Residence Time Distribution

The **residence time distribution** (RTD) of a chemical reactor is a probability distribution function that describes the amount of time that a fluid element could spend inside the reactor.

Prof. Danckwerts introduced the concept of `fluid element', meaning a small volume of fluid where continuous properties, such as concentration, can still be defined. The RTD function, external residence time distribution, $E(t)$, measures the time that the various fractions of `fluid element' reside in the reactor (macromixing); it gives no information about the mixing details at a molecular level (micromixing). The expressions of the RTD functions can be derived for the ideal reactors, as well as for any association of PFR and CSTR elements.

Chemical Engineers employ the RTD to characterize the mixing and flow within reactors and to compare the behavior of real reactors to their ideal models. This is useful, not only for trouble shooting existing reactors, but in estimating the yield of a given reaction and designing future reactors.

The concept was first proposed by MacMullin and Weber in 1935, but was not used extensively until Prof. P.V. Danckwerts analyzed a number of important RTDs in 1953.

Theory

An RTD curve for a reasonably well-mixed reactor

The theory of residence time distributions generally begins with three assumptions:

1. The reactor is at steady-state,

2. Transports at the inlet and the outlet takes place only by advection, and

3. The fluid is incompressible (v = constant).

The incompressibility assumption is not required, but compressible flows are more difficult to work with. A further level of complexity is required for multi-phase reactors, where a separate RTD will describe the flow of each phase, for example bubbling air through a liquid.

The distribution of residence times is represented by **an external residence time distribution or an exit age distribution, $E(t)$**. The function $E(t)$ has the units of time^{-1} and is defined such that:

$$\int_0^\infty E(t)dt = 1$$
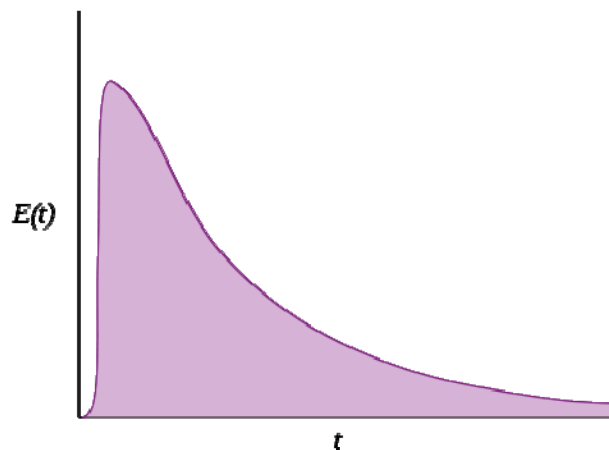
A typical CSTR RTD curve.

The fraction of the fluid that spends a given duration, t inside the reactor is given by the value of $E(t)dt$.

The fraction of the fluid that leaves the reactor with an age time less that t_1 is

$$F(t_1) = \int_0^{t_1} E(t)dt$$

where $F(t)$ is called "cumulative distribution".

Thus, the fraction of the fluid that leaves the reactor with an age greater that t_1 is:

$$1 - F(t_1) = 1 - \int_0^{t_1} E(t)dt = \int_{t_1}^{\infty} E(t)dt$$

The average residence time is given by the first moment of the age distribution:

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

If there are no dead, or stagnant, zones within the reactor, then t_m will be equal to τ, the residence time calculated from the total reactor volume and the volumetric flow rate of the fluid: $\tau = V/v = t_m$

The higher order central moments can provide significant information about the behavior of the function $E(t)$. For example, the second central moment indicates the variance (σ^2), the degree of dispersion around the mean.

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

The third central moment indicates the skewness of the RTD and the fourth central moment indicates the kurtosis (the "peakedness").

One can also define an internal age distribution $I(t)$ that describes the reactor contents. This function has a similar definition as $E(t)$: the fraction of fluid within

the reactor with an age of t is $I(t)dt$. As shown by Danckwerts, the relation between $E(t)$ and $I(t)$ can be found from the mass balance:

$$I(t) = \frac{1}{\tau}\left(1 - \int_0^t E(t)dt\right); \quad E(t) = -\tau\frac{dI(t)}{dt}$$

Determining the RTD Experimentally

Residence time distributions are measured by introducing a non-reactive tracer into the system at the inlet. The concentration of the tracer is changed according to a known function and the response is found by measuring the concentration of the tracer at the outlet.

The selected tracer should not modify the physical characteristics of the fluid (equal density, equal viscosity) and the introduction of the tracer should not modify the hydrodynamic conditions. A suitable tracer material for RTD-experiments should exhibit similar physical properties, *i.e.* viscosity, diffusion coefficient, density, to the flow medium and in particular the materials used should behave inertly, not adhere or adsorb on to the reactor walls and be easily detectable. In particular this last aspect is of critical importance for the design of an optimal system to measure residence time distributions in microreactors.

The experimental determination of the residence time distribution requires a well-defined introduction of a tracer species into the reactor inlet and the detection of its transient concentration leaving the reactor outlet. In general, the change in tracer concentration will either be a *pulse* or a *step*. Other functions are possible, but they require more calculations to deconvolute the RTD curve, $E(t)$.

Pulse Experiments

This method required the introduction of a very small volume of concentrated tracer at the inlet of the reactor, such that it approaches the dirac delta function. Although an infinitely short injection cannot be produced, it can be made much smaller than the mean residence time of the vessel. If a mass of tracer, M, is introduced into a vessel of volume V and an expected residence time of τ, the resulting curve of $C(t)$ can be transformed into a dimensionless residence time distribution curve by the following relation:

$$E(t) = \frac{vC(t)}{N_0}$$

$$dN = vC(t)dt; \quad N_0 = \int_0^\infty vC(t)dt$$

where N_0, v, $C(t)$ indicate the total amount of tracer, volume flow rate, and concentration of tracer measured at outlet with residing time $= t$.

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

Step Experiments

In a step experiment, the concentration of tracer at the reactor inlet changes abruptly from 0 to C_0. The concentration of tracer at the outlet is measured and normalized to the concentration C_0 to obtain the non-dimensional curve $F(t)$ which goes from 0 to 1: $F(t) = \dfrac{C(t)}{C_0}$

The step- and pulse-responses of a reactor are related by the following:

$$F(t) = \int_0^t E(t)dt \qquad E(t) = \frac{dF(t)}{dt}$$

The value of the mean residence time and the variance can also be deduced from the function $F(t)$:

$$t_m = \int_0^\infty tE(t)dt = \int_0^1 tdF(t) = -\int_0^1 td[1-F(t)] = \int_0^\infty [1-F(t)]dt$$

$$\sigma^2 = \int_0^\infty (t-t_m)^2 E(t)dt = \int_0^1 (t-t_m)^2 dF(t) = \int_0^1 t^2 dF(t) - t_m^2 = 2\int_0^\infty t[1-F(t)]dt - t_m^2$$

A step experiment is often easier to perform than a pulse experiment, but it tends to smooth over some of the details that a pulse response could show. It is easy to numerically integrate an experimental pulse response to obtain a very high-quality estimate of the step response, but the reverse is not the case because any noise in the concentration measurement will be amplified by numeric differentiation.

RTDs of ideal and real reactors

The residence time distribution of a reactor can be used to compare its behavior to that of two ideal reactor models: the PFR and the CSTR (or mixed-flow reactor). This characteristic is important in order to calculate the performance of a reaction with known kinetics.

Plug Flow Reactors

In an ideal PFR, there is no mixing and the fluid elements leave in the same order they arrived. Therefore, fluid entering the reactor at time t will exit the reactor

at time $t + \tau$, where τ is the residence time of the reactor. The residence time distribution function is therefore a dirac delta function at τ.

$$E(t) = \sigma(t - \tau)$$

The variance of an ideal plug-flow reactor is zero.

The RTD of a real reactor deviate from that of an ideal reactor, depending on the hydrodynamics within the vessel. A non-zero variance indicates that there is some dispersion along the path of the fluid, which may be attributed to turbulence, a non-uniform velocity profile, or diffusion. If the mean of the $E(t)$ curve arrives earlier than the expected time τ, it indicates that there is stagnant fluid within the vessel. If the RTD curve shows more than one main peak, it may indicate channeling, parallel paths to the exit, or strong internal circulation.

CSTRs

An ideal CSTR is based on the assumption that the flow at the inlet is completely and instantly mixed into the bulk of the reactor. The reactor and the outlet fluid have identical, homogeneous compositions at all times. An ideal CSTR has an exponential residence time distribution:

$$E(t) = \frac{1}{\tau} e^{-\frac{t}{\tau}}$$

In reality, it is impossible to obtain such rapid mixing, especially on industrial scales where reactor vessels may range between 1 and several tens of cubic meters, and hence the RTD of a real reactor will deviate from the ideal exponential decay. For example, there will be some finite delay before $E(t)$ reaches its maximum value

and the length of the delay will reflect the rate of mass transfer within the reactor. Just as was noted for a PFR, an early mean will indicate some stagnant fluid within the vessel, while the presence of multiple peaks could indicate channeling, parallel paths to the exit, or strong internal circulation. Short-circuiting fluid within the reactor would appear in an RTD curve as a small pulse of concentrated tracer that reaches the outlet shortly after injection.