Unsteady-State Residence-Time Distribution in Perfectly Mixed Vessels

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While addressing some difficulties in the modeling of unsteady-state residence-time distribution (RTD), the care of perfectly mixed systems was considered. By an extension of the boundary condition domain, the traditional unfeasible concept of fresh and original populations was discarded to achieve a solution valid for all the fluid elements in a single vessel. This result enabled the development of the unsteady-state RTD for N vessels in series in the form of a joint probability density function. The relationship between the joint RTD and the combined RTD was also established. Numerical simulations were performed under various time varying flow patterns. The proposed solution can be applied to RTD-based models of chemical reactors operating under unsteady-state conditions. Potential applications in polymer reaction engineering are briefly outlined.

Introduction

The effect of the residence-time distribution (RTD) on reactor performance was well established and researched during the 1950–1975 period (Danckwerts, 1953, 1958; Cha and Fan, 1963; Hulbert and Katz, 1964; Himmelblau and Bischoff, 1968; Chen, 1971). At that time, most of the interest was focused on RTD under steady flow conditions. Recently, however, the incorporation of unsteady-state models into predictive control schemes has become commonplace (McAuley and MacGregor, 1992), partly due to advances in computational processor speed. In order to produce dynamic models that accurately reflect the physical reality, the effect of RTD on system performance under unsteady flow conditions must then be considered.

Despite a great deal of research in the RTD field, the unsteady-state region remains an area that requires further investigation. While the general balance describing unsteady-state RTD has been well-established (Hulbert and Katz, 1964), the rigor of the final model solution, its computational efficiency, and applicability need some clarification. In chemical engineering, RTD is applied to reactor models in order to account for the effects of the ageing of the reactor contents. For example, the activity of a catalyst that interacts with other components in a reactor is a function of the reactor dynamics, characterized by real time, t, as well as the duration of exposure of the catalyst to the reaction environment, characterized by residence-time or catalyst age, θ. For cases wherein the inlet and exit flows vary with real time, a reactor model that accounts for unsteady-state RTD leads to a complex system of ODEs, PDEs, and sometimes integral equations. They are computationally tedious and expensive, raising questions about the feasibility of RTD incorporation. In addition, the boundary conditions associated with the partial differential equation resulting from RTD modeling are not as yet rigorously established. Previously, they were defined without connection to physical reality (Hulbert and Katz, 1964; Himmelblau and Bischoff, 1968; Chen, 1971), rendering the resulting models of interest only academically. Furthermore, each of the two boundary conditions involved generates the RTD solution only in a particular (t, θ) domain. When obtaining the global solution, the concept of two populations (fresh and original) used to be employed in order to maintain consistency between the domain of the solution and the domain of the boundary conditions (Zacca, 1995). This complicates the final mathematical result and renders the previous models impractical for solving more general RTD models, for example, the model of vessels in series. We then find that there is much room for improvement in the field of mathematical modeling of unsteady-state RTD. We overcome the problem of having distinct populations by employing a fundamental material balance and extending the boundary-condition domain for the fresh population. This novel approach also enables us to address the problem of unsteady-state RTD for vessels in series.

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Previous Attempts at Modeling

None of the research available in the literature provides a suitable starting point for the development of unsteady-state residence-time distribution for vessels in series. The steady-state RTD was first developed by MacMullin and Weber (1935) for both a single vessel as well as a cascade of vessels. Danckwerts (1953, 1958) and Zwietering (1959) popularized the RTD concept in chemical-reaction engineering by giving it a convenient organizational structure, and employed it to assess the effect of imperfect mixing on the efficiency in blenders and homogeneous reactors. However, these developments applied only to steady-state conditions. Hulbert and Katz (1964) derived an expression that was restricted to the evolution of RTD from an arbitrary initial state to a steady-state pattern. Cha and Fan (1963) treated the unsteady-state RTD, but only for special cases, such as sinusoidally varying flows or constant entrance and variable exit flows. In obtaining the unsteady-state RTD for a single vessel, Nauman (1969) employed a theoretical method based on the concept of a tracer input signal. He developed the unsteady-state RTD for a single vessel, but effectively employed a two-population concept, which does not extend itself easily to vessels in series. On the other hand, Chen (1971) and Zacca et al. (1995, 1996) applied population-balance modeling in obtaining the unsteady-state RTD for a single vessel, but had some unspecified functions in the final solution. For the case of vessels in series, an integrated flow variable was introduced by Niemi (1977), and, more recently, Fernandez-Sempere et al. (1995), in order to derive an unsteady-state RTD that was restricted to the case of a constant vessel holdup. Chen and Hu (1993) derived the more descriptive joint RTD by employing statistical theory, but only for the case of steady flow conditions.

Before developing a refined mathematical model of unsteady-state RTD, we present the framework proposed by previous authors in their modeling attempts. Hulbert and Katz (1964) approached the problem of unsteady-state RTD via population-balance modeling. For the case of a single vessel, they demonstrated that the governing PDE is

$$\frac{\partial w}{\partial t} + \frac{\partial w}{\partial \theta} = \sum_k f_k(t,\theta). \tag{1}$$

The RTD $w(t,\theta)$ is often presented in the following normalized form:

$$I(t,\theta) = \frac{w(t,\theta)}{\int_0^\infty w(t,\theta')d\theta'} = \frac{w(t,\theta)}{H(t)}, \tag{2}$$

where the fluid holdup $H(t)$ results from the unsteady-state total material balance over the vessel:

$$\frac{d}{dt}H = \sum_k \int_0^\infty f_k(t,\theta)d\theta. \tag{3}$$

Equation 1 represents the general relationship between the distribution $w(t,\theta)$, real time t, and age θ, as well as flows across the boundaries of the vessel. The requisite boundary conditions (BC) for the governing PDE were presented by Zacca (1995) in the following form:

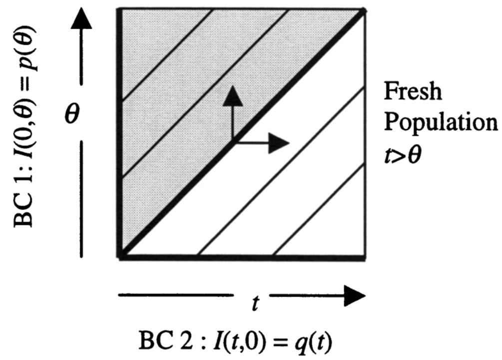

Figure 1. Two population domains in the (t,θ)-plane.

$$\text{BC 1:} \quad I(0,\theta) = p(\theta) \tag{4}$$

$$\text{BC 2:} \quad I(t,0) = q(t). \tag{5}$$

He considered these boundary conditions to be independent, each referring to a different solution domain in the (t,θ)-plane. These domains correspond to two distinct fluid element populations present in the vessel. The fluid elements that were already in the vessel at time $t = 0$ constitute the *original population*, and for this population $t \le \theta$. In turn, the *fresh population* involves only those fluid elements that entered the vessel at $t > 0$. Therefore, in this domain $t > \theta$. Figure 1 illustrates the two domains corresponding to original and fresh populations. It is known from the theory of characteristics that BC 1 generates the solution to Eq. 1 in the original population domain, whereas BC 2 generates the solution in the fresh population domain. The flow rates across the vessel boundaries for $t \le 0$ determine the initial age distribution function $p(\theta)$, whereas the flows for $t > 0$ determine $q(t)$.

Zacca (1995) proposed that the function $q(t)$ in BC 2 is the inverse of the mean residence-time $\tau_{in}(t)$, where $\tau_{in}(t)$ is based on the entrance flow $h_{in}(t)$ rather than the exit flow $h_{out}(t)$. For the case of perfect mixing, his solution in the fresh population domain is

$$I(t,\theta) = \frac{1}{\tau_{in}(t-\theta)} \exp\left(-\int_{t-\theta}^{t} \frac{dt'}{\tau_{in}(t')} \right), \tag{6}$$

where $\tau_{in}(t)$ is available from the flow characteristics. In turn, for the original population, corresponding to BC 1, Zacca obtained:

$$I(t,\theta) = I(0,\theta - t)\exp\left(-\int_0^t \frac{dt'}{\tau_{in}(t')} \right), \tag{7}$$

which unfortunately contains the unknown function $I(0, \theta - t)$. As Zacca (1995) admits, the presence of two populations makes the final solution and its application in chemical-reactor engineering fairly complicated. It will be shown in the present article that this complication makes further extension of the RTD model untenable, for example, to the case of vessels in series. Therefore, we seek to eliminate the two-

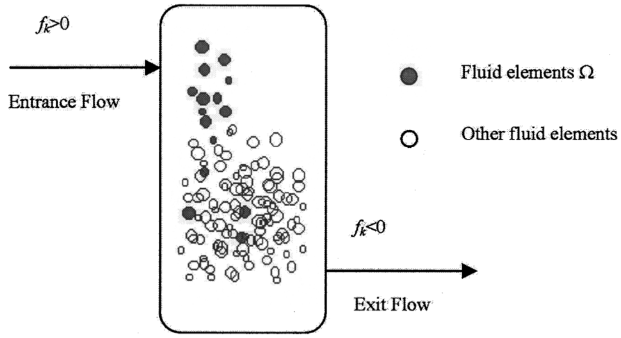

Figure 2. Fluid element sets.

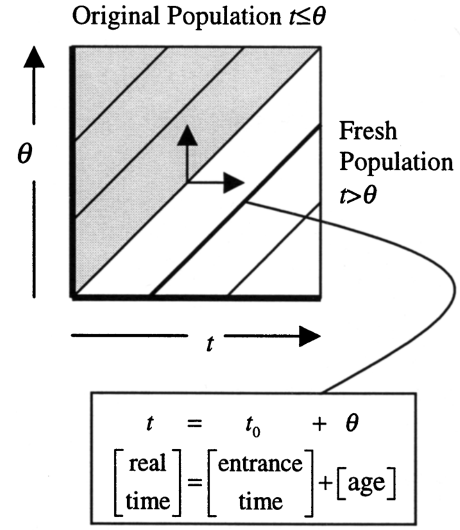

Figure 3. Process of ageing.

population nature of the problem. As our logical starting point, we will employ a fundamental balance over the number of fluid elements in the vessel, since it applies to both the fresh and original populations.

Governing Equation for Unsteady-State RTD

Our developments apply to a completely segregated fluid where the assumption of perfect mixing holds for the macroscopic elements of the fluid, rather than its individual molecules. Possible examples of completely segregated fluids are distinct packets of fluid in the case of continuous phases, or solid particles, liquid droplets, and gas bubbles in the case of dispersed phases.

RTD is usually derived from a combined description of the ageing of fluid elements within the vessel and their flow across its boundaries. Let t_0 be the entrance time of the fluid elements belonging to the age range $\theta = [0,\ \Delta\theta]$ that entered the vessel in the time interval $[t_0,\ t_0 + \Delta t]$, where both $\Delta\theta$ and Δt are infinitesimally small. This entrance time interval will be the only distinguishing characteristic between this set of fluid elements, denoted Ω, and all other elements, as shown in Figure 2.

For set Ω, the following equation relates the three time variables involved, viz., real time t, age θ, and entrance time t_0:

$$t = t_0 + \theta. \tag{8}$$

Equation 8 describes the process of ageing, and can be geometrically interpreted as the characteristic line on the (t,θ)-plane, as shown in Figure 3.

We define the internal RTD function $w(t,\theta)$ such that the product $w(t,\theta)\Delta\theta$ represents the number of fluid elements at time t in the vessel with ages in the range $[\theta,\ \theta + \Delta\theta]$. Similarly, we define the flow-rate age distribution $f_k(t,\theta)$ such that $f_k(t,\theta)\Delta\theta$ is the contribution to the rate at which fluid elements with age range $[\theta,\ \theta + \Delta\theta]$ flow into or out of the vessel via stream k. We adopt the convention that for flow into the vessel, $f_k(t,\theta) > 0$.

Let us consider fluid elements in age range $[\theta - \Delta\theta,\ \theta]$ in the vessel at time t. The entrance time for these fluid elements is given by $t_0 = t - \theta$. After Δt time units have elapsed, all these elements will be older by $\Delta\theta = \Delta t$. Hence, they will then belong to the age range $[\theta,\ \theta + \Delta\theta]$. The number of elements in this range will not be identical to that in $[\theta - \Delta\theta,\ \theta]$ due to material exit flow. A balance over the number of elements of age range $[\theta,\ \theta + \Delta\theta]$ and time frame $[t,\ t + \Delta t]$ is thus given by

$$w(t,\theta)\Delta\theta = w(t - \Delta t, \theta - \Delta\theta)\Delta\theta + \sum_k f_k(t - \Delta\theta, \theta - \Delta\theta)\Delta\theta\Delta t. \tag{9}$$

On substituting $\Delta\theta = \Delta t$, and taking the limit $\Delta\theta \to 0$, we have:

$$\lim_{\Delta\theta \to 0} \frac{w(t,\theta) - w(t - \Delta\theta, \theta - \Delta\theta)}{\Delta\theta} = \sum_k f_k(t,\theta). \tag{10}$$

By applying l' Hopital's rule to the lefthand side, we obtain:

$$\begin{aligned} LHS &= \frac{d}{d\Delta\theta}\left[w(t,\theta) - w(t - \Delta\theta, \theta - \Delta\theta)\right]_{\Delta\theta = 0} \\ &= \left[-\frac{d}{d\Delta\theta}\left[w(t - \Delta\theta, \theta - \Delta\theta)\right]\right]_{\Delta\theta = 0} \\ &= -\left[\frac{\partial w}{\partial t}\frac{\partial(t - \Delta\theta)}{\partial\Delta\theta} + \frac{\partial w}{\partial\theta}\frac{\partial(\theta - \Delta\theta)}{\partial\Delta\theta}\right]_{\Delta\theta = 0} = \frac{\partial w}{\partial t} + \frac{\partial w}{\partial\theta}, \end{aligned} \tag{11}$$

which leads to the PDE given by Eq. 1. According to the general theory of first-order linear PDEs, Eq. 1 can be reduced to an ODE by the method of characteristics. The first derivative along the characteristic line is

$$\frac{dw}{dt} = \frac{\partial w}{\partial t} + \frac{\partial w}{\partial\theta}\frac{\partial\theta}{\partial t} = \frac{\partial w}{\partial t} + \frac{\partial w}{\partial\theta}. \tag{12}$$

Hence, if we restrict our attention to the case of one entrance and one exit flow, the equation governing unsteady-state RTD becomes

$$\frac{dw}{dt} = f_{\text{in}}[t,\theta(t)] - f_{\text{out}}[t,\theta(t)], \tag{13}$$

with $\theta(t) = t - t_0$. When there is no recycle, the inlet flow to the reactor can be regarded as containing only fluid elements with zero age. Therefore, for $\theta > 0$, $f_{in}(t,\theta)$ vanishes and Eq. 13 reduces to

$$\frac{dw}{dt} = -f_{out}[t,\theta(t)]. \tag{14}$$

Unsteady-State RTD for a Perfectly Mixed Vessel

Fresh population domain

The particular form of the flow-rate age distribution $f_{out}(t,\theta)$ depends on the model of mixing assumed for the vessel. Under the perfect mixing assumption, this can be obtained by noting that the age distribution of the fluid elements is identical at all points in the vessel, including points precisely at the exit. Mathematically, the latter is expressed as

$$I(t,\theta) = E(t,\theta). \tag{15}$$

The external age distribution $E(t,\theta)$ refers to fluid elements that have just exited the vessel, and is defined such that $E(t,\theta)\Delta\theta$ is the fraction of fluid elements at the exit in age range $[\theta, \theta + \Delta\theta]$. The same fraction also can be obtained by dividing $f_{out}(t,\theta)\Delta\theta$, the exit flow rate of fluid elements belonging to the same age range, by the total exit flow rate $h_{out}(t)$. The external age distribution then becomes

$$E(t,\theta) = \frac{f_{out}(t,\theta)}{h_{out}(t)}. \tag{16}$$

Thus, according to Eq. 15, for perfect mixing, we have

$$f_{out}(t,\theta) = I(t,\theta)h_{out}(t) = \frac{w(t,\theta)}{H(t)}h_{out}(t) = \frac{w(t,\theta)}{\tau_{out}(t)}. \tag{17}$$

Finally, the governing ODE for unsteady-state RTD under perfect mixing is

$$\frac{d}{dt}w[t,\theta(t)] = -\frac{w[t,\theta(t)]}{\tau_{out}(t)}. \tag{18}$$

The initial condition to this equation can be obtained by considering only the fluid elements that have just entered the vessel and so belong to the zero age range $\theta = [0, \Delta\theta]$, where $\Delta\theta \to 0$. In this age range, the entrance flow rate must also be accounted for. The general balance of fluid elements, in the form of Eq. 9, can be used for this purpose:

$$w(t_0,0)\Delta\theta = w(t_0 - \Delta\theta, -\Delta\theta)\Delta\theta + f_{in}(t_0,0)\Delta\theta\Delta\theta - f_{out}(t_0,0)\Delta\theta\Delta\theta. \tag{19}$$

There are obviously no fluid elements in the vessel bearing negative ages, so the term $w(t_0 - \Delta\theta, -\Delta\theta)\Delta\theta$ can be ignored. Since the entrance flow consists entirely of age-zero fluid elements, the term $f_{in}(t_0,0)\Delta\theta$ equals $h_{in}(t_0)$. As a result, with the finite function, f_{out}, and taking the limit $\Delta\theta \to 0$, the requisite initial condition of Eq. 18 assumes the form:

$$w(t_0,0) = h_{in}(t_0). \tag{20}$$

After solving the governing ODE given the initial condition just obtained, we obtain

$$w(t, t - t_0) = h_{in}(t_0)\exp\left(-\int_{t_0}^{t}\frac{dt'}{\tau_{out}(t')}\right). \tag{21}$$

When applying the characteristic line equation and rewriting Eq. 21 in terms of the normalized age distribution, the final solution for the fresh population becomes

$$I(t,\theta) = \frac{h_{in}(t-\theta)}{H(t)}\exp\left(-\int_{t-\theta}^{t}\frac{dt'}{\tau_{out}(t')}\right) \quad t \geq \theta \geq 0. \tag{22}$$

We note that Zacca's solution for RTD in the same domain is

$$I(t,\theta) = \frac{h_{in}(t-\theta)}{H(t-\theta)}\exp\left(-\int_{t-\theta}^{t}\frac{dt'}{\tau_{in}(t')}\right). \tag{23}$$

Although the difference between these solutions might appear to be significant at first glance, they are equivalent, as shown in Appendix A. However, the advantage of the solution presented here is that it can be extended to the original population as well, finally resulting in a global solution to unsteady-state RTD.

Extension to the original population

As Zacca (1995) admits, the presence of two populations makes solution of RTD-based models of chemical reactors complicated. We illustrate this by considering a system of vessels in series. We wish to develop a complete historical record of the time spent by the fluid elements in each of the vessels. The fluid elements in a particular vessel are characterized by more than one residence time as a result of the residence in the preceding vessels. Such a "historical" record can be properly expressed in terms of a joint probability density $\rho_i(t,\theta)$, which is a function of real time t and ages (θ_1, θ_2, . . ., θ_i). This is a more general age distribution than the traditionally obtained combined RTD. The latter describes the probability of a fluid element having spent a total of $\theta_T = \theta_1 + \theta_2 + \cdots + \theta_N$ time units in all N vessels of the cascade, implying that it does not distinguish between the ages spent in the different vessels. In order to obtain a more general result for unsteady-state flow conditions, we wish to determine the joint probability of a fluid element having spent $\theta_1, \theta_2, \ldots, \theta_i$ time units in vessels 1, 2, . . ., $i \leq N$, respectively. The required joint probability density $\rho_i(t, \boldsymbol{\theta})$, $i \leq N$, is defined such that the product $\rho_i(t, \boldsymbol{\theta})\prod_{j=1}^{i}\Delta\theta_j$ represents the fraction of fluid elements currently residing in vessel i, identified by the age range $[\theta_i, \theta_i + \Delta\theta_i]$, which previously occu-
pied vessels 1, 2, . . ., $i-1$ for $[\theta_1, \theta_1 + \Delta\theta_1]$, $[\theta_2, \theta_2 + \Delta\theta_2]$, . . ., $[\theta_{i-1}, \theta_{i-1} + \Delta\theta_{i-1}]$ periods of time, respectively.

When attempting to derive the joint RTD by using the two-population concept, a complicated solution results. Let us consider a system of two vessels in series. What is the joint RTD for fluid elements exiting vessel number two? If we adopt the fresh/original population approach, we begin by developing the joint RTD in vessel 1:

$$\rho_1(t,\theta_1) = \begin{cases} \rho_1^{\mathrm{I}}(t,\theta_1) & \text{for} \quad \theta_1 > t \quad \text{(original population RTD, vessel 1)} \\ \rho_1^{\mathrm{II}}(t,\theta_1) & \text{for} \quad \theta_1 \le t \quad \text{(fresh population RTD, vessel 1)}. \end{cases}$$

We note that two populations are required in constructing ρ_1. This is due to the presence of two different boundary conditions, which generate different functional forms of the RTD function, namely, $\rho_1^{\mathrm{I}}(t,\theta_1)$ and $\rho_1^{\mathrm{II}}(t,\theta_1)$. Similarly, we develop the RTD in vessel 2, but find that the complexity of the solution is increasing, as shown below:

$$\rho_2(t,\theta_1,\theta_2) = \begin{cases} \rho_2^{\mathrm{I}}(\rho_1^{\mathrm{I}};t,\theta_1,\theta_2) & \text{for} \quad \theta_1 > t,\ \theta_2 > t \quad \text{(original pop. RTD, vessel 1; original pop. RTD, vessel 2)} \\ \rho_2^{\mathrm{I}}(\rho_1^{\mathrm{II}};t,\theta_1,\theta_2) & \text{for} \quad \theta_1 \le t,\ \theta_2 > t \quad \text{(fresh pop. RTD, vessel 1; original pop. RTD, vessel 2)} \\ \rho_2^{\mathrm{II}}(\rho_1^{\mathrm{I}};t,\theta_1,\theta_2) & \text{for} \quad \theta_1 > t,\ \theta_2 \le t \quad \text{(original pop. RTD, vessel 1; fresh pop. RTD, vessel 2)} \\ \rho_2^{\mathrm{II}}(\rho_1^{\mathrm{II}};t,\theta_1,\theta_2) & \text{for} \quad \theta_1 \le t,\ \theta_2 \le t \quad \text{(fresh pop. RTD, vessel 1; fresh pop. RTD, vessel 2)}. \end{cases}$$

Since there are two functional forms of ρ_1 and because there are two different boundary conditions that apply in vessel 2, four functional forms are required to generate the joint RTD in vessel 2. It becomes obvious that, in general, to obtain the joint RTD for N vessels, we require 2^N different functional forms.

The complexity increases even further if the systems concerned exhibit moving discontinuities of the RTD surface as a result of discontinuous flow rates. According to Zacca, these discontinuities can be accounted for by introducing further fresh populations. Unfortunately, such a procedure further fragments the solution domain. Figure 4 illustrates the example of three discontinuities in the system entrance flow rate in a single vessel, occurring at instances d_1, d_2, and d_3. It is evident that Zacca's proposal necessitates the presence of as many as eight populations. The problem is exacerbated by the presence of more than one vessel, as described earlier.

The inherent complexity of the multiple-population approach led Zacca to acknowledge that the resulting rigorous bookkeeping of the emerging populations can make generic dynamic modeling intractable unless further simplifications or assumptions are called for. It is thus preferable to obtain a solution that overcomes the difficulties associated with multiple populations. On analyzing Zacca's solution more closely, we note that the fundamental difference between the original and fresh populations is merely the identity of fluid elements, which is determined by the domain of the entrance time, t_0. The fresh population enters the vessel in the domain $t > 0$, whereas the original population enters in the domain $t \le 0$. If we could extend the domain of the boundary condition for the fresh population in order to include the original population domain, we would be able to obtain the required global solution.

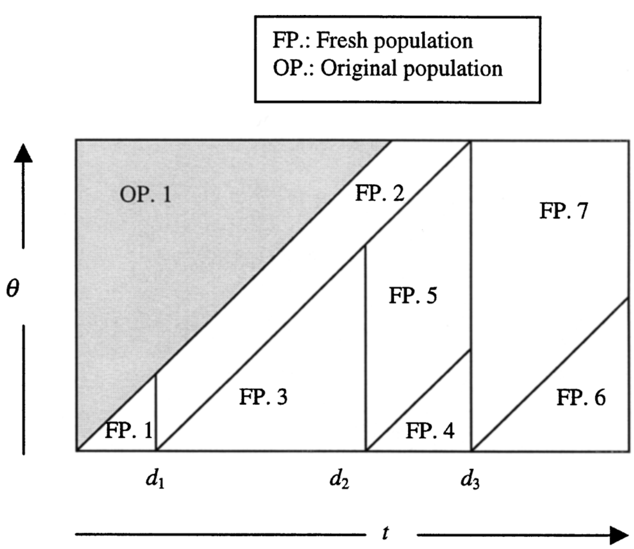

Figure 4. Three input discontinuities under two-population framework.

During the development of the unsteady-state RTD of the fresh population, the only reason that attention was restricted to the $0 \le \theta \le t$ domain was the inherent assumption that the entrance flow rate, $h_{\mathrm{in}}(t)$, was known just for $t \ge 0$. Since this function appears in Eq. 22 in the form, $h_{\mathrm{in}}(t-\theta)$, we require $t \ge \theta$ in order to remain within the time domain for which the entrance flow rate was known. However, if we assume that $h_{\mathrm{in}}(t)$ is also available beyond the solution domain $[0\ t]$, say in a certain interval $[t_1, 0)$, where t_1 is negative, then the solution propagates to the domain $0 < \theta \le (t - t_1)$, which is the large triangle shown in Figure 5. By doing so, we have effectively extended the physically meaningful boundary condition for the fresh population such that it applies to the original population as well. The required global solution can be obtained by simply adopting the fresh population solution represented by Eq. 22. It is important to note that since $h_{\mathrm{in}}(t)$ is only known for $t \ge t_1$, the new domain is confined to the region determined by $t \ge 0$ and $\theta = [0, -t_1]$.

Consequently, the resulting solution

$$I(t,\theta) = \frac{h_{\mathrm{in}}(t-\theta)}{H(t)} \exp\left(- \int_{t-\theta}^{t} \frac{h_{\mathrm{out}}(t')\, dt'}{H(t')} \right)$$

$$\text{(all fluid elements, } t > 0,\ 0 \le \theta \le -t_1) \quad (24)$$

is mathematically simpler than the previous ones, since just a single equation is required and the fragmentary solution domain also has been avoided. Hence, in contrast to the efforts of Zacca, we require neither rigorous bookkeeping nor simplifications in general dynamic modeling of unsteady-state RTD.

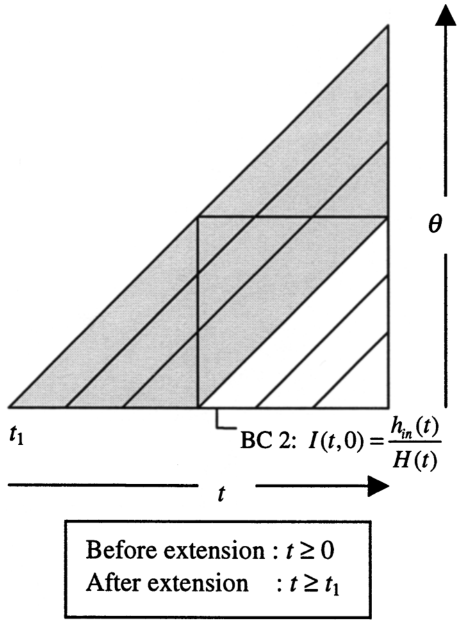

Figure 5. Extension of the boundary-condition domain.

The effective determination of the RTD surface from Eq. 24 requires that integration be performed for each pair (t,θ). Computation time can be significantly reduced, however, by introducing the function $\alpha(t)$, defined as an average ratio of real time to the mean residence time:

$$\alpha(t) = -\int_0^t \frac{h_{\text{out}}(t')dt'}{H(t')}, \quad (25)$$

which, when substituted in Eq. 24, yields:

$$I(t,\theta) = \frac{h_{\text{in}}(t-\theta)}{H(t)} \exp[\alpha(t) - \alpha(t-\theta)]. \quad (26)$$

It is evident from Eq. 26 that the entrance and exit flow rates as well as the holdup must be known for $t < 0$ to use the preceding equation effectively. The question that immediately arises concerns the amount of data that are then required. In other words, how far back in real time need we go in obtaining the flow-rate history? If the vessel was indeed operated in the non-steady-state mode prior to $t = 0$, then to predict RTD in the entire age range $\theta = [0\ \infty]$, an infinite amount of data would be required. However, if we accept that there exists a certain practical upper limit on the age, say $\theta_{\max}$, above which the number of fluid elements in the vessel is negligible, that is, $w(t,\theta \geq \theta_{\max}) \cong 0$, then a finite domain in which the flow rates and holdup need to be known can be predefined. As such, we require information regarding the flow only in the time interval $[-\theta_{\max},\ t]$ in order to obtain the RTD solution in the domain $\{(t,\theta)\colon t \geq 0,\ 0 \leq \theta \leq \theta_{\max}\}$. For the case of the perfectly mixed vessel, $\theta_{\max}$ can typically be expressed as $k\tau$, where k results from the tolerance for which the number of fluid elements is chosen to be negligible.

Simulation results

In order to demonstrate the effect of time-varying flows across the boundaries of the vessel on the RTD, we present three elementary case studies involving: (1) constant entrance and exit flow rates, (2) step change in either flow, and (3) sinusoidal variation in either flow.

Case 1: Steady Flow Conditions. Figure 6 presents simulation results for steady-state flow conditions. Under these conditions, the entrance flow rate is equal to that of the exit, both do not vary with time, and hence, the holdup is also constant. Note that the function $\alpha(t)$, as defined by Eq. 25, is an average ratio of real time to mean residence time. Thus, for steady flows, $\alpha(t)$ varies proportionally with real time. Consequently, the RTD pattern generated by Eq. 26 is the well-known exponential decay with age that remains unaffected for all real time.

Case 2: Step Change in System Flow Rates. Figures 7 and 8 illustrate the effect of step increasing the entrance flow rate and decreasing the exit flow rate, respectively. It might be expected that an increase in the entrance flow rate has the same impact on the system performance as a decrease by the same amount in the exit flow rate. This is true of the holdup, as can be seen by comparing the corresponding subplots. However, the two RTDs exhibit markedly different patterns. For example, when the entrance flow rate increases at $t = 150$ as shown in Figure 7, the number of the age-zero fluid elements immediately increases, resulting in an RTD step increase in the entire $t \geq \theta$ domain. This is a consequence of the direct dependence of RTD on the entrance flow rate, as easily can be seen in Eq. 22, where $h_{\text{in}}(t)$ appears as a multiplying factor. On the other hand, the age-zero fluid elements are not affected by a changing exit flow rate. When the exit flow rate decreases at $t = 150$, the holdup increases, so the elements spend on average more time in the vessel. For this reason, in contrast to the situation observed in Figure 7, the RTD rate decrease with age becomes weaker as the exit flow rate is reduced, as shown in Figure 8.

Case 3: Sinusoidal System Flow Rates. Sinusoidal fluctuations in the entrance and exit flow rates result in the nonuniform patterns shown in Figures 9 and 10, respectively. For entrance flow fluctuations, the sine wave appears immediately on the $\theta = 0$ boundary, since the number of age-zero fluid elements in the vessel is directly affected by the entrance flow rate. It is interesting to note that these fluctuations impact on the RTD pattern by propagating along the characteristic lines $t = \theta + t_0$. The effect of a sinusoidal variation in the exit flow rate results in similar propagation behavior, as discussed in Case 2 for the case of exit flow decrease. Likewise, the effect of the exit flow is reflected through the indirect agency of holdup, which affects the function $\alpha(t)$, and so eventually the RTD.

The case studies presented here function as an elementary set of possible changes in flow rate across the boundaries of the vessel. As such, they can be used to infer, at least qualitatively, the variation in RTD with changing process flow rates. It is also significant that due to the elimination of the multi-

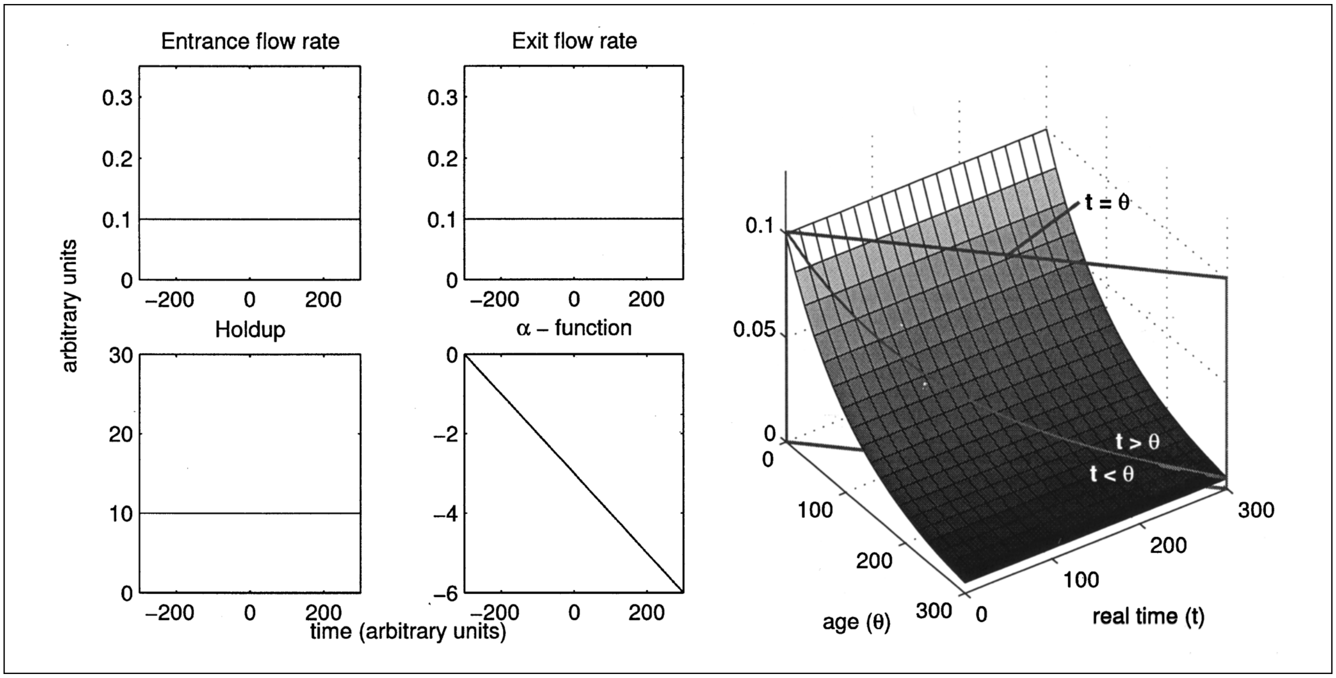

Figure 6. Residence-time distribution $w(t,\theta)$ under steady flow conditions.

ple-population concept and the use of the $\alpha(t)$ function, minimal computational effort was required in generating these simulation results. Therefore, the proposed unsteady-state RTD is feasible for general dynamic reactor modeling, especially in particulate mass and energy balancing encountered in polymer reaction engineering.

Vessels in Series

Dynamic RTD model

Due to the developments presented in the previous sections, we are now in a position to obtain the unsteady-state RTD for the system of N perfectly mixed vessels in series

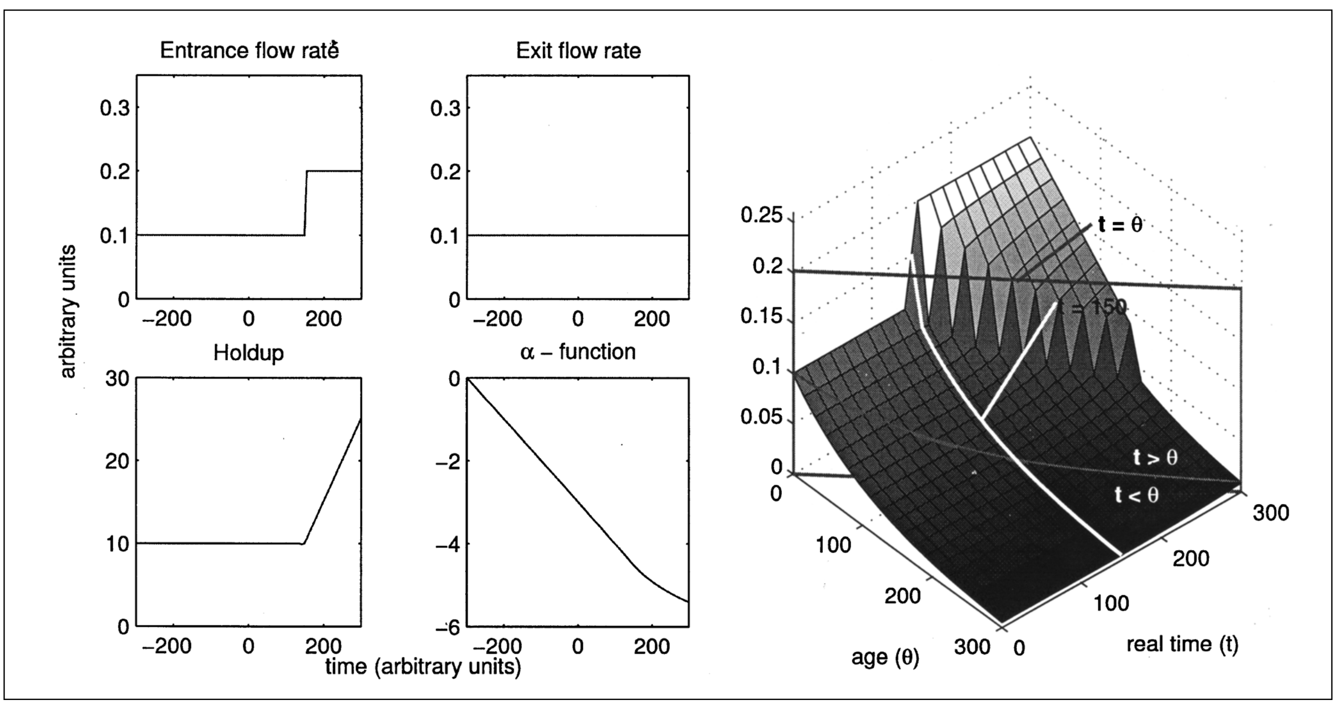

Figure 7. Residence-time distribution $w(t,\theta)$ under increasing entrance flow rate.

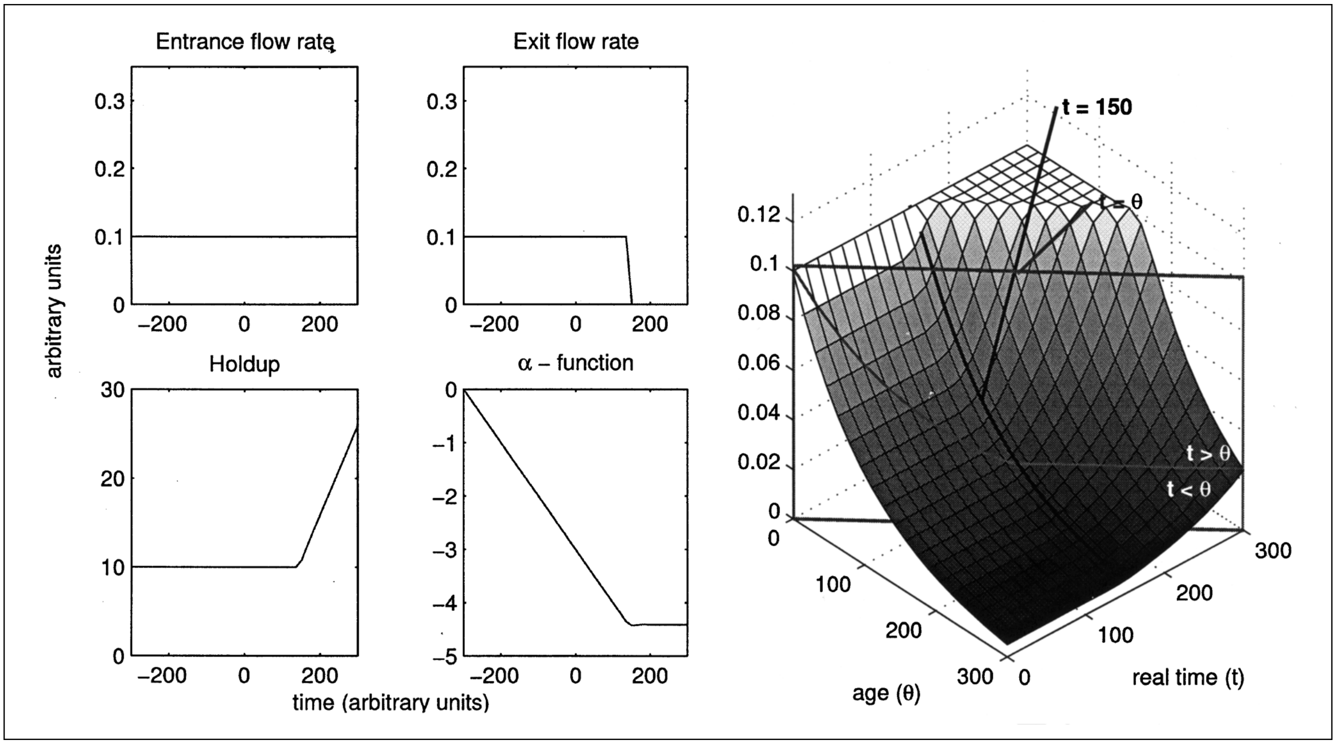

Figure 8. Residence-time distribution $w(t,\theta)$ under decreasing exit flow rate.

shown in Figure 11. We assume here that there is no delay time between vessels, hence $h_{i+1}(t)$, the exit flow from vessel i, is equal to the entrance flow to vessel $i+1$. According to Eq. 22, the solution to unsteady-state RTD for a single perfectly mixed vessel is

$$I_i(t,\theta_i) = \frac{h_i(t-\theta_i)}{H_i(t)} \exp\left(-\int_{t-\theta_i}^{t} \frac{dt'}{\tau_i(t')}\right), \quad (27)$$

where the exit-flow-based mean residence time in vessel i is

$$\tau_i(t) = \frac{H_i(t)}{h_{i+1}(t)}. \quad (28)$$

However, for a cascade of vessels, the fluid elements in a particular vessel are characterized by more than one residence time as a result of the residence in the preceding vessels. We have already introduced the joint probability density $\rho_i(t, \boldsymbol{\theta})$, which stores this historical record. For the sake of convenience, we use the age-characteristic vector $\boldsymbol{\theta} = [\theta_1, \theta_2, \ldots, \theta_N]$. In effective construction of $\rho_i(t, \boldsymbol{\theta})$, it is necessary to account for the ageing of fluid elements in the vessel of interest as well as in the preceding vessels. Let us consider fluid elements bearing age characteristic $\boldsymbol{\theta}$ at time t in vessel N. These elements would have entered vessel 1 at time $t-(\theta_1+\theta_2+\cdots+\theta_N)$, resided there for θ_1 time units, and exited at time $t-(\theta_2+\theta_3+\ldots+\theta_N)$. To simplify the notation, we introduce the variable

$$t_{0,i}(t,\boldsymbol{\theta}) = t - \sum_{j=i}^{N} \theta_j, \quad (29)$$

which represents the entrance time to vessel i for the fluid elements characterized by $\boldsymbol{\theta}$ at time t. Hence, $t_{0,i}$ is the entrance time to vessel i, whereas $t_{0,i+1}$ is the exit time, or the entrance time to vessel $i+1$. Given that the fluid elements exit vessel 1 at time $t_{0,2}$, the fraction of fluid elements with age characteristic $\boldsymbol{\theta}$ that resided in vessel 1 for θ_1 time units is $\rho_1(t_{0,2},\boldsymbol{\theta})\Delta\theta_1$. According to Eq. 22, we have

$$\rho_1(t_{0,2},\boldsymbol{\theta}) = I_1(t_{0,2},\theta_1) = \frac{w_1(t_{0,2},\theta_1)}{H_1(t_{0,2})} = \frac{h_1(t_{0,1})}{H_1(t_{0,2})} \exp\left(-\int_{t_{0,1}}^{t_{0,2}} \frac{dt'}{\tau_1(t')}\right). \quad (30)$$

In turn, the fraction of fluid elements that resided in vessel 2 for θ_2 time units, given that they resided in vessel 1 for θ_1, is $\rho_2(t_{0,3},\boldsymbol{\theta})\Delta\theta_1\Delta\theta_2$. The joint probability density $\rho_2(t_{0,3},\boldsymbol{\theta})$ can be obtained by considering the age distribution in $h_2(t)$, the total entrance flow to vessel 2. The number of fluid elements characterized by $\boldsymbol{\theta}$ in this flow is the fraction $\rho_1(t_{0,2},\boldsymbol{\theta})\Delta\theta_1$ multiplied by $h_2(t)$, the total entrance flow rate to vessel 2. We can define $g_i(t,\boldsymbol{\theta})$ such that $g_i(t,\boldsymbol{\theta})\prod_{j=1}^{i-1}\Delta\theta_j$ represents the fluid elements in the entrance flow to vessel i that have resided in the preceding vessels 1, 2, . . ., $i-1$ for $\theta_1, \theta_2, \ldots, \theta_{i-1}$ time units. Therefore, the flow-rate age distribution in the entrance flow to vessel 2 is given by

$$g_2(t_{0,2},\boldsymbol{\theta}) = \rho_1(t_{0,2},\boldsymbol{\theta})h_2(t_{0,2}). \quad (31)$$

In deriving the joint probability density $\rho_2(t_{0,3},\boldsymbol{\theta})$, we replace the total entrance flow-rate $h_i(t)$ in the general Eq. 27

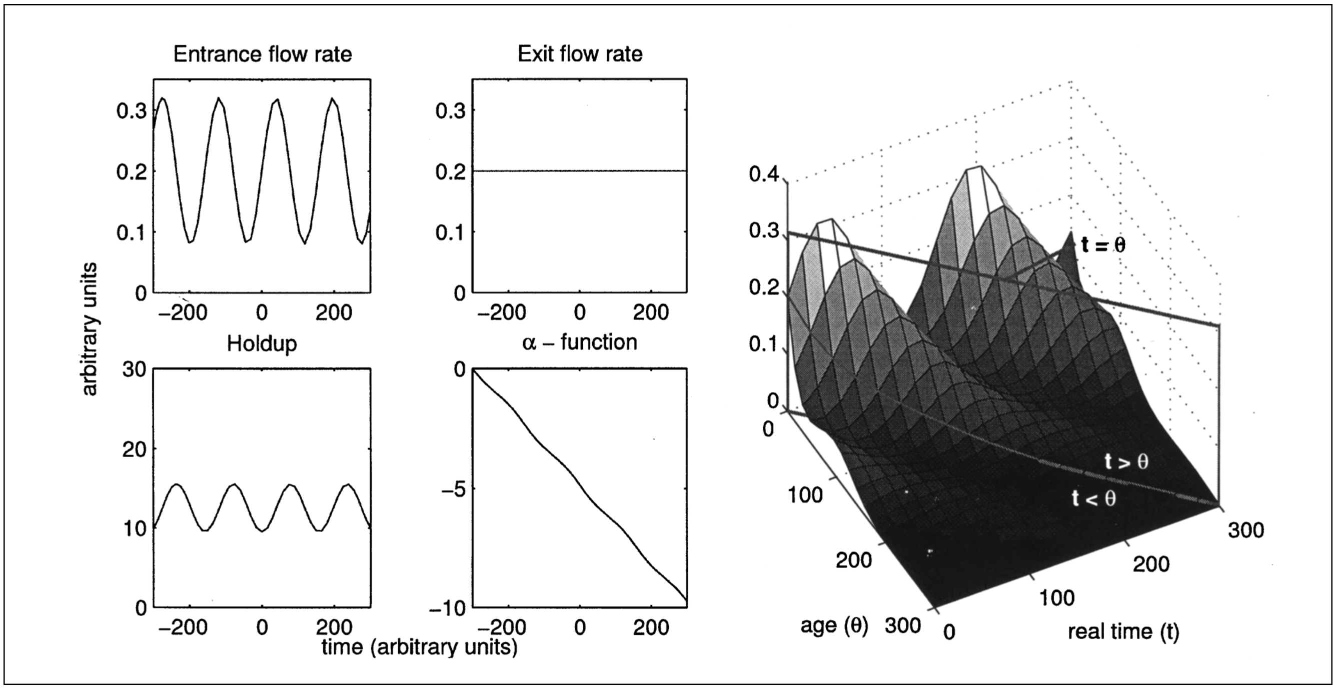

Figure 9. Residence-time distribution $w(t,\boldsymbol{\theta})$ under sinusoidal entrance flow.

by the flow-rate distribution $g_2(t_{0,2},\boldsymbol{\theta})$, as shown below:

$$\rho_2(t_{0,3},\boldsymbol{\theta}) = \frac{g_2(t_{0,2},\boldsymbol{\theta})}{H_2(t_{0,3})}\exp\left(-\int_{t_{0,2}}^{t_{0,3}}\frac{dt'}{\tau_2(t')}\right)$$
$$= \rho_1(t_{0,2},\boldsymbol{\theta})\frac{h_2(t_{0,2})}{H_2(t_{0,3})}\exp\left(-\int_{t_{0,2}}^{t_{0,3}}\frac{dt'}{\tau_2(t')}\right) \quad (32)$$

On substituting Eq. 30 in Eq. 32 we obtain:

$$\rho_2(t_{0,3},\boldsymbol{\theta})$$
$$= \frac{h_1(t_{0,1})}{H_1(t_{0,2})}\frac{h_2(t_{0,2})}{H_2(t_{0,3})}\exp\left(-\int_{t_{0,1}}^{t_{0,2}}\frac{dt'}{\tau_1(t')}\right)\exp\left(-\int_{t_{0,2}}^{t_{0,3}}\frac{dt'}{\tau_2(t')}\right)$$
$$= \frac{h_1(t_{0,1})h_2(t_{0,2})}{H_1(t_{0,2})H_2(t_{0,3})}\exp\left(-\int_{t_{0,1}}^{t_{0,2}}\frac{dt'}{\tau_1(t')}-\int_{t_{0,2}}^{t_{0,3}}\frac{dt'}{\tau_2(t')}\right). \quad (33)$$

Similarly, the joint probability density function of the fluid elements with age characteristic $\boldsymbol{\theta}$ (which resided in vessel 3 for θ_3, given that they resided in vessel 1 for θ_1, and in vessel 2 for θ_2) is

$$\rho_3(t_{0,4},\boldsymbol{\theta}) = \rho_2(t_{0,3},\boldsymbol{\theta})\frac{h_3(t_{0,3})}{H_3(t_{0,4})}\exp\left(-\int_{t_{0,3}}^{t_{0,4}}\frac{dt'}{\tau_3(t')}\right)$$
$$= \frac{h_1(t_{0,1})h_2(t_{0,2})h_3(t_{0,3})}{H_1(t_{0,2})H_2(t_{0,3})H_3(t_{0,4})}$$
$$\exp\left(-\int_{t_{0,1}}^{t_{0,2}}\frac{dt'}{\tau_1(t')}-\int_{t_{0,2}}^{t_{0,3}}\frac{dt'}{\tau_2(t')}-\int_{t_{0,3}}^{t_{0,4}}\frac{dt'}{\tau_3(t')}\right). \quad (34)$$

When comparing Eqs. 30, 32, and 34, we conclude that the joint probability density for vessel i may be generalized as:

$$\rho_i(t_{0,i+1},\boldsymbol{\theta}) = \left(\prod_{j=1}^{i}\frac{h_j(t_{0,j})}{H_j(t_{0,j+1})}\right)\exp\left(-\sum_{j=1}^{i}\int_{t_{0,j}}^{t_{0,j+1}}\frac{dt'}{\tau_j(t')}\right). \quad (35)$$

The preexponential factor can be expressed in terms of the mean residence time $\tau_i(t)$ if we rewrite Eq. 35 in the form

$$\rho_i(t_{0,i+1},\boldsymbol{\theta})$$
$$= \frac{h_1(t_{0,1})}{H_i(t_{0,i+1})}\left(\prod_{j=2}^{i}\frac{h_j(t_{0,j})}{H_{j-1}(t_{0,j})}\right)\exp\left(-\sum_{j=1}^{i-1}\int_{t_{0,j}}^{t_{0,j+1}}\frac{dt'}{\tau_j(t')}\right). \quad (36)$$

Therefore, by noting that $h_i(t)$ is the exit flow rate from vessel $i-1$ and applying the definition of the mean residence time based on the exit flow rate as given by Eq. 28, we obtain:

$$\rho_i(t_{0,i+1},\boldsymbol{\theta}) = \frac{h_1(t_{0,1})}{H_i(t_{0,i+1})}\frac{\exp\left(-\sum_{j=1}^{i}\int_{t_{0,j}}^{t_{0,j+1}}\frac{dt'}{\tau_j(t')}\right)}{\prod_{j=1}^{i-1}\tau_j(t_{0,j+1})}. \quad (37)$$

In addition, to simplify the form of this solution, we can define:

$$\alpha_i(t) = -\int_0^t\frac{dt'}{\tau_i(t')} \quad (38)$$

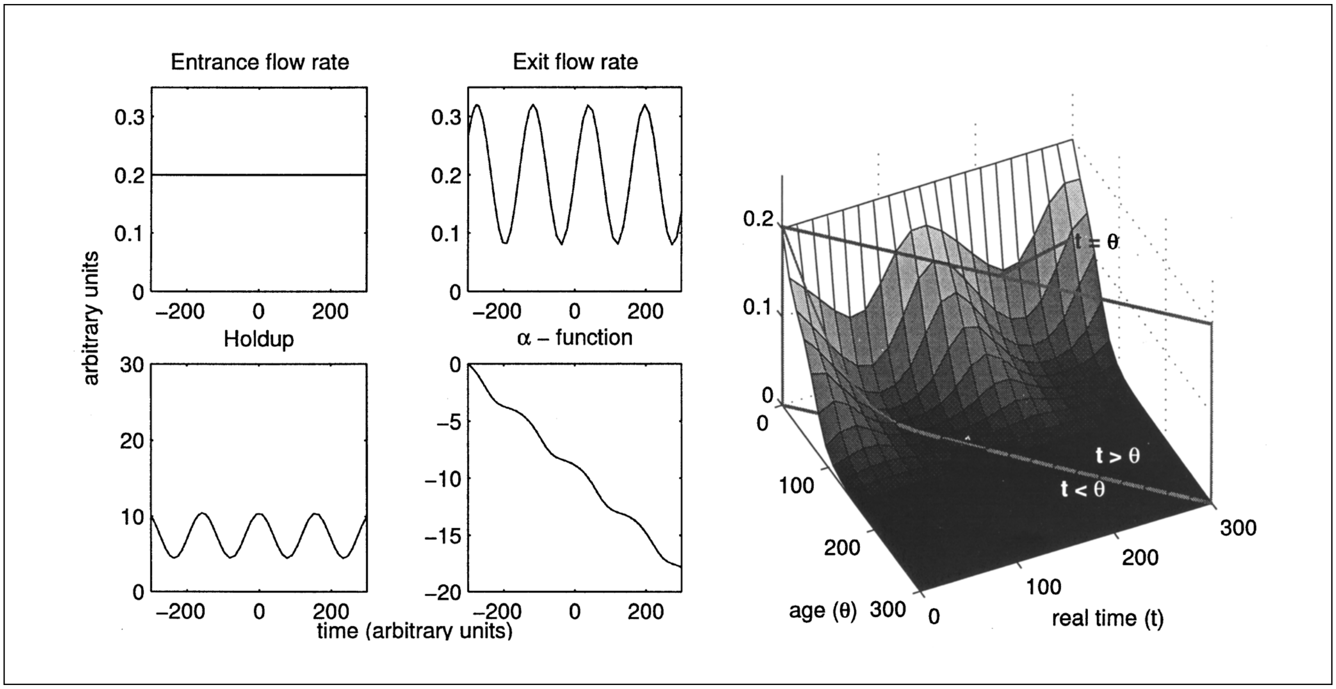

Figure 10. Residence-time distribution $w(t,\theta)$ under sinusoidal exit flow.

and

$$\boldsymbol{\tau}'(t,\boldsymbol{\theta}) = \left[\tau_1'(t,\boldsymbol{\theta}),\tau_2'(t,\boldsymbol{\theta}),\ldots,\tau_{N-1}'(t,\boldsymbol{\theta}),\tau_N'(t,\boldsymbol{\theta})\right]$$
$$= \left[\tau_1(t_{0,2}),\tau_2(t_{0,3}),\ldots,\tau_{N-1}(t_{0,N-2}),\frac{H_N(t)}{h_1(t_{0,1})}\right]. \tag{39}$$

Noting that $t_{0,N+1}=t$, the joint probability density function for vessel N becomes

$$\rho_N(t,\boldsymbol{\theta}) = \frac{\exp\left(\sum_{i=1}^{N}\left[\alpha_j(t_{0,j+1})-\alpha_j(t_{0,j})\right]\right)}{\prod_{i=1}^{N}\tau_i'(t,\boldsymbol{\theta})}. \tag{40}$$

Henceforth, we shall refer to this function as the joint RTD for vessels in series. This joint RTD is sufficient to describe the unsteady-state RTD for all fluid elements in a cascade of N vessels under the assumption of perfect mixing and zero delay time between the vessels. Thus far, we have referred to $\rho_N(t,\boldsymbol{\theta})$ as the joint probability density function without rigorous qualification. However, as is shown in Appendix B, this function is indeed the joint probability in a mathematical sense.

Combined residence-time distribution

We define the combined RTD $\rho_T(t,\ \theta_T)$ such that the term $\rho_T(t,\ \theta_T)\Delta\theta_T$ is the fraction of fluid elements that have resided in the cascade for a total of $[\theta_T,\ \theta_T+\Delta\theta_T]$ time units in all N vessels, where $\theta_T=\theta_1+\theta_2+\cdots+\theta_N$. In contrast to the joint RTD, the combined RTD does not distinguish between the residence times spent by the fluid in the individual vessels. We can obtain the relationship between the combined and joint RTD by integrating the joint RTD over all

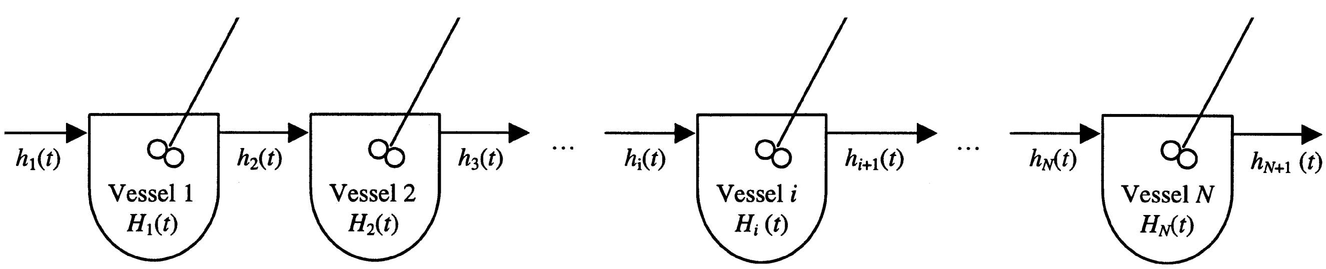

Figure 11. Perfectly mixed vessels in series.

possible ages under the constraint $\theta_T = \theta_1 + \theta_2 + \cdots + \theta_N$, as shown below:

$$\int_0^{\theta_T} \rho_T(t,\theta_T')\, d\theta_T' = \int_0^{\theta_T} \cdots \int_0^{\theta_T - \Sigma_{i=3}^N \theta_i} \int_0^{\theta_T - \Sigma_{i=2}^N \theta_i} \rho_N(t,\boldsymbol{\theta})\, d\theta_1 d\theta_2 \cdots d\theta_N. \tag{41}$$

Equation 41 effectively represents the fraction of fluid elements that have spent a total of θ_T time units in the system. In order to obtain $\rho_T(t, \theta_T)$ explicitly, the preceding relationship must be differentiated with respect to the total age, θ_T:

$$\rho_T(t,\theta_T) = \frac{d}{d\theta_T}\left[\int_0^{\theta_T} \cdots \int_0^{\theta_T - \Sigma_{i=3}^N \theta_i} \int_0^{\theta_T - \Sigma_{i=2}^N \theta_i} \rho_N(t,\boldsymbol{\theta})\, d\theta_1 d\theta_2 \cdots d\theta_N\right]. \tag{42}$$

When demonstrating the validity of this relationship, we consider the case of steady flow conditions. In particular, for identical vessels, where $H_{i+1}(t)/h_i(t) = \tau = \text{const.}$, the joint RTD given by Eq. 36 becomes

$$\rho_N(t,\boldsymbol{\theta}) = \frac{1}{\tau^N} \exp\left(-\frac{1}{\tau}\sum_{i=1}^N \theta_i\right). \tag{43}$$

Consequently, for a two-vessel system, the combined RTD can be obtained by the application of Eq. 42. The requisite integration gives

$$K = \int_0^{\theta_T} \int_0^{\theta_T - \theta_2} \frac{1}{\tau^2} \exp\left(-\frac{1}{\tau}[\theta_1 + \theta_2]\right) d\theta_1\, d\theta_2 = \int_0^{\theta_T}\left[-\frac{1}{\tau}\exp\left(-\frac{\theta_T}{\tau}\right) - \frac{1}{\tau}\exp\left(-\frac{\theta_2}{\tau}\right)\right] d\theta_2 = \left(1 - \frac{\theta_T}{\tau}\right)\exp\left(-\frac{\theta_T}{\tau}\right) + 1, \tag{44}$$

and differentiation with respect to θ_T finally yields:

$$\rho_T(\theta_T) = \frac{dK}{d\theta_T} = \frac{\theta_T}{\tau^2}\exp\left(-\frac{\theta_T}{\tau}\right). \tag{45}$$

The preceding result is consistent with the well-known tanks in series ($N = 2$) model originally developed by MacMullin and Weber (1935):

$$\rho_T(\theta_T) = \frac{\theta_T^{N-1}}{(N-1)!\,\tau^N}\exp\left(-\frac{\theta_T}{\tau}\right). \tag{46}$$

Here, we stress that the joint RTD provides us with a complete historical record of the fluid elements in the reactor system, whereas the combined RTD only reveals a distribution with respect to the total age. RTD theory is usually applied in reactor technology to predict the exit conversion from a reactor system. For such an application, the combined RTD is useful only for cases in which the total age is sufficient to characterize the conversion in a fluid element. This occurs in just two special cases, namely, when the reaction is zero or first order and the reaction conditions (such as temperature and pressure) are the same in all reactors in the system. For all other cases, the combined RTD is not sufficient to predict the mean exit conversion, and the more general joint RTD is required.

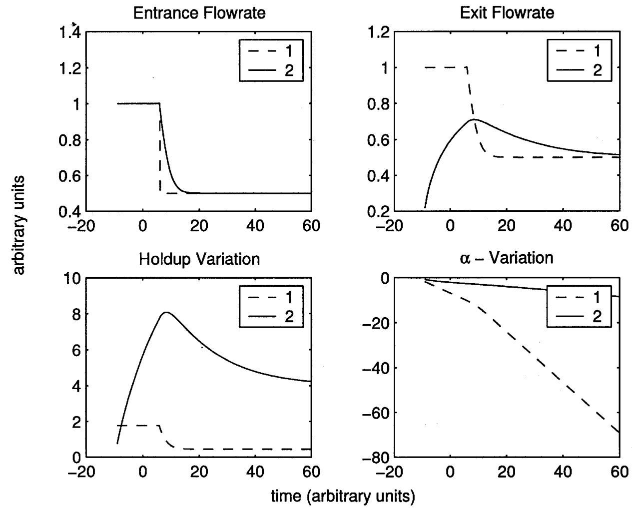

Figure 12. Flow conditions for two vessels in series: $h_2(t) = 0.75\sqrt{H_1(t)}$ and $h_3(t) = 0.25\sqrt{H_2(t)}$.

Simulation results

In order to illustrate the effect of unsteady flows on the joint RTD, we consider here the case of two vessels in series, where the entrance flow rate to the first vessel undergoes a step decrease. It often happens that the exit flow from a vessel is affected by the holdup. For example, the gravity-driven exit flow rate from a liquid-phase storage tank is approximately proportional to the square root of the level in the tank, which is, in turn, linearly dependent on the holdup in the vessel. Therefore, here we employ the relationship $h_{i+1} = k\sqrt{H_i(t)}$. The vessels' overall flow performance is illustrated in Figure 12 for the case of a step decrease in the entrance flow rate to vessel 1 at $t = 5$. Figure 13 illustrates the joint RTD in vessel 2 at different time instances. After $t = 5$, the induced step discontinuity results in a moving front on the RTD surface, and its progress is evident at $t = 7$. As time passes, this front is "washed out" of the system, which eventually exhibits a steady-state RTD pattern. This simulation exercise serves to illustrate that the RTD model presented here for vessels in series can quite easily incorporate even extreme unsteady-state conditions, including flow discontinuities.

Conclusions

A rigorous model of unsteady-state residence-time distribution (RTD) was developed from the fundamental material

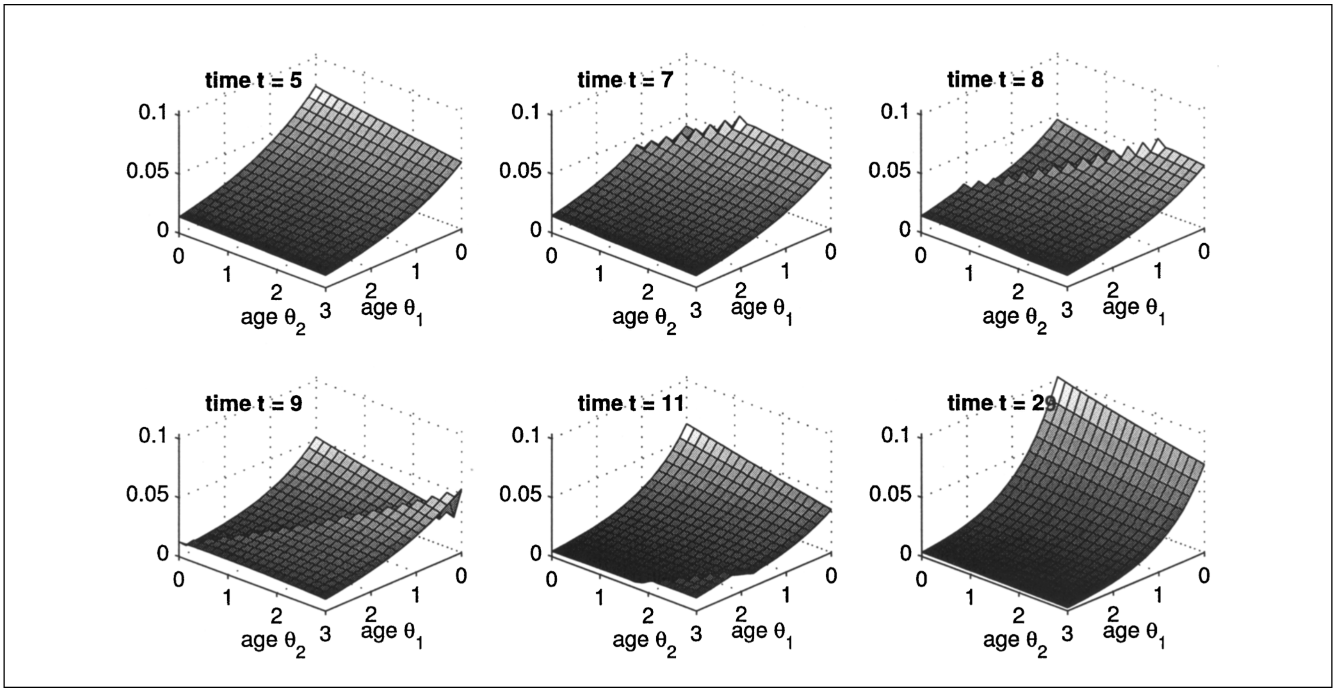

Figure 13. Joint RTD in vessel 2, $\rho_2(t,\theta)$.

balance of fluid elements. The case of a single perfectly mixed vessel was first considered. It was shown, by an extension of the fresh population-boundary condition, that the unfeasible concept of two populations could be avoided, and a single-equation solution describing the RTD of fluid elements belonging to both the fresh and original population was derived. This extension also allowed for the generalization of the case of a single vessel to a system of N vessels in series. The solution obtained was presented in the form of a joint probability density function. The relationship between the resulting "multiage" joint RTD and the traditionally used "total-age" combined RTD was established. Numerical simulations were performed that illustrated that the proposed model can predict RTD for continuous as well as discontinuous flow characteristics, such as step changes in system flow rates.

One important potential application of unsteady-state RTD is evident in polymer reaction engineering. A topic of great importance is the transition from one polymer product grade to another as a result of changing reactor feed. In order to study and optimize such a change, a dynamic model of a reactor that incorporates time-varying system inputs and outputs is required. Under such a model, the RTD of polymer particles in the reactor varies with time. Since the catalyst is subject to several site transformations affecting its overall activity, the time of exposure of the catalyst to the reactor conditions, characterized by RTD, determines its activity, which significantly impacts on the properties of the polymer produced. Therefore, the unsteady-state RTD model presented here can be used to obtain the required dynamic model of the heterogeneous reactor, which can, in turn, be applied to predict the course of polymer product grade transition under unsteady flow conditions.

Notation

$E(t,\theta)$ = exit residence-time distribution (normalized)
$f(t,\theta)$ = flow distribution function
$h(t)$ = flow rate
$H(t)$ = vessel holdup
$I(t,\theta)$ = internal residence-time distribution (normalized)
t = real time
$w(t,\theta)$ = internal residence-time distribution (not normalized)

Greek letters

θ = residence time
$\rho_i(t,\boldsymbol{\theta})$ = joint residence-time distribution
$\rho_T(t,\boldsymbol{\theta})$ = combined residence time distribution
$\tau_{in}(t)$ = mean residence time based on entrance flow rate

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Appendix A: Presented Model vs. Population-Balance Model

At first glance, the solution developed in this article, namely,

$$I(t,\theta) = \frac{h_{\text{in}}(t-\theta)}{H(t)} \exp\left(-\int_{t-\theta}^{t} \frac{h_{\text{out}}(t')\,dt'}{H(t')} \right), \quad \text{(A1)}$$

is different from the solution derived by Zacca (1995), given by Eq. 6, since the arguments of the holdup and the basis of the mean residence time in the integrand differ. However, if both equations are equivalent, we should be able to arrive at one form from the other. By applying the total material balance for a single vessel to Eq. A1, as shown below:

$$\frac{dH}{dt} = h_{\text{in}}(t) - h_{\text{out}}(t), \quad \text{(A2)}$$

we obtain:

$$I(t,\theta) = \frac{h_{\text{in}}(t-\theta)}{H(t)} \exp\left(-\int_{t-\theta}^{t} \frac{\left(-\frac{dH}{dt'} + h_{\text{in}}(t') \right) dt'}{H(t')} \right)$$
$$= \frac{h_{\text{in}}(t-\theta)}{H(t)} \exp\left(\int_{H(t-\theta)}^{H(t)} \frac{dH}{H} - \int_{t-\theta}^{t} \frac{h_{\text{in}}(t')\,dt'}{H(t')} \right), \quad \text{(A3)}$$

which finally results in the form proposed by Zacca, as follows:

$$I(t,\theta) = \frac{h_{\text{in}}(t-\theta)}{H(t-\theta)} \exp\left(-\int_{t-\theta}^{t} \frac{dt'}{\tau_{\text{in}}(t')} \right). \quad \text{(A4)}$$

Appendix B: Verification of the Joint RTD as a Probability Function

It will be demonstrated that the RTD function for a cascade of vessels proposed in this study is indeed a joint probability function. First, we find that the function

$$\rho_N(t,\boldsymbol{\theta}) = \left(\prod_{i=1}^{N} \frac{h_i(t_{0,i})}{H_i(t_{0,i+1})} \right) \exp\left(-\sum_{i=1}^{N} \int_{t_{0,i}}^{t_{0,i+1}} \frac{dt'}{\tau_i(t')} \right) \quad \text{(B1)}$$

is nonnegative, as required. Second, we verify that integration of $\rho_N(t,\boldsymbol{\theta})$ over all possible ages from 0 to ∞ is unity. Certainly, Eq. B1 can be written in the form:

$$\rho_N(t,\boldsymbol{\theta}) = \left(\prod_{i=1}^{N} \frac{h_i\left(t - \sum_{j=i} \theta_i\right)}{H_i\left(t - \sum_{j=i+1} \theta_i\right)} \right) \exp\left(-\sum_{i=1}^{N} \int_{t-\Sigma_{j=i}\theta_j}^{t-\Sigma_{j=i+1}\theta_j} \frac{dt'}{\tau_i(t')} \right) = \left(\frac{h_1\left(t - \theta_1 - \sum_{i=2} \theta_i\right)}{H_l\left(t - \sum_{i=2} \theta_i\right)} \right)$$
$$\exp\left(-\int_{t-\theta_1-\Sigma_{i=2}\theta_i}^{t-\Sigma_{i=2}\theta_i} \frac{dt'}{\tau_1(t')} \right) \left[\prod_{i=2}^{N} \frac{h_i\left(t - \sum_{j=i} \theta_j\right)}{H_i\left(t - \sum_{j=i+1} \theta_j\right)} \exp\left(-\sum_{i=2}^{N} \int_{t-\Sigma_{j=i}\theta_j}^{t-\Sigma_{j=i+1}\theta_j} \frac{dt'}{\tau_i(t')} \right) \right]. \quad \text{(B2)}$$

The factor in the square brackets is not a function of θ_1. Therefore, when integrating with respect to θ_1, we can write

$$\int_0^\infty \rho_N(t,\boldsymbol{\theta})\, d\theta_1 = \prod_{i=2}^{N} \frac{h_i\left(t - \sum_{j=i} \theta_j\right)}{H_i\left(t - \sum_{j=i+1} \theta_j\right)} \exp\left(-\sum_{i=2}^{N} \int_{t-\Sigma_{j=i}\theta_j}^{t-\Sigma_{j=i+1}\theta_j} \frac{dt'}{\tau_i(t')} \right)$$
$$\times \int_0^\infty \frac{h_l\left(t - \theta_1 - \sum_{i=2} \theta_i\right)}{H_l\left(t - \sum_{i=2} \theta_i\right)} \exp\left(-\int_{t-\theta_1-\Sigma_{i=2}\theta_i}^{t-\Sigma_{i=2}\theta_i} \frac{dt'}{\tau_1(t')} \right) d\theta_1. \quad \text{(B3)}$$

In order to evaluate the integral with respect to θ_1 on the righthand side, we refer to the solution for a single perfectly mixed vessel. According to Eq. 22, for any θ-independent time shift a, we have

$$\int_0^\infty I(t,\theta)\, d\theta = \int_0^\infty I(t-a,\theta)\, d\theta$$
$$= \int_0^\infty \frac{h_{\text{in}}(t-\theta-a)}{H(t-a)} \exp\left[-\int_{t-\theta-a}^{t\text{-}a} \frac{h_{\text{out}}(t')}{H(t')} dt' \right] d\theta = 1. \quad \text{(B4)}$$

Since the integral in Eq. B3 has the same form as that in Eq. B4 for $a = \sum_{i=2} \theta_i$, we have (note that a does not include θ_1):

$$\int_0^\infty \rho_N(t,\boldsymbol{\theta})\, d\theta_1 = \prod_{i=2}^{N} \frac{h_i\left(t - \sum_{j=i} \theta_j\right)}{H_i\left(t - \sum_{j=i+1} \theta_j\right)} \exp\left(-\sum_{i=2}^{N} \int_{t-\Sigma_{j=i}\theta_j}^{t-\Sigma_{j=i+1}\theta_j} \frac{dt'}{\tau_i(t')}\right) \times 1. \quad \text{(B5)}$$

When integrating over θ_2, we proceed in a similar way:

$$\int_0^\infty \rho_N(t,\boldsymbol{\theta})\, d\theta_1 = \prod_{i=2}^{N} \frac{h_i\left(t - \sum_{j=i} \theta_j\right)}{H_i\left(t - \sum_{j=i+1} \theta_j\right)} \exp\left(-\sum_{i=2}^{N} \int_{t-\Sigma_{j=i}\theta_j}^{t-\Sigma_{j=i+1}\theta_j} \frac{dt'}{\tau_i(t')}\right) = \frac{h_2\left(t - \theta_2 - \sum_{i=3} \theta_i\right)}{H_2\left(t - \sum_{i=3} \theta_i\right)} \exp\left(-\int_{t-\theta_2-\Sigma_{i=3}\theta_i}^{t-\Sigma_{i=3}\theta_i} \frac{dt'}{\tau_2(t')}\right) \left[\prod_{i=3}^{N} \frac{h_i\left(t - \sum_{j=i} \theta_j\right)}{H_i\left(t - \sum_{j=i+1} \theta_j\right)} \exp\left(-\sum_{i=3}^{N} \int_{t-\Sigma_{j=i}\theta_j}^{t-\Sigma_{j=i+1}\theta_j} \frac{dt'}{\tau_i(t')}\right)\right] \quad \text{(B6)}$$

Once more, noticing that the factor in square brackets is not a function of θ_2, we can write:

$$\int_0^\infty \int_0^\infty \rho_N(t,\boldsymbol{\theta})\, d\theta_1\, d\theta_2 = \left[\prod_{i=3}^{N} \frac{h_i\left(t - \sum_{j=i} \theta_j\right)}{H_i\left(t - \sum_{j=i+1} \theta_j\right)} \exp\left(-\sum_{i=3}^{N} \int_{t-\Sigma_{j=i}\theta_j}^{t-\Sigma_{j=i+1}\theta_j} \frac{dt'}{\tau_i(t')}\right)\right] \times \int_0^\infty \frac{h_2\left(t - \theta_2 - \sum_{i=3} \theta_i\right)}{H_2\left(t - \sum_{i=3} \theta_i\right)} \exp\left(-\int_{t-\theta_2-\Sigma_{i=3}\theta_i}^{t-\Sigma_{i=3}\theta_i} \frac{dt'}{\tau_i(t')}\right) d\theta_2 = \prod_{i=3}^{N} \frac{h_i\left(t - \sum_{j=i} \theta_j\right)}{H_i\left(t - \sum_{j=i+1} \theta_j\right)} \exp\left(-\sum_{i=3}^{N} \int_{t-\Sigma_{j=i}\theta_j}^{t-\Sigma_{j=i+1}\theta_j} \frac{dt'}{\tau_i(t')}\right) \times 1. \quad \text{(B7)}$$

Hence, it is evident that we can eliminate the distribution with respect to the age in vessel i simply by splitting off from $\rho_i(t,\boldsymbol{\theta})$ the part that depends on θ_i and integrating with respect to θ_i from 0 to ∞, to yield a value of one for that factor. Consequently, if we integrate over all N age variables, we obtain:

$$\int_0^\infty \cdots \int_0^\infty \int_0^\infty \rho_N(t,\boldsymbol{\theta})\, d\theta_1\, d\theta_2 \cdots d\theta_N = 1. \quad \text{(B8)}$$

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