Published in *Chem. Eng. Sci.*, **61** (2006), 6213–6217

Danckwerts' law for mean residence time revisited

Timo Gottschalk and Herold G. Dehling

Fakultät für Mathematik, Ruhr-Universität Bochum
Universitätsstraße 150, 44780 Bochum, Germany

Alex C. Hoffmann

Department of Physics and Technology, The University of Bergen
Allegaten 55, 5007 Bergen, Norway

Abstract

This paper shows that Danckwerts' law for mean residence time in a vessel with continuous and steady throughflow holds for a stochastic model based on a Markov chain for the particle spatial position, under a set of three very general conditions on the transfer probabilities. These are natural conditions and represent mass balance conditions on the transfer between spatial regions in the process. It is shown that a stochastic model for particle residence time distribution with these three conditions may describe almost any physical flow configuration, and also covers published mathematical RTD models, independent of their mathematical form or the nature of the associated boundary conditions, models for which Danckwert's law has hitherto been shown to be satisfied on a case-by-case basis. Two examples, namely those birth-death Markov chains and fluidized bed models are discussed.

1 Introduction

Since P. V. Danckwerts' original paper (Danckwerts (1953)) the study of residence time distribution (RTD) in vessels with continuous throughflow has become a valuable tool in process technology, and has been investigated in a number of articles.

Common to all models for RTD is that Danckwerts' law for mean residence time: $T'_m = \frac{V'}{v'}$ with V' the vessel volume and v' the continuous and steady volumetric throughflow must be satisfied. This can be a challenge both in numerical and analytical RTD modelling (e.g. Golz and Dorroh (2001) and Szymczak and Ladd (2003)).

Preprint submitted to Elsevier Science *25 November 2006*

There exists a vast number of different RTD models. They can roughly be divided into four categories (Wen and Fan (1975)):

(1) Models derived from a known flow profile;
(2) models based on flow with superimposed axial dispersion;
(3) compartment models and
(4) models based on fitting the RTD to some known stochastic distribution function.

In the categories 2 and 3 the conditions at the inflow and outflow boundaries need to be specified. These boundary conditions can be classified as:

(1) "Open" boundaries, where inflow is allowed through the outflow boundary and *vice-versa*.
(2) "Closed" boundaries, where such flows are not allowed.

For instance, for the simple plug flow with axial dispersion model, an open outflow boundary condition would allow material elements to diffuse back into the reactor through the outflow boundary.

Also combinations of the four types of RTD models mentioned above are used, see, for instance, Levenspiel (1999) or Wen and Fan (1975). The study of RTD for heterogeneous systems is still a quite open field.

Only a few articles have extended Danckwerts' general theory.

Gibilaro (1969) significantly extended Danckwerts' law to subregions. By considering a first order reaction taking place only in a subregion of the vessel with volume V_s', performing a mass balance over the entire vessel and taking the limit of the reaction rate constant to 0 after differentiating the mass balance equation, Gibilaro showed that the mean residence time in this subregion is equal to $\frac{V_s'}{v'}$.

Fan et al. (1995) rewrote Danckwerts' work into stochastic *parlange*, assigning a stochastic variable to the residence time of a particle (or fluid element) in the process. They also extended Danckwerts' theory to a reactor in the start-up phase.

A new approach for studying the particle dynamics and RTD in processes is to formulate *stochastic models* (Dehling et al. (1999); Harris et al. (2002)). In this, a stochastic variable is assigned to the spatial position of a particle, and the particle's dynamics is modelled by allowing this variable to undergo a Markov process.

This paper presents a set of natural and very general conditions that are sufficient for Danckwerts' law to hold for a generic RTD model based on assigning a stochastic variable to the spatial position of a particle, and allowing this variable to undergo a Markov process. These conditons, as the model itself, have a simple and intuitive physical significance.

Fan et al. (1985) have computed residence time distributions for some specific Markov chain models. They did not consider the issue of general conditions for the validity of Danckwerts' law, which is the focus of the present paper. The conditions formulated here can thus be used as a criterion for Danckwerts' law to hold also for their specific models.

We start by presenting the model and deriving the conditions under which Danckwerts' law holds for it. Then we discuss the physical significance.

2 A general RTD model satisfying Danckwerts' law based on a Markov chain with conditions

We consider the position of a particle or fluid element in a vessel of volume V' with volumetric inflow and outflow v'. Both space and time are discretized, each spatial cell has volume $\Delta V'$, and the length of a time interval is $\Delta t'$. We use these two magnitudes as scales for volume and time, so that the dimensionless volume of the vessel is $N = V'/\Delta V'$, the dimensionless time is $t = t'/\Delta t'$, and the dimensionless residence time $T = T'/\Delta t'$. The dimensionless volumetric throughflow becomes $v = v'\Delta t'/(\Delta V')$. Necessarily $v \leq 1$, which imposes the restriction $\Delta t' \leq \frac{\Delta V'}{v'}$ on the length of the time interval.

The particle's position (at each timestep n) is described by a random variable, $(X_n)_{n\geq 0}$, and space is discretized so that the state space for X_n is finite: $\{1, 2, 3, \ldots, N+1\}$. We let the process of particle movement be Markovian, i.e. without memory, and denote the transfer probabilities by $p_{ij} := P(X_n = j|X_{n-1} = i)$. The p_{ij} thus denote the probability that the particle transfers to cell j in timestep n, given that it was in cell i in time step $n-1$ and constitute an $(N+1) \times (N+1)$ transfer matrix $\mathbf{P}$.

The probability distribution of the particle's position models the concentration profile of a pulse of infinitely many non-interacting particles introduced in an inlet cell with index 1 at time $n = 0$. The outlet is modeled by an absorbing cell with index $N+1$, i.e. $p_{N+1i} = 0$ for all $i \neq N+1$. We denote the $N \times N$ transfer matrix without the absorbing cell by $\mathbf{Q}$.

We note that the n-times transition probabilities are given as $p^n_{ij} := P(X_n = j|X_0 = i) = (\mathbf{P}^n)_{ij} = (\mathbf{Q}^n)_{ij}$ for $1 \leq i, j \leq N$. The last equality holds because the $(N+1)th$ cell is absorbing. Now:

$$(\mathbf{I}-\mathbf{Q})\sum_{n=0}^{k}\mathbf{Q}^n = \mathbf{I}-\mathbf{Q}^{k+1}. \tag{1}$$

The condition that the absorbing state is reachable from every state implies that $\mathbf{Q}^{k+1} \to 0$ for $k \to \infty$, so that:

$$(\mathbf{I}-\mathbf{Q})\sum_{n=0}^{\infty}\mathbf{Q}^n = \mathbf{I}. \tag{2}$$

Thus the matrix $\mathbf{I}-\mathbf{Q}$ is invertible with inverse $(\mathbf{I}-\mathbf{Q})^{-1} = \sum_{n=0}^{\infty}\mathbf{Q}^n$. The expected total life time for the particle in cell j if it starts in cell i is:

$$\begin{aligned} E\left[\sum_{n=0}^{\infty} \mathbb{1}_{\{X_n=j\}} \middle| X_0 = i\right] &= \sum_{n=0}^{\infty} (\mathbf{Q}^n)_{ij} \\ &= \left(\sum_{n=0}^{\infty}\mathbf{Q}^n\right)_{ij} = (\mathbf{I}-\mathbf{Q})^{-1}_{ij}, \end{aligned} \tag{3}$$

where the indicator function $\mathbb{1}_{\{X_n=j\}}$ is equal to 1 in $\{X_n = j\}$ and else 0. $\sum_{n=0}^{\infty} (\mathbf{Q}^n)_{ij}$ is the total probability for transference from i to j.

The time that the Markov chain is in the non-absorbing states, or the life time, is: $T = \sum_{j=1}^{N}\sum_{n=0}^{\infty} \mathbb{1}_{\{X_n=j\}}$, the expected value of which is:

$$\begin{aligned} E\Big[T|X_0 = i\Big] &= \sum_{j=1}^{N} E\left[\sum_{n=0}^{\infty} \mathbb{1}_{\{X_n=j\}} \middle| X_0 = i\right] \\ &= \sum_{j=1}^{N} (\mathbf{I}-\mathbf{Q})^{-1}_{ij}. \end{aligned} \tag{4}$$

Now we impose the following conditions on the transfer probabilities:

a) $\sum_{j=1}^{N} p_{j1} = 1 - v$
b) $\sum_{j=1}^{N} p_{ji} = 1$ for all $2 \leq i \leq N$
c) $\sum_{j=1}^{N} p_{jN+1} = v$.

Since the matrix $\mathbf{I}-\mathbf{Q}$ is invertible, the matrix equation:

$$(\mathbf{I}-\mathbf{Q})^t x = e_1, \tag{5}$$

where $e_1 := (1, 0, \ldots, 0)^t$ is an N-dimensional vector, has a unique solution, which, by the standard rules for solving matrix equations, is the first row of the matrix $(\mathbf{I}-\mathbf{Q})^{-1}$. By conditions a) and b) $\sum_{i=1}^{N} (\mathbf{I}-\mathbf{Q})^t_{1i} = v$ and $\sum_{i=1}^{N} (\mathbf{I}-\mathbf{Q})^t_{ji} = 0$ $(2 \leq j \leq N)$, so that the N-dimensional vector: $x_0 := \frac{1}{v}(1, \ldots, 1)$ is the solution to Equation (5). By Equation (4), the expected residence time in the non-absorbing states, which constitute the vessel is:

$$E\Big[T|X_0 = 1\Big] = \sum_{j=1}^{N} (\mathbf{I} - \mathbf{Q})^{-1}_{1j} = \frac{N}{v}. \tag{6}$$

3 Physical significance

The N non-absorbing cells constitute the vessel, and the absorbing cell $N+1$ the outlet. We base the analysis on unit cell volume, so the volume of the vessel is N and the volumetric inflow and outflow are v. Equation (6) is therefore a statement of Danckwerts' law for the mean residence time.

The probability of the particle occupying a given cell $p(n,i)$ can be seen as the fraction of a pulse of marked material in that cell. The transition probabilities times the position probability $p_{ij}p(n,i)$ can be seen as the flow of marked material from cell i to cell j during time step n.

The requirement that the absorbing state must be reachable from all other states translates to the requirement that there must be no zones in the vessel that are completely "dead".

None of the above depends on the *form* of $\mathbf{P}$, and the analysis can therefore be applied to any stacking of cells in 1, 2 or 3 dimensions and any distribution of material movement in the vessel. Specifically as long as the outlet is reachable from all cells, the degree of "deadness" of partially dead regions, such as those discussed by Danckwerts (1953) in connection with "hold-back", has no influence on the mean residence time. In addition to this the mean residence time distribution is invariant to changes in the geometry of the vessel.

Conditions a), b) and c) simply describe volume conservation within the vessel. Condition b) says that the volume that flows into a cell (marked and unmarked material) is the same as what flows out, and conditions a) and c) that the volume flowing into the reactor is the same as that which flows out.

Gibilaro's result also holds in the presented model. By Equation (3) the expected residence time in cell j, when starting in cell 1, is $(\mathbf{I} - \mathbf{Q})^{-1}_{1j}$. Since we found that the first row of $(\mathbf{I}-\mathbf{Q})^{-1}$ is given by $x_0 := \frac{1}{v}(1, \ldots, 1)$, the expected residence time in each cell is $\frac{1}{v}$. Physically we can make cells arbitrarily small, and combine any arbitrary number N_s of them to create any subregion of volume $\frac{N_s}{N}$, for which the expected residence time is thus $\frac{N_s}{v}$, which is Gibilaro's result.

The state of boundaries (open or closed) has therefore no influence on the validity of Danckwerts' law in this model since we can choose to consider any

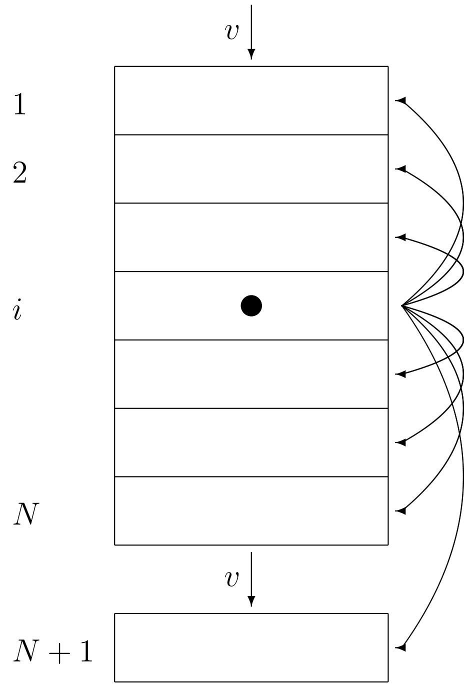

Fig. 1. Vessel split in cells $1 \ldots N$ with entrance in cell 1 and exit in cell $N+1$, inflow/outflow v, the particle in cell i and possible transition pathes indicated by the arrows with transfer probabilities p_{ij}.

subregion including or excluding the boundary cells 1 and $N+1$ in contrast to the classical treatment for compartment models, dispersed plugflow or series of ideal mixers (see Beek et al. (1999), Levenspiel (1999) and Wen and Fan (1975)).

4 Examples

a), b) and c) specify conditions on the transition matrix $\mathbf{P}$ that imply the validity of Danckwerts' law for the resulting Markov process model. Since Danckwerts' law is an empirical fact in continuous reactors containing one type of particles, any physically relevant Markov models for the motion of a single particle of the same type must satisfy a), b) and c). In this section we will investigate the consequences of these equations for a stochastic model for particle transport in fluidized beds. The model was proposed by Hoffmann and Paarhuis (1990) and subsequently refined by Dehling et al. (1999).

The model is based on ideas of Rowe and Partridge (1962) about the physical processes governing particle transport in batch fluidized beds. Adapted to continuous fluidized beds, these processes are

- transport upward in bubble wakes and deposition on top of the bed
- transport down in the bulk due to the exit flow of particles and to the removal of material low in the bed in bubble wakes
- dispersion due to the disturbance of the bulk material by fluidization bubbles.

We are considering a radially symmetric reactor with inflow of particles at the top and outflow at the bottom. We divide the reactor into N horizontal compartments of equal size. The compartments are labelled with indices i, $1 \leq i \leq N$, where $i = 1$ denotes the top compartment and $i = N$ the bottom, see Figure 2. Moreover, we add an additional state representing the exterior of the reactor. Particles that leave the reactor enter this state which gets the label $N + 1$.

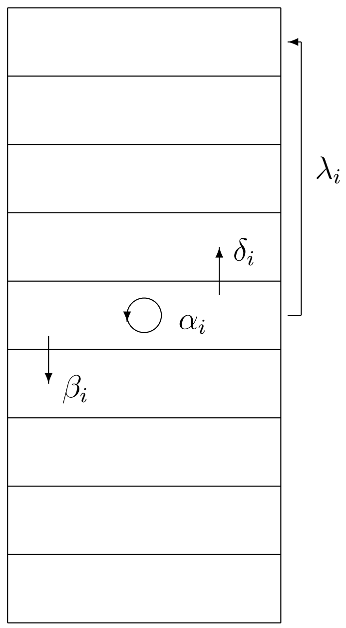

Fig. 2. Radially symmetric reactor with transition probabilities

A particle that is presently in state i can only make one of four possible transitions, namely stay where it is, move one cell ahead or back or move all the way to the top of the reactor. While the first three of these transitions model the last two processes identified by Rowe and Partridge, the last transition models the first of these physical processes.

The probabilities for the four possible transitions are denoted by α_i, β_i, δ_i and λ_i respectively and we demand $\alpha_i + \beta_i + \delta_i + \lambda_i = 1$. For the entrance cell a move back is not possible, and thus we put $\delta_1 = 0$. The exterior is an absorbing boundary, hence $\alpha_{N+1,N+1} = 1$. In this way we get the following transition probabilities for $3 \leq i \leq N$:

$$\begin{aligned} p_{i,i-1} &= \delta_i \\ p_{i,i} &= \alpha_i \\ p_{i,i+1} &= \beta_i \\ p_{i,1} &= \lambda_i. \end{aligned}$$

For $i = 2$ we modify these equations to get

$$\begin{aligned} p_{2,1} &= \delta_2 + \lambda_2 \\ p_{2,2} &= \alpha_2 \\ p_{2,3} &= \beta_2. \end{aligned}$$

At the boundaries, i.e. for $i = 1$ and $i = N + 1$, we have

$$\begin{aligned} p_{1,1} &= \alpha_1 \\ p_{1,2} &= \beta_1 \\ p_{N+1,N+1} &= 1. \end{aligned}$$

All the other transition probabilities are equal to zero.

For the fluidized bed transport process, the general conditions a) and c) become

$$\alpha_1 + \delta_2 + \sum_{i=2}^{N} \lambda_i = 1 - v \tag{7}$$

$$\beta_N = v. \tag{8}$$

Condition b) now becomes

$$\alpha_i + \beta_{i-1} + \delta_{i+1} = 1 \tag{9}$$

for $2 \leq i \leq N - 1$ and for $i = N$

$$\alpha_N + \beta_{N-1} = 1. \tag{10}$$

These conditions can be simplified by using the fact that $\alpha_i + \beta_i + \delta_i + \lambda_i = 1$ for $2 \leq i \leq N$, and $\alpha_1 + \beta_1 = 1$. Thus condition (9) is equivalent to

$$\beta_{i-1} - \delta_i = \lambda_i + (\beta_i - \delta_{i+1}) \tag{11}$$

for $2 \leq i \leq N - 1$ and

$$\beta_{N-1} - \delta_N = \lambda_N + v. \tag{12}$$

Iterating (11) and using (12) we thus attain

$$\beta_{i-1} - \delta_i = v + \sum_{j=i}^{N} \lambda_j, \tag{13}$$

for $2 \le i \le N$. Note that (7) together with $\alpha_1 + \beta_1 = 1$ yields

$$\beta_1 - \delta_2 = v + \sum_{j=2}^{N} \lambda_j,$$

and thus (13) holds for all $1 \le i \le N$. Together with $\beta_N = v$, (13) is actually equivalent with a), b) and c). Thus if (13) holds for all $1 \le i \le N$ and if $\beta_N = v$, Danckwerts' law holds!

Condition (13) has a natural intuitive interpretation. The left hand side equals the netflow in the bulk phase through the membrane separating the i-th and the $(i-1)$-st cell. This flow has to be equal to the sum of the outflow of particles and the wake flow, at this point, as otherwise material will accumulate in one of the cells

Notation

$\mathbf{I}$	identity matrix
N	number of cells/dimensionless vessel volume
N_s	number of cells in a subregion/dimensionless subregion volume
$\mathbf{P}$	transfer probability matrix with elements $p_{i,j}$
$\mathbf{Q}$	transfer probability matrix between non-absorbing cells, elements $q_{i,j}$
t'	time, s
t	dimensionless time
T'	residence time, s
T	dimensionless residence time
V'	volume of vessel, m^3
V'_s	volume of subregion, m^3
v'	volumetric throughflow, m^3/s
v	dimensionless volumetric throughflow
X_n	stochastic variable representing the cell containing the particle at time step n
x_n	vector of position probabilities at time step n
$\Delta t'$	length of a time interval/time scale, s
$\Delta V'$	volume of a spatial cell/volume scale, m^3
$\delta_i,\ \alpha_i,\ \beta_i$	probabilities of moving one cell back, staying in cell, or moving one cell forward, resp.
λ_i	dimensionless probability rate of particle moving from cell i to cell 1
$\mathbb{1}$	indicator function

References

Beek, W. J., Muttzall, K. M. K., van Heuven, J. W., 1999. Transport Phenomena, 2nd Edition. John Wiley and Sons.

Danckwerts, P. V., 1953. Continuous flow systems. Chem. Eng. Sci. 2, 1–13.

Dehling, H. G., Hoffmann, A. C., Stuut, H. W., 1999. Stochastic models for transport in a fluidized bed. SIAM J. Appl. Math. 60, 337–358.

Fan, L. T., Too, J. R., Nassar, R., 1985. Stochastic simulation of residence time distribution curves. Chem. Eng. Sci. 40(9), 1743–1749.

Fan, L. T., Shen, B. C., Chou, S. T., 1995. Stochastic modeling of transient residence-time distributions during start-up. Chem. Eng. Sci. 50, 211–221.

Gibilaro, L. G., 1969. Residence time distributions in regions of continuous flow systems. Chem. Eng. Sci. 34, 697–702.

Golz, W. J., Dorroh, J. R., 2001. The convection-diffusion equation for a finite domain with time varying boundaries. Applied Mathematics Letters 14, 983–988.

Harris, A. T., Thorpe, R. B., Davidson, J. F., 2002. Stochastic modelling of the particle residence time distribution in circulating fluidised bed risers. Chem. Eng. Sci. 57, 4779–4796.

Hoffmann, A. C., Paarhuis, H. A., 1990. Study of the particle residence time distribution in vertically moving fluidized beds. IChemE Symp. Ser. 121, 37–49.

Levenspiel, O., 1999. Chemical reaction engineering, 3rd Edition. John Wiley and Sons.

Rowe, P. N., Partridge, B. A., 1962. Particle movement caused by bubbles in a fluidised bed. In: Interaction Between Fluids & Particles, P. A. Rottenburg (hon. ed). Instn. of Chem. Engrs., London, pp. 135–142.

Szymczak, P., Ladd, A. J. C., 2003. Boundary conditions for stochastic solutions of the convection-diffusion equation. Physical Review E 68, 036704–1–036704–12.

Wen, C. Y., Fan, L. T., 1975. Models for flow systems and chemical reactors. Dekker.