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Research Article

Derivation of a Multiparameter Gamma Model for Analyzing the Residence-Time Distribution Function for Nonideal Flow Systems as an Alternative to the Advection-Dispersion Equation

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A new residence-time distribution (RTD) function has been developed and applied to quantitative dye studies as an alternative to the traditional advection-dispersion equation (AdDE). The new method is based on a jointly combined four-parameter gamma probability density function (PDF). The gamma residence-time distribution (RTD) function and its first and second moments are derived from the individual two-parameter gamma distributions of randomly distributed variables, tracer travel distance, and linear velocity, which are based on their relationship with time. The gamma RTD function was used on a steady-state, nonideal system modeled as a plug-flow reactor (PFR) in the laboratory to validate the effectiveness of the model. The normalized forms of the gamma RTD and the advection-dispersion equation RTD were compared with the normalized tracer RTD. The normalized gamma RTD had a lower mean-absolute deviation (MAD) (0.16) than the normalized form of the advection-dispersion equation (0.26) when compared to the normalized tracer RTD. The gamma RTD function is tied back to the actual physical site due to its randomly distributed variables. The results validate using the gamma RTD as a suitable alternative to the advection-dispersion equation for quantitative tracer studies of non-ideal flow systems.

1. Introduction

Researchers have used the distribution of residence times to examine the characteristics of a nonideal flow reactor or system. The residence-time distribution (RTD) was first proposed to analyze chemical reactor performance in a paper by MacMullin and Weber in 1935 [1–3]. Only after Danckwerts' publication of "Continuous flow systems. Distribution of residence times," in 1953, was the RTD theory organized in a more structured manner and most of the distributions were classified [2–5]. Many people still use Danckwerts' work as their foundation for analysis of systems with the RTD model. The residence-time distribution of a system characterizes the mixing that happens in a system. The residence-time distribution function is quantified by the term $E(t)$. $E(t)$ describes quantitatively the amount of time that different fluid particles have spent in the system. $E(t)$ is also a probability density function (PDF) that defines the probability that a particle entering the system will remain there for a time t (see [1–8] for a thorough explanation of the background theory to mixing and RTD). Equation (1) is generally used to determine the RTD function [2, 7] as

$$E(t) = \frac{C(t)}{\int_0^\infty C(t)\,dt}, \tag{1}$$

where $C(t)$ is the concentration of the tracer over time and the plot of concentration versus time is the tracer breakthrough curve.

It is important to note that all molecules will eventually leave the system (this is also a method used to normalize the distribution) [2, 3, 8], thus

$$\int_0^{\infty} E(t)\,dt = 1. \tag{2}$$

Two important parameters derived from the RTD function are the mean residence time (t_m) [2, 7] as

$$t_m = \frac{\int_0^{\infty} tE(t)\,dt}{\int_0^{\infty} E(t)\,dt} = \int_0^{\infty} tE(t)\,dt \tag{3}$$

and the first moment about the mean of the RTD function (distribution variance or σ^2) [2] as

$$\sigma^2 = \int_0^{\infty} (t - t_m)^2 E(t)\,dt. \tag{4}$$

Although the RTD was originally applied to designing chemical reactors, the RTD has been used in a variety of other applications (see [1–28] and their references for both a thorough discussion of the RTD and its widespread applications). The RTD has also been referred to in the literature as the detention-time distribution (DTD) [29], transit-time distribution (TTD) [30], travel-time distribution [31–33], and hydraulic residence-time distribution (HRTD) [34, 35]. Some researchers concentrate their efforts on obtaining the parameters derived from the RTD function to characterize the flow patterns that they are analyzing [36, 37].

Generally, the main model used to describe the residence-time distribution of a system has been the one-parameter advection-dispersion equation or model (AdDE) [7, 19, 21–28, 31, 33]. In the literature, the AdDE has also been called the axial dispersion or diffusion equation or model (AxDE) or (ADM) [2, 3, 5, 6, 8–10, 13–15, 18]; the advection diffusion equation or "diffusion with bulk flow equation" [10]; or the convection dispersion or diffusion equation (CDE) [18, 38, 39]. The advection-dispersion equation exhibits an RTD function curve which can appear Gaussian based on the conditions [19]. The AdDE model with its single parameter and Gaussian-shaped curves is inadequate for visualizing the nonideal flow RTD [9, 19, 27, 28]. Also, it is true that the symmetric AdDE Gaussian-shaped curve predicts a finite tracer concentration at time = 0, but this is not true for the AdDE solution at that time. Lastly, the Gaussian-shaped curve of the advection-dispersion equation does not adequately display the fullness of tracer breakthrough curves that generally have long upper tails [27]. Thus, we decided to derive an RTD function for non-ideal flow systems by combining two, two-parameter gamma distributions. The gamma distribution resembles many natural processes and has been used widely in complex applications, thus it is a good model for non-ideal flow systems (see [29–33, 40–51] for both a thorough discussion of the gamma distribution and its various applications).

This jointly combined four-parameter gamma model allows for more flexibility to account for the nonlinear aspects [30, 31] of a non-ideal flow system than the single parameter AdDE model; however, the gamma distribution's two parameters (α, β) do not have a clearly associated physical interpretation [30] as does the AdDE model with the Péclet number. To address this issue, the gamma distribution for the RTD was derived based on the assumption that the tracer travel distance and linear velocity of the system were gamma-distributed random variables. This assumption solves the problems regarding the physical interpretation as $\alpha_1\beta_1$ is associated with the mean travel distance of the tracer molecules while $(\alpha_2 - 1)\beta_2$ is associated with the mean travel linear velocity (mean travel distance/mean time in the system). Thus we assume that the solute moves with the water. We also assume that the ratio $\alpha_1\beta_1/(\alpha_2 - 1)\beta_2$ is approximately equal to the mean residence time or the mean time in the system (t_m). The resulting four-parameter model is robust and better able to fit the normalized tracer RTD curve. In addition, the model parameters' relation to the linear velocity and the travel distance of the actual system simplifies the parameterization of the model by reducing the degrees of freedom from four to two.

Regarding non-ideal flow systems, we are assuming the system is isothermal and homogeneous and that the volume changes during the tracer study are assumed to be negligible [5, 6]. We are also assuming that the time domain is steady state rather than transient. The authors in [2, 5–8] provide a thorough explanation of non-ideal flow systems.

2. Derivation of the Four-Parameter Gamma Distribution RTD Model

We are assuming that the residence time of tracer particles is similar to travel times of discrete water molecules in a non-ideal flow system along flow paths. The flow paths for discrete water particles vary in length, local hydraulic gradient, and cross-section. Tracer sample concentration as a measure of the tracer flux at a given time is randomly distributed, but the approach developed in this paper does not apply a residence-time distribution directly to the concentration data. Instead, the arrival of molecules at the sampling point at a particular time is seen as a random event dependent on the distance traveled and speed of travel. Thus, the relation between travel distance and velocity reflected in the space time (τ) for a non-ideal flow system as follows:

$$\tau = \frac{V_{\mathrm{eq}}}{Q} = \frac{\overline{L}A_{\mathrm{eq}}}{\overline{v}A_{\mathrm{eq}}} = \frac{\overline{L}}{\overline{v}}, \tag{5}$$

where both L and v represent independent random variables.

For modeling non-ideal flow systems, addressing the interaction of L and v is important because their independent values relate directly to important characteristics of the system. Specifically, those important characteristics are the following: distance traveled and the straight-line distance between the injection and sampling point(s), localized hydraulic gradient(s), and flow cross-section(s) along the flow path. For this reason, describing the tracer breakthrough curve in terms of a distribution derived from the joint PDF for L and v should provide better insight regarding the RTD for a non-ideal flow system.

The literature suggests that the gamma distribution does well in describing tracer breakthrough curves for non-ideal flow systems [27–33]. The gamma distribution, which is frequently used as a probability model for waiting times, seems to adequately reflect the "long tail to the right" often observed in tracer breakthrough curves [22]. Based on this observation we assumed that L and v are independent random variables (irv) that have gamma PDFs as follows:

$$f_L(x_1) = \frac{x_1^{\alpha_1-1}e^{-x_1/\beta_1}}{\Gamma(\alpha_1)\beta_1^{\alpha_1}}; \quad \alpha_1 \geq 1;\ \beta_1 \geq 0,\ x_1 \geq 0, \tag{6}$$

where α_1 and β_1 are the shape and scale parameters of the two-parameter gamma distribution, respectively, and $\Gamma(\alpha)$ is the gamma function [40–45] as

$$\Gamma(\alpha) = \int_0^\infty x^{\alpha-1}e^{-x}dx,$$
$$f_v(x_2) = \frac{x_2^{\alpha_2-1}e^{-x_2/\beta_2}}{\Gamma(\alpha_2)\beta_2^{\alpha_2}}; \quad \alpha_2 \geq 1;\ \beta_2 \geq 0,\ x_2 \geq 0, \tag{7}$$

where α_2 and β_2 are the shape and scale parameters of the two-parameter gamma distribution, respectively and $\Gamma(\alpha)$ is the gamma function [40–45].

$$f(x) = \frac{x^{\theta-1}e^{-x/\varphi}}{\varphi^\theta\Gamma(\theta)}; \quad x > 0;\ \theta,\varphi > 0, \tag{8}$$

this is the general formula for a two-parameter gamma distribution where θ and φ are the shape and scale parameters of the distribution, respectively, and $\Gamma(\theta)$ is the gamma function [52].

The following mathematical discussion and (9)–(15) are from [52] "The distribution of residence time (t) is derived from the Mellin convolution of the distribution of quotients of random variables where the PDF of the quotient

$$Y = \frac{X_1}{X_2} = (X_1)\left(\frac{1}{X_2}\right), \tag{9}$$

where $Y = t$ and $X_1 = L$ and $X_2 = v$ of two nonnegative irv's with PDFs $f_L(x_1)$ and $f_v(x_2)$ is expressible as the Mellin convolution

$$h_2(y) = \int_0^\infty x_2 f_L(yx_2) f_v(x_2)\,dx_2, \tag{10}$$

of $f_L(x_1)$ and $g_2(1/x_2)$. This is established by utilizing a transformation

$$Y = \frac{X_1}{X_2}, \quad X_2 = X_\mathbf{2}, \tag{11}$$

the inverse of which is

$$X_1 = YX_\mathbf{2}, \qquad X_2 = X_\mathbf{2}. \tag{12}$$

As the Jacobian of the transformation of (12) is

$$J = \begin{vmatrix} \dfrac{\partial x_1}{\partial y} & \dfrac{\partial x_1}{\partial x_2} \\ \dfrac{\partial x_2}{\partial y} & \dfrac{\partial x_2}{\partial x_2} \end{vmatrix} = \begin{vmatrix} x_2 & y \\ 0 & 1 \end{vmatrix} = x_2, \tag{13}$$

the joint PDF $f(x_1,x_2) = f_L(x_1)f_v(x_2)$ is transformed into $g(y,x_2)$, where

$$g(y,x_2) = f_L(yx_2)f_v(x_2)|J| = x_2 f_L(yx_2)f_v(x_2). \tag{14}$$

On integrating (14) with respect to x_2, one obtains the Mellin convolution {in our case the PDF for the residence time (t) is given by the marginal probability in (15)}

$$h_2(y) = \int_0^\infty g(y,x_2)\,dx_2 = \int_0^\infty x_2 f_L(yx_2)f_v(x_2)\,dx_2. \tag{15}$$

Equation (15) represents the PDF of the quotient random variable $Y = X_1/X_2$"

$$f_L(yx_2) = \frac{x_2 y^{\alpha_1-1}e^{-x_2y/\beta_1}}{\Gamma(\alpha_1)\beta_1^{\alpha_1}},$$
$$f_v(x_2) = \frac{x_2^{\alpha_2-1}e^{-x_2/\beta_2}}{\Gamma(\alpha_2)\beta_2^{\alpha_2}},$$
$$h_2(y) = \int_0^\infty x_2\left(\frac{x_2 y^{\alpha_1-1}e^{-x_2y/\beta_1}}{\Gamma(\alpha_1)\beta_1^{\alpha_1}}\right)\left(\frac{x_2^{\alpha_2-1}e^{-x_2/\beta_2}}{\Gamma(\alpha_2)\beta_2^{\alpha_2}}\right)dx_2 \tag{16}$$

make constant

$$C = \frac{y^{\alpha_1-1}}{\Gamma(\alpha_1)\Gamma(\alpha_2)\beta_1^{\alpha_1}\beta_2^{\alpha_2}}, \tag{17}$$

$$h_2(y) = C\int_0^\infty x_2^{\alpha_1+\alpha_2-1}e^{-x_2(y/\beta_1+1/\beta_2)}dx_2. \tag{18}$$

The solution to (18) provides the PDF of the residence time or the combined four-parameter gamma distribution RTD model noted as $E(t)$ in (19) as follows:

$$E(t) = \frac{\Gamma(\alpha_1+\alpha_2)}{\Gamma(\alpha_1)(\alpha_2)}\left(\frac{\beta_1}{\beta_2}\right)^{\alpha_2}\left(\frac{t^{\alpha_1-1}}{(t+\beta_1/\beta_2)^{\alpha_1+\alpha_2}}\right), \quad \alpha_1,\alpha_2,\beta_1,\beta_2 \geq 0 \tag{19}$$

taking the first moment of (19) about the mean using (3) gives

$$t_m = \left(\frac{\beta_1}{\beta_2}\right)\left(\frac{\alpha_1}{\alpha_2-1}\right), \tag{20}$$

where the mean travel distance is

$$L = \alpha_1\beta_1 \tag{21}$$

and the mean travel linear velocity is

$$v = (\alpha_2-1)\beta_2. \tag{22}$$

Taking the second moment of (19) about the mean using (4) gives

$$\sigma^2 = \left(\frac{\beta_1}{\beta_2}\right)^2\left(\frac{\alpha_1}{\alpha_2-1}\right)\left(\frac{\alpha_1+1}{\alpha_2-2}-\frac{\alpha_1}{\alpha_2-1}\right). \tag{23}$$

The individual distributions of L and v provide insight into predicting the characteristics of the transformed distribution.

Assistance in deriving the intermediate steps between equations (18) and (19), between equations (19) and (20), and between equations (19) and (23) came from [53–56].

3. Advection-Dispersion Equation RTD Model

The one-parameter advection-dispersion equation RTD model is obtained from the dimensionless effluent tracer concentration in (24) which is derived from the solution to Danckwerts' "Open-Open System Boundary Conditions" and then applying (1) to (24) to produce (25) [2, 3] as

$$\Psi(1,\theta) = \frac{C_T(L,t)}{C_{T_0}} = \frac{1}{2\sqrt{\pi\theta/\mathrm{Pe}}} \exp\left[\frac{-(1-\theta)^2}{4\theta/\mathrm{Pe}}\right]. \quad (24)$$

Equation (24) is derived in [2, 3] as

$$E(t) = \frac{\Psi(1,\theta)}{\int_0^\infty \psi\, d\theta}. \quad (25)$$

Equation (25) is modified from the $E(t)$ presented in [2, 7].

The Péclet number (Pe) in (24) is computed via (26) after both the mean residence time and the distribution variance are calculated

$$\frac{\sigma^2}{t_m^2} = \frac{2}{\mathrm{Pe}} + \frac{8}{\mathrm{Pe}^2}. \quad (26)$$

Equation (26) is derived in [2] as

$$t_m = \left(1 + \frac{2}{\mathrm{Pe}}\right)\tau, \quad (27)$$

and solving (27) provides the space time (τ) [2].

4. Laboratory Setup for the Validation of the Four-Parameter Gamma RTD Model

A steady-state, non-ideal reactor of glass tubes was set up in the laboratory to simulate a plug-flow reactor (PFR). The glass tubing was borosilicate glass with an inner diameter of 0.4 cm. The flow path model consisted of 1.4 m straight segments of glass tubing. The straight segments of glass tubing were connected by 180° elbows made of Teflon tubing. The radius of each elbow was 0.079 m and the inner diameter of the Teflon tubing was 0.4 cm. The linear length of the system was 32 m. The system was calibrated such that flow rate in the system was maintained at 2.0-mL/min. The injection mechanism to introduce the conservative tracer was a syringe delivering a volume of 5 mL for each trial. Two trials were conducted using 10 ppm of the tracer dye rhodamine WT-20 and 10 ppm Zn, zinc chloride (ZnCl2). Discharge samples of the simulated PFR were collected at 20-minute intervals and analyzed using fluorometry and inductively coupled plasma optical emission spectrometry (ICP-OES) for rhodamine and zinc chloride, respectively. The rhodamine WT-20 tracer data was applied to the gamma and AdDE RTD models.

5. Results and Discussion

The results of the tracer study were used to develop the residence-time distribution (RTD) function. The RTD function ($E(t)$) for contaminant molecules in a non-ideal flow system is a probability density function (PDF) which can be interpreted to define the probability that contaminant particles present in the influent at time equals zero will arrive at the effluent after a time. The RTD is depicted as a plot of $E(t)$ versus time as time goes from zero to infinity (or a reasonably long time where the RTD approaches zero) [2–4, 6–8].

$E(t)$ was determined by injecting a pulse of a conservative tracer (rhodamine WT-20) into the reactor, described in Section 4, at time $(t) = 0$ and then measuring the tracer concentration in the effluent as a function of time. The concentration and time data necessary for computing $E(t)$ was compiled in the Calc spreadsheet program of LibreOffice [57]. Using the Solver for Nonlinear Programming LibreOffice Calc extension [58], we computed the Péclet number (Pe) from (26) using the DEPS (Differential evolution and particle swarm optimization) algorithm [59].

Equation (28) represents the solution to the one-parameter advection-dispersion equation residence-time distribution function at time $\theta = 0$. In this case the solution is infinity, although a finite tracer concentration should be expected for the initial time interval. Therefore, to compare the 3 RTD models, we disregard the RTD at time = 0 as

$$\begin{aligned}\Psi(1,\theta=0) &= \frac{C_T(L,t)}{C_{T_0}} \\ &= \frac{1}{2\sqrt{\pi\times 0/\mathrm{Pe}}} \exp\left[\frac{-(1-0)^2}{4\times 0/\mathrm{Pe}}\right] \approx \infty.\end{aligned} \quad (28)$$

Equation (28) is derived in [2, 3] and is the same as (24) except that $\theta = 0$ and

$$E(t) = \frac{\Psi(1,\theta=0)}{\int_0^\infty \psi\, d\theta} \approx \infty. \quad (29)$$

Equation (29) is modified from the $E(t)$ presented in [2, 7] and is the same as (25), except that $E(t)$ is shown to be approximately equal to ∞.

The normalized forms of the RTD for the tracer, the AdDE model, and the gamma model were computed in LibreOffice Calc. In order to determine the better RTD model, either the AdDE or the gamma, we had to calculate the mean-absolute deviation (MAD) [60] from the tracer RTD model using (30) as follows:

$$\mathrm{MAD} = n^{-1}\sum_{i=1}^{n} \left|y_i - \hat{y}_i\right|, \quad (30)$$

where n represents the number of values where y_i and $\hat{y}_i$ differ, y_i is either the value of the AdDE or gamma RTD model, and $\hat{y}_i$ is the value of the tracer RTD model [60].

The MAD associated with the gamma RTD model was approximately 0.16 while the MAD for the AdDE RTD model was approximately 0.26.

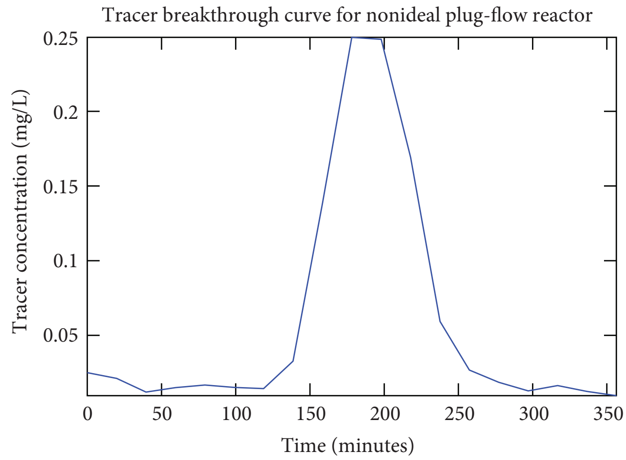

Figure 1: Tracer concentration versus time for the laboratory experiment. These data were used to determine the mean, variance, and Péclet number for the plug-flow reactor.

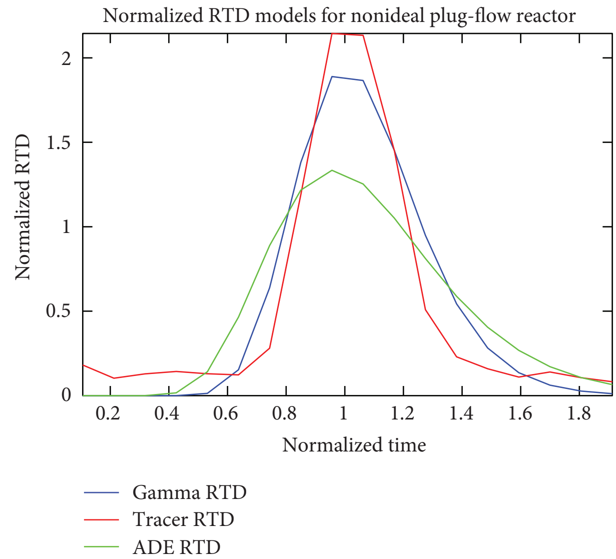

Figure 2: Comparing the normalized forms of the advection-dispersion equation RTD and the gamma RTD models to the normalized tracer RTD model for the laboratory tracer study.

We used the DEPS algorithm to determine the four parameters (α_1, β_1, α_2, β_2) to use in the gamma RTD model which provided a lower MAD than that produced from the AdDE model. Both a script and function files [61] were written in the M-file language of the numerical computation program GNU Octave [62]. GNU Octave uses either the FLTK toolkit [63] or gnuplot [64] to produce graphs. The following graphs in this paper were created using gnuplot rather than the FLTK toolkit. The script and function files used the four parameters for the gamma RTD model to solve equations (19)–(23) for the normalized gamma RTD model. The script and function files were also used to produce the graphs for the tracer breakthrough curve and the comparison of the normalized RTD curves. The graphical results of the laboratory, quantitative tracer study using rhodamine WT-20 are shown in Figures 1 and 2.

Figure 1 shows the tracer breakthrough curve.

The results for the laboratory plug-flow reactor rhodamine dye study conducted are as follows The mean residence time (t_m) is ≈186 minutes which is from (3), the variance of the distribution (σ^2) is ≈3276 $\min^2$ which is from (4), the dimensionless Péclet number is ≈25 which is from (26), and the space time (τ) is ≈172 minutes which is from (27).

To compare the 3 RTD models to each other (gamma from (19), advection-dispersion equation (AdDE) from (25), and tracer from (25)), we had to normalize each of the RTDs with dimensionless time.

Figure 2 shows the comparison of the three normalized RTD models.

The results for the normalized gamma RTD model's interpretation of the laboratory plug-flow reactor rhodamine dye study conducted using $\alpha_1 \approx 50$, $\alpha_2 \approx 50$, $\beta_1 \approx 0.61$, and $\beta_2 \approx 0.59$ are as follows.

The dimensionless mean residence time or mean time in the system (t_m) is ≈1.07 mean minutes which is from (20), the mean travel distance of tracer molecules is ≈32 mean meters which is from (21), the mean travel linear velocity (mean travel distance of tracer molecules/mean time in the system) is ≈30 mean meters/minute which is from (22), and the dimensionless variance of the distribution (σ^2) is ≈0.05 mean $\min^2$ which is from (23). The mean travel distance of ≈32 mean meters is approximately equal to the straight-line horizontal distance of 32 meters for the laboratory reactor.

In an ideal plug-flow reactor (PFR) the apparent reactor velocity should be strongly correlated to the velocity of the peak of the tracer curve. This strong correlation is based on the shape of the velocity profile. In our study, the apparent reactor velocity (volumetric flow rate/area of the tube) is ≈9.55 meters/hour compared to the velocity of the peak of the tracer curve (mean travel distance of tracer molecules/mean residence time), obtained from the gamma RTD model, of ≈9.77 meters/hour. The velocity obtained from the gamma RTD model has a good correlation to the apparent reactor velocity with ≈2.3% error.

6. Conclusions

The normalized form of the gamma RTD function had a better fit with the tracer RTD function than the advection-dispersion equation RTD function. The mean-absolute deviation (MAD) from the normalized tracer RTD function for the normalized gamma RTD function was ≈0.16 compared to ≈0.26 for the normalized AdDE RTD model. The lower MAD value for the normalized gamma RTD function was also displayed visually in Figure 2.

As previously discussed in Section 5, the initial time value had to be removed from the comparison of the three normalized RTD models due to the normalized AdDE RTD function computing a value of ∞ at this time. This flaw presents a major setback in using the one-parameter advection-dispersion equation RTD function.

In addition, the normalized gamma RTD function allows for the calculation of the mean travel linear velocity and the mean travel distance which are obtained from the α and β parameters obtained from the best fit of the normalized gamma RTD to the normalized tracer RTD. The mean velocity and the mean distance traveled are tied back to the actual physical site due to the relation with time between the length and the linear velocity. This information is not available with the normalized AdDE RTD function.

For those reasons, we conclude that the jointly combined four-parameter gamma distribution RTD function better models the non-ideal flow present in the laboratory plug-flow reactor than the one-parameter advection-dispersion equation RTD function. Thus, the gamma RTD function is a suitable alternative to the advection-dispersion equation RTD function for quantitative tracer studies of other non-ideal flow systems.

Abbreviations

L:	Travel distance
v:	Velocity
t or T:	Time
t_m:	Mean residence time
σ^2:	Distribution variance
θ:	Dimensionless time
$C(t)$:	Concentration over time
C_T:	Concentration at time t
C_{T0}:	Concentration at time $t = 0$
V:	Reactor or system volume
V_{eq}:	Equivalent volume
A_{eq}:	Equivalent area
eq:	Equivalent
Q:	Volumetric flow rate
τ:	Space time
irv:	Independent random variable
RTD:	Residence-time distribution
$E(t)$:	Residence-time distribution function
TTD:	Transit time distribution
DTD:	Detention time distribution
HRTD:	Hydraulic residence-time distribution
AdDE or ADE:	Advection-dispersion equation
AxDE:	Axial dispersion equation
ADM:	Axial dispersion model
CDE:	Convection dispersion equation
PDF:	Probability density function
PFR:	Plug-flow reactor
Pe:	Péclet number
MAD:	Mean-absolute deviation
DEPS:	Differential evolution and particle swarm optimization algorithm.

Future Work

We will compare the four-parameter gamma RTD function to the advection-dispersion equation RTD function for a quantitative dye study that was performed at Mammoth Cave National Park, Ky, USA.

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