Applications of a Statistical Theory in Residence Time Distributions

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Since the concept of residence time distribution was introduced by Danckwerts (1953), it has attracted extensive research activities and has been considered a key parameter in chemical reaction engineering (Nauman and Buffham, 1983; Smith, 1981), including reactive processing and devolatilization of polymers in screw extruders (Lambla, 1992). Much work dealing with the residence time distribution has been based primarily on the distributions of two idealized reactors that pervade the residence time theory, called the continuously stirred tank reactor (CSTR) and the plug-flow reactor. While the residence time density (RTD) functions of these idealized systems or their combinations can be calculated theoretically, the RTD functions in most practical systems have to be obtained experimentally, particularly for screw extruders. With only a few exceptions, both theoretical derivations and experimental measurements of a RTD function reported in standard textbooks or in the literature are virtually all done using the classical mass-balance approach: monitoring the concentration response at the outlet to a given change in concentration of a species at the inlet. The inherent definition of the RTD function in terms of probability, on the other hand, has often been largely overlooked, and its importance seems not to be fully appreciated. One would expect that the statistical view of the RTD function could allow direct use of well established statistical theories and mathematical manipulations, thus offering a much easier alternative of deriving RTD functions of simple systems. The objectives of this work are twofold: 1. to provide insights into the relations of a RTD function between its mathematical formalism and its physical implications, or its practical application potential; 2. to demonstrate advantages of the statistical concept over the traditional mass-balance approach in deriving the RTD functions in systems consisting of idealized reactors in series, in parallel, or in a more complicated manner.

Theoretical Background

For a system consisting of n subsystems in series (Figure 1 in which the individual residence time density functions, $f_1(t)$ $f_2(t), \ldots, f_n(t)$, are statistically independent, the overall residence time density function $f(t)$ can be related to the individual ones in the Laplace domain by (Nauman and Buffham 1983):

$$\bar{f}(s) = \bar{f}_1(s)\bar{f}_2(s) \ldots . \bar{f}_n(s) \quad (1$$

or in the time domain by:

$$f(t) = \int_0^t f_1(\tau_1) \int_0^{t-\tau_1} f_2(\tau_2) \ldots$$

$$\int_0^{\tau_{n-3}-\tau_{n-2}} f_{n-1}(\tau_{n-1}) f_n(\tau_{n-2}-\tau_{n-1}) d\tau_{n-1} \ldots d\tau_2 d\tau_1 \quad (2$$

Equation 2, to the authors' knowledge, is not available i standard textbooks or in the literature.

For a combination of two subsystems, Eq. 2 reduces to:

$$f(t) = \int_0^t f_1(\tau) f_2(t-\tau) d\tau \quad (3$$

Equation 3 is recognized as the convolution integral for statistically independent systems (Nauman and Buffham, 1983)

Physical Implications of Statistical Independenc

Although the mathematical formalisms of Eq. 1 have bee discussed by Nauman and Buffham (1983), its physical implications concomitant with the assumption that the $f_i(t)$ ar statistically independent remain to be elaborated. Subsequently, we show that this statistic independence requires perfect mixing or uniform concentrations that exist at ever boundary that connects two subsystems without backflow.

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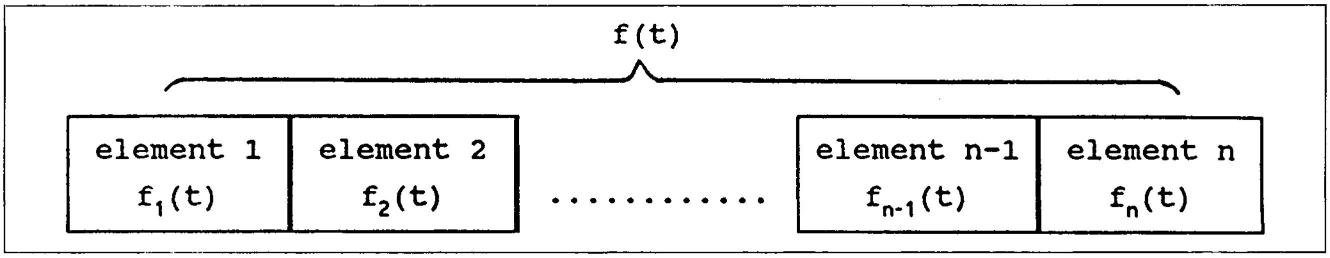

Figure 1. *n* statistically independent subsystem in series.

For simplicity, a system consisting of two subsystems is considered (Figure 2). If a perfect mixing exists at the boundary of the two subsystems, the concentration response at the boundary $C_i(t)$ to a concentration change C_0 at the inlet of the first subsystem is the same across the entire boundary. If $C_i(t)$ is viewed as the input concentration function of the species to the second subsystem, the response at its outlet $C(t)$ is then:

$$C(t) = \int_0^t C_i(t-\theta) f_2(\theta) d\theta \tag{4}$$

A remark is made here that Eq. 4 was derived first by Danckwerts (1953) with an error to be corrected: the upper integral limit of Eq. 39 or 40 in his original article should be t, not ∞.

If C_0 is a step function, the cumulative RTD function or step response of the first subsystem $F_1(t)$ can be expressed as:

$$F_1(t) = C_i(t)/C_0 \tag{5}$$

Introduction of Eq. 5 into Eq. 4, with rearrangements of the resulting expression, yields the overall cumulative residence time distribution function of the overall system $F(t)$:

$$F(t) = \frac{C(t)}{C_0} = \int_0^t F_1(t-\theta) f_2(\theta) d\theta \tag{6}$$

Differentiation of both sides of Eq. 6 leads to the overall $f(t)$:

$$f(t) = \frac{dF(t)}{dt} = \int_0^t f_1(t-\theta) f_2(\theta) d\theta + F(0) f_2(t) \tag{7}$$

Introduction of $\tau = t - \theta$ into Eq. 7, along with the fact that $F(0) = 0$, leads to:

$$f(t) = \int_0^t f_1(\tau) f_2(t-\tau) d\tau \tag{8}$$

which is the same as Eq. 3.

It follows from the above discussion that a perfect mixing or a uniform concentration at the boundary is a sufficient condition for Eq. 3 to be valid. Similar arguments also apply to a system consisting of more than two subsystems. It should be emphasized that in addition to a perfect mixing at the boundaries, the validity of Eq. 2 or 3 also requires that each of the subsystems is a closed system. In other words, particles in the downstream subsystem do not communicate with those in the adjacent or other upstream subsystems through some mechanism of transport. This is not to say that particles within a subsystem cannot communicate: in fact, communication among particles within a subsystem can be as much as in a CSTR or as little as in a plug-flow reactor.

Applications of the Statistical Theory

RTD in CSTR in series

Case 1: Identical CSTR in Series. Traditionally, the RTD of n CSTRs in series is derived from the tracer concentration response to a step function input (Smith, 1981). From tracer mass balances, the concentration response of tank j is obtained:

$$C_j = \frac{Q}{V_j} e^{-tQ/V_j} \int_0^t C_{j-1} e^{tQ/V_j} dt \tag{9}$$

where Q is the flow rate, and V_j is the volume of tank j. If the tanks are of the same volume, the following relation holds:

$$\frac{Q}{V_j} = \frac{n}{\bar{t}} \tag{10}$$

where n is the number of tanks, and $\bar{t}$ is the overall mean residence time in n tanks. The overall cumulative residence time distribution function can then be obtained by establishing mass balances for n tanks:

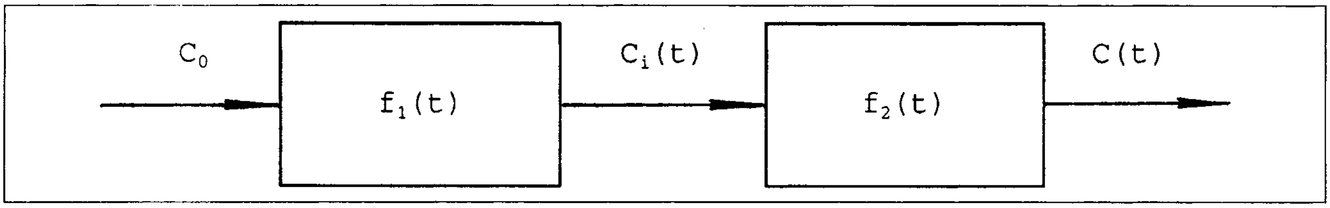

Figure 2. Two subsystems in series.

$$F(t)=1-e^{-nt/\bar{t}}\left[1+\frac{nt}{\bar{t}}+\frac{1}{2!}\left(\frac{nt}{\bar{t}}\right)^2+\ldots+\frac{1}{(n-1)!}\left(\frac{nt}{\bar{t}}\right)^{n-1}\right] \tag{11}$$

Differentiation of both sides of Eq. 11 yields the $f(t)$ function:

$$f(t)dt=\frac{n}{(n-1)!}\left(\frac{nt}{\bar{t}}\right)^{n-1}e^{-nt/\bar{t}}d\left(\frac{t}{\bar{t}}\right) \tag{12}$$

Since the RTD functions of the individual tanks are statistically independent of each other because of a perfect mixing that exists at any boundary between two tanks, derivation of Eqs. 11 and 12 can be achieved using the theory presented above (Eq. 2 or 3). It is well known that the $f(t)$ function of a single CSTR is:

$$f(t)=\frac{1}{\bar{t}}e^{-t/\bar{t}} \tag{13}$$

The use of Eq. 3 easily yields the $f(t)$ of two identical tanks in series:

$$f(t)=\int_0^t\left(\frac{1}{\bar{t}_s}e^{-\tau/\bar{t}_s}\right)\left(\frac{1}{\bar{t}_s}e^{-(t-\tau)/\bar{t}_s}\right)d\tau=\frac{t}{\bar{t}_s^2}e^{-t/\bar{t}_s} \tag{14}$$

where $\bar{t}_s$ is the mean residence time of a single tank. Similarly, $f(t)$ of n identical tanks in series can be obtained using Eq. 2, and it has the following form:

$$f(t)=\frac{1}{\bar{t}_s(n-1)!}\left(\frac{t}{\bar{t}_s}\right)^{n-1}e^{-t/\bar{t}_s} \tag{15}$$

Equation 15 can be recast into Eq. 11 by first noting that $\bar{t}=n\bar{t}_s$ and then integrating both sides of Eq. 15 from time 0 to time t.

Case 2: CSTRs of Different Volumes in Series. The advantage of Eq. 2 or 3 is much more relevant when the volumes of stirred tanks are different. For two stirred tanks in series of unequal volumes, the overall $f(t)$ of these two tanks can be obtained using Eq. 3:

$$f(t)=\int_0^t\left(\frac{1}{\bar{t}_1}e^{-\tau/\bar{t}_1}\right)\left(\frac{1}{\bar{t}_2}e^{-(t-\tau)/\bar{t}_2}\right)d\tau=\frac{e^{-t/\bar{t}_1}-e^{-t/\bar{t}_2}}{\bar{t}_1-\bar{t}_2} \tag{16}$$

Although Eq. 16 can also be derived from the mass-balance approach, it will be tedious and time-consuming for a large number of CSTRs in series. In contrast, the use of Eq. 2 easily yields the overall $f(t)$ of three tanks in series:

$$f(t)=\frac{\bar{t}_1e^{-t/\bar{t}_1}}{(\bar{t}_1-\bar{t}_2)(\bar{t}_1-\bar{t}_3)}+\frac{\bar{t}_2e^{-t/\bar{t}_2}}{(\bar{t}_2-\bar{t}_1)(\bar{t}_2-\bar{t}_3)}+\frac{\bar{t}_3e^{-t/\bar{t}_3}}{(\bar{t}_3-\bar{t}_1)(\bar{t}_3-\bar{t}_2)} \tag{17}$$

and that of n tanks in series:

$$f(t)=\sum_{j=1}^{n}\frac{\bar{t}_j^{n-2}e^{-t/\bar{t}_j}}{(\bar{t}_j-\bar{t}_1)(\bar{t}_j-\bar{t}_2)\ldots(\bar{t}_j-\bar{t}_{j-1})(\bar{t}_j-\bar{t}_{j+1})\ldots(\bar{t}_j-\bar{t}_n)} \tag{18}$$

Integration of both sides of Eq. 18 leads to the cumulative residence time distribution:

$$F(t)=\sum_{j=1}^{n}\frac{\bar{t}_j^{n-1}(1-e^{-t/\bar{t}_j})}{(\bar{t}_j-\bar{t}_1)(\bar{t}_j-\bar{t}_2)\ldots(\bar{t}_j-\bar{t}_{j-1})(\bar{t}_j-\bar{t}_{j+1})\ldots(\bar{t}_j-\bar{t}_n)} \tag{19}$$

RTD in a combination of a CSTR and a tubular laminar flow reactor (TLFR) in series

Figure 3 is a schematic representation of the combined system. $f(t)$ of a TLFR is (Smith, 1981):

$$f(t)=\begin{cases}0 & t<t_{\min}\\ \dfrac{\bar{t}_1^2}{2t^3} & t\geq t_{\min}\end{cases} \tag{20}$$

where $t_{\min}$ and $\bar{t}_1$ are the minimum and mean residence times, and $t_{\min}=\bar{t}_1/2$.

Considering the perfect mixing that exists between CSTR and TLFR, the overall $f(t)$ can be obtained easily using Eq. 3:

$$f(t)=\int_{t_{\min}}^{t}\frac{\bar{t}_1^2}{2\tau^3}\frac{1}{\bar{t}_2}e^{-(t-\tau)/\bar{t}_2}d\tau=\int_0^{t-t_{\min}}\frac{\bar{t}_1^2}{2(t-\tau)^3}\frac{1}{\bar{t}_2}e^{-\tau/\bar{t}_2}d\tau \tag{21}$$

where $\bar{t}_2$ is the mean residence time of the CSTR.

Equation 21 can be expanded to:

$$f(t)=\frac{e^{-\xi}}{\bar{t}_2}\left[e^{\zeta}(1+\zeta)-\zeta^2\left(\ln\frac{\bar{t}_1}{2}+\zeta+\frac{1}{2\cdot 2!}\zeta^2+\frac{1}{3\cdot 3!}\zeta^3+\ldots\right)\right]-\frac{\zeta^2}{\bar{t}_2}\left[1/\xi^2+1/\xi-e^{-\xi}\left(\ln t+\xi+\frac{1}{2\cdot 2!}\xi^2+\frac{1}{3\cdot 3!}\xi^3\ldots\right)\right] \tag{22}$$

where $\zeta=\bar{t}_1/2\bar{t}_2$, and $\xi=t/\bar{t}_2$.

Note that Eq. 21 or 22 can also be derived from the mass-balance approach, but it needs more work (cf, Appendix 1). The identical RTD expressions derived from both the mass-balance approach and the statistical theory for a combination of a CSTR and a TLFR further confirms that as long as a two-dimensional perfect mixing is ensured at every boundary between two subsystems, the relation between the overall residence time density function $f(t)$ and the individual ones $f_i(t)$ is then given by Eq. 2.

RTD in TLFRs in series

If a two-dimensional perfect mixing is ensured across the section of the boundary between two tubular laminar flow reactors, the overall $f(t)$ can also be obtained using Eq. 3:

$$f(t)=\int_{t_{01}}^{t-t_{02}}\left(\frac{2t_{01}^2}{\tau^3}\right)\left(\frac{2t_{02}^2}{(t-\tau)^3}\right)d\tau=\int_{t_{01}}^{t-t_{02}}\frac{4t_{01}^2t_{02}^2}{\tau^3(t-\tau)^3}\,d\tau \tag{23}$$

where t_{01} and t_{02} are the minimum residence times of the first and the second TLFRs.

When $t_{01} = t_{02} = t_0$, Eq. 23 can be recast into:

$$f(t)=\frac{16t_0^4}{t^2}\left[\frac{2t_0-t}{t_0^2(t-t_0)^2}+\frac{3}{2}\left(\frac{t+2t_0}{t^2t_0^2}-\frac{3t-2t_0}{t^2(t-t_0)^2}\right)+\frac{6}{t^3}\ln\left(\frac{t-t_0}{t_0}\right)\right] \tag{24}$$

Otherwise, the expanded expression is a bit too long to be written down here.

Certainly Eq. 2 or 3 can also be applied to series-parallel configurations with ease if perfect mixing exists at every boundary of interest, as the $f(t)$ function of a parallel configuration is simply related to the individual $f_i(t)$ functions by:

$$f(t)=\Sigma x_i f_i(t) \tag{25}$$

where x_i is the volumetric flow rate fraction passing through subsystem i of the parallel configuration. Thus, a series-parallel configuration reduces to a series one.

Discussion

It has been shown that for a system consisting of n subsystems, a perfect mixing or a uniform concentration in every boundary is a sufficient condition for the subsystems to be statistically independent so that Eq. 2 or 3 is valid. In comparison to the traditional mass-balance approach, Eq. 2 or 3 provides a much easier alternative to derive the overall RTD function of a system involving the idealized reactors (CSTR and TLFR). The Laplace transform (Eq. 1) may do a better job than Eq. 2 or 3 when the transform and inverse transform of a RTD function are readily available, which is the case for CSTRs in series.

The statistical theory is useful particularly for reactors-in-series, in which flow paths are long and narrow, or the length-diameter ratio (L/D) is large. A typical example of this is a (single or twin) screw extruder, of which the ratio is usually much larger than 20. In this case, a fluid passing through the channels can be easily mixed to a sufficient extent by the presence of mixing elements (such as kneading discs and calender gaps). In chemical reactors, a flow may be sufficiently rearranged by valves, fittings or flow paths of sharply changing geometries at the boundaries of reactors so that Eq. 2 or 3 can be applied. Experimental verification and practical applications of the theory in screw extruders will be addressed in a companion article (Chen et al., 1993).

Concluding Remarks

This work has shown applications of a statistical theory (Eq. 2 or 3) to derive the residence time distribution (RTD) functions of some idealized reactors in series including continuously stirred tank reactors and tubular laminar flow reactors. In comparison to the traditional mass-balance approach, this theory offers a much easier alternative, particularly when the reactors are of different volumes and/or of different types. More importantly, this theory can be used to derive the RTD of a combination of any reactors in series from the individual RTDs regardless of their volumes and types, provided that mixing at the boundaries is two-dimensionally perfect and that the reactors involved are closed systems.

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Notation

$C(t)$ = concentration response to a step function, kg/m^3
C_0 = step function of concentration, kg/m^3
$C_i(t)$ = concentration response at a boundary, kg/m^3
$f(t)$ = overall residence time density function, s^{-1}
$f_i(t)$ = residence time density function of subsystem i, s^{-1}
$\bar{f}(s)$ = Laplace transform of $f(t)$ function
$F(t)$ = overall cumulative RTD function
$F_i(t)$ = cumulative residence time distribution of subsystem i
Q = volumetric flow rate, m^3/s
t = time, s
$\bar{t}$ = mean residence time, s
$\bar{t}_i$ = mean residence time of subsystem i, s
$t_{\min}$ = minimum residence time of a TLFR, s
$\bar{t}_s$ = mean residence time of a CSTR, s
V_j = volume of tank j, m^3
x_i = volumetric flow rate fraction of subsystem i

Greek letters

ζ = $\bar{t}_1/2\bar{t}_2$ in Eq. 22
ξ = $t/\bar{t}_2$ in Eq. 22
θ = dummy variable of integration in Eqs. 4, 6 and 7
τ = dummy variable of integration in Eqs. 2, 3, 8, 14, 16, 21

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Appendix 1: Mass-Balance Approach to Derive Eq. 21

Consider a TLFR and a CSTR connected in series (Figure A1). At time 0, a concentration step function from 0 to C_0 enters the TLFR; after time t, the concentration response at the boundary between the CSTR and the TLFR is $C_i(t)$, and that at the outlet of the CSTR is $C(t)$. Writing a mass balance for the CSTR yields:

$$\frac{dC(t)}{dt}=\frac{Q}{V}\left[C_i(t)-C(t)\right]=\frac{1}{\bar{t}_2}\left[C_i(t)-C(t)\right] \tag{A1}$$

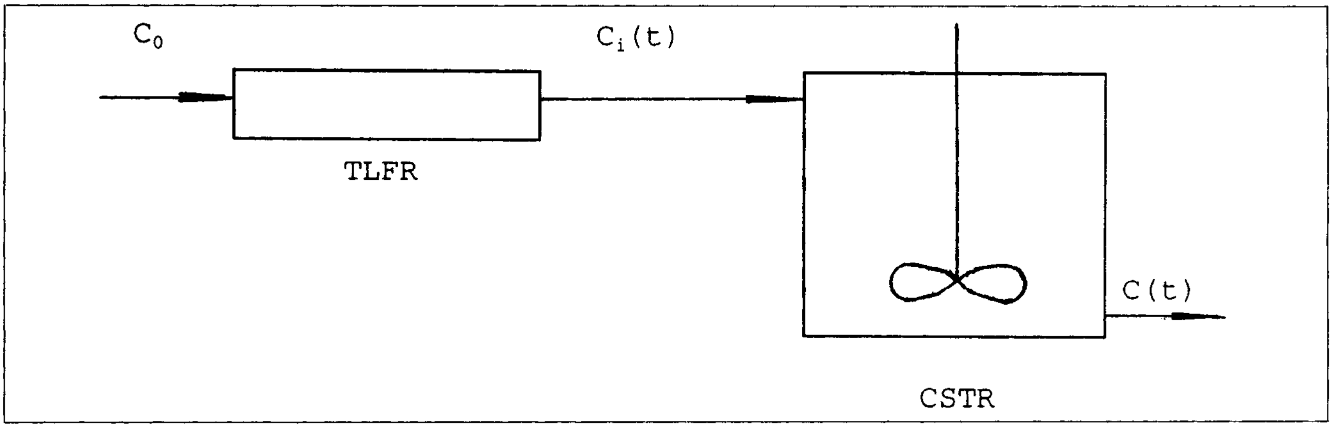

Figure A1. Combination of a TLFR and a CSTR in series.

where Q is the volumetric flow rate, V is the volume of the CSTR, and $C_i(t)$ can be related to the cumulative RTD function of the TLFR:

$$C_i(t) = C_0 F_1(t) = C_0 \left[1 - \frac{1}{4}\left(\frac{\bar{t}_1}{t}\right)^2\right] \qquad \text{(A2)}$$

Introducing the cumulative RTD in the whole combination $F(t)$ which by definition is equal to $C(t)/C_0$, and Eq. A2 into Eq. A1 yields:

$$\frac{dF(t)}{dt} + \frac{1}{\bar{t}_2} F(t) = \frac{1}{\bar{t}_2} - \frac{1}{4\bar{t}_2}\left(\frac{\bar{t}_1}{t}\right)^2 \qquad \text{(A3)}$$

The solution to Eq. A3 is:

$$F(t) = \frac{e^{-t/\bar{t}_2}}{\bar{t}_2}\left\{\int_{t_{\min}}^{t}\left[1 - \frac{1}{4}\left(\frac{\bar{t}_1}{t}\right)^2\right] e^{t/\bar{t}_2} dt\right\} \qquad \text{(A4)}$$

where $t_{\min} = \bar{t}_1/2$.

Differentiation of both sides of Eq. A4 leads to Eq. 21.

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