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Residence time distribution in ideal reactors

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2. When to determine RTD?
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4. Evaluation of RTD
5. RTD of PFR/CSTR

Residence Time

- How does long each molecule stay in the reactor (the residence time)?

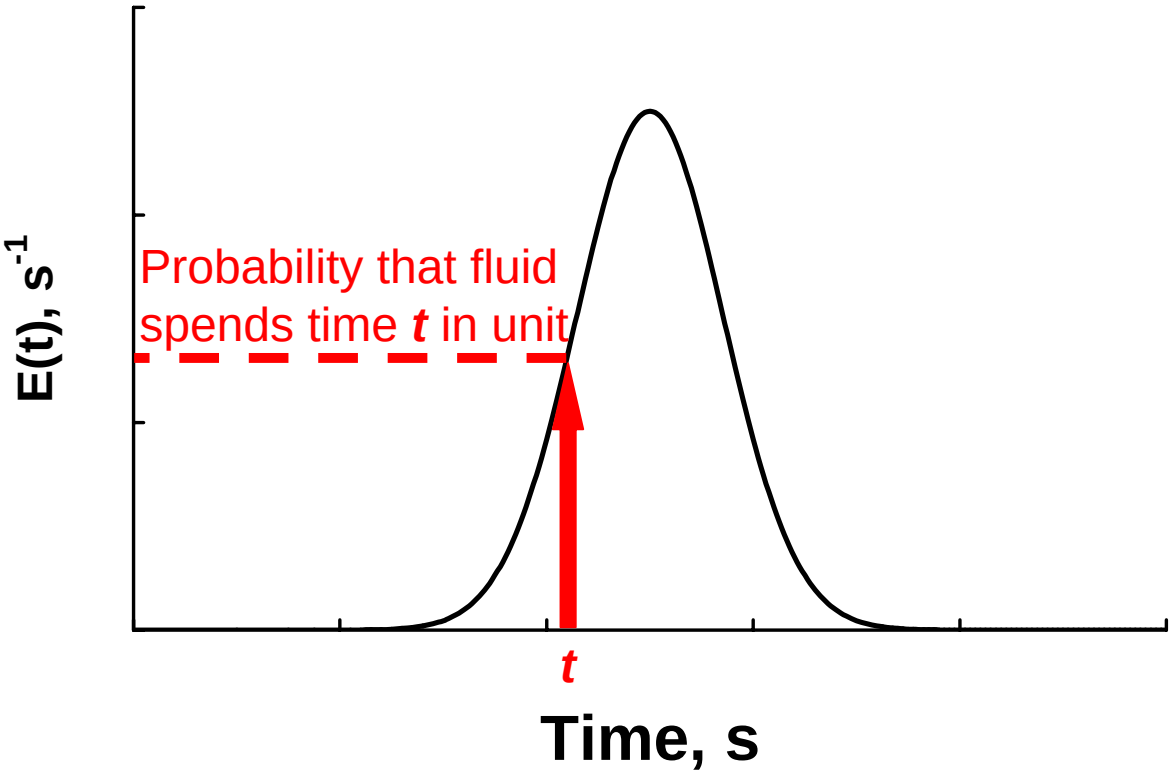
$$\tau = \frac{\text{Reactor volume}}{\text{volumetric flow rate through reactor}} \qquad \boxed{\tau = \frac{V}{v}}$$

We need to know enough about the fluid to design the reactor. In most cases it is sufficient to know the average residence time

- ***Residence time distribution*** function (E-function) tells us quantitatively how long each fluid element spends in the reactor.
  - E(t) probability of residence time τ=t in unit
  - E·dt the fraction of fluid with an age between t and t + dt in the exit stream.

Residence Time (2)

$$\int_0^\infty E \cdot dt = 1$$



When to determine RTD?

- Laboratory reactors:

  typically assumed to be ideal

  sometimes deviations determined experimentally
- Pilot-scale reactors

  Take into account non-ideality of real reactors in scale-up
- Demonstration units

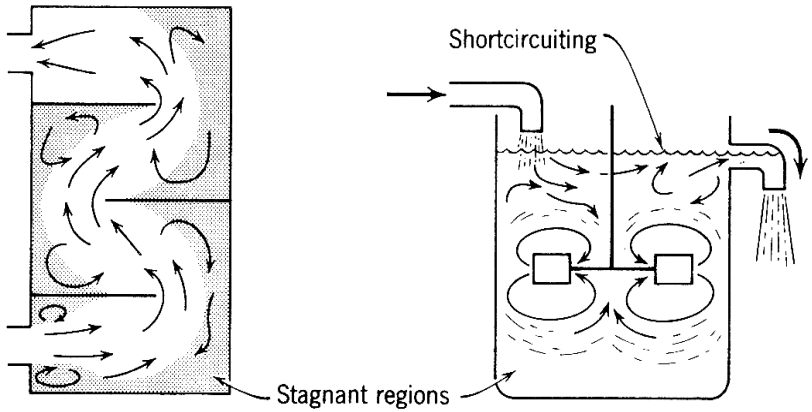
  Take into account non-ideality of real reactors in scale-up
- Production units

  Test to investigate observed non-design behaviour of unit(s)

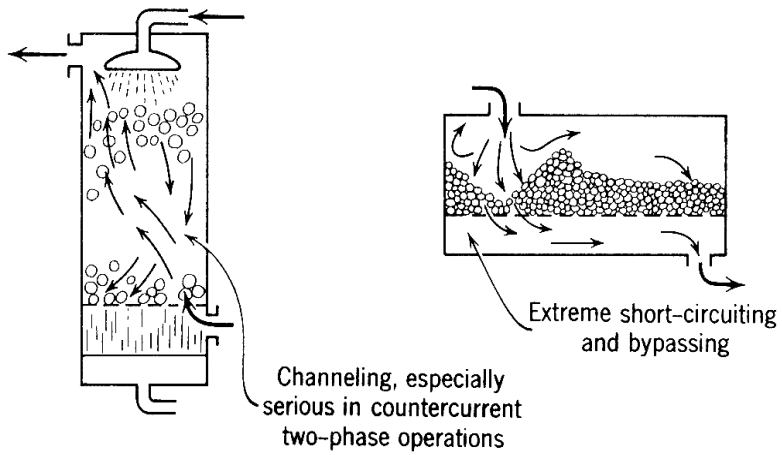
When to determine RTD?

- Basic reactor design

  Assume ideal flow behaviour (complete back mixing ***CSTR*** no back mixing ***PFR***)



- Deviation from the ideal can be considerable.
- *Causes of non-ideal flow*:
  - Channelling
  - Recycling
  - Bypassing
  - Stagnant zones



O. Levenspiel, "Chemical Reaction Engineering," 2nd Ed., John Wiley & Sons, 1972, pp 254

How to determine RTD?

- The RTD is determined by injecting a tracer into the feed stream of a reactor and measuring its concentration in the outlet stream.

- The tracer can take various forms, but must have certain properties:
  - Inert (Not allowed to react with other components in the reactor feed)
  - Easily measurable

- Examples of tracers include
  - Chemical molecules or atoms
  - Radioactive molecules
  - Energy (temperature)

Measuring the RTD

•*The are two methods for determining the residence time distribution* :

•Pulse input

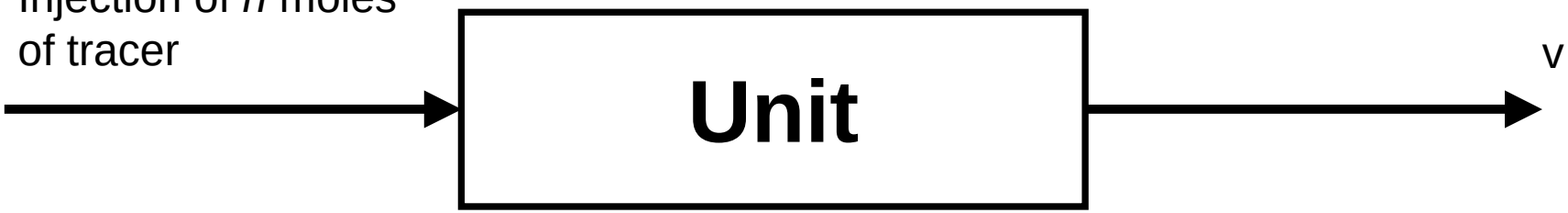
A finite amount of an inert tracer is injected at t=0 into a feed stream in a short period of time. The outlet concentration is measured as a function of time.

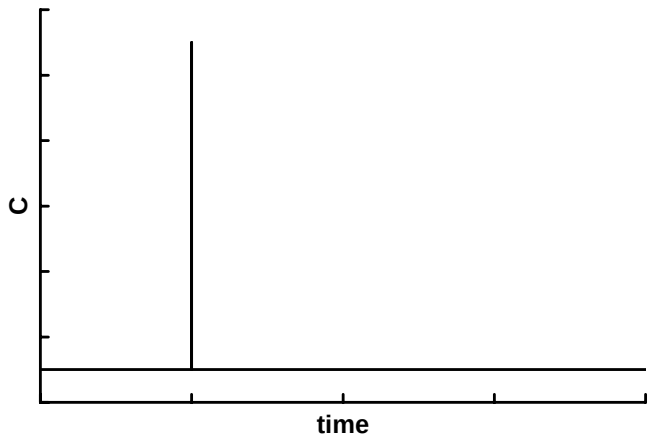
•Step input

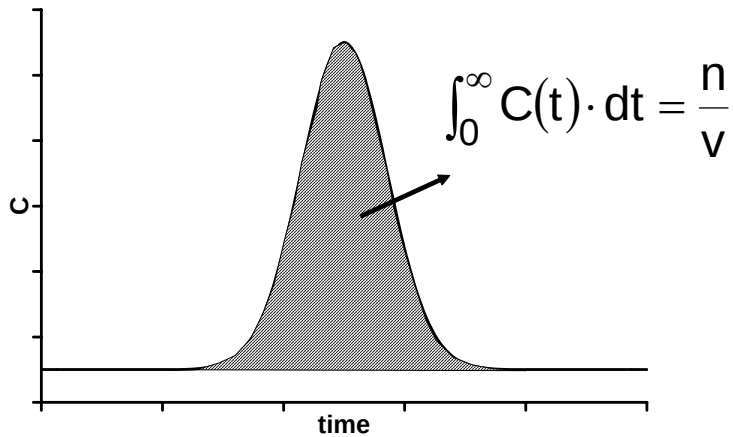
The concentration of the tracer is increased at t=0. The change in the concentration in the outlet is measured as a function of time

Measuring the RTD – Pulse input

Injection of *n* moles of tracer







$$E(t) = \frac{C(t)}{\int_0^\infty C(t)\,dt} = \frac{C(t)}{n/v}$$

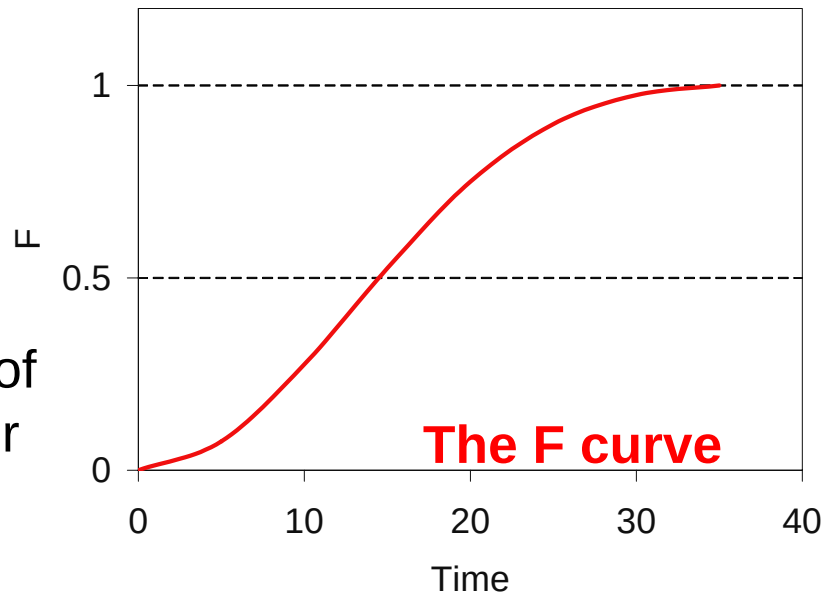
Measuring the RTD - step input

A constant amount of tracer is added to the feed stream.

$$C_0(t) = \begin{cases} 0 & t < 0 \\ C_0(\text{constant}) & t \geq 0 \end{cases}$$

$$F(t) = \frac{C(t)}{C_0}$$

–The F curve represents the fraction of fluid exiting the reactor that is younger than age t_1:



E curve is the differential of the F curve

$$E(t) = \frac{dF}{dt} = \frac{d}{dt}\left[\frac{C(t)}{C_0}\right]_{step}$$

Measuring the RTD

With either method care must be taken that the mass balance closes around the unit

- Pulse input:
  - All of the tracer injected must be accounted for

$$\int_0^\infty C(t)\,dt = C_{tracer,aliquot} \cdot v_{aliquot}$$

- Step Input:
  - The concentration finally reached must equal the inlet concentration

$$C(t_\infty) = C_0(t)$$

RTD from experimental data
Pulse input

The following data represent a continuous response to a pulse input into a closed vessel that will be used as a chemical reactor. Plot the exit age distribution E.

Time t, min	0	5	10	15	20	25	30	35
Tracer Output concentration, g/l	0	3	5	5	4	2	1	0

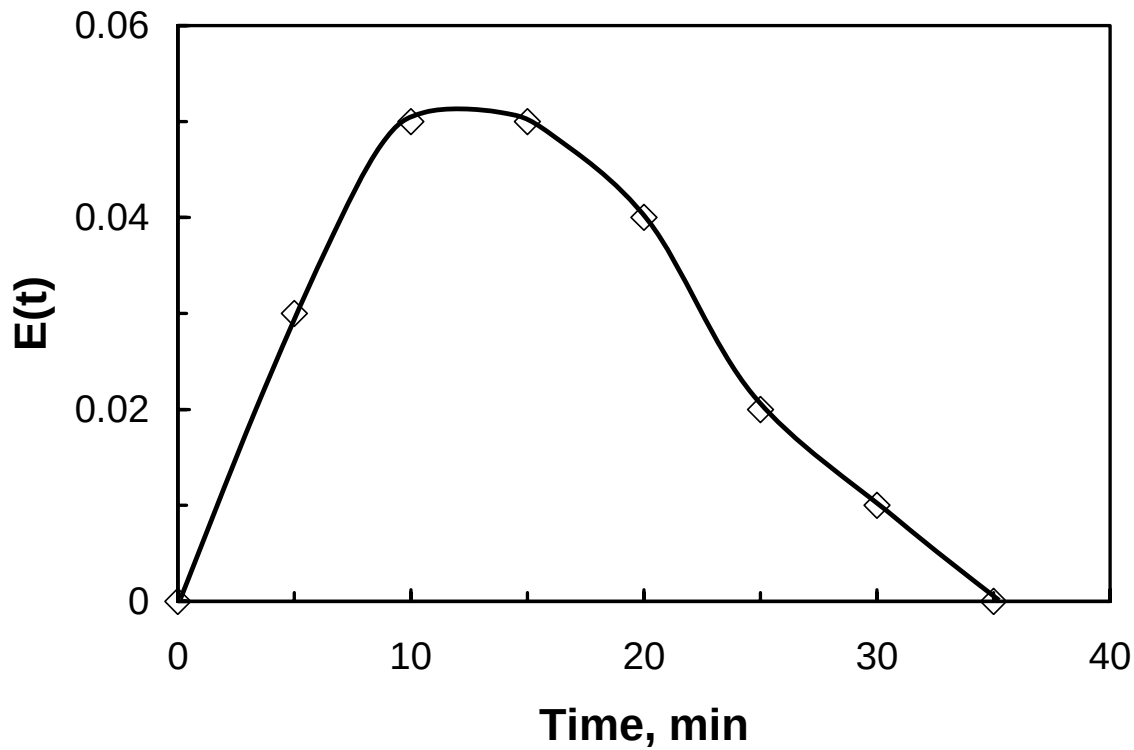
RTD from experimental data
Pulse input

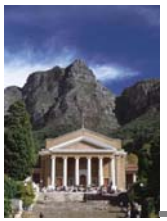
Time t, min	C_{tracer} g/l	C_{avg}	Δt	$C_{avg} * \Delta t$	***E***	E_{avg}	$E_{avg} * \Delta t$
0	0	1.5	5	7.5	***0***	0.015	0.075
5	3	4	5	20	***0.03***	0.04	0.2
10	5	5	5	25	***0.05***	0.05	0.25
15	5	4.5	5	22.5	***0.05***	0.045	0.225
20	4	3	5	15	***0.04***	0.03	0.15
25	2	1.5	5	7.5	***0.02***	0.015	0.075
30	1	0.5	5	2.5	***0.01***	0.005	0.025
35	0				***0***		
			Q:	***100***		Sum:	1

Use trapezoidal rule to improve accuracy

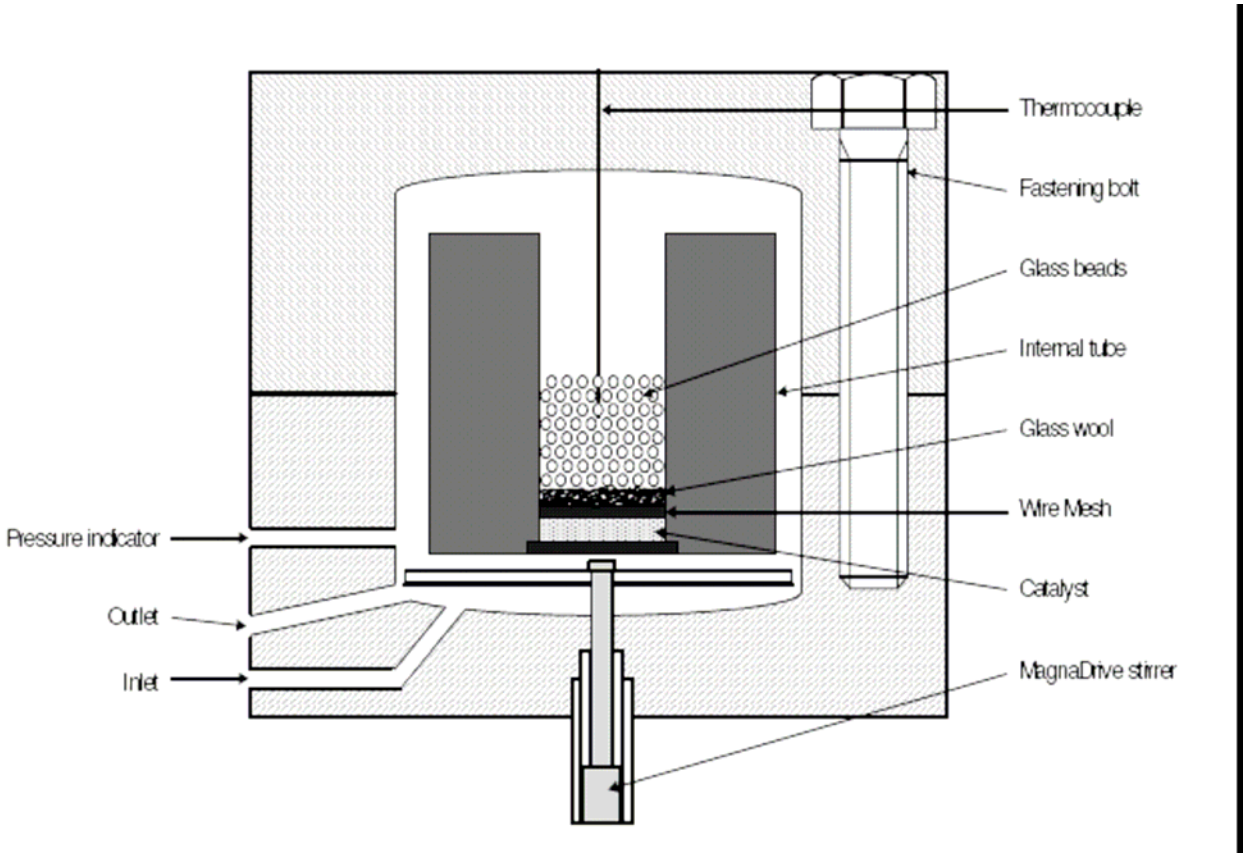
Check results by integrating E*dt

RTD from experimental data
Pulse input



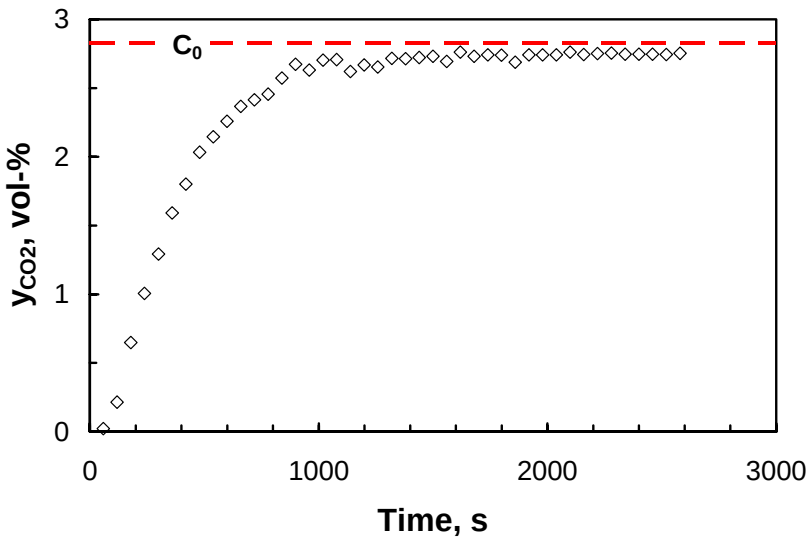


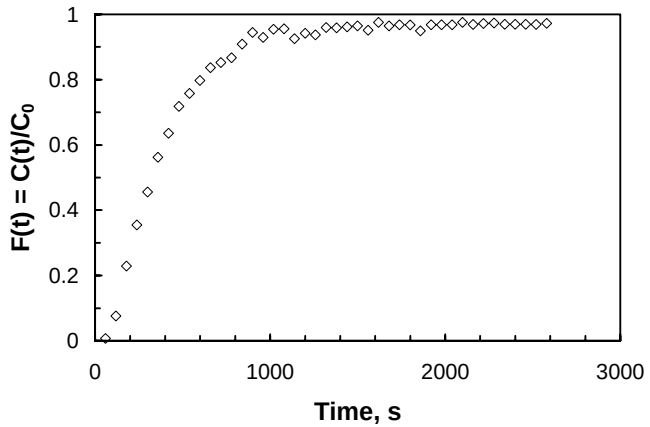
RTD from experimental data step input

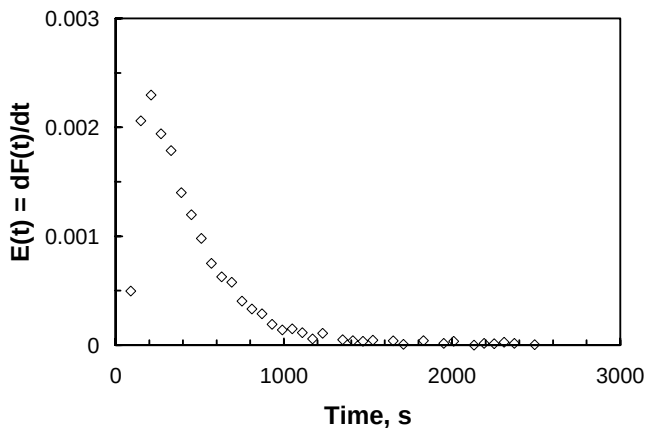


Berty reactor

RTD from experimental data step input







Evaluation of RTD

Mean Residence time

The mean or average residence time:

$$t_m = \frac{\int_0^\infty t \cdot C \cdot dt}{\int_0^\infty C \cdot dt} = \int_0^\infty t \cdot E \cdot dt$$

It can be derived that the mean residence time is simply equal to the space time:

$$\boxed{t_m = \tau = \frac{V}{v}}$$

But be careful with dead zones

Variance

It is often more interesting to know how much of a spread in the residence time distribution there is. This is commonly measured by the variance:

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

Skewness

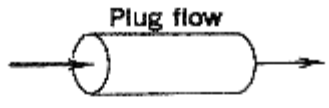
This is not often used but measures the extent to which the distribution is skewed to one side or another.

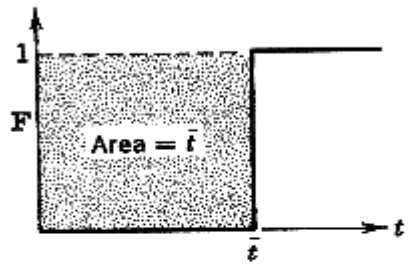
$$s^3 = \frac{1}{\sigma^{3/2}} \cdot \int_0^\infty (t - t_m)^3 \cdot E \cdot dt$$

RTD in Ideal Reactors

Plug flow reactors (PFR)

For perfect plug flow, all molecules spend exactly the same amount of time in the reactor (simplest type of reactor to consider).

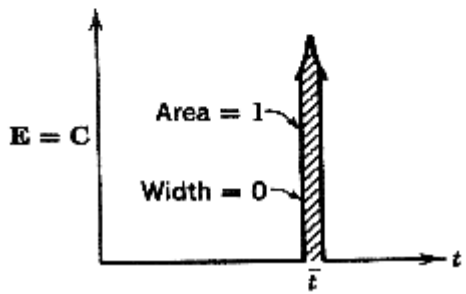




The residence time distribution follows a Dirac delta function:

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

$$\delta(x) = \begin{cases} 0 & \text{when } x \neq 0 \\ \infty & \text{when } x = 0 \end{cases}$$



O. Levenspiel, “Chemical Reaction Engineering,” 2nd Ed., John Wiley & Sons, 1972

RTD in Ideal Reactors

Continued stirred tank reactor (CSTR)

In ideal CSTR, concentration at all points in the reactor identical

The unsteady state mass balance over the reactor, after an injection at t=0 is then:

$$\text{in} - \text{out} = \text{accumulation}$$

$$0 - v \cdot C = V \cdot \frac{dC}{dt}$$

– C is both the reactor and outlet concentration.

• Integrating with $C = C_0$ at t=0 gives the concentration time profile:

$$C(t) = C_0 \cdot e^{-t/\tau}$$

$$E(t) = \frac{C(t)}{\int_0^\infty C(t)\,dt} = \frac{C_0 \cdot e^{-t/\tau}}{\int_0^\infty C_0 \cdot e^{-t/\tau}\,dt} = \frac{e^{-t/\tau}}{\tau}$$

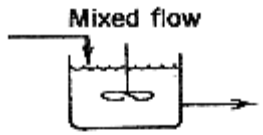
RTD in Ideal Reactors

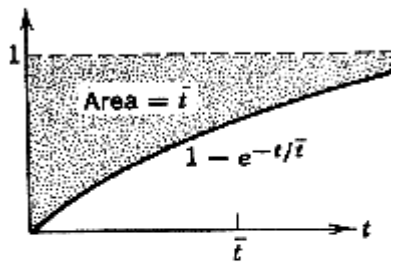
Continued stirred tank reactor (CSTR)

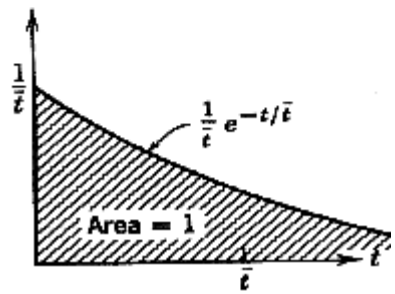
Characteristics of E-curve:

Area → 1

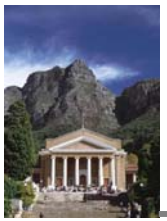
Intercept: $1/\tau$





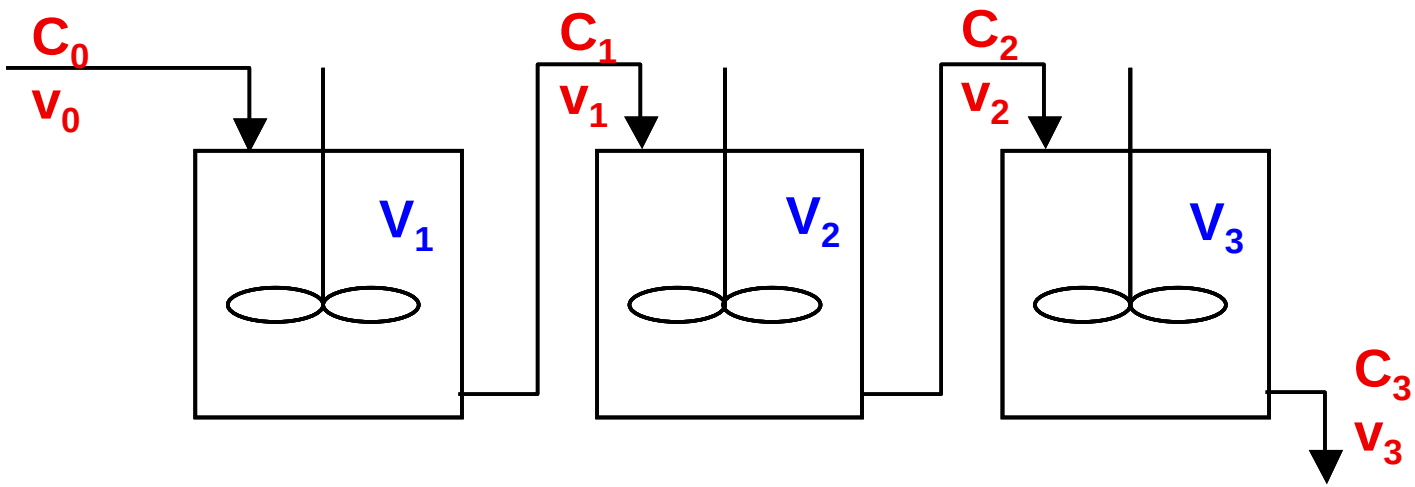


O. Levenspiel, “Chemical Reaction Engineering,” 2nd Ed., John Wiley & Sons, 1972,



RTD in Ideal Reactors

Tank in series model



A reactor can often be considered as a series of perfectly mixed zones (tanks) with the fluid moving from one zone to the next.

Typically, the zones are assumed to be equally sized

PFR can be viewed as an infinite number of CSTRs in series

RTD in Ideal Reactors

Tank in series model

Considering outlet from the first tank:

$$C_1(t) = C_0 \cdot e^{-t/\tau_i} = C_0 \cdot e^{-t \cdot v / V_i}$$

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

Normal CSTR

For the second tank:

$$V_i \frac{dC_2}{dt} = v \cdot C_1 - v \cdot C_2 = v \cdot C_0 \cdot e^{-t/\tau_i} - v \cdot C_2$$

Mole Balance

This can be integrated to give

$$C_2(t) = \frac{C_0 \cdot t}{\tau_i} \cdot e^{-t/\tau_i}$$

Similarly for the third tank:

$$C_3(t) = \frac{C_0 \cdot t^2}{2\tau_i^2} \cdot e^{-t/\tau_i}$$

RTD in Ideal Reactors

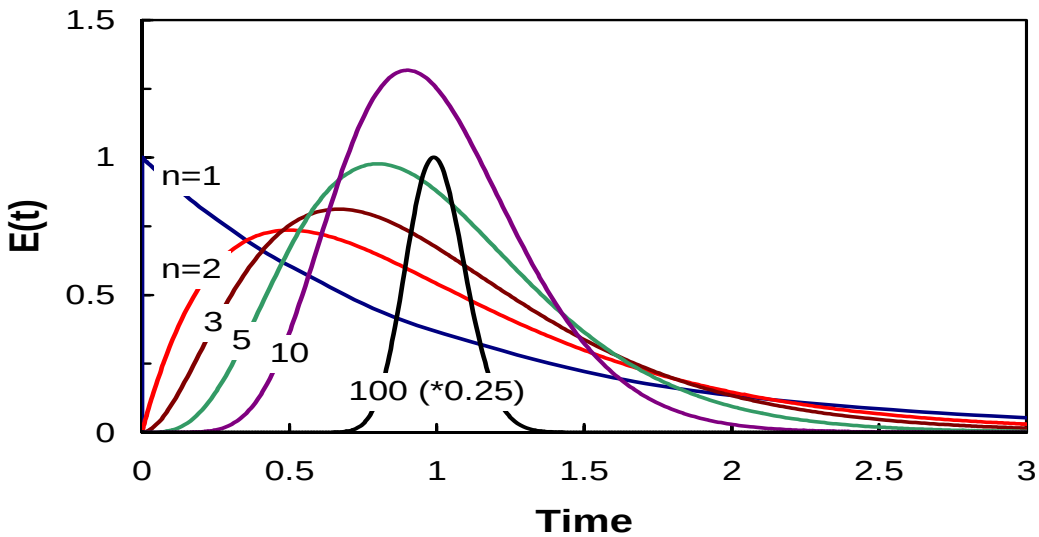
Tank in series model – E-curve

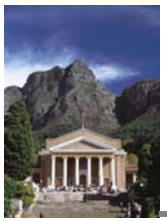
For 3 reactors in series

$$E(t) = \frac{C_3(t)}{\int C_3(t)\,dt} = \frac{t^2}{2\tau_i^3} \cdot e^{-t/\tau_i}$$

In general

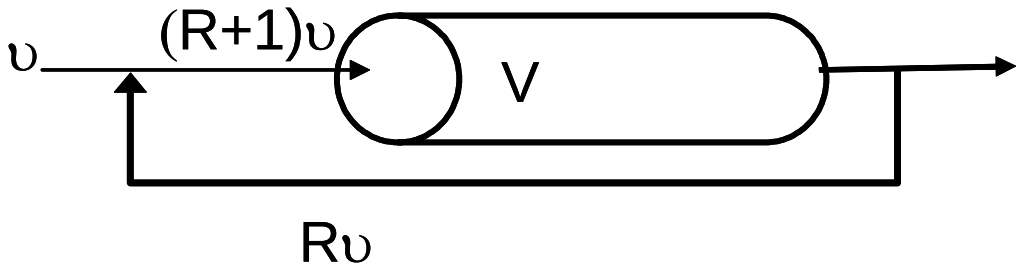
$$E(t) = \frac{t^{n-1}}{(n-1)!\,\tau^n_i} \cdot e^{-t/\tau_i}$$

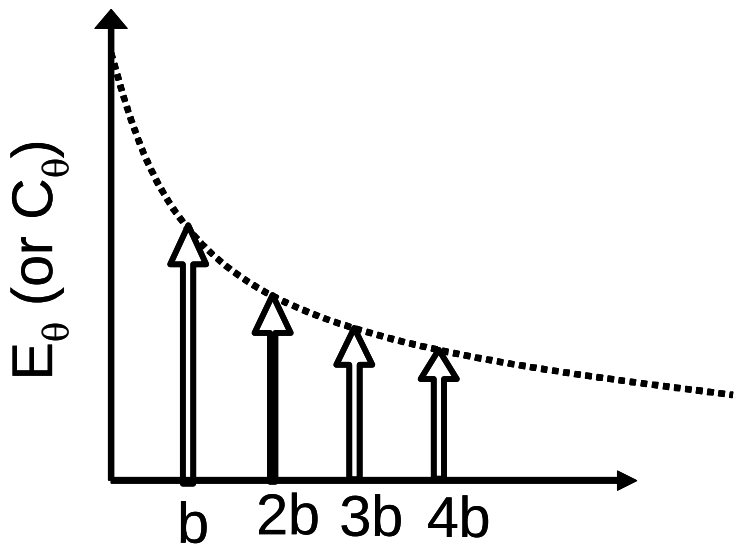




RTD in Ideal Reactors

Recycle reactor





RTD in Ideal Reactors

Laminar flow reactors

Parabolic flow profile:

fluid in the centre spends the shortest time in the reactor.

The velocity profile is given as follows:

$$U = U_{max}\left[1-\left(\frac{r}{R}\right)^2\right] = 2U_{avg}\left[1-\left(\frac{r}{R}\right)^2\right] = \frac{2v}{\pi R^2}\left[1-\left(\frac{r}{R}\right)^2\right]$$

U_{max} is the centre velocity

U_{avg} is the average velocity through the tube

The time spent in the reactor for the fluid element at radius r is:

$$t(r) = \frac{L}{U(r)} = \frac{\pi R^2}{2\upsilon_0}\cdot\left[\frac{L}{1-(r/R)^2}\right] = \frac{\tau}{2\left[1-(r/R)^2\right]} \qquad t_{min} = \frac{L}{U_{max}} = \frac{\tau}{2}$$

RTD in Ideal Reactors

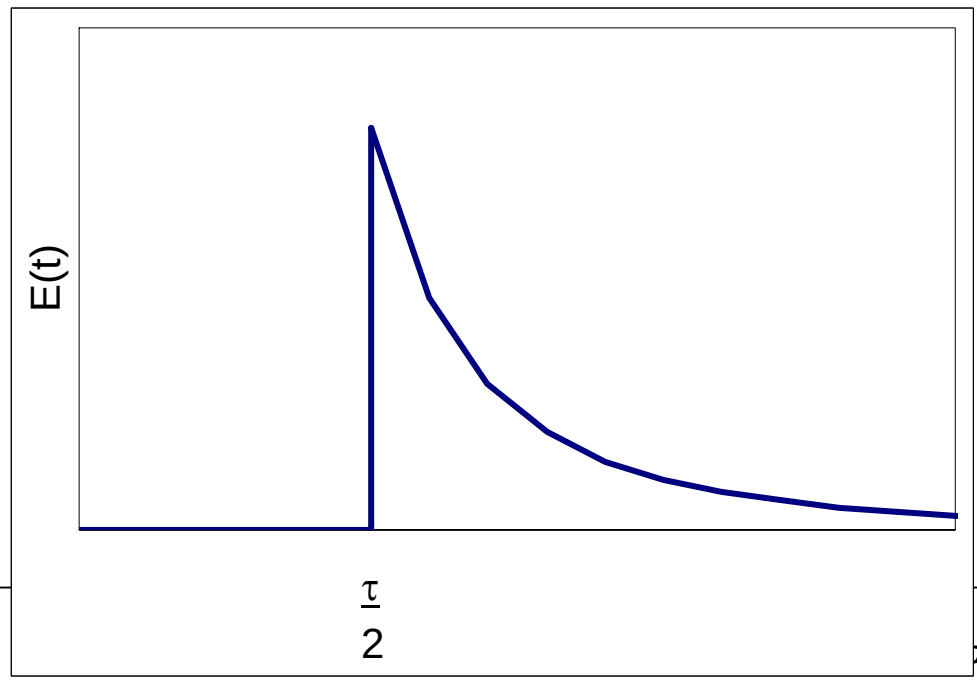
Laminar flow reactors

The fraction of fluid moving through the shell between r and (r + Δr) is:

$$\frac{dv}{v_0} = \frac{U(r)\, 2\pi r\, dr}{v_0}$$

E-curve for laminar flow (see e.g. Fogler 13.4.3)

$$E(t) = \begin{cases} 0 & t < \frac{\tau}{2} \\ \frac{\tau^2}{2t^3} & t \geq \frac{\tau}{2} \end{cases}$$



Segregation Model

Conversion from tracer information

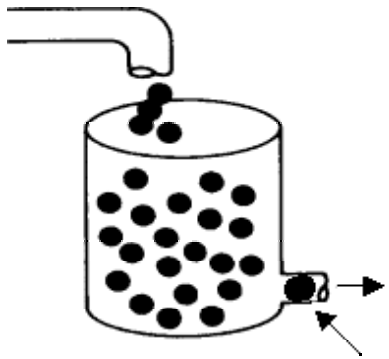
Valid for linear processes: Each fluid element does not react with any other

Mixing occurs as late as possible (at the reactor exit)

A number of flow patterns may give the same RTD curve.

This is not a problem with linear processes, as all will give the same conversion.

$$\begin{pmatrix}\text{mean}\\ \text{concentration}\\ \text{in exit stream}\end{pmatrix} = \sum_{\substack{\text{All}\\ \text{exit}\\ \text{elements}}} \begin{pmatrix}\text{conc. of reac tan t}\\ \text{left in element}\\ \text{of age between}\\ t \text{ and } t+dt\end{pmatrix} \cdot \begin{pmatrix}\text{fraction of exit}\\ \text{stream of age}\\ \text{between}\\ t \text{ and } t+dt\end{pmatrix}$$



$$\overline{C}_A = \int_{t=0}^{\infty} C_{A,\text{element}}\, E\, dt$$

[H. Scott Fogler, "Elements of Chemical reaction Engineering" 4th Ed., Prentice Hall, 2006]

Types of Reactions

Irreversible first order reaction:

$$\ln \frac{C_{A,element}}{C_{A,0}} = -k \cdot t \qquad \text{or} \qquad C_{A,element} = C_{A,0}\, e^{-k \cdot t}$$

$$\overline{C}_A = C_{A,0} \int_{t=0}^{\infty} e^{-k \cdot t}\, E\, dt$$

Reversible first order reaction:

$$\overline{C}_A = C_{A,0} \int_{t=0}^{\infty} \left[1 - X_{Ae} + X_{Ae} e^{-k \cdot t / X_{Ae}}\right] E\, dt$$

Successive first order reactions: A → R → P

$$\overline{C}_R = \frac{C_{A,0} \cdot k_1}{k_2 - k_1} \int_{t=0}^{\infty} \left[e^{-k_1 \cdot t} - e^{-k_2 \cdot t}\right] E\, dt$$

These equations can then be solved if E is known.