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## MICRO-MIXING IN CONTINUOUS PARTICULATE REACTORS

F. K. CRUNDWELL

Department of Chemical Engineering, University of the Witwatersrand, Private Bag 3, WITS, Johannesburg, 2050 South Africa

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**Abstract**—Previous work in the mathematical modelling of particulate (or heterogeneous) reactors has used either the segregated model or the number balance. There has been no mention of the effects of micro-mixing, nor mention of the relationship between these two approaches. This work shows that the relationship between these two equations is concerned with the micro-mixing in a particulate reactor. The number balance for the extremes of micro-mixing is derived. These models are the segregated model and the maximum-mixedness model. Analytical solutions to these equations are obtained for the case in which the order of reaction with respect to the concentration in the gas or liquid phase is zero. It was shown that if the concentration in the gas or liquid phase remains unaffected by the course of the reaction, then the segregated and maximum-mixedness models are identical. In all other cases the performance calculations yield results which depend on the conditions of micro-mixing in the reactor. Numerical solutions for other cases are also discussed. It is shown that the segregated model predicts greater conversions than the maximum-mixedness model for shrinking-particle kinetics (e.g. roasting or leaching).

### 1. INTRODUCTION

Danckwerts (1958) recognised that the state of mixing in a reactor with a given residence-time distribution,  $F(t)$ , may fall between two limiting cases. The first case is that in which the feed to the reactor is dispersed on entering the reactor into discrete packets or elements of fluid. These elements of fluid are small compared to the reactor volume and they are uniformly distributed throughout the reactor. The elements remain intact while in the reactor, so that each element behaves as a batch reactor. In other words, each element has a unique history which can be determined by an examination of the contents of the element. This model of the mixing in a reactor is referred to as the segregated model.

In contrast, the second case is that in which the contents of the reactor are uniformly mixed on a molecular scale. Elements of fluid do not contain molecules that have entered the reactor at the same time. Rather, there is a continuous exchange of contents, or mixing, between elements which leave the reactor at the same moment. This means that each element of fluid has no single history. Zwietering (1959) called this the maximum-mixedness model. He stipulated conditions for the maximum-mixedness reactor. These conditions require all molecules that leave the reactor at the same moment to be mixed for the duration of their stay in the reactor.

The difference between these two cases is a result of the degree of micro-mixing that is achieved in the reactor. Zwietering (1959) observed that, for a given  $F(t)$ , mixing occurs at the latest possible moment in the segregated model, and at the earliest possible moment in the maximum-mixedness reactor.

Zwietering (1959) showed that these two models of the micro-mixing in a reactor gave different results for the performance of the reactor, except for a limited number of cases. One such case, in which there is no difference between the two models, is that in which the reaction is first-order (or pseudo-first-order). This is to be expected, since a molecule in a first-order reaction does not interact with its environment. In other words, whether a molecule reacts or not depends only on the time it has spent in the system, and not on its interaction with its neighbours. Thus each molecule can be regarded as a batch reactor, and both the segregated and maximum-mixedness reactors give the same result.

Danckwerts (1958) and Zwietering (1959) both restricted their discussion of micro-mixing to homogeneous systems. On the other hand, particulate reactions are important in a number of industrial processes. Examples include mineral flotation, crystallisation, leaching and fluid-bed roasting. Bacterial populations are also regarded as particulate systems if corpuscular models are used (Ramkrishna, 1979).

The concepts of segregation and micro-mixing are particularly important in heterogeneous systems. For example, when bacterial populations of different physiological states are mixed, the biomass does not form a biomass of a single new (average) state. Instead, the mixed biomass comprises portions which retain their previous physiological states (Fredrickson, 1992). In this sense, the biomass is segregated.

In other particulate processes, the disperse phase consists of particles, each of which is an aggregate of molecules physically separate from the continuous

phase. Because of this physical separateness, the particles themselves have often been regarded as the same entities as the volume elements of fluid referred to in the discussion of micro-mixing. Each particle is then regarded as a batch reactor which reacts with a constant continuous phase concentration, and the segregated model is used to describe the overall conversion. It is in this form that the segregated model has been widely used to model continuous reactors for particulate systems (Levenspiel, 1972, Chap. 12).

However, it is possible to formulate a different segregated model that is more akin to the segregated model of Danckwerts and Zwietering. Consider the following model. The feed, consisting of both particles and fluid, is broken into volume elements containing both particles and fluid. Each of these volume elements remains intact and behaves as a batch reactor, and the probability of a volume element having left the system after time  $t$  is given by  $F(t)$ . This model is conceptually identical to the segregated model referred to in the discussion of micro-mixing for homogeneous systems.

Thus the physical separateness of the particles from the continuous phase is different from the concept of segregation spoken of in the context of micro-mixing. Central to the concept of micro-mixing is the history of each element of fluid in the reactor. In the segregated reactor, each element has a well-defined history. In the maximum-mixedness reactor, each element of fluid has no discernible history. The particles are themselves segregated only if they have a discernible history, that is to say that some particle properties are a measure of the time that the particle has spent in the reactor. This is not true in general, since by an elementary argument a particle could arrive in the reactor with a property value, say of size  $l$ , or react to that value, that is, react to size  $l$ .

This paper expands Zwietering's work on segregated and maximum-mixedness models to include heterogeneous systems. We derive the number balance equations describing the segregated and maximum-mixedness reactors for particulate systems, and discuss the implications that micro-mixing has for modelling particulate processes. We show that the results for particulate systems in which both phases have the same residence-time distribution are conceptually similar to the case for premixed homogeneous reactors.

## 2. THE CONDITION OF SEGREGATION AND MAXIMUM-MIXEDNESS IN PARTICULATE REACTORS

Consider a steady-state continuous system. Material comes into the system without any age, and acquires age,  $\Gamma$ , in proportion to the duration of stay in the system. The age ceases to increase when the material leaves the system, and the age on final departure is the residence time,  $t$  (Nauman and Buffham, 1983). The residual life,  $\lambda$ , is the time the material still

has to spend in the reactor, and is given by

$$\Gamma + \lambda = t. \quad (1)$$

The action of mixing is to divide the material entering the system into small volume elements, called "points" (Danckwerts, 1958). Points are defined at a particular moment, and need not retain their identity with time. The contents within each point are mixed, and may have different ages and residual lives due to mixing between points.

In a particulate system, the material that enters or leaves may contain both molecules and particles. These molecules and particles are distinct. Molecules change character and acquire a new identity on reaction; particles, however, change only the value of some characteristic property on reaction. The particles are referred to as the disperse phase, while the molecular constituents are referred to as the continuous phase. The molecular species that reacts with the particles will be referred to as the continuous-phase reactant.

Each point in the system contains both disperse and continuous phases. Particles and molecules acquire age identically, and we consider the case in which the residence-time distribution for both phases is identical. [This is equivalent to assuming the particles of the disperse phase and the molecules of the continuous phase in the feed to the reactor are mixed. The case in which the two phases have different residence-time distributions is analysed by considering unmixed feed streams. Ritchie and Tobgy (1978) have prepared a review of the models for the case of an un-premixed feed to a homogeneous chemical reactor.]

The micro-mixing is then considered to be segregated if the ages (of both particles and molecules) within each point are identical. The distribution of ages within each point is therefore a step function centred on the average age of the point. This is equivalent to saying that each point has a unique history.

On the other hand, the micro-mixing in the system is considered to be maximum-mixed if all the material leaving the system at some moment was mixed for the duration of stay in the system. Points with equal residual lives are mixed, which is to say that they have identical age distributions. This is equivalent to saying that points do not have a unique history.

## 3. THE NUMBER BALANCE DESCRIPTION OF A PARTICULATE PROCESS

The number balance is a general method for the description of the disperse phase in a particulate process (Hulburt and Katz, 1964). The number balance is premised on the concept of conservation of number, that is, since particles are distinct they can be counted. This principle has been applied to a large variety of particulate processes, such as crystallisation, leaching, combustion, roasting, flotation and comminution.

Hulburt and Katz (1964) presented the population balance in detail, defining the state, or condition, of

a particle and the position within the reactor of a particle in terms of the phase coordinates.

However, in chemical engineering, it is often more useful to define the population balance in terms of volume-averaged number densities. Thus, we define  $n(l, t) dl$  as the number of particles per unit volume in the system at any moment with particle coordinates  $l_i, i = 1, \dots, N$ , in the range  $l_i$  to  $l_i + dl_i$  for  $i = 1, \dots, N$ .  $N$  represents the total number of particle coordinates. Examples of such particle coordinates are the size of the particle in such processes as crystallisation or leaching, or the loading of an adsorbent onto resin or carbon in water treatment plants.

For the case of a continuous-flow system the number balance is written as (Hulburt and Katz, 1964; Randolph and Larson, 1971; Herbst, 1979)

$$\frac{\partial n(l, t)}{\partial t} + \sum_i^N \frac{\partial [R_i(l)n(l, t)]}{\partial l_i} = \frac{1}{\tau} \left[ n^0(l) - n_e(l, t) \right] + B(l, t) + D(l, t) \quad (2)$$

where  $n^0(l)$  is the particle density in the flow to the system,  $n_e(l, t)$  is the particle density leaving the system,  $\tau$  is the mean residence-time, and the two terms  $B(l, t)$  and  $D(l, t)$  represent the birth processes (such as nucleation) and the death processes (such as fission, or breakage).  $R_i(l)$  represents the kinetics of the reaction, and is the rate of change of  $l_i$  with respect to time,  $dl_i/dt$ .

The terms on the left-hand side of eq. (2) represent the accumulation of material in the reactor and the change in the number density due to reaction. The terms on the right-hand side of eq. (2) represent the flow of material to and from the reactor, the birth of particles in the reactor by processes such as nucleation, and the death of particles in the reactor by such processes as the disappearance of a mother cell due to the formation of daughter cells.

We assume that the number density  $n(l, t)$  is real and continuous.

The derivation of eq. (2) has been discussed in detail by Randolph and Larson (1971) and by Herbst (1979); the reader unfamiliar with the number balance is referred to these texts for an exposition.

In this work we do not consider any birth or death processes, and will consider only one particle coordinate, denoted as  $l$ . This is done only to simplify the mathematics of the problem, and is not a limitation of these concepts.

Usually the well-mixed assumption is made, so that number density leaving the system is the same as that in the system. Therefore, the number balance for the case of no birth or death processes is written as

$$\frac{\partial n(l, t)}{\partial t} + \frac{\partial [R(l)n(l, t)]}{\partial l} = \frac{1}{\tau} \left[ n^0(l) - n(l, t) \right]. \quad (3)$$

Implicit in this formulation of the volume-averaged number balance is the assumption of the residence-

time distribution of a single ideally mixed continuous tank, and the assumption that the environment in the system to which the particles are exposed is homogeneous. The second assumption means that the concentration of continuous-phase reactant throughout the system at all times is independent of position.

In the sections that follow, we will derive the volume-averaged number balance for the extremes of micro-mixing, that is, for the segregated system and the maximum-mixed system.

#### 4. THE NUMBER BALANCE FOR THE SEGREGATED REACTOR

Slurry which is fed to the reactor is divided into small packets of slurry which remain intact for the duration of their stay in the reactor. Each packet behaves as a batch reactor, and the probability of a packet leaving the reactor with residence time between  $t$  and  $t + dt$  is  $f(t) dt$ . Therefore, the number density of solids leaving the reactor is given by

$$n(l) dl = \int_0^\infty n(l, t) f(t) dt dl. \quad (4)$$

$n(l, t)$  is evaluated from the solution of the batch number balance

$$\frac{\partial n(l, t)}{\partial t} + \frac{\partial [R(l)n(l, t)]}{\partial l} = 0. \quad (5)$$

If birth and death processes need to be considered in the description of the reactor, then terms describing these processes can be added to eq. (5).

This differential equation has the initial condition that  $n(l, t) = n^0(l)$  at  $t = 0$ . The boundary condition is given by either  $n(l, t) = 0$  at  $l = 0$  if  $R(l)$  is a growth process or by  $n(l, t) = 0$  at  $l = \infty$  if  $R(l)$  is a shrinkage process.

For a process in which particle shrinkage occurs the solution to the number balance using these boundary conditions may result in particles with a negative value for their size. This is as a result of not including a death term in the number balance to account for particles vanishing at size zero. Clearly a negative value for the size of a particle is not meaningful; for this reason the moments of the distribution must be carefully calculated, beginning at size zero and increasing to the largest size.

The batch number balance must be solved in conjunction with the material balance in each packet:

$$C(t) = C^0 - \eta [\mu_3^0 - \mu_3(t)] \quad (6)$$

where  $C(t)$  is the concentration of continuous-phase reactant in each packet,  $C^0$  is the inlet concentration,  $\eta$  is a stoichiometric factor, and the amount of material in the disperse phase per unit volume is given by  $\mu_3(t) = \int_0^\infty l^3 n(l, t) dl$  (the third moment of the number density). The stoichiometric factor,  $\eta$ , determines how much continuous-phase reactant is consumed on reaction. If  $\eta = 0$  then none of the continuous-phase

reactant is consumed, and if  $\eta = 1$  then  $C(t) \rightarrow 0$  as the reaction conversion tends to 1.

The solution of eq. (6) is obtained by the method of characteristics (Aris and Amundson, 1973, pp. 83–124), and is given by

$$n(l, t) dl = n^0(L) dL \quad (7)$$

where  $n^0(L)$  is the number density in the feed.  $L$ , the particle size at zero conversion, and  $l$  are related by the solution of the equation:

$$t = \int_L^l \frac{dl}{R(l)} \quad (8)$$

An outline of the solution to quasi-linear partial differential equations using the method of characteristics is given in Section 6.2.

The segregated model is usually written in terms of the conversion,

$$1 - X = \frac{\int_0^\infty l^3 n(l) dl}{\int_0^\infty L^3 n^0(L) dL} \quad (9)$$

Substituting eqs (4), (7) and (8) into eq. (9) gives

$$1 - X = \frac{\int_0^\infty \int_0^\infty l^3 n^0(L) f(t) dL dt}{\int_0^\infty L^3 n^0(L) dL} \quad (10)$$

Noting that  $(l/L)^3 = 1 - X(t)$  where  $X(t)$  is the conversion for a particle of initial size  $L$ , we can write eq. (10) as

$$1 - X = \int_0^\infty \int_0^\infty [1 - X(t)] m^0(L) f(t) dL dt \quad (11)$$

where  $m^0(L)$  is the particle-size density of the feed on a mass basis. This is the usual form that segregated model is written (Rueher, 1979; Bartlett, 1971; Peters, 1991; Papangelakis *et al.*, 1990).

## 5. THE NUMBER BALANCE FOR THE MAXIMUM-MIXEDNESS REACTOR

Zwietering's representation of a maximum-mixedness reactor is as a side-stream reactor with the feed arranged to obtain a required residence-time distribution,  $F(t)$ .

The number balance for the maximum-mixedness reactor is given by the following partial differential equation:

$$\frac{\partial R(l)n(l, \lambda)}{\partial l} - \frac{\partial n(l, \lambda)}{\partial \lambda} = \frac{f(\lambda)}{1 - F(\lambda)} [n^0(l) - n(l, \lambda)] \quad (12)$$

The derivation of this equation is given in the Appendix.

Birth and death processes have not been introduced in this equation. This may be necessary for a complete description of crystallisation, or bioreactors.

The amount of continuous-phase reactant that reacts is proportional to the amount of material in the disperse phase that reacts. At any point  $\lambda$  the amount of material in the disperse phase per unit volume is given by  $\mu_3 = \int_0^\infty l^3 n(l, \lambda) dl$  (the third moment of the number distribution). Performing a material balance on the continuous phase gives

$$C(\lambda) = C^0 - \eta [\mu_3^0 - \mu_3(\lambda)] \quad (13)$$

where  $C^0$  is the concentration of continuous-phase reactant in the feed to the system and  $C(\lambda)$  is the concentration at point  $\lambda$  in the continuous phase.  $\eta$  represents the amount of the continuous-phase reactant that is consumed on reaction with the particles. If  $\eta = 0$ , then no continuous-phase reactant is consumed (zero-order reaction or  $C$  is in excess), or if  $\eta = 1$ , then  $C \rightarrow 0$  as the conversion of solids tends to one (stoichiometric amount of continuous-phase reactant is added).

We have assumed that there is no volume change on reaction, and that the disperse and continuous phases have the same residence-time distribution.

In order to calculate the conversion, we require the particle distribution at the reactor exit, i.e.  $n(l, \lambda)$  at  $\lambda = 0$  [or  $C(\lambda)$  at  $\lambda = 0$ ]. The boundary condition for eq. (12) is that  $n(l, \lambda)$  is bounded and positive at  $\lambda = \infty$ , i.e.  $\partial n / \partial \lambda = 0$  at  $\lambda = \infty$ . The other boundary condition depends on whether the particle reaction results in growth or shrinkage of  $l$ . If particle growth is considered then the condition is that  $n(l, \lambda) = 0$  at  $l = 0$ , while if shrinkage is considered the condition is that  $n(l, \lambda) = 0$  at  $l = \infty$ . The comments on the boundary conditions for the shrinkage process in Section 5 also apply here.

## 6. RESULTS

### 6.1. Maximum-mixedness reactor with residence-time distribution of an ideal mixer

For an ideal mixer, the residence-time distribution is given by

$$F(t) = 1 - e^{-t/\tau} \quad (14)$$

and the residence-time density is given by

$$f(t) = \frac{1}{\tau} e^{-t/\tau} \quad (15)$$

Therefore, for any arbitrary particulate kinetics  $R(l)$  eq. (12) becomes

$$\frac{\partial n(l, \lambda)}{\partial \lambda} = \frac{\partial [R(l)n(l, \lambda)]}{\partial l} + \frac{1}{\tau} [n^0(l) - n(l, \lambda)] \quad (16)$$

The solution of this equation is  $\partial n / \partial \lambda = 0$ . This means that  $n(l, \lambda)$  and  $C(\lambda)$  are constant for all  $\lambda$ , and they can be found from the solution of the equations:

$$\frac{\partial [R(l)n(l)]}{\partial l} = \frac{1}{\tau} [n^0(l) - n(l)] \quad (17)$$

$$C = C^0 + \eta (\mu_3^0 - \mu_3) \quad (18)$$

These equations [(17) and (18)] are the usual form of

the number balance written for a well-mixed continuous tank, which is given by eq. (3).

Therefore, the usual number balance when written for a well-mixed particulate reactor [eq. (3)] is identical to the solution to the equation describing the maximum-mixed reactor with a residence-time distribution for an ideally mixed tank, that is, an  $F(t)$  given by eq. (14).

This is analogous to the homogeneous system, where the mass balance written for a well-mixed tank (the usual CSTR mass balance) is equivalent to the solution to the maximum-mixedness reactor with a residence-time distribution of an ideally mixed tank, that is, an  $F(t)$  given by eq. (14).

### 6.2. Segregated model with constant continuous-phase reactant concentration

Consider a segregated reactor in which the exit concentration of continuous-phase reactant is the same as the inlet concentration. This describes a reaction in which the dependence of the rate of growth or shrinkage,  $R(l)$ , is independent of the continuous-phase reactant concentration. This reaction is zero-order with respect to concentration. This case also arises when the continuous-phase reactant in the continuous phase is in such excess that its concentration remains unchanged on leaving the reactor. In other words the reaction is pseudo-zero-order.

This case is described by the following equations:

$$n(l) = \int_0^{\infty} n(l, t) f(t) dt. \quad (19)$$

$n(l, t)$  is evaluated from the solution of the batch number balance:

$$\frac{\partial n(l, t)}{\partial t} + \frac{\partial [R(l)n(l, t)]}{\partial l} = 0. \quad (20)$$

Equation (20) is a quasi-linear partial differential equation and can be solved by the method of characteristics (Aris and Amundson, 1973, pp. 83–124). The technique of the method of characteristics is illustrated by eqs (21)–(24). According to the method of characteristics, the solution is found from the system of ordinary differential equations:

$$\frac{dl}{R(l)} = \frac{dt}{1} = \frac{dn(l)}{-R'(l)n(l)} \quad (21)$$

where  $R'(l)$  is the derivative of  $R(l)$  with respect to  $l$ . The solution to this set of equations follows directly from eq. (21) and is given by

$$n(l, t) = \frac{R(r)n^0(r)}{R(l)} \quad (22)$$

where  $r$  is evaluated from the expression

$$t = \int_r^l \frac{dl}{R(l)}. \quad (23)$$

$n^0(r)$  is the functional form of the initial number density evaluated at  $r$ .

Therefore, the segregated model for this case is

$$n(l) = \int_0^{\infty} \frac{R(r)n^0(r)}{R(l)} f(t) dt. \quad (24)$$

The solution of the segregated model for this case may be illustrated by an example. Consider a process in which the particles either diminish in size on reaction, such as a dissolution reaction, or increase in size on reaction. The kinetics of the solid–fluid reaction, that is, the rate of change of particle size, can be described by the following equation if no product layer forms on reaction (Le Blanc and Fogler, 1987):

$$R(l) = \frac{l^\beta C}{\alpha(1 - \beta)} \quad (25)$$

where  $\alpha$  and  $\beta$  are parameters, and  $C$  is the continuous-phase reactant concentration, which we consider to be a constant in this example. If the particles shrink in size on reaction,  $\alpha$  is negative, and if they grow in size on reaction,  $\alpha$  is positive. The constant  $\beta$  is zero if the kinetics are controlled by the rate of the surface reaction. If the kinetics are controlled by the transport of material to or from the particle surface, then  $\beta$  is  $-1$  for small particles where the slip velocity is assumed to be negligible, or  $\beta$  is  $-\frac{1}{2}$  for larger particles where the slip velocity is significant (Le Blanc and Fogler, 1987).

From eq. (23),  $r$  is given by

$$r = (l^{1-\beta} + tC/\alpha)^{1/(1-\beta)} \quad (26)$$

and the number density for a segregated reactor in this case is

$$n(l) = \int_0^{\infty} l^{-\beta} (l^{1-\beta} + tC/\alpha)^{\beta/(1-\beta)} \times n^0[(l^{1-\beta} + tC/\alpha)^{1/(1-\beta)}] f(t) dt. \quad (27)$$

### 6.3. Maximum-mixedness model with constant continuous-phase reactant concentration

Consider a similar situation as in Section 6.2 above, but for the case of the maximum-mixedness reactor. Again consider the reaction to be zero-order, or pseudo-zero-order, so that the concentration of continuous-phase reactant,  $C$ , remains constant.

In this case the maximum-mixedness reactor is described by

$$\frac{\partial R(l)n(l, \lambda)}{\partial l} - \frac{\partial n(l, \lambda)}{\partial \lambda} = \frac{f(\lambda)}{1 - F(\lambda)} [n^0(l) - n(l, \lambda)]. \quad (28)$$

Equation (28) is a quasi-linear first-order partial differential equation; the analytical solution to eq. (28) may be found by the method of characteristics (Aris and Amundson, 1973, pp. 83–124). The technique is the same as that outlined for eq. (20), and for this reason the solution procedure is not repeated here. The solution to this equation is given by

$$n(l, \lambda) = \frac{1}{R(l) [1 - F(\lambda)]} \int_\lambda^{\infty} R(r)n^0(r)f(\lambda) d\lambda \quad (29)$$

where  $r$  is evaluated from the equation

$$\lambda = \int_0^l \frac{dl}{R(l)}. \quad (30)$$

The reactor performance is evaluated using the exit conditions, that is, at  $\lambda = 0$ . This gives

$$n(l) = \frac{1}{R(l)} \int_0^\infty R(r) n^0(r) f(\lambda) d\lambda. \quad (31)$$

This result is the same as that which was obtained in Section 6.2 above for the segregated reactor under similar conditions, given by eq. (24).

Therefore, the segregated and maximum-mixedness reactors are identical if the concentration in the continuous phase remains constant. In other words, the segregated and maximum-mixed models are identical if the reaction is zero-order, or pseudo-zero-order with respect to the concentration of the reactant in the continuous phase.

This result is different to the case for homogeneous reactors, in which these two models are identical only if the reaction is first-order or pseudo-first-order in reactant concentration.

#### 6.4. Numerical solutions to micro-mixing models

Solutions of the equations describing the segregated and maximum-mixedness models were obtained for the residence-time densities for one, two and three tanks-in-series. The equations were expressed in dimensionless form using the following variables:

$$n(l) = \frac{n(l)}{n_T}, \quad \lambda = \frac{\lambda}{\bar{t}}, \quad l = \frac{l}{\bar{t}}, \quad C = \frac{C}{C^0}, \quad t = \frac{t}{\bar{t}}, \quad (32)$$

$$\mu_3 = \frac{\mu_3}{\mu_3^0}, \quad R(l, C) = \frac{\bar{t}R(l)}{l} = \frac{l^\beta C}{\alpha(1-\beta)}, \quad \alpha = \frac{\alpha \bar{t}^{1-\beta}}{C^0 \bar{t}}.$$

When the kinetics of the reaction for a dissolution reaction are expressed in this dimensionless form,  $\alpha$  represents the reaction time for complete conversion for a particle of the average size.

The equations for the segregated model in dimensionless form are

$$n(l) dl = \int_0^\infty n(l, t) f(t) dt dl \quad (33)$$

$$\frac{\partial n(l, t)}{\partial t} + \frac{\partial [R(l, C)n(l, t)]}{\partial l} = 0 \quad (34)$$

$$C(t) = C^0 - \eta[1 - \mu_3(t)] \quad (35)$$

and the equations for the maximum-mixedness model are

$$\begin{aligned} \frac{\partial [R(l, C)n(l, \lambda)]}{\partial l} - \frac{\partial n(l, \lambda)}{\partial \lambda} \\ = \frac{f(\lambda) [n^0(l) - n(l, \lambda)]}{1 - F(\lambda)} \end{aligned} \quad (36)$$

$$C(\lambda) = 1 - \eta[1 - \mu(\lambda)]. \quad (37)$$

The performance of the reactor was expressed in terms of the conversion:

$$X = 1 - \mu_3. \quad (38)$$

A gamma distribution was used as the feed distribution:

$$n^0(l) = \frac{1}{\Gamma(p)} l^{p-1} \exp(-pl). \quad (39)$$

The dimensionless variance  $\sigma^2 = 1/p$  used had a value of  $\frac{1}{2}$ .

The equations for both models were solved using a finite difference technique to approximate the differentials (Press *et al.*, 1989). The computational results were checked by comparison with the analytical solutions, given in Sections 6.2 and 6.3.

Table 1 compares the results of the calculation of conversion achieved in the reactor when  $\beta = 0$  and  $\beta = -1$ . When surface reaction is rate controlling, then the volume rate of shrinkage is proportional to the surface area, and  $\beta$  has the value of zero. However, if film transfer is rate controlling and the particles are sufficiently small that the film-transfer coefficient is

Table 1. Effect of micro-mixing on the performance of heterogeneous reactors when  $\eta = 1$

	$\beta = 0$		$\beta = -1$
	$\alpha = -0.5$	$\alpha = -1.5$	$\alpha = -0.5$
<i>One tank</i>			
Segregated	0.624	0.412	0.370
Maximum-mixedness	0.574	0.390	0.354
<i>Two tanks</i>			
Segregated	0.810	0.610	0.547
Maximum-mixedness	0.751	0.573	0.519
<i>Three tanks</i>			
Segregated	0.879	0.715	0.643
Maximum-mixedness	0.830	0.676	0.616

inversely proportional to the particle size, then  $\beta$  has a value of  $-1$ .

Table 1 shows the strong influence the mechanism of reaction has on the conversion achieved in the continuous reactor. For the same value of the time for complete conversion of the average-sized particle in the distribution,  $\alpha$ , there is almost a factor of two difference in the conversion achieved for both segregated and maximum-mixedness reactors.

Figure 1 shows that for a stoichiometric factor of 1, and a value of  $\beta = 0$ , and for a residence-time distribution given by eq. (14), the segregated model predicts a higher conversion than the maximum-mixedness model. This difference shows that for the case of a residence-time distribution for a single tank the models are not identical.

This figure also shows that the difference between these two cases becomes smaller as the residence time increases. This is because as the mean residence-time increases, the reactor begins to approximate a batch reactor; this is as expected, since the condition of micro-mixing plays no role in the performance of a batch reactor.

Figures 2 and 3 show the results for four different models, including two models referred to here as the tanks-in-series model and the partially segregated model.

The tanks-in-series model is that in which the number balance for a single tank, given by eqs (17) and (18), is repeated in series. The number balance for a single tank and the maximum-mixedness model with an  $f(t)$  of a single well-mixed tank [eq. (15)] are

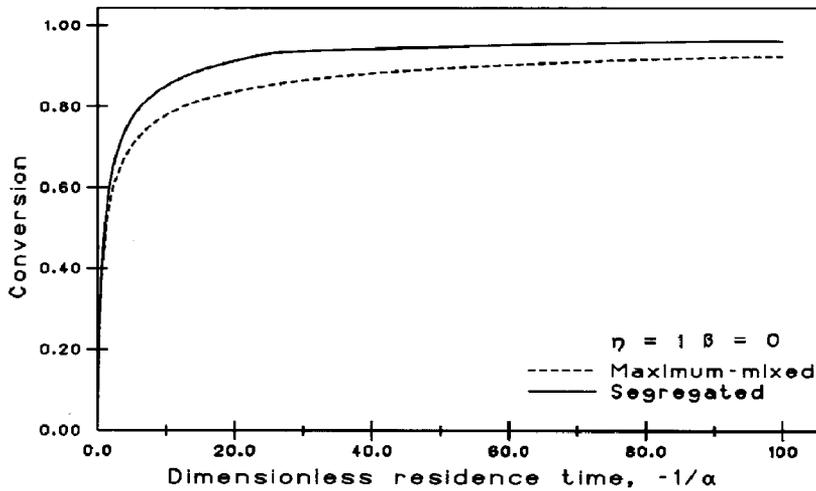


Fig. 1. The conversion calculated from the segregated and maximum-mixedness models for residence-time distributions of one ideally mixed tank.

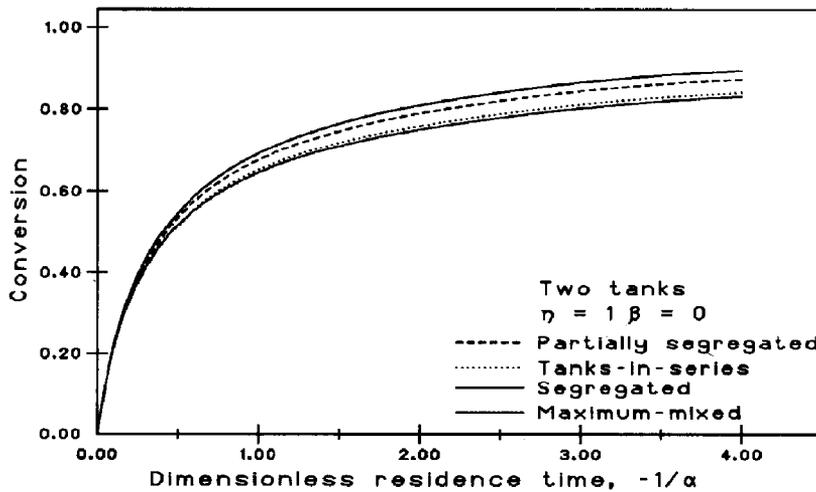


Fig. 2. The conversion calculated from the segregated and maximum-mixedness models for residence-time distributions of two tanks-in-series. Also included are the models for a series of two tanks using the number balance applied to two tanks (tanks-in-series) and using the segregated reactor with the residence time of a single ideal mixer repeated twice (partially segregated).

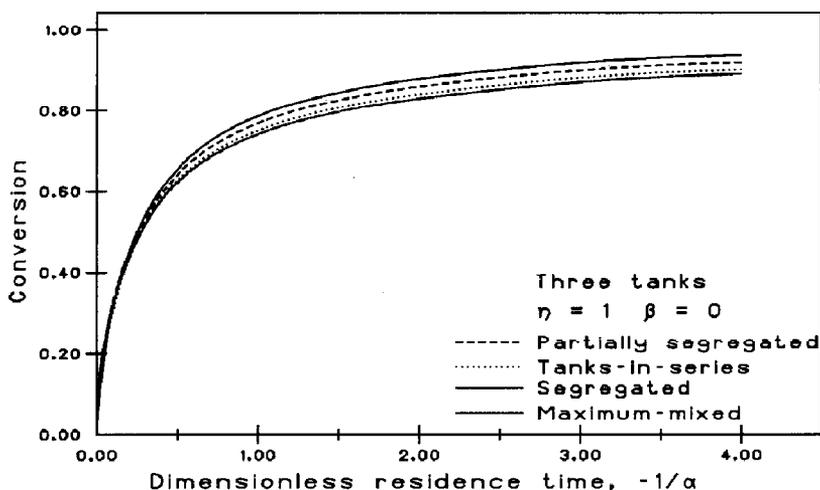


Fig. 3. The conversion calculated from the segregated and maximum-mixedness models for residence-time distributions of three tanks-in-series. Also included are the models for a series of three tanks using the number balance for the series of three tanks (tanks-in-series) and using the segregated reactor with the residence time of an ideal mixer repeated thrice (partially segregated).

identical. This means that each tank is maximum-mixed. On leaving the tank, mixing occurs, and then the material enters the next tank. Therefore, a series of  $N$  tanks modelled in this manner is not the same as the maximum-mixedness model with an  $f(t)$  for  $N$  tanks in series.

The partially segregated model is that in which a single segregated tank is repeated in series. The single segregated tank is described by the segregated model, eqs (4)–(6) with an  $f(t)$  for a single ideally mixed tank described by eq. (15). This means that each tank is segregated. On leaving the tank, mixing, or randomisation, of the segregated volume elements occurs between the tanks before material enters the next tank. This model for a series of  $N$  tanks is clearly not the same as the segregated model with an  $f(t)$  for  $N$  tanks in series.

These figures show that there is a difference in the conversion predicted by these models. The largest difference in the conversion data shown in these figures is 7.67% [ $-1/a = 25$  for  $f(t)$  for a single well-mixed tank and first-order kinetics]. If we consider the difference in  $a$  for fixed conversion, there is a much larger difference. An examination of the data in Fig. 1 at a conversion of 0.9 indicates that there is a factor of approximately four between the values of  $-1/a$  for the two models. This indicates that the values of the rate constant calculated will differ by a factor of four depending on which state of mixing is assumed.

## 7. DISCUSSION

Previous work has described particulate reactors using the segregated model, given by eq. (11), or by the number balance, given by eq. (3). The relationship between these two models has never been explored.

The key to the understanding of this relationship lies in the state of micro-mixing in the continuous reactor.

The segregated model assumes that the fluid entering the reactor is broken up into volume elements of fluid that each remain intact and behave as individual batch reactors during their passage through the reactor.

The population balance for a well-mixed tank reactor assumes that the reactor is a continuous-stirred-tank reactor, and the fluid in the reactor is well-mixed on a molecular level. This model, as written in eq. (3), assumes the residence-time distribution for a single tank, and is not applicable to other residence-time distributions.

The condition of micro-mixing is important in distinguishing these models. In order to explore the effect of micro-mixing on the performance of the particulate reactor, the number balance for particulate reactors has been formulated for the extremes of micro-mixing: the segregated number balance, given by eq. (4), and the maximum-mixedness number balance, given by eq. (12).

The analytical solutions to these models showed that the segregated and maximum-mixedness reactors are identical for the special case in which the concentration in the continuous phase remains constant throughout the course of the reaction.

This can be explained in the following way: if the rate of change of size is independent of the continuous phase concentration, that is, the particle kinetics are zero-order or pseudo-zero-order with respect to the gas- or liquid-phase concentration, then the rate at which the particle changes size is independent of its environment. Each particle is then a batch reactor, and micro-mixing has no effect on the performance of the reactor.

This is analogous to the case of first-order kinetics in homogeneous reactors. If the rate of reaction is first-order in a homogeneous system, then no interaction between the molecules is required for reaction. Each molecule then behaves as a batch reactor, and micro-mixing has no effect on the reactor performance.

Therefore, the condition for the equivalence of the segregated model and the maximum-mixedness model is different for a homogeneous reactor (that the reaction is first-order) and for a particulate reactor (that the reaction is zero-order). However, the underlying concept that determines these conditions for the equivalence of the models is the same for both homogeneous and particulate reactors.

For all other cases the segregated model [eq. (4)] and the maximum-mixed model [eq. (12)] will describe extremes of micro-mixing, and will predict different performances for the reactor.

Numerical solutions for the number balances were used to compare the predictions of reactor performance for these two models for various residence-time distributions. The differences in the conversion achieved in the reactors can be up to 7.67%, if the concentration in the continuous phase drops to zero as the conversion approaches one.

The differences reported here may increase significantly as the order of reaction with respect to the concentration of continuous-phase reactant increases. For example, the kinetics of the bacterial leaching of pyrite are essentially autocatalytic, in that as the bacteria consume pyrite they multiply. For this process the differences between these models will be magnified. They may also increase if birth and death processes, such as those needed to model bacterial populations and crystallisers, are included in the number balance.

In this work, we have considered the case in which both the phases had the same residence-time distribution. For this to be the case, the feed stream to the reactor must be completely mixed (premixed feed stream). The more general case, and that more likely to be found in practice, is that the residence-time distributions for the phases will be different, and the feed stream is therefore un-premixed. The model of the reactor in which the feed stream to the reactor is un-premixed may be analysed by considering that the two components enter the reactor as separate feed streams. Treleaven and Tobgy (1971) examined the case for maximum-mixedness in homogeneous reactors. Future work could be the analysis particulate reactors with un-premixed feed streams. Such reactors could be analysed using the number balance by the methods of Treleaven and Tobgy (1971).

## 8. CONCLUSIONS

This work has extended the pioneering research of Zwietering to include the discussion of heterogeneous reactors. The results of this work will enable workers in the field of heterogeneous reactions to determine

the effects of micro-mixing on the performance of the system under study. Such effects have been illustrated to be large. An accurate model of the system would therefore require an accurate model for the micro-mixing achieved in the system.

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## NOTATION

$B(l, t)$	birth function, $B(l, t) dl dt$ represents the number of particles arriving in the particle coordinate intervals $l_i$ to $l_i + dl_i$ for $i = 1, \dots, N$ during the time interval $t$ to $t + dt$ by birth processes, such as nucleation of crystals, or cell division of bacteria
$C$	concentration in fluid phase
$D(l, t)$	death function, $D(l, t) dl dt$ represents the number of particles leaving the particle coordinate intervals $l_i$ to $l_i + dl_i$ for $i = 1, \dots, N$ during the time interval $t$ to $t + dt$ by death processes, such as attrition of crystals, or cell division of bacteria
$f(t)$	residence-time density
$F(t)$	residence-time distribution
$l$	a single particle coordinate, such as particle size
$l_i$	particle coordinates
$L$	particle coordinate at time $t = 0$
$n(l)$	number density per unit volume w.r.t. $l$
$n^0(l)$	number density per unit volume w.r.t. $l$ in inlet to reactor
$n_e(l, t)$	number density per unit volume w.r.t. $l$ of particles in exit from the reactor
$N$	number particle coordinates, such as size or loading in the case of an adsorption process onto resin or carbon
$R_i(l)$	rate of change of $l_i$ , $dl_i/dt$ ; incorporates the kinetics of reaction
$t$	time, or residence time
$X$	conversion
<i>Greek letters</i>	
$\alpha$	parameter in rate of change of $l$ , eq. (25)
$\beta$	parameter in rate of change of $l$ , eq. (25)
$\Gamma$	age of volume element in reactor, eq. (1)
$\eta$	stoichiometric number, eq. (6)
$\lambda$	residual life of volume element in reactor, eq. (1)
$\mu_3(t)$	third moment of the number density [ $= \int_0^\infty l^3 n(l, t) dl$ ]
$\tau$	mean residence time

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#### APPENDIX: DERIVATION OF THE NUMBER BALANCE FOR THE MAXIMUM-MIXEDNESS REACTOR

Let  $\lambda$  be the residual life of the slurry at any point along the length of the reactor,  $q$  be the flow rate of the slurry at the

point along the length of the reactor where the life expectancy is  $\lambda$ ,  $\Delta q$  be the amount of slurry added to the reactor between life expectancy  $\lambda$  and  $\lambda + \Delta\lambda$ , and let  $\Delta v$  be the volume of the reactor that contains slurry with residual life between  $\lambda$  and  $\lambda + \Delta\lambda$ . We define  $n(l, \lambda) \Delta l \Delta \lambda$  as the number of particles per unit volume with size between  $l$  and  $l + \Delta l$ , and with life expectancy between  $\lambda$  and  $\lambda + \Delta\lambda$ . We can calculate  $n(l, \lambda) \Delta l \Delta \lambda$  from the number balance performed over the differential element  $\lambda$  to  $\lambda + \Delta\lambda$  for particles in the size class  $l$  to  $l + \Delta l$ :

Number in by flow at  $\lambda + \Delta\lambda$ :

$$|n(l, \lambda) \Delta l q|_{\lambda + \Delta\lambda}$$

Number in by flow at  $\lambda$ :

$$|n(l, \lambda) \Delta l q|_{\lambda}$$

Into differential element by flow from side-streams:

$$n^0(l) \Delta l \Delta q$$

Into size class by growth:

$$|R(l, C)n(l, \lambda) \Delta v|_l$$

Out of size class by growth:

$$|R(l, C)n(l, \lambda) \Delta v|_{l + \Delta l}$$

The number balance for this differential element gives

$$\begin{aligned} |n(l, \lambda) \Delta l q|_{\lambda + \Delta\lambda} + |R(l, C)n(l, \lambda) \Delta v|_l + n^0(l) \Delta l \Delta q \\ = |n(l, \lambda) \Delta l q|_{\lambda} + |R(l, C)n(l, \lambda) \Delta v|_{l + \Delta l} \end{aligned}$$

The quantities  $q$ ,  $\Delta q$  and  $\Delta v$  are related to the total flow rate to the reactor  $Q$  and the residence-time distribution,  $F$ , by the following relationships (Nauman and Buffham, 1983):

$$q = q(\lambda), \quad q(0) = Q$$

$$q/Q = 1 - F(t)$$

$$\Delta q/Q = f(\lambda) \Delta \lambda$$

Substituting these relationships, and taking the limits as  $\Delta\lambda \rightarrow 0$  and as  $\Delta l \rightarrow 0$ , gives

$$\frac{\partial R(l)n(l, \lambda)}{\partial l} - \frac{\partial n(l, \lambda)}{\partial \lambda} = \frac{f(\lambda)}{1 - F(\lambda)} [n^0(l) - n(l, \lambda)]. \quad (12)$$