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Residence Time Distribution (RTD) theory is revisited and tracer technology discussed. The background of RTD following Danckwerts ideas is presented by introducing “distribution” functions for residence time, internal age and intensity function and how to experimentally obtain them with tracer techniques (curves C and F of Danckwerts). Compartment models to describe fluid flow in real reactors are reviewed and progressive modeling of chromatographic processes discussed in some detail. The shortcomings of Standard Dispersion Model (SDM) are addressed, the Taylor-Aris model discussed and the Wave Model of Westerterp’s group introduced. The contribution of Computational Fluid Dynamics (CFD) is highlighted to calculate RTD from momentum and mass transport equations and to access spatial age distribution and degree of mixing. Finally smart RTD and future challenges are discussed.
1. Introduction

I learned Residence Time Distribution (RTD) 50 years ago in a Chemical Reaction Engineering (CRE) course given by Jacques Villermaux (Villermaux, 1972) at ENSIC (Nancy, France) when doing my doctoral work. I appreciated his “system dynamics” approach in the modeling of real reactors. From those days I remember a seminar from Levenspiel (Levenspiel, 1973) given on September 17, 1973 (I still keep my notes...) at the “Centre de Cinétique Physique et Chimique”, the CNRS laboratory directed by P. Le Goff where I was working. Levenspiel mixed English and French in his beautiful and pedagogical presentation. I tell my students that if they read and understand Levenspiel’s book (Levenspiel, 1972) it is more than enough; the original is always better than photocopies... He stressed that the task of an engineer is to transform raw materials into products, hopefully with increasing value. He pointed out that the output of a reactor depends on the input type, kinetics, mode of contact, etc. We can summarize as shown in Fig. 1:

Output = f(input, kinetics, nature of the fluid flow, state of mixing)

In the case of fluid flow he mentioned two approaches: the one by hydraulics (civil engineering) based on correlations (practical but not general) and fluid mechanics approach (involving mathematics and theorems...). How to conciliate these lines was the challenge taken by Prandtl (Prandtl, 1904) in 1904: instead of solving equations he simplified them and that is the beginning of the Modern Fluid Mechanics.

The RTD theory is linked to the name of Danckwerts and his seminal paper (Danckwerts, 1953) in 1953. I was reading recently the book “Life on the edge” (Varey, 2012) about P. V. Danckwerts. His chemistry background from Oxford (“we had laboratories in the cellars and all the kinetic results were said to be catalyzed by cigarette smoke” (Danckwerts, 1986), the attendance of MIT course to learn the tricks of Chemical Engineering (ChE) is very well documented there. The simplicity and clarity of presentation are due may be to his non-mathematical background (as Danckwerts said “At the age of 30 I had never used a slide-rule or heard about differential equations” (Danckwerts, 1986).

In 1983 I spent a sabbatical year at the Université de Technologie de Compiegne (UTC) and as a result of the interaction with E. Brunier, G. Antonini and A. Zoulalian, RTD was tackled by solving the complete set of equations for flow and mass transport of a passive tracer (Brunier et al., 1984) in line with the approach mentioned in the book by Nauman and Buffham (Nauman and Buffham, 1983). This problem was later solved in 2004 with new...
CFD tools (Fluent) and published with education goal (Madeira et al., 2004).

In the middle of 90's I came across a series of papers by Westerterp's group (Westerterp, 1995; Westerterp et al., 1995, 1996; Kronberg et al., 1996; Benneker et al., 1997) about what they called "wave model" where the limitations of the SDM (Standard Dispersion Model) were discussed. My interest on this topic was renewed during ISCRE 22 in Maastricht when Westerterp delivered a talk to the representatives of the Working Party of EFChE on CRE (Westerterp, 2012); unfortunately Westerterp passed away on August 24, 2013. In more recent years a series of papers (Liu, et al., 2004).

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The outlet concentration is simply the tracer outlet concentration, \( c_{out} \), "leaves'. The normalized outlet tracer concentration versus time, \( \frac{E(t)}{Et} \), is the step function or Dirac delta function. Similarly for a

2. RTD theory of Danckwerts and tracer methodology

2.1. Residence time distribution \( E(t) \), internal age distribution, \( I(t) \) and intensity function, \( \Lambda(t) \)

Danckwerts (Danckwerts, 1953) (1953) approached the study of fluid flow in reactors in a brilliant and simple way: "introduce a pulse of tracer into the fluid entering the reactor and see when it leaves". The normalized outlet tracer concentration versus time, \( E(t) \) is the Residence Time Distribution (RTD). Here the normalized outlet concentration is simply the tracer outlet concentration, \( c_{out} \), normalized by the area under the curve \( c_{out}(t) \) versus time, i.e.,

\[
E(t) = \frac{c_{out}(t)}{\int_0^\infty c_{out}(t) \, dt} \quad (1)
\]

The study of RTD of flowing fluids and its consequences can be put under the umbrella of tracer technology. This is important for chemical engineers (Levenspiel and Bischoff, 1963; Shinnar, 1977), researchers in the medical field (Weinstein and Dudukovic, 1975), environment (Zvirin and Shinnar, 1976), etc to diagnose the reactor ill-functioning, drug distribution in the body, dispersion of pollutants in rivers, etc. When I taught this subject at the University of Virginia in 1988 students "saw" the application of RTD in a Department Seminar where Michael J. Angelo from Merck Chemical Manufacturing Division talked about pharamcokinetic models (Angelo, 1988)

Danckwerts built a theory based on the characterization of fluid elements of the population inside the reactor using two characters: age or internal age, \( t_i \), and of the population leaving the reactor: residence time, \( t_r \). Then he introduced the "distribution" relative to each character; the residence time distribution \( E(t) \) defined as \( E(t) \, dt \) being the fraction of fluid elements leaving the reactor with residence time between \( t \) and \( t + dt \). Similarly the internal age distribution \( I(t) \), a decreasing monotonic function, was defined as \( I(t) \, dt \) being the fraction of fluid elements inside the reactor with age between \( t \) and \( t + dt \).

When I taught RTD in undergraduate CRE course I made an analogy with the population in a country (Rodrigues, 1981); obviously the life of the newborn babies born today will follow the same pattern of those babies born before... the number of elements \( n(t) \) will decrease with time and after 110 years or so all "left" the system. If \( n(t) \) decreases suddenly near time zero it means high birth mortality rate in a given population or a by-pass (short-circuit) in reactors.

The intensity function \( \Lambda(t) \) was defined as \( \Lambda(t) \, dt \) being the fraction of fluid elements inside the reactor that, in each class of internal ages, has zero life expectancy (it means that those fluid elements will leave the reactor immediately after). These theoretical "distribution" functions are related by

\[
\Lambda(t) = \frac{E(t)}{Et} \quad (2)
\]

where \( \tau = \frac{t}{Q_0} \) is the space time of the fluid flowing through the reactor volume \( V \) with a volumetric flowrate \( Q_0 \). This is a result from the fact that in a time interval \( dt \), the amount of fluid leaving the reactor with residence time between \( t \) and \( t + dt \), \( \int_{Q_0} E(t) \, dt \), is the fraction of the amount of fluid inside the reactor with age between \( t \) and \( t + dt \), \( V(t) \), which has zero life expectancy, \( \Lambda(t) \, dt \).

For a general reactor these theoretical distribution functions \( E(t), I(t) \) and \( \Lambda(t) \) are shown in Fig. 2.

For the extreme cases of plug flow and perfect mixing the "theoretical" functions \( E(t), I(t) \) and \( \Lambda(t) \) are shown in Fig. 3. In a perfectly mixed reactor young molecules and old molecules have equal probability of escaping the reactor \( \Lambda(t) = \frac{1}{\tau} \); hopefully in the analogy of RTD and population studies that is not the situation and certainly not in this time of COVID-19.

2.2. How to get the RTD, \( E(t) \) from tracer experiments: Linking theory and experiments

The next question is how to experimentally have access to \( E(t) \). This brings the tracer technology to the center of the arena (Fig. 4). The response of the reactor to an impulse of tracer, \( c_{out} \), normalized by a reference concentration, \( c_0 = \frac{c_{out}}{c_{in}} \), is the experimental C curve of Danckwerts, \( C(t) \). It should be noted that \( n \) is the amount of tracer injected which should appear at the outlet and therefore \( n = Q_0 \int_0^\infty c_{out}(t) \, dt \). The experimental C curve is directly related with the RTD, \( E(t) \) by:

\[
C(t) = \tau E(t) \, \delta(C(t)) = E(\theta) \quad (3)
\]

where \( \theta = \frac{t}{Q_0} \) is the time normalized by the space time. The inlet tracer concentration when \( n \) moles of tracer are injected instantaneously in a fluid stream with flowrate \( Q_0 \) is \( C_{in}(t) = c_0 \delta(t) \), where \( \delta(t) \) is the impulse or Dirac delta function. Similarly for a step input of tracer \( C_{in} = c_0 H(t) \), where \( H(t) \) is the unit Heaviside step function, the normalized reactor response is the F curve of Danckwerts, i.e., \( F(t) = \frac{c_{out}}{c_{in}} \). Furthermore, as a consequence of system linearity, the response to an impulse is the derivative of the response to a step input since the Dirac delta function is the derivative of the step function, i.e., \( \delta(C(t)) = \frac{dF(t)}{dt} \) and therefore the RTD, \( E(t) \) can be obtained from the experimental curve F of Danckwerts by:

\[
E(t) = \frac{dF(t)}{dt} \quad (4)
\]

The mass conservation of the tracer in a tracer experiment where the inlet concentration is a step of magnitude \( c_0 \) is:
Q_0c_0 = Q_0c_{out} + \frac{d}{dt} \left( Vc_0 \int_0^t I(t) dt \right) \tag{5}

which leads to a relation between the experimental F curve of Danckwerts and the internal age distribution I(t):

1 = F(t) + \tau I(t) \Rightarrow I(t) = \frac{1 - F(t)}{\tau} \tag{6}

where 1 - F(t) = P(t) is the purge function, response of the system to a negative step going from an initial tracer concentration c_0 to zero.

2.3. Relation between RTD, E(t) and the system transfer function, G(s): A system dynamics approach.

It is also interesting to note that the RTD is the inverse Laplace transform of the transfer function G(s), i.e.,

\[ E(t) = L^{-1}G(s) \tag{7} \]

To recall the transfer function of a dynamical system is just the ratio between the Laplace transforms of output and input tracer concentrations. In the case of an impulse input the Laplace transform is simply \( L\{c_\text{in}(t)\} = L\{e^\alpha \delta(t)\} = e^{\alpha \tau} \) and so:

\[ G(s) = \frac{L[I_{\text{out}}(t) \big|_{c_\text{in}}]}{e^{\alpha \tau}} = L[E(t)] = \int_0^\infty e^{-st}E(t)dt \tag{8} \]

This relation allows the calculation of the moments of E(t) from G(s) and its derivatives at s = 0. The transfer function G(s) is the generating function of moments of E(t), i.e.,

\[ G(s) = \mu_0 - \mu_1 s + \frac{\mu_2}{2} s^2 + \cdots + (-1)^n \frac{\mu_n}{n!} s^n + \cdots \tag{9} \]

where the moments of n\textsuperscript{th} order of the RTD, can be calculated from G(s) and its derivatives for s = 0 (Van der Laan theorem (Van der Laan, 1958)).

\[ \mu_n = \int_0^\infty t^n E(t) dt = (-1)^n \frac{d^n G(s)}{ds^n} \big|_{s=0} \tag{10} \]

In the presence of a first-order irreversible reaction with kinetic constant k the transfer function is \( G_r(s) = G(s + k) \).

2.4. Conversion in real reactors: Combining information on reaction kinetics from batch reactors and nature of fluid flow with residence time distribution.

Finally the chemical engineer uses the hydrodynamic characterization to connect the nature of fluid flow in a real reactor with the
reaction kinetics obtained in a batch reactor, \( c_{\text{batch}}(t) \) and predict the average outlet concentration in a real reactor in steady state:

\[
\langle c_{\text{out}} \rangle = \int_0^\infty E(t)c_{\text{out}}(t)\,dt
\]

This result is valid for first-order reactions. It is easily derived by considering the real reactor as an assembly of plug flow reactors in parallel, each with a space time corresponding to a residence time \( t \) which can take values from zero to infinite. This model assumes completely segregated flow, i.e., molecules flowing through the plug flow with space time \( t \) do not mix with molecules flowing through the other plug flow reactors with different residence times...

For other reaction kinetics equation Eq. (11) gives the limit when the flow is completely segregated; in the limit of maximum mixedness the Zwiertering equation (Eq. (12)) holds (Zwiertering, 1959).

\[
\frac{dc}{dt} = R(c) + \Lambda(t)[c(t) - c_0]
\]

where \( R(c) \) is the rate of reaction, \( c_0 \) is the feed concentration and the outlet concentration \( c(0) \) is obtained by integrating in the direction of decreasing \( t \) using \( \frac{dc}{dt} = 0 \).

2.5. Remarks on the measurement of RTD and its use for reactor diagnosis

A tracer is ideally a solute able to follow the path of the fluid travelling through the reactor and should be easy to detect and not disturb the flow. Data analysis is facilitated if the tracer is inert, nonvolatile (for liquid phase tracers), non-absorbed (for gas phase tracers) or non-adsorbed (in fluid-solid systems).

Various types of tracer detection can be used in laboratory and at industrial scale tests such as UV–Vis, conductivity, online Near Infrared (NIR) spectroscopy, radioactive tracers, etc. Bérard et al (Bérard et al., 2020) presented RTD examples ranging from applications in static mixers, tubular loop reactor, structured packings for catalytic distillation, continuous powder blending using some of the above mentioned techniques for tracer detection. A recent review of the use of radiotracers in chemical industry was published by Sheoran et al (Sheoran et al., 2018) emphasizing the need for radioactive decay correction and tail correction and listing techniques and the potential of the method of moments in chromatography has been discussed in detail in a report from IAEA (2008).

For impulse tracer input the data treatment is simple: the outlet tracer concentration \( c_{\text{out}}(t) \) (or a signal proportional to it) is divided by the area under the curve \( c_{\text{out}} \) versus time \( t \) (i.e., number of moles of tracer injected divided by the volumetric flowrate = \( n/Q \)) as indicated by Eq (1) to give directly the RTD, \( E(t) \).

If \( t > \tau \) it indicates the presence of short-circuit and the fraction of tracer by-passed is \( 1 - e^{-t/\tau} \) on the other hand if \( t < \tau \) the system has dead zones and the fraction of the reactor volume occupied by dead zones is \( 1 - \xi \). These tools have been applied by the author to an industrial polymerization reactor where a short-circuit around 6% of the feed flowrate was observed (Rodrigues, 1981).

For step input of tracer \( c_{in} = c_0H(t) \) the data treatment is also simple; first the outlet signal is normalized by \( c_0 \) leading to the Danckwerts \( F(t) \) curve and the RTD is just the time derivative of \( F(t) \).

When the inlet tracer concentration \( c_{in}(t) \) is not a perfect Dirac impulse, both inlet and outlet signals \( c_{in}(t) \) and \( c_{out}(t) \) are recorded (or two signals at different points along the reactor) and these two signals are related with the RTD, \( E(t) \) through the convolution integral

\[
\langle c_{\text{out}} \rangle = \int_0^\infty c_0(t-t')E(t')\,dt' \quad \text{or} \quad c_{\text{out}}(t) = c_0(t) * E(t)
\]

The RTD, \( E(t) \) is obtained by deconvolution or as the inverse of the transfer function, i.e., the ratio of Laplace transforms of the outlet and inlet signals, as indicated above in Eq (8).

The interpretation of RTD data has been discussed in many publications; for example Leclerc et al (Leclerc et al., 2000) and Martin (Martin, 2000) analyzed data from measurements in industrial processes and the potential of the method of moments in chromatography has been discussed in detail in a report by Qamar and Seidel-Morgenstern (Qamar and Seidel-Morgenstern, 2016).

3. Models to describe fluid flow in real reactors

3.1. Nuclei elements and compartment models

A class of models (compartment models) can be built by assembling nuclei elements in order to represent tracer experiments in real reactors. Those nuclei elements are: i) perfectly mixed reactor; ii) plug flow reactor; iii) laminar flow reactor, iv) recycle; v) bypass or short-circuit; vi) dead zones and viii) stagnant zones. Nuclei-elements are shown in Fig. 5.

Typical models of this class such as Cholette and Cloutier (Cholette and Cloutier, 1959), Adler and Hovorka (Adler et al., 1961), plug flow with recycle (Villermaux, Lavoisier (1993), tank in series with recycle (Levenspiel, 2012) and unified time delay model (Buffham and Gibilaro, 1970) are shown in Fig. 6.

(a) The Cholette and Cloutier model (Fig. 6a) of a stirred tank reactor with space time \( \tau = \frac{n}{V} \)

considers a by-pass flowrate \( \alpha Q_o \) and a dead zone with volume \( (1 - \beta) V \); the model has three parameters: \( \alpha, \beta, \tau \). The transfer function \( G(s) \) is:

\[
G(s) = \frac{1}{1 + \frac{1}{\tau s}}
\]

and the RTD is:

\[
E(t) = \alpha \delta(t) + (1 - \alpha) \left( \frac{(1 - \alpha)}{\tau s} \right) e^{-\frac{\tau - \tau_d}{\tau}}
\]

(b) The basic unit of the Adler and Hovorka model (Fig. 6b) of a real reactor is a cell with total volume \( V \) and feed flowrate \( Q_o \) combining a plug flow reactor of volume \( V_p \) and a perfectly mixed stirred tank of volume \( V_s \) exchanging mass with a stagnant zone of volume \( V_m \). The flowrate exchanged is \( \beta Q_o \). The transfer function is now:

\[
G(s) = \frac{e^{-\frac{\tau_s}{\tau_m}}}{\left(1 + \frac{1}{\tau_s + \tau_m} - \frac{\beta}{\tau_m}\right)}
\]
The model parameters are $V_p/V$, $V_f/V$ and $\beta$. For $\beta = 0$ the model reduces to the Kramers system (plug flow and perfectly mixed reactor in series).

(c) The plug flow with recycle flowrate $RQ_0$ (Fig. 6c) is a good example of recirculation systems. The transfer function is:

$$G(s) = \frac{e^{-\frac{t}{\tau}}}{1 + R - Re^{-\frac{t}{\tau}}}$$

and the RTD is a series of impulses with decreasing strength:

$$E(t) = \sum_{i=0}^{\infty} \frac{1}{1 + R \left( \frac{R}{1+R} \right)^i} \delta (t - (i+1)\tau)$$

In the above equations $R$ is the recycle ratio: ratio between the recycle flowrate ($RQ_0$) and feed flowrate ($Q_0$).

(d) The model of tanks in series with volumes $\rho V$ and $(1 - \rho)V$ with recycle $RQ_0$ is shown in Fig. 6d. The system is a second-order system with damping factor $\zeta = \frac{\sqrt{(1-\rho)}\sqrt{1+\rho}}{2\sqrt{\rho(1-\rho)}}$ and a time constant $\tau_{\text{system}} = \frac{\sqrt{(1-\rho)}}{\sqrt{1+\rho}}$ where the space time of the reactor is $\tau = \frac{V_f}{Q_0}$. The RTD is now:

$$E(t) = \frac{\zeta}{\sqrt{\zeta^2 - 1}} \frac{e^{\frac{t}{\tau}}}{\tau} \left[ e^{\frac{t}{\tau}} - e^{\frac{2t}{\sqrt{\zeta^2 - 1}}} \right]$$

(e) The unified time delay model of a packed bed in its version of discrete cells in series is shown in Fig. 6e. The model parameters are the minimum transit time of a fluid element which is not delayed in the main flow region with volume $V_s = \frac{V}{Q_0}$ and the mean delay time $t_D$ ($t_D = V_D/q$ where $q$ is the lateral flowrate in each discrete cell) for a delay time distribution in lateral zones. The transfer function is:

$$G(s) = \left\{ 1 + \frac{1}{\tau D (\tau s + 2g_D(s))} \right\}^{-1}$$

where $\alpha = \frac{q}{Q_0}$ and $g_D(s)$ is the transfer function of the lateral zone with an exponential time delay distribution $g_D(s) = (1 + \tau_D s)^{-1}$. 

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**Fig. 5.** Nuclei elements of compartment models.

**Fig. 6.** Examples of “complex” models: (a) Cholette and Cloutier, (b) Adler and Hovorka, (c) plug flow with recycle and (d) tanks in series with recycle and (e) unified time delay model.
A recent review on compartmental modeling can be found elsewhere (Jourdan et al., 2019).

3.2. Application to NETmix® reactor

The NETmix® reactor is shown in Fig. 7. It is a network of chambers connected by channels (Martins et al., 2007; Laranjeira et al., 2009). It is a technology for static mixing which has been patented (Lopes et al., 2004) and successfully used industrially for the production of hydroxyapatite nanoparticles (Silva et al., 2008; Gomes et al., 2009). The model assumes that the chambers are perfectly mixed reactors and the channels are plug flow systems. The RTD can be derived easily for such model

\[ E(\theta) = \frac{n_x}{(1 - \alpha)(n_x - 1)!} \left( \frac{n_x(\theta - \alpha)}{1 - \alpha} \right)^{n_x-1} e^{-\frac{n_x}{1 - \alpha} H(\theta - \alpha)} \]  

In Equation (21) the segregation parameter is \( \alpha = \frac{V_{\text{channels}}}{V_{\text{network}}} \) and the network is an alternate sequence of \( n_x \) piston flow channels and perfectly mixed chambers finishing with one piston flow channel at the exit; the normalized time is \( \theta = \frac{t}{s} \) and the space time is the network volume divided by the total flowrate. Fig. 8 shows RTD of a Netmix reactor for \( n_x = 50 \) and various values of the segregation parameter \( \alpha \).

Advanced-Flow™ Reactors (AFR) from Corning (Suranani et al., 2018) have also been used in a number of applications from biodiesel to the production of Active Pharmaceutical Ingredients (APIs) in pharma industry. It is interesting to note the patented HEART design of the mixers elements (Figure 9).

3.3. Staged models and Standard dispersion model (SDM)

The more used models to describe fluid flow in packed bed columns are the staged model and the standard dispersion model (SDM) or plug dispersion flow model.

3.3.1. Staged model and the chromatography plate theory of Martin and Synge

One important application of the staged model was in the modeling of chromatographic processes - the Plate theory of Martin and Synge (Martin and Synge, 1941). The column is viewed as a cascade of \( J \) mixing cells in series each one containing a volume of fluid phase \( v_f \) and a volume of solid phase \( v_s \); the space time is \( \tau = \frac{Jv_f}{Q_0} \) and the partition of solute between phases or capacity factor is \( \xi = m \frac{v_s}{v_f} \) where \( m \) is the slope of the adsorption equilibrium isotherm relating concentrations of solute in the solid and fluid phases at the interface. The retention time (first moment of the chromatographic peak) is then \( t_r = \tau (1 + \xi) \). The system transfer function is:

\[ G(s) = \prod_i g_i(s) = \left( 1 + \frac{t_r s}{J} \right)^{-j} \]  

Fig. 7. NETmix® reactor: (a) Network of channels and chambers and (b) photo of an industrial unit (www.fluidinova.com).
Cascade and to my knowledge was first reported by Mac Mullin and Weber (MacMullin and Weber, 1935) in 1935 although the title of that paper could be confusing.

The model above considers instantaneous equilibrium between the solute in fluid phase and in the adsorbed phase. We know that the behaviour of a fixed bed chromatographic or adsorption column is governed by equilibrium and kinetic factors (hydrodynamics, heat/mass transfer).

If we add a degree of complexity in the above model by considering a finite mass transfer rate between fluid and solid phases we have a new model MCE: Mixing cells in Cascade with Exchange (Villermaux, 1972). Model equations are the mass balance over a mixing cell, the kinetic law of mass transfer between phases and the equilibrium law at the interface:

$$Q_0 c_0 = Q_0 c_i + V_i \frac{dc_i}{dt} + V_i \frac{d(n_i)}{dt}$$

$$k_m n_i \left( \frac{n_i}{m} \right) = \frac{d(n_i)}{dt}$$

where $Q_0$ is the feed flowrate, $c_i$ is the fluid solute concentration, $n_i$ is the adsorbed phase concentration at the particle/fluid interface in equilibrium with $c_i$, $(n_i)$ is the average particle concentration , $a_p$ is the particle specific area and $k_m$ is the mass transfer coefficient between bulk fluid and particle.

By putting $t_m = \frac{c_i}{k_m a_p}$ the transfer function $G(s)$ is:

$$G(s) = \left\{ 1 + \frac{c_i}{J} \left( 1 + \frac{c_i}{J m^s + 1} \right) \right\}^{-J}$$

The moments of the chromatographic peak are: $t_r = \tau (1 + \xi)$ and $\tau^2 = \frac{t_r^2}{c_i}$.

### 3.3.2. Standard dispersion model (SDM)

The plug diffusional model or Standard Dispersion model (SDM) in its simple version superimposes plug flow and axial dispersion. From the second Fick's law and considering a plane source of tracer in a quiescent medium we obtain:

$$c(z, t) = \frac{N}{2 \sqrt{\pi D} t} \exp \left( \frac{-z^2}{4 D t} \right)$$

In the above Eq. (28), $c(z, t)$ is the concentration in axial direction $z$ at time $t$ and $D$ is axial diffusion.

Now if the fluid is moving with velocity $u$ in a tube with length $L$, the residence time distribution will be

$$E(\theta) = \frac{\sqrt{Pe}}{2 \sqrt{\pi \theta}} \exp \left( - \frac{Pe(1 - \theta^3)}{4 \theta} \right)$$

where the concentration was normalized by $c^0 = N/L$ , the dimensionless time is $\theta = t/\tau$ and the Peclet number is $Pe = u \tau$ based on the reactor length.

Alternatively one can start with the mass balance of tracer in a volume element of a bed with porosity $\varepsilon$ packed with non-permeable particles showing the contribution of convection, accumulation and axial dispersion:

$$u_0 \frac{\partial c}{\partial z} + \varepsilon \frac{\partial c}{\partial t} = \varepsilon D_m \frac{\partial^2 c}{\partial z^2}$$

### 3.3.3. Advanced-Flow Reactors (AFR) from Corning

![Advanced-Flow Reactors (AFR) from Corning](image)

Fig. 8. RTD for a Netmix reactor; $n_i = 50$ number of piston flow channels and $\alpha = \frac{V_{network}}{V}$ increasing from 0.01, 0.1, 0.25, 0.5 and 0.75 (reprinted from Laranjeira et al, AIChEJ, 55, 2226–2243 (2009), with permission from Wiley).

The moments of the chromatographic peak are: $t_r = \tau (1 + \xi)$ and $\tau^2 = \frac{t_r^2}{c_i}$.

and the outlet normalized concentration is:

$$E(t) = \frac{1}{t_r} \left( \frac{t}{t_r} \right)^{J-1} \int_0^t e^{-J/\bar{t}}$$

The moments of $E(t)$ are $\mu_0 = 1$, $\mu_1 = \tau (1 + \xi)$ and the variance is $\sigma^2 = \tau^2/J$; the peak maximum is $t_{\text{max}} = \bar{t}_r (J - 1)/J$ and the peak width at mid-height for high $J$ , is $2\sigma = 2 \bar{t}_r / \sqrt{J}$. In the case of homogeneous systems without adsorbent/catalyst particles $\xi = 0$ and the first moment of $E(t)$ is simply the space time $\bar{t}_r = \tau = V/Q_{in}$. This result holds for the model of Mixing Cells in chemical engineering science 230 (2021) 116188
z = L \left( \frac{\partial c}{\partial z} \right)_z = 0 

(30b)

to get the RTD, Equation (29), where the space time is redefined as 
\[ \tau = \frac{z}{u_1} \] and \( \text{Pe} = \frac{u_1 L}{D ax} \).

The axial dispersion contains the contribution of molecular diffusion \( D_m \) and eddy dispersion due to the presence of the packing; at high Reynolds number the random walk theory of diffusion allows us to calculate Bodenstein numbers for axial \( Bo_{ax} = \frac{u_0}{\sqrt{D_m}} = 2 \) and radial dispersion, \( Bo_{rad} = \frac{u_0}{D_m} = 8 \).

For a packed bed with porous particles the mass balance for inert, passive tracer in a bed volume element is:

\[ u_0 \frac{\partial c_{pi}}{\partial t} + e \frac{\partial c_{pi}}{\partial z} + (1 - e) \phi \frac{\partial c_{pi}}{\partial t} = e D_m \frac{\partial^2 c_{pi}}{\partial z^2} \]

(31)

and at the particle level the mass balance writes as:

\[ \frac{\partial c_{pi}}{\partial t} = D_{pe} \left( \frac{\partial^2 c_{pi}}{\partial z^2} + \frac{2}{r} \frac{\partial c_{pi}}{\partial r} \right) \]

(32)

Obviously in a tracer experiment in a bed with porous particles what we are measuring is an "apparent axial dispersion"

\[ D \approx D_{ax} \approx \frac{v}{1 + \frac{v}{1 + \frac{v}{v}} T d e f^2} \]

(33)

where the interstitial velocity is \( u_1 \), the ratio of fluid in the particle pores and outside particles is \( v = \frac{v}{1 + \frac{v}{v}} \), and the intraparticle diffusion time constant is \( \tau_d = \frac{d_p}{D_{pi}} \). Alternatively one can write a relation between the "apparent Peclet number" \( \text{Pe} = \frac{u_1}{\varepsilon D_{ax}} \) and \( \text{Pe} \):

\[ \frac{\text{Pe}}{1 + \frac{\text{Pe}}{1 + \frac{\text{Pe}}{\text{Pe}}}} \]

(33a)

or

\[ 1 = \frac{1}{\text{Pe}} + \frac{\text{Pe}}{1 + \frac{\text{Pe}}{\text{Pe}}} \]

(33b)

where the parameter \( z = \frac{\text{Pe}}{\text{Pe}} \) is the ratio of the time constants for diffusion and convection. Only when intraparticle diffusion is very fast and \( z \) goes to zero we are measuring axial dispersion free of intrusion of pore diffusion. This is illustrated in Fig. 10 showing the apparent Peclet number, \( \text{Pe} \) versus \( \text{Pe} \).

Van Deemter, Zuiderweg and Klinkenberg viewed the column as a continuous system (Van Deemter et al., 1956) with flow described by the plug dispersion model; for linear systems the transfer function is:

\[ G(s) = \exp \left\{ \frac{\text{Pe}}{2} \left[ 1 - \sqrt{1 + \frac{4\tau s(1 + M(s))}{\text{Pe}}} \right] \right\} \]

(34)

where \( M(s) = \frac{s}{\tau s} \). The variance is obtained by replacing \( 1/f \) by \( 2/\text{Pe} \). The response to a step input of tracer is (Danckwerts, 1953)

\[ F(t) = \frac{1}{2} \left[ 1 - \text{erf} \left( \sqrt{\frac{\text{Pe} (1 - \frac{1}{2})}{2}} \right) \right] \]

(35)

Danckwerts used this result to experimentally show for the first time, according to Amundson (Amundson, 1986), that \( Bo_{ax} \) was close to 2.

3.3.2.3. Notes on boundary conditions for the Standard dispersion model (SDM). The proper boundary conditions for the SDM have been discussed for a long time (Wehner and Wilhelm, 1956; Levenspiel and Smith, 1957; Brenner, 1962) since the publication of Danckwerts paper (Danckwerts, 1953) in 1953. The so-called Danckwerts boundary conditions given in Eqs 30a and 30b correspond to "closed-to-diffusion" boundaries. Other boundary conditions used for SDM are those of infinite reactor (open-to-diffusion), Eq 36a, semi-infinite reactor (open to diffusion at the inlet), Eq 36b and open-to-diffusion at the outlet, Eq 36c

\[ z = -\infty \quad c = c^i \quad \text{limited} \]

\[ z = +\infty \quad c = c_{in} \quad \text{limited} \]

(36a)

\[ z = 0, \quad c = c_{in}(t) \]

(36b)

\[ z = 0, \quad uc(0^+) = uc(0^-) = 0 \quad D_{ax} \quad \text{limited} \]

(36c)

For practical purposes the RTDs from SDM for various types of boundary conditions are similar if \( \text{Pe} \) is sufficiently high. A detailed discussion of this topic for transient reactor was provided by Parulekar and Ramkrishna (Parulekar et al., 1982).

3.3.3. The Taylor-Aris model for flow in tubes

G. I. Taylor pioneer work describes how a solute travels in a capillary where a solvent is moving in laminar flow (Taylor, 1953). It seems, according to Batchelor (Batchelor, 1981) that "Taylor learnt about this problem from an animal physiologist who was measuring the rate of flow of blood in arteries by injecting a small volume of highly conducting liquid (tracer) at some point and measuring the change of conductivity with time at another point downstream". Dispersion is an unsteady diffusion process characterized with an effective diffusion coefficient or dispersion coefficient which measures the rate at which the solute spreads axially and is proportional to the ratio axial convection/radial (transverse) molecular diffusion.

Fig. 11 shows the velocity profile, reference coordinates and band profiles of the solute at various times. The velocity \( u(r) \) in a channel with radius \( r_0 \) for laminar flow is given by Eq (37) where \( u \) is the mean fluid velocity.

\[ u(r) = 2u \left[ 1 - \left( \frac{r}{r_0} \right)^2 \right] \]

(37)

At short times axial convection is the dominant mechanism and the slug of solute introduced at time zero takes the parabolic shape imposed by the velocity profile. This leads to radial concentration gradients and so at higher times radial molecular diffusion con-
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Fig. 11. Velocity profile and dispersion of a slug in a tube.

The area-averaged concentration profile is:

\[
\bar{c}(z,t) = \frac{N/\pi r_0^2}{\sqrt{4\pi D't}} \exp \left( -\frac{(z-\mu t)^2}{4D't} \right)
\]

The limiting case of pure convection holds if the time constants for radial diffusion, \( D_r \), and axial diffusion, \( D_z \), are both higher than the convective time constant \( L/u \), i.e., \( Pe \gg L/r_0 \) and \( Pe \gg r_0/L \) respectively. Similarly axial diffusion is controlling if \( \frac{D_r}{D_z} \approx \frac{1}{K} \) or \( \frac{D_z}{D_r} \approx \frac{1}{K} \). These results are condensed in Fig. 12 adapted from Aris (Aris, 1994).

Taylor (Taylor, 1954) extended his approach to turbulent flow in tubes and provided conditions to use experiments of dispersion of solutes in a solvent flowing in a tube to measure molecular diffusion (Taylor, 1954). The Taylor-Aris method was used by McCalley (Mc Calley, 2002) to measure diffusion coefficients in monolith reversed-phase columns.

The Taylor description can be extended to include adsorption at the wall of the channels and diffusion at the wall surface \( D_z \); in that case the zone migrates at a velocity:

\[
u^* = \frac{u}{1 + K}
\]

and the effective diffusion coefficient will be given a form of Golay equation (Golay, 1968):

\[
D' = \frac{D + KD_z}{1 + K} + \frac{u^2r_0^2}{48D} \left( \frac{1 + 6K + 11K^2}{1 + K} \right)
\]

where \( K \) is the adsorption equilibrium parameter for linear isotherms.

3.4. Progressive modeling and perfusion chromatography

The measurement of effective diffusivity in large pore catalysts can use a chromatographic method and tracer technology. The analysis of results (Ahn, 1980) with a conventional model showed that effective diffusivity was changing with flowrate. A closer look to the problem assuming mass transport not only by diffusion in pores \( D_0 \) but also by convection (pore velocity \( v_0 \)) and the equivalence with the conventional model in which both mechanisms were lumped in an apparent \( D_0 \), allowed us to show (Rodrigues et al., 1982) that:

\[
\bar{D}_0 = D_0 \frac{1}{f(\lambda)}
\]

Here the intraparticle Peclet number is \( \lambda = \frac{u_0 r_0}{D_0} \) and \( f(\lambda) = \frac{1}{2} \left( \frac{1}{\lambda} - 1 \right) \). The apparent diffusivity is augmented by convection and the enhancement factor is \( 1/f(\lambda) \). This result shown in Fig. 13 explains the functioning of perfusion chromatography (Afeyan et al., 1990a, 1990b, 1991c; Rodrigues et al., 1991).
For a passive tracer the "lumped" diffusion/convection model for the particle with slab geometry is:

$$D_e \frac{\partial^2 c}{\partial z^2} = \frac{\partial c}{\partial t}$$

and the particle transfer function is:

$$g_p(s) = \frac{c(s)}{c_i} = \frac{\tanh(\sqrt{s} \tau_d s)}{\sqrt{s} \tau_d s}$$

with an apparent diffusion time constant $\tau_d = D_e / \bar{D}_e$. Model equivalence leads to Eq. (46).

A practical application of this concept is on the chromatographic separation of proteins. The pore velocity can be estimated from the equality between relative pressure drop at bed and particle scales assuming that Darcy’s law is valid; the result is $v_0 = au$ where $a$ is the ratio of particle and bed permeabilities. The Van Deemter equation for conventional packings was modified by Rodrigues (Rodrigues et al., 1991; Rodrigues, 1993) where the C term shows the effect of intraparticle convection.

$$HETP = A + B \frac{u}{v} + Cf(k)u$$

Fig. 14 shows HETP versus $u$ for conventional and perfusive adsorbents. At low velocities $f(k) \approx 1$; however, at high velocities $f(k) \approx \frac{1}{2}$ and the last term of Rodrigues equation (51) becomes constant. The HETP reaches a plateau which only depends on the particle permeability and pressure gradient (convection-controlled limit). The C term of Van Deemter equation is reduced, the column performance is improved and the speed of separation is increased without losing efficiency.

### 4. Shortcoming of Standard dispersion model (SDM) and the Wave model

The SDM described by Eq (30) and Danckwerts boundary conditions, eqs (30a) and (30b) has raised doubts concerning several points, which may be considered as drawbacks of the model. Westerterp (Westerterp, 2012) listed some of those concerns, namely:

i) The basic idea of SDM is that axial dispersion is superimposed to plug flow; however plug flow means that radial dispersion is infinitely fast but in packed beds the Bodenstein number for radial dispersion is not zero;

ii) The physical significance of boundary conditions has been questioned along the years (Petho and Noble, 1982). The inlet boundary condition means a sudden fall more pronounced for small Peclet numbers although this fall certainly happens in a perfectly mixed reactor by definition;

iii) In packed beds backmixing can occur as shown by Hiby (Hiby, 1962) but does not exist in 1D flow;
iv) As pointed out in 1962 by Westerterp (Westerper and Landsman, 1962; Westerper and Meyberg, 1962) axial dispersion under the same flow conditions depends on the measurement technique; also Jasti and Fogler (Jasti and Fogler, 1992) noticed that $D_{ax}$ was influenced by flow reversal;

v) Laminar flow cannot be handled by the SDM

In the “Wave Model” axial dispersion results from the fact that fluid velocity in axial direction is not uniform. It means that some fluid streams travel at velocity $u + v$ higher than the average velocity $u$, while others travel at velocity $u - v$ lower than the average velocity as shown in a simplistic way in Fig. 15.

Assuming no chemical reaction and equal cross section areas occupied by both streams mass balances for each stream are:

$$\frac{\partial c_1}{\partial t} + (u + v) \frac{\partial c_1}{\partial z} = k \left(\frac{c_2 - c_1}{2}\right)$$  \hspace{1cm} (52a)

$$\frac{\partial c_2}{\partial t} + (u - v) \frac{\partial c_2}{\partial z} = k \left(\frac{c_2 - c_1}{2}\right)$$  \hspace{1cm} (52b)

where $k$ is the exchange coefficient between both streams (relaxation time constant) expressed in sec$^{-1}$.

The average concentration $c$ and the dispersion flux $j_d$ are given by $c = (c_1 + c_2)/2$ and $j_d = v(c_1 - c_2)/2$, respectively; the conservation equation for mass becomes:

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial z} + \frac{j_d}{\partial z} = 0$$  \hspace{1cm} (53)

with the dispersion flux satisfying

$$j_d + \tau_m \frac{\partial j_d}{\partial t} + \tau_m u \frac{\partial j_d}{\partial z} = -D_{ax} \frac{\partial c}{\partial z}$$  \hspace{1cm} (54)

where $D_{ax} = v^2/k$ and $\tau_m = \frac{1}{k}$.

The initial and boundary conditions are now:

$$t = 0, \quad c = c_0(z), \quad j = j_0(z)$$  \hspace{1cm} (54a)

$$z = 0, \quad c = c_0(t), \quad j = j_0(t)$$  \hspace{1cm} (54b)

Instead of one parameter $D_{ax}$ in SDM, there is now one more parameter, the relaxation time constant $\tau_m = \frac{1}{k}$.

It is important to notice that the laws of basic momentum transfer (Newton’s law), mass transfer by diffusion (Fick’s law) and heat conduction (Fourier’s law) assume infinite velocity of propagation of signals; this problem is eliminated in Maxwell formulation for momentum transfer (Maxwell, 1952), mass transfer by diffusion (Rodrigues and Minceva, 2005) and heat transfer (Liu et al., 1999). For mass transfer in quiescent media we have a description similar to Cattaneo (Cattaneo, 1958) equation for heat transfer by conduction (Turner, 1972).

$$j_d + \tau \frac{\partial j_d}{\partial t} = -D \frac{\partial c}{\partial z}$$  \hspace{1cm} (55)

It is also interesting to note that the transfer function of the fixed bed in the case of the Wave Model becomes:

$$G(s) = \exp\left[\frac{Pe}{2(1 - Pe \frac{\tau_m}{s})}\left(1 - \frac{4\tau_m(1 + \tau_m)}{1 - Pe \frac{\tau_m}{s}}\right)\right]$$  \hspace{1cm} (56)

Again the SDM is recovered when $\tau_m \to 0$. The transfer function of the wave model is obtained simply from the one of SDM model by replacing $Pe$ by $Pe/(1 - Pe \frac{\tau_m}{s})$. The SDM model will be applicable when $Pe \frac{\tau_m}{s} \ll 1$.

The relationship between the wave (relaxation) model and diffusion model of longitudinal dispersion accompanied by chemical reaction was discussed by Moshinskii (Moshinskii, 2003). Also Jordanidis et al (Jordanidis et al., 2003) critically compared the wave model and the standard dispersion model for various exothermic reactions and concluded that the main difference is in the description of energy transport; discrepancies are more significant for fast processes with steep temperature and concentration profiles along the reactor.

5. RTD calculations from momentum and mass transport equations and CFD modeling

Levenspiel (Levenspiel, 2002) summarizes the progress on the study of fluid flow as follows: “In the 19th century there were two approaches to study fluid flow: hydrodynamics (dealt with ideal frictionless fluid; highly mathematical stuff) and hydraulics developed by civil engineers “who amassed mountains of tables of pressure drop and head loss of fluids in open and closed channels of all sort...”. At the beginning of the 20th century Prandtl said “Hydrodynamics has little significance for the engineer because of the great mathematical knowledge required for an understanding of it and the negligible possibility of applying its results. Therefore engineers put their trust in the mass of empirical data collectively known as the “science of hydraulics”. “Prandtl was the genius who patched together these different disciplines with his simple boundary layer theory. The result is modern fluid mechanics”. Although this view is shared by some authors (Anderson, 2010), others associate L-Prandtl and G.I.Taylor (Kundu and Ira, 2000; Batchelor, 1992) as founders of modern fluid mechanics.

On the other hand numerical methods for the solution of PDE’s exist and the combination of two solid disciplines appears with a new name: “Computational Fluid Dynamics”. As Krishna said once in a CHEMPOR meeting in Lisbon (Krishna, 1998) CFD results from Numerical Methods and Fluid Mechanics using computers. More than thirty years ago, I published (Brunier et al., 1984) a paper with French colleagues in ISCREB: “Residence time distribution in laminar flow through reservoirs from momentum and mass transport equations”. It is a problem of 2-D flow in a reservoir of length L and height H where a stationary laminar flow exists between inlet and outlet. The model equations include momentum transport under steady state condition in terms of vorticity and stream function formulation; the flow field is obtained and the tracer mass transport is described by a convection–diffusion equation leading to the RTD:
and future challenges (at least in terms of computer cost!), the spatial distribution of the instantaneous fluid particle age $a(x,t)$ as introduced by Sandberg (1981). The balance of the fluid age is then

$$\frac{\partial a}{\partial t} + (v \cdot \nabla) a = 1$$

(63)

This was called by Simcik et al (Simcik et al., 2012) the Smart RTD (SRTD). While RTD only gives the distribution of the internal age $l(t)$ for steady flow, the SRTD gives the space–time distribution of the instantaneous fluid age $a(x,t)$ for unsteady state flow in general. This approach was also discussed by Liu and Tilton (Liu and Tilton, 2010), Balle and Le Cloirec (Balle and Le Cloirec, 2000) and Liu (Liu, 2011) who performed 2D simulations in a single phase reactor.

The mean age $a$ is the first moment of age calculated as:

$$a(x) = \int_0^\infty tc(x,t)dt / \int_0^\infty c(x,t)dt$$

(64)

The denominator is invariant and equal to the ratio of the total amount of tracer in the pulse to the volumetric flowrate. Liu presented a method to predict the tracer concentration and mixing in CFSTRs with mean age distribution (Liu, 2011). The mean age theory was extended to multiphase systems by Russ and Berson (Russ and Berson, 2016). CFD solutions of mean age allow spatial and time resolution within the flow field.

The study of mixing processes needs somehow a parameter to quantify the “goodness of mixing” based on experimental measurements (Zwietering, 1959; Danckwerts, 1952, 1958). Liu (Liu, 2011) presented a method for the calculation of the degree of mixing in steady continuous flow systems. The age $x$ of a molecule is the time that has elapsed since the molecule entered the reactor; the average age of all molecules in the flow is $\bar{x}$. The variance of the ages of all molecules will be:

$$\text{var}x = (x - \bar{x})^2$$

(65)

and the variance of mean age all over the whole reactor volume $V$ is

$$\text{var}a = (a - \bar{x})^2$$

(66)

6. How to access age distribution and state of mixing, smart RTD and future challenges

6.1. Spatial distribution of internal age $a(x,t)$ and Smart RTD

The exit concentration of a reactor $c_{out}$ can in general be obtained by solving the equations for flow and tracer mass balance; for incompressible flows they are:

$$\rho \frac{\partial v}{\partial t} + \rho (v \cdot \nabla) v = -\nabla p + \mu \nabla^2 v + \rho g$$

(61)

$$\frac{\partial c}{\partial t} + (v \cdot \nabla) c = D \nabla^2 c$$

(62)
The degree of mixing of Zwietering (Zwietering, 1959) was defined as

$$J = \frac{(\bar{a} - \bar{x})^2}{(\bar{a} - \bar{x})^2}$$  \hspace{1cm} (67)

Therefore from RTD one calculate the distribution of internal ages, $I(t_c)$ and obtain the variance of the ages of all molecules $\text{var}$. However, to get $J$ one still needs the spatial distribution of mean age to calculate the variance of mean age $\text{var}$. In a CSTR the variance of mean age is zero and $J = 0$; for completely segregated system $J = 1$. The calculation of the degree of mixing was possible with the work of Liu and Tilton (Liu and Tilton, 2010) who derived the governing equations for all moments of age from the time dependent concentration equation and equation for the mean age

$$\frac{\partial c}{\partial t} + \nabla \cdot (uc) = \nabla \cdot (D \nabla c)$$  \hspace{1cm} (68)

$$\nabla \cdot (ua) = \nabla \cdot (D \nabla a) + 1$$  \hspace{1cm} (69)

leading to

$$\nabla \cdot (uM_n) = \nabla \cdot (D \nabla M_n) + nM_{n-1}$$  \hspace{1cm} (70)

where $M_n$ is the $n^{th}$ moment of age calculated from the tracer concentration at every spatial position $x$:

$$M_n(x) = \int_0^\infty t^nc(x,t)dt / \int_0^\infty c(x,t)dt$$  \hspace{1cm} (71)

The Zwietering degree of mixing can now be written as

$$J = \frac{\bar{a}_n^2 - \bar{x}^2}{(\bar{a}_n^2 - \bar{x}^2)}$$  \hspace{1cm} (72)

CFD is a powerful tool to help process development in chemical engineering and examples in stirred tanks and static mixers have been discussed by LaRoche (LaRoche, 2005), Liu (Liu, 2012), Khapre et al. (Khapre et al., 2016). One example at hand is the study of mixing and its mechanisms addressed in detail in the book by Ottino (Ottino, 1989). It is interesting to learn that in a note published in 1987 by Franjione and Ottino (Franjione and Ottino, 1987) they presented some calculations showing that numerical tracking of the interface in mixing involving fast reactions between fluids was an enormous task with the computing power at the time. Recently, Matos et al (Matos et al., 2018) introduced a new method Lagrangian Mixing Simulation (LMS) to track the flow front between two fluids in a mixer. LMS uses Eulerian velocity field from CFD simulations to calculate the instantaneous rate of interfacial area generation and segregation scales and it was applied to CFD simulations of flow in 2D Confined Impinging Jets (Fig. 17).

6.2. Looking ahead

The concept of RTD is spread through many areas from solid processing (continuous blenders, extruders, rotary drums, fluidized beds) used in continuous manufacturing of chemicals, plastics, polymers, food, catalysts and pharmaceutical products (Gao et al., 2012), to hydrodynamic modeling of real systems (liquid–liquid systems (Nogueira et al., 2016), simulated moving bed (Fangueiro Gomes et al., 2015, 2016), cascades of stirred tanks (Toson et al., 2019), continuous flow polymerization (Reis et al., 2019).

Tracer technology (Levenspiel, 2012; Aris, 1994; Wei, 1990) has many applications outside the traditional chemical engineering (Shook, 2005) and extensions of the traditional RTD have appeared, (Claudel et al., 2000; Dantas et al., 2014; Morscheidt et al., 2013) and still experimental improvements are reported (Bérard et al., 2020).

The recent push of continuous flow chemistry in pharmaceutical industry and the development of milli–and microreactors renewed the interest on RTD for the characterization of the flow behavior in such devices (Gobert et al., 2017; Siguemoto et al., 2020).

I am particularly interested in less conventional applications of RTD theory. I will mention two topics. One of those areas is Perfume Engineering (Teixeira et al., 2013) with the aim of predicting the trail of perfumes or sillage (Pereira et al., 2018; Benaim and Brahms, 2018). Briefly a perfume is commonly viewed as a mixture of top notes, middle notes and base notes in a solvent. Some perfumers will say there are no middle notes and what matters is the diffusivity of top and base notes containing fast and slow diffusing molecules (Benaim and Brahms, 2018). Therefore measurements of diffusivities of perfumery raw materials (PRM) in air are required to address the effect of molecule (Tovar et al., 2019) and skin adsorption.

A second area is related to archeology concerning the application of diffusion-adsorption-decay models for dating bones (Sambridge et al., 2012). But in our everyday life the measurement of RTD is routinely made in our main research activity on Cyclic separation/reaction processes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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