangle = 0.25$, and further data as indicated in the figure. Observe that, at the reactor entrance, where conditions are relatively mild, the value of p is very low. As we proceed towards the hot-spot area, conditions become more severe and the value of p increases rapidly. Near the hot-spot region, conditions are most dangerous and p reaches its maximum value. In the tail behind the hot spot, conditions become less severe again and p decreases rapidly to zero.

For the packed bed given in Fig. 7, the value of p is much lower than unity for all values of ω and we can write

$$\langle \ln(1-p) \rangle \approx \langle -p \rangle = -\langle p \rangle. \quad (30)$$

As indicated in the figure, $\langle p \rangle = 0.0042$. In a cooled tube we have between 1000 and 100,000 particles, say $N_p \approx 10^4$. Then according to eq. (7), $q = 1 - e^{-42}$; so q equals unity. In other words, we can be certain that for the situation given in Fig. 7 a run away will be ignited by a pellet run away. So, unless the value of $\langle p \rangle$ is extremely small, run away of the bed will always occur.

3.7. Maximum conversion in a cooled tubular reactor

In Fig. 8 relations between q and ζ_{out} and the coolant temperature T_c are given. With varying coolant temperature, the numbers NRU , ψ and $\Delta\Theta_{ad}$ also vary, as indicated above the figure. For $T_c = 600$ K we obtain the situation given in Fig. 7, where $q \approx 1$ and $\zeta_{out} \approx 0.29$. With increasing coolant temperature, the conversion ζ_{out} increases, till at $T_c = 603$ K there is a sudden, sharp increase in ζ_{out} due to a reactor run away. From Fig. 8 we also see that, at a coolant temperature of $T_c = 593$ K, there is already a 10% probability that a run away will be initiated by a pellet run away. For $T_c = 598$ K this probability is already 90% and for $T_c = 600$ K we can be sure that a full run away will be ignited by a pellet run away, as shown before. Hence, here we have an example of a pellet run away dominating over a reactor run away.

In a cooled tubular reactor, typically 50–10,000 reactor tubes are operated in parallel inside the same jacket containing the coolant. Because of the large number of tubes, the probability that a pellet run away initiates a run away on reactor level roughly equals the percentage of tubes in which this actually

happens. A tube suffering a run away will become inactive, because, due to the high reaction temperatures involved, the catalyst is deactivated completely. The inactive tubes do not necessarily have to be plugged, as some vulnerable active species also, e.g. small metal crystallites, may have been destroyed. So through the inactive tubes gas may continue to flow, the reactant is simply not converted anymore in those tubes. In the case when a tube has indeed been plugged, the remaining tubes become loaded at a higher flow rate, which also results in an overall conversion decrease. Consequently, if in the active tubes we achieve a conversion ζ_{at} , in the whole reactor the conversion ζ_r will be only

$$\zeta_r = (1 - q)\zeta_{at}. \quad (31)$$

If we plot q , ζ_{at} and ζ_r vs the coolant temperature for the conditions as given in Fig. 8, Fig. 9 is obtained. For low coolant temperatures, conditions are very mild and no run aways occur; thus, $q = 0$ and conversion is low. As T_c increases conditions become more severe, tubes suffer run aways here and there and ζ_r becomes lower than ζ_{at} . For an even higher T_c the increase in conversion of the active tubes is outweighed by the decrease in the number of active tubes and ζ_r actually decreases with increasing T_c . Eventually, ζ_r becomes zero because all the tubes in the reactor jacket have suffered run away. This point is reached for this specific example before a run away can be ignited by the reactor run-away mechanism. Hence, there is a maximum value $\zeta_{r,max}$ for the conversion in the cooled tubular reactor.

3.8. Operation of a cooled tubular reactor

Figure 10 shows what happens in a reactor which had a temporary fluctuation in the coolant temperature. For the data given in Section 3.7, we have a cooled tubular reactor operating at a coolant temperature of 580 K. A temporary fluctuation occurs, during which the coolant temperature increases for a short time to 593 and 596 K, respectively. After the fluctuation the control system returns T_c to 580 K. We can observe that a number of tubes have become inactivated because of pellet run aways causing a full single-tube run away. The conversion drops because of this fluctuation. Furthermore, it can be observed that $T_c = 580$ K is too low a coolant temperature for the case under consideration.

After start-up and in fine tuning the reactor to maximum capacity by slowly increasing T_c , a number of individual tubes will always suffer run away as we approach maximum capacity. After having determined this point we should take great care never to exceed the optimum value of T_c , or better yet to keep the temperature somewhat below this value in order to cope with operational perturbations without immediately inactivating a number of additional tubes.

3.9. Design of a cooled tubular reactor

The model discussed here can also be used for the design of a cooled tubular reactor. We take a certain

$$\text{NRU}=0.1 ; \text{NTU}=20 ; \psi=10 ; \Delta\theta_{ad}=9.6 ; \langle\phi_0\rangle=-0.05 ;$$

$$\sigma_{\phi_0}/\langle\phi_0\rangle=0.25 ; \text{Le}=1$$

Fig. 7. Axial profiles of the chance p of a pellet run away, the bed temperature Θ and the conversion ζ .

cooled tubular reactor with say 6000 tubes, $D_t = 5$ cm, $L_t = 10$ m, $\Delta T_{ad} = 2500^\circ\text{C}$ (for further data see Table 1). The coolant temperature, T_c , and the catalyst particle diameter, d_p , can be chosen freely. Our aim is to find the optimum value for d_p . For too low a

value of d_p , the effective radial heat conductivity in the tubes becomes low, thereby increasing the danger of reactor run away. For too high a value of d_p , the possibility of pellet run aways is large. Somewhere in between there must be an optimum particle diameter.

$$\begin{aligned} NRU &= 0.1 * \exp(10 * (1 - 600/T_c)) ; NTU = 20 ; \psi = 10 * 600/T_c ; \\ \Delta\theta_{ad} &= 9.6 * 600/T_c ; \langle\phi_0\rangle = 0.05 ; \sigma_{\phi_0}/\langle\phi_0\rangle = 0.25 ; Le = 1 ; \\ N_p &= 10^4 \end{aligned}$$

Fig. 8. Probability q that a run away on reactor level is initiated by pellet run away and the conversion at the reactor outlet ζ_{out} vs the coolant temperature T_c .

Since only the values of T_c and d_p are unknown we calculate NRU , ψ , NTU , $\Delta\theta_{ad}$, $\langle\phi_0\rangle$, $\sigma_{\phi_0}/\langle\phi_0\rangle$ and N_p as a function of T_c and d_p . To this end, literature correlations have been used for U , $\langle\phi_0\rangle$ and $\sigma_{\phi_0}/\langle\phi_0\rangle$.

For every individual particle diameter, d_p , we can draw a figure like Fig. 9, resulting in a maximum obtainable reactor conversion $\zeta_{r,max}$, and the corresponding values of $T_{c,opt}$ and q_{opt} for that value of d_p , see Fig. 11. Two regions can be distinguished. For low

$$\begin{aligned} \text{NRU} &= 0.1 * \exp(10 * (1 - 600/T_c)) ; \text{NTU} = 20 ; \psi = 10 * 600/T_c ; \\ \Delta\theta_{\text{ad}} &= 9.6 * 600/T_c ; \langle\phi_0\rangle = 0.05 ; \sigma_{\phi_0}/\langle\phi_0\rangle = 0.25 ; \text{Le} = 1 ; \\ N_p &= 10^4 \end{aligned}$$

Fig. 9. Percentage q of tubes suffering run away due to pellet run away, conversion ζ_{at} achieved in an active tube and the total conversion ζ_r achieved in the reactor, respectively, vs the coolant temperature T_c .

d_p -values, reactor run away dominates, while for high d_p -values pellet run away dominates. For $d_p = 1$ cm or five particles on a tube diameter we reach the optimum. The conversion here equals $\zeta_{r,\text{max}} = 0.20$.

For the whole range of d_p -values, q_{opt} remains roughly in the range 1–2%. So a small percentage of

the tubes have to suffer run away, otherwise we have very low coolant temperatures and pay a heavy price in the form of too low a conversion.

This more or less academic example demonstrates the existence of an optimum particle diameter. This is not a very practical conclusion, since both particle

$$\begin{aligned} \text{NRU} &= 0.1 \cdot \exp(10 \cdot (1 - 600/T_c)) ; \text{NTU} = 20 ; \psi = 10 \cdot 600/T_c ; \\ \Delta\theta_{\text{ad}} &= 9.6 \cdot 600/T_c ; \langle \phi_0 \rangle = 0.05 ; \sigma_{\phi_0} / \langle \phi_0 \rangle = 0.25 ; \text{Le} = 1 ; \\ N_p &= 10^4 \end{aligned}$$

Fig. 10. The effect of a small temperature fluctuation to $T_{c, \max} = 593$ K and of a large fluctuation to $T_{c, \max} = 596$ K on the overall conversion.

Table 1. Data used for the design discussed in Fig. 11

Physical data of the gas	Data reactor
$\lambda_g = 0.04$ W/m K	$L_t = 10$ m
$\rho_g = 4$ kg/m ³	$D_t = 5$ cm
$C_{p,g} = 1000$ J/kg K	$N_t = 6000$
$a_g = 1 \times 10^{-5}$ m ² /s	$\varepsilon = 0.5$
$v_g = 5 \times 10^{-6}$ m ² /s	
$D_g = 5 \times 10^{-6}$ m ² /s	
Data particles	System properties
$\lambda_s = 0.5$ W/m K	$C_{in} = 30$ mol/m ³
Ring-shaped catalyst:	$\phi_v = 5$ m ³ /s
inner radius $\times$ outer radius	$(-\Delta H) = 370$ kJ/mol
$\times$ height $= \frac{1}{12} d_p \times \frac{1}{2} d_p \times \frac{1}{3} d_p$	$k_0 = 2.5 \times 10^4$ 1/s
$d_p = 6V_p/A_p$	$E_a/R = 7200$ K
$V_p = 125/144 d_p^3$	

Note: The overall heat transfer coefficient U was calculated from correlations recommended by Westerterp *et al.* (1987):

$$U = \frac{25 + 42d_p}{1 + 0.17d_p^{1.25}} \text{ (W/m}^2 \text{ K) with } d_p \text{ in cm.}$$

and tube diameters are determined by a number of other factors. In practice, of course, the entrance temperature and feed concentrations are the most important design parameters. Furthermore, the particle geometry usually has been determined already much earlier in the process development stage, based on pore-diffusion limitation and pressure-drop calculations. The example here, however, illustrates the model and states that optimization of pellet vs reactor run away may also be a point for consideration.

4. CONCLUSIONS

Cooled tubular reactor design and operation are determined to a large extent by the objective of avoiding run away. We discussed two types of run away, pellet and reactor run away. It is economically desirable to operate close to run-away limits. We obtain the highest conversion if the conditions in the tubes are such that the pellet and reactor run-away mechanisms are in balance. This determines the optimum

$$\begin{aligned} \text{NRU} &= 3.0 \times 10^5 \cdot \exp(-7200/T_c) ; \text{NTU} = (12 + 20 \cdot d_p) / (1 + 0.17 \cdot d_p^{1.25}) ; \\ \psi &= 7200/T_c ; \Delta\theta_{ad} = 2775/T_c ; \langle \phi_0 \rangle = 2.1 \times 10^{-4} \cdot d_p^{-1.50} ; \\ \sigma_{\phi_0} / \langle \phi_0 \rangle &= 0.10 \cdot d_p^{-0.50} ; \text{Le} = 2.0 ; N_p = 2.3 \times 10^4 \cdot d_p^{-3} \\ \text{FOR FORMULAE ABOVE USE } T_c &\text{ IN K AND } d_p \text{ IN cm} \end{aligned}$$

Fig. 11. The maximum conversion achieved $\zeta_{r,max}$, the corresponding coolant temperature $T_{c,opt}$ and the percentage q_{opt} of tubes which suffers run away, respectively, as a function of the particle diameter d_p .

amount of particles on a diameter inside a cooled tubular reactor.

Because of the pellet-scale statistical behaviour, a certain percentage of the tubes will always suffer run away if we operate close to the run-away region. The catalyst in the tubes which have suffered run away will usually be permanently damaged because of the high temperatures involved in run away. Every fluctuation in the coolant temperature, reactor pressure or reactor load can damage a certain number of the tubes. In operation, fluctuations will occur often, and there-

fore the performance of the cooled tubular reactor will deteriorate with time. The more the precision with which the reactor is operated, the lower the number of large fluctuations, and therefore the slower the performance decline in the time. Obviously, if some sort of calamity occurs, e.g. a sudden high increase in coolant temperature, we will immediately have a full run away and destroy the catalyst in all tubes.

We used rather crude assumptions for the models, so they only give a rough idea of the significance of pellet-scale statistical behaviour. A better study using

more refined models should be made in future as soon as more quantitative information becomes available on statistics of pellet-scale properties. Finally, we have to observe that generally the activity of catalyst pellets is also a stochastic quantity with a certain distribution. Due to the manufacturing process not all pellets will contain the same amount or quality of active species. This pellet activity distribution will alter the distribution of ϕ_0 in eq. (27). The distribution obtained can be incorporated in reactor design and operation models in an identical manner as discussed above.

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NOTATION

a_g	thermal diffusivity of the gas, m ² /s
A_p	external surface area of the catalyst pellet, m ²
C_g	concentration of reactant in the gas phase, mol/m ³
C_{in}	reactor inlet concentration of the reactant, mol/m ³
C_p	concentration of the reactant in the internal catalyst pores, mole/m ³
$C_{p,g}$	specific heat of gas, J/kg K
C_ω	concentration of the reactant in the bed at the location ω , mol/m ³
d_p	particle diameter equivalent to a sphere ($= 6V_p/A_p$), m
D_t	tube diameter, m
$\mathcal{D}$	($= \theta_{ac} - 4\theta_g - 4\theta_g^2$), dimensionless
D_g	diffusion coefficient of the reactant in the gas phase, m ² /s
E_a	energy of activation, J/mol
$f_{k_g}(k_g)$	density distribution of k_g , s/m
$f_{\phi_0}(\phi_0)$	density distribution of ϕ_0 , dimensionless
$-\Delta H$	reaction enthalpy: for exothermic reactions $-\Delta H > 0$; for endothermic reactions $-\Delta H < 0$, J/mol reactant converted
$k(T_p)$	reaction rate constant per unit of catalyst volume and at pellet temperature T_p [$= k_0 \exp(-E_a/RT_p)$], 1/s
k_0	frequency factor per unit of catalyst volume, 1/s
k_g	pellet mass transfer coefficient of the reactant, m/s
$k_{g,ra}$	value of k_g for which run away of the catalyst pellet occurs, m/s
$\langle k_g \rangle$	average value of k_g for all the particles in the packed bed, m/s
Le	Lewis number ($= a_g/D_g$), dimensionless
L_t	tube length, length of the packed bed, m
NRU	number of reaction units [$= e^{-\psi}(1 - \varepsilon)k_0 L_t/v_0$], dimensionless
NTU	number of heat transfer units [$= 4UL_t/(\rho_g C_{p,g} v_0 D_t)$], dimensionless

N_p	number of particles in a packed bed or reactor, dimensionless
N_t	number of parallel tubes in a cooled tubular reactor, dimensionless
p	probability that a pellet exhibits run away, dimensionless
Pr	Prandtl number ($= v_g/a_g$), dimensionless
q	probability that a run away on reactor level is initiated by a pellet run away, dimensionless
q_{opt}	value of q obtained when the coolant temperature is tuned such that the maximum conversion is achieved, dimensionless
R	gas constant, 8.314 J/mol K
Re	particle Reynolds number ($= v_0 d_p/v_g$), dimensionless
Sc	Schmidt number ($= D_g/v_g$), dimensionless
Sh	particle Sherwood number ($= k_g d_p/D_g$), dimensionless
$\langle Sh \rangle$	average number of Sh for all pellets in the packed bed, dimensionless
T_{ac}	activation temperature ($= E_a/R$), K
T_c	coolant temperature, K
$T_{c,opt}$	coolant temperature for which the maximum conversion is achieved, K
T_g	gas temperature, K
T_{in}	reactor gas inlet temperature, K
T_p	temperature of a catalyst pellet, K
T_ω	temperature in the bed at the location ω , K
ΔT_{ad}	adiabatic temperature rise locally around the pellet [$= C_g(-\Delta H)/(\rho_g C_{p,g})$], K
$\Delta T_{ad,R}$	adiabatic temperature rise at the reactor entrance [$= C_{in}(-\Delta H)/(\rho_g C_{p,g})$], K
U	overall heat transfer coefficient between the packed bed and the wall, W/m ² K
v_0	superficial gas velocity based on the empty tube, m/s
V_p	volume of catalyst pellet, m ³
V_t	reactor or tube volume, m ³
z	axial coordinate, m

Greek letters

α_p	heat transfer coefficient between pellet and gas, W/m ² K
ζ	dimensionless conversion of the reactant in the bed [$= (C_{in} - C_\omega)/C_{in}$]
ζ_{at}	conversion achieved in an active tube, dimensionless
ζ_{out}	conversion of reactant at reactor outlet, dimensionless
ζ_r	overall conversion achieved in a reactor, dimensionless
$\zeta_{r,max}$	maximum conversion that can be achieved by tuning the coolant temperature T_c , dimensionless
θ_{ac}	dimensionless activation temperature [$= E_a/(R\Delta T_{ad})Le^{+2/3}$]
θ_g	dimensionless gas temperature ($= T_g/\Delta T_{ad}Le^{+2/3}$)
θ_p	dimensionless particle temperature ($= T_p/\Delta T_{ad}Le^{+2/3}$)

Θ	dimensionless bed temperature $[= (T_w - T_c)/T_c]$
$\Delta\Theta_{ad}$	dimensionless adiabatic temperature rise $[= (-\Delta H)C_{in}/(\rho_g C_{p,g} T_c)]$
λ_g	heat conductivity of the gas, W/m K
λ_s	heat conductivity of the solid catalyst, W/m K
ν_g	kinematic viscosity of the gas, m ² /s
ρ_g	density of the gas, kg/m ³
σ_{k_g}	standard deviation in k_g , m/s
σ_{ϕ_0}	standard deviation in ϕ_0 , dimensionless
Σ	measure of the relative standard deviation $\{= \ln[1 + (\sigma_{k_g}/\langle k_g \rangle)^2] = \ln(1 + \sigma_k^2) = \ln[1 + (\sigma_{\phi_0}/\langle \phi_0 \rangle)^2]\}$, dimensionless
ϕ_0	ratio of the mass transfer rate to the reaction rate for an infinitely high temperature $[= k_g A_p/(k_0 V_p)]$, dimensionless
$\langle \phi_0 \rangle$	average value of ϕ_0 for all pellets in the packed bed, dimensionless
$\phi_{0,ra}$	value of ϕ_0 for which run away of a pellet occurs, dimensionless
ψ	dimensionless energy of activation or Arrhenius number $(= E_a/RT_c)$
ω	dimensionless axial coordinate $(= z/L_t)$

REFERENCES

- Aerov, M. E., Todes, O. M. and Narinskii, D. A., 1979, *Apparatus Containing a Stationary Granular Bed*. Khimiya, Leningrad [cited by Fedoseev and Shanin (1986)].
- Denton, W. H., 1951, In *Proceedings of the General Discussion on Heat Transfer*, pp. 370–381. Institution of Mechanical Engineering and American Society of Mechanical Engineering, London.
- Eigenberger, G., 1972, Dynamic behaviour of the catalytic fixed-bed reactor in the region of multiple steady states. I. Influence of heat conduction in two phase models. *Chem. Engng Sci.* 27(11), 1909–1915.
- Fedoseev, V. N. and Shanin, O. I., 1986, Statistical characteristics of convective transfer in a fixed granular bed. *Inz.-Fiz. Zh.* 51(2), 194–198.
- Kirillov, V. A., Matros, Y. S. and Sorokin, V. N., 1972, Hydrodynamic conditions in the free space of a catalyst bed. *Dokl. Akad. Nauk. SSSR* 206(6), 1409–1414.
- Liu, S. L. and Amundson, N. R., 1962, Stability of adiabatic packed bed reactors—elementary treatment. *Ind. Engng Chem. Fundam.* 1, 200–208.
- Liu, S. L. and Amundson, N. R., 1963, Stability of adiabatic packed bed reactors—effect of axial mixing. *Ind. Engng Chem. Fundam.* 2(3), 183–189.
- Liu, S. L., Aris, R. and Amundson, N. R., 1963, Stability of nonadiabatic packed bed reactors. An elementary treatment. *Ind. Engng Chem. Fundam.* 2, 12–20.
- Westertorp, K. R., van Swaaij, W. P. M. and Beenackers, A.

A. C. M., 1987, *Chemical Reactor Design and Operation*. Wiley, Chichester.

Wijngaarden, R. J., 1988, The scaling up of cooled tubular reactors. Ph.D. thesis, Twente University, Enschede.

APPENDIX: DERIVATION OF EQ. (18)

For a catalyst pellet and a first-order reaction the following balances hold:

$$\alpha_p A_p (T_p - T_g) = k(T_p) C_p V_p (-\Delta H) \quad (A1)$$

$$k_g A_p (C_g - C_p) = k(T_p) C_p V_p \quad (A2)$$

with $k(T_p) = k_0 \exp(-E_a/RT_p)$. According to the Chilton-Colburn analogy

$$\frac{\alpha_p}{k_g} = \rho_g C_{p,g} Le^{+2/3}. \quad (A3)$$

Eliminating C_p and α_p gives

$$\frac{T_p - T_g}{\Delta T_{ad} Le^{-2/3}} = \left[1 + \frac{k_g A_p}{k(T_p) V_p} \right]^{-1} \quad (A4)$$

with

$$\Delta T_{ad} = \frac{C_g (-\Delta H)}{\rho_g C_{p,g}}. \quad (A5)$$

Introducing

$$\theta_g = T_g / \Delta T_{ad} Le^{+2/3} \quad (A6)$$

$$\theta_p = T_p / \Delta T_{ad} Le^{+2/3} \quad (A7)$$

$$\theta_{ac} = E_a / (R \Delta T_{ad}) Le^{+2/3} \quad (A8)$$

$$\phi_0 = k_g A_p / k_0 V_p \quad (A9)$$

we obtain

$$\theta_p - \theta_g = \left[1 + \phi_0 \exp\left(\frac{\theta_{ac}}{\theta_p}\right) \right]^{-1}. \quad (A10)$$

Taking derivatives of both sides and equating them leads to

$$1 = \frac{\theta_{ac} \phi_0 \exp\left(\frac{\theta_{ac}}{\theta_p}\right)}{\theta_p^2 \left[1 + \phi_0 \exp\left(\frac{\theta_{ac}}{\theta_p}\right) \right]^2}. \quad (A11)$$

From eqs (A10) and (A11) we can eliminate θ_p . From eq. (A10) follows

$$\phi_0 \exp\left(\frac{\theta_{ac}}{\theta_p}\right) = \frac{1 - \theta_p + \theta_g}{\theta_p - \phi_g}. \quad (A12)$$

Substituting into eq. (A11) leads to a quadratic equation in θ_p and θ_g . Solving for θ_p gives two roots, the smaller of which gives the ignition temperature, the higher, the extinction temperature. For run away we eventually obtain for ϕ_0 at run away eq. (18).

A real root is only found, when

$$\mathcal{D} = \theta_{ac} - 4\theta_g - 4\theta_g^2 > 0. \quad (A13)$$

The maximum slope of the heat production rate curve is found in its inflection point, for which $\mathcal{D} = 0$. This gives the so-called trifurcation point.