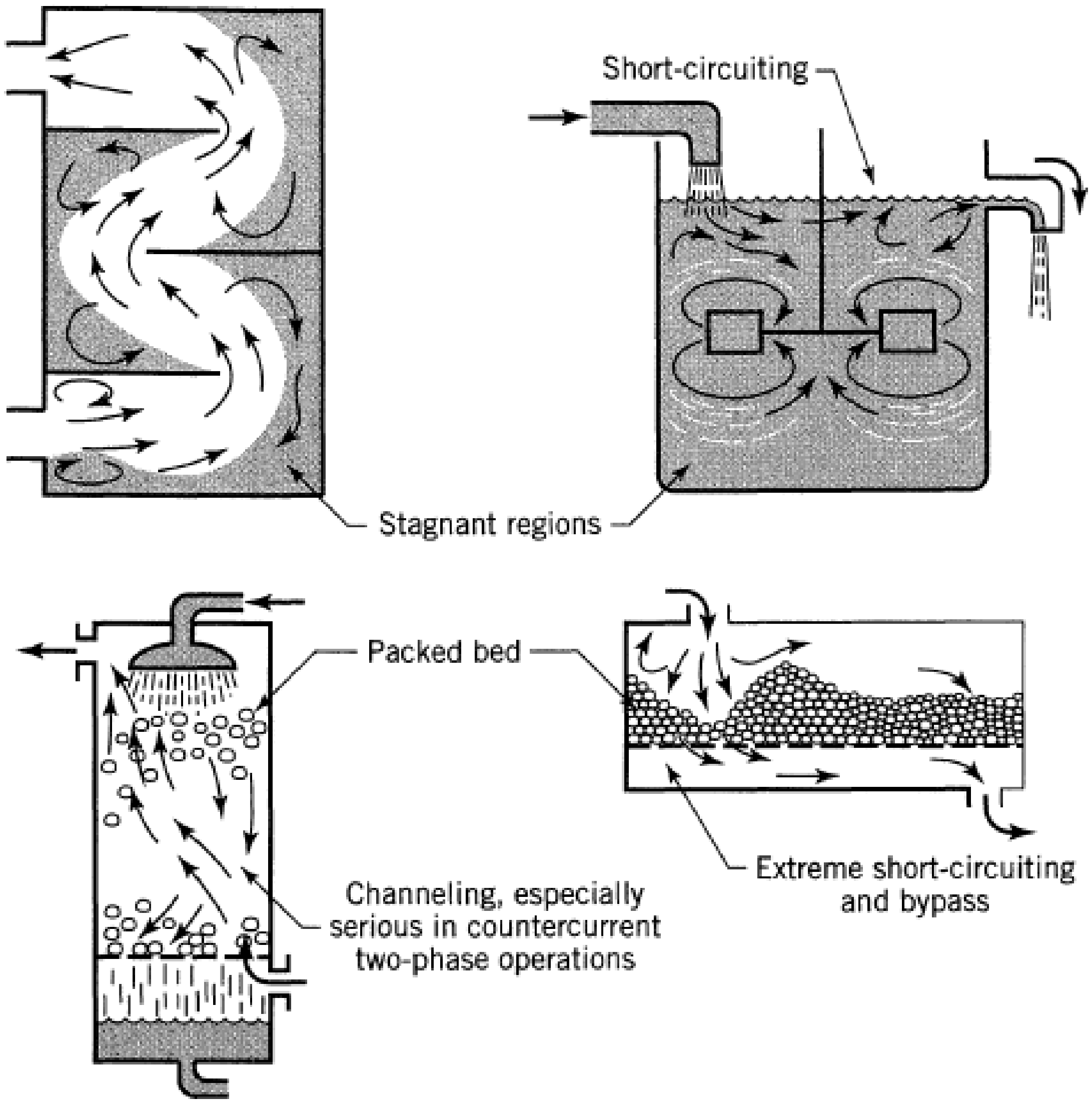
4. Non ideal flow, residence time distribution

- **The three main reactor types developed thus far - batch, continuous-stirred-tank, and plug-flow reactors - are useful for modeling many complex chemical reactors.**
- **Up to this point we have neglected a careful treatment of the fluid flow pattern within the reactor.**
- **In this lecture we explore some of the limits of this approach and develop methods to address and overcome some of the more obvious limitations.**

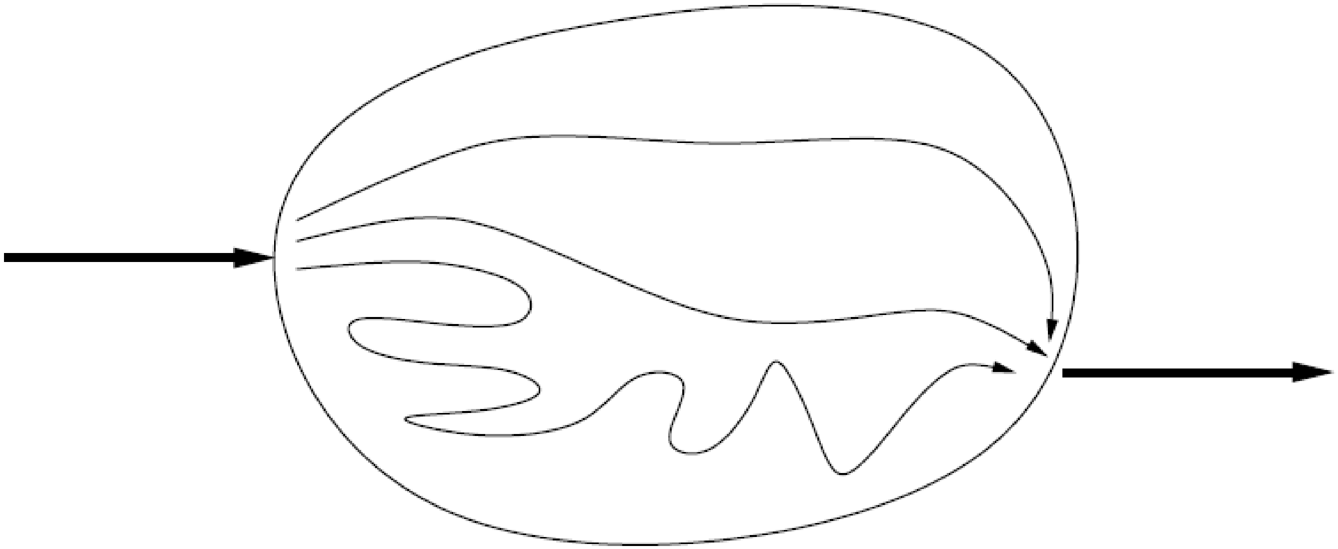
- **Deviation from the two ideal flow patterns can be caused by channeling of fluid, by recycling of fluid, or by creation of stagnant regions in the vessel.**



- **If we know precisely what is happening within the vessel, thus if we have a complete velocity distribution map for the fluid in the vessel, then we should, in principle, be able to predict the behavior of a vessel as a reactor. Unfortunately, this approach is impractical, even in today's computer age.**

Residence-Time Distribution : Definition

- Consider an arbitrary reactor with single feed and effluent streams depictedin the following figure



- Without solving for the entire flow field, which might be quite complex, we would like to characterize the flow pattern established in the reactor at steady state.
- The residence-time distribution (RTD) of the reactor is one such characterization or measure of the flow pattern.

- **Imagine we could slip some inert tracer molecules into the feed stream and could query these molecules on their exit from the reactor as to how much time they had spent in the reactor.**

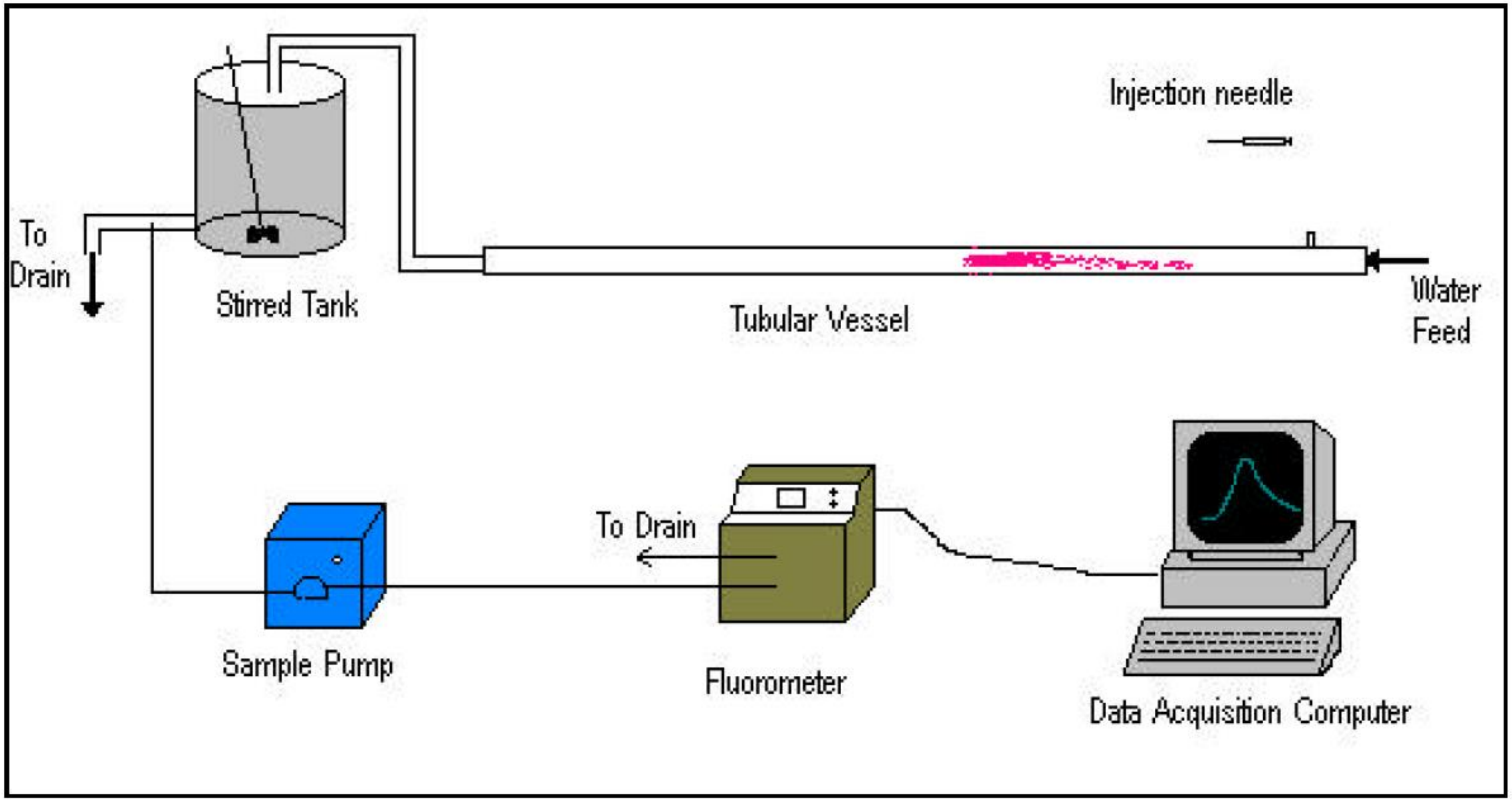
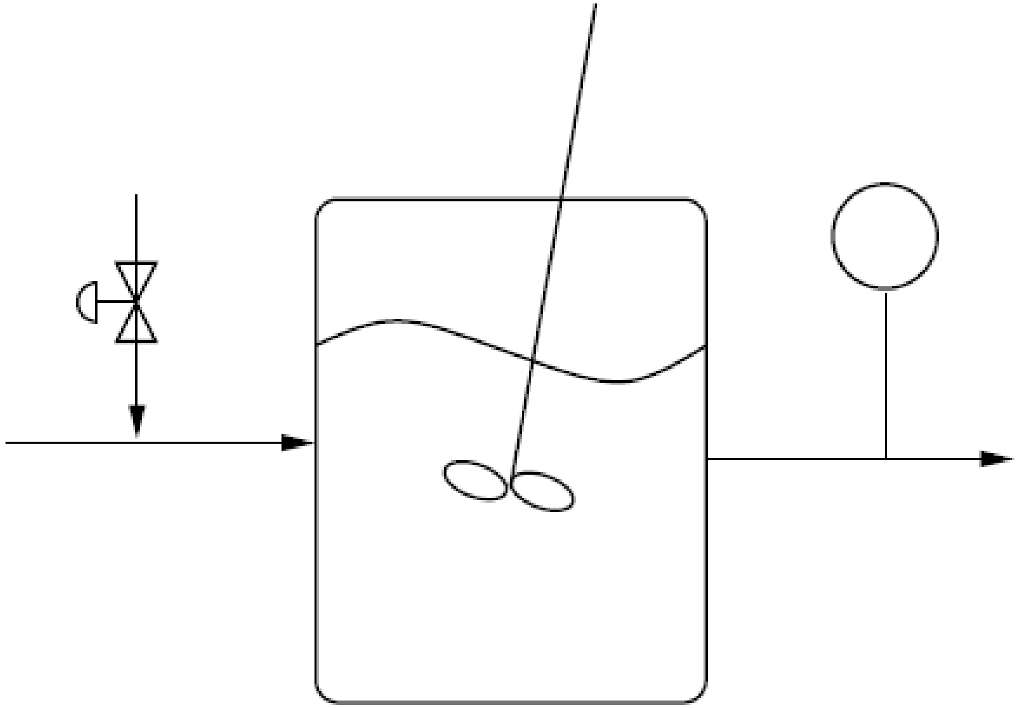


Figure 1 - RTD Experimental Setup

- **Some of the tracer molecules might happen to move in a very direct path to the exit; some molecules might spend a long time in a poorly mixed zone before finally ending their way to the exit.**
- **Due to their random motions as well as convection with the established flow, which itself might be turbulent, we would start recording a distribution of residence times and we would create the residence-time probability density or residence-time distribution.**
- **If the reactor is at steady state, and after we had collected sufficient residence-time statistics, we expect the residence-time distribution to also settle down to a steady function.**

Continuous-stirred-tank reactor - CSTR

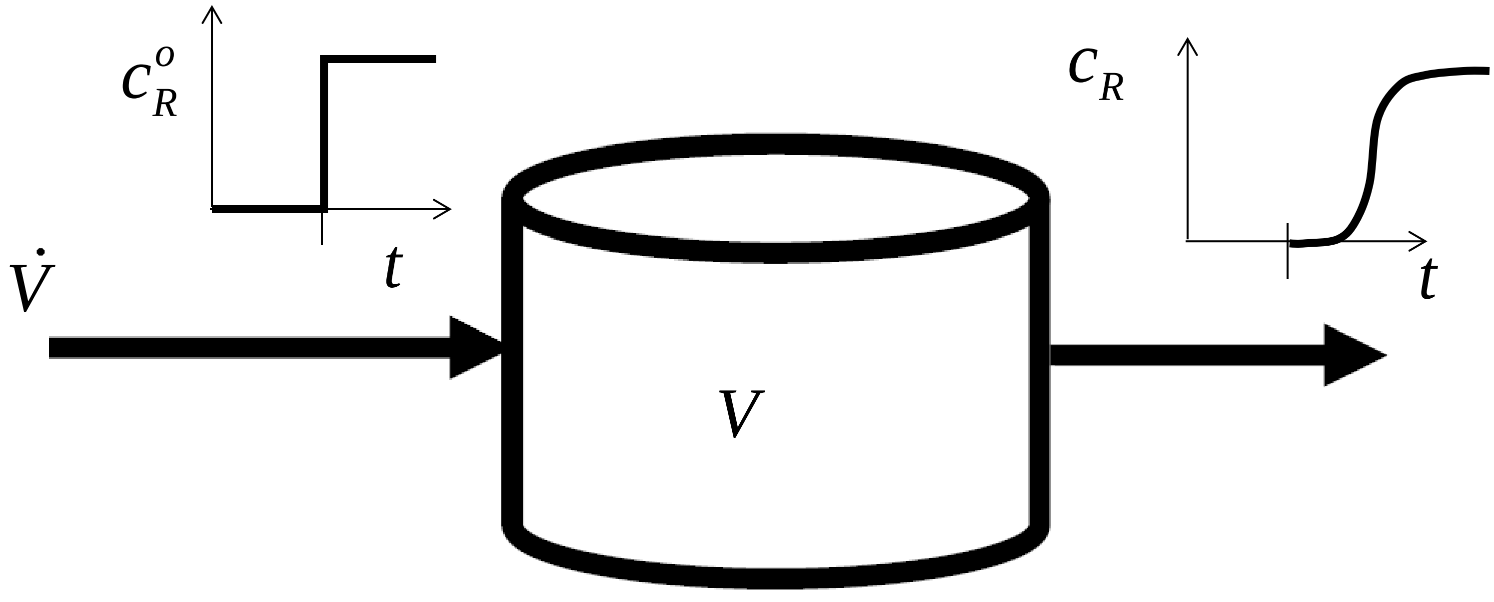
We next examine again the well-stirred reactor.



- Consider the following step-response experiment: a clear fluid with flowrate $\dot{V}$ enters a well-stirred reactor of volume V

- At time zero we start adding a small flow of a tracer to the feed stream and measure the tracer concentration in the effluent stream.

- We expect to see a continuous change in the concentration of the effluent stream until, after a long time, it matches the concentration of the feed stream.



- **Assuming constant density, the differential equation governing the balance of red dye, c_R, in the reactor follows from equation**

$$V_R \frac{dc_R}{dt} = \dot{V}\left(c_R^o - c_R\right)$$

$$t = 0, c_R = 0$$

- **We introduce average residence time**

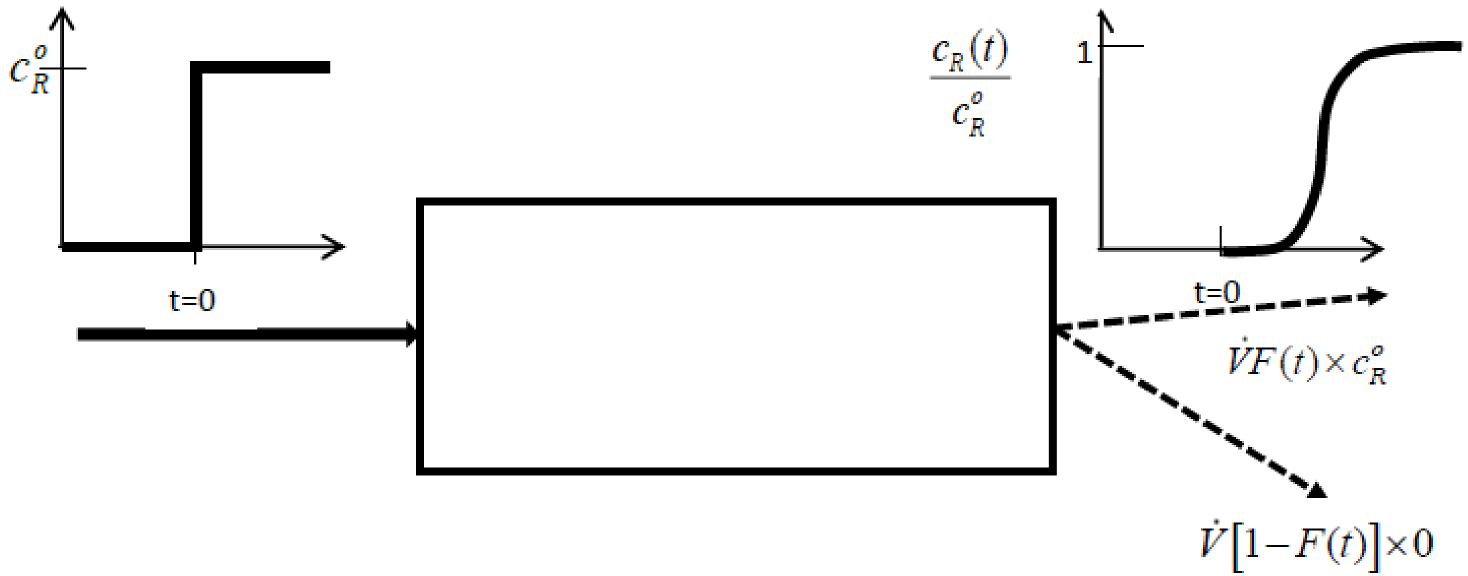
$$\bar{\tau} = \frac{V}{\dot{V}}$$

- **Solution of red color dye balance becomes**

$$c_R(t) = c_R^o\left(1 - e^{-\frac{t}{\bar{\tau}}}\right)$$

Cumulative Residence Time Distribution function (*F* – function)

***F(τ)* – The fraction of fluid of the effluent stream which has been in the reactor time less than τ**



$$\dot{V}c_R(t)=\dot{V}\left[1-F_{CSTR}(t)\right]\times 0+\dot{V}F_{CSTR}(t)\times c_R^o$$

$$F_{CSTR}(\tau)=\frac{c_R(\tau)}{c_R^o}=1-e^{-\frac{\tau}{\bar{\tau}}}$$

Residence Time Distribution (RTD) function (E– function)

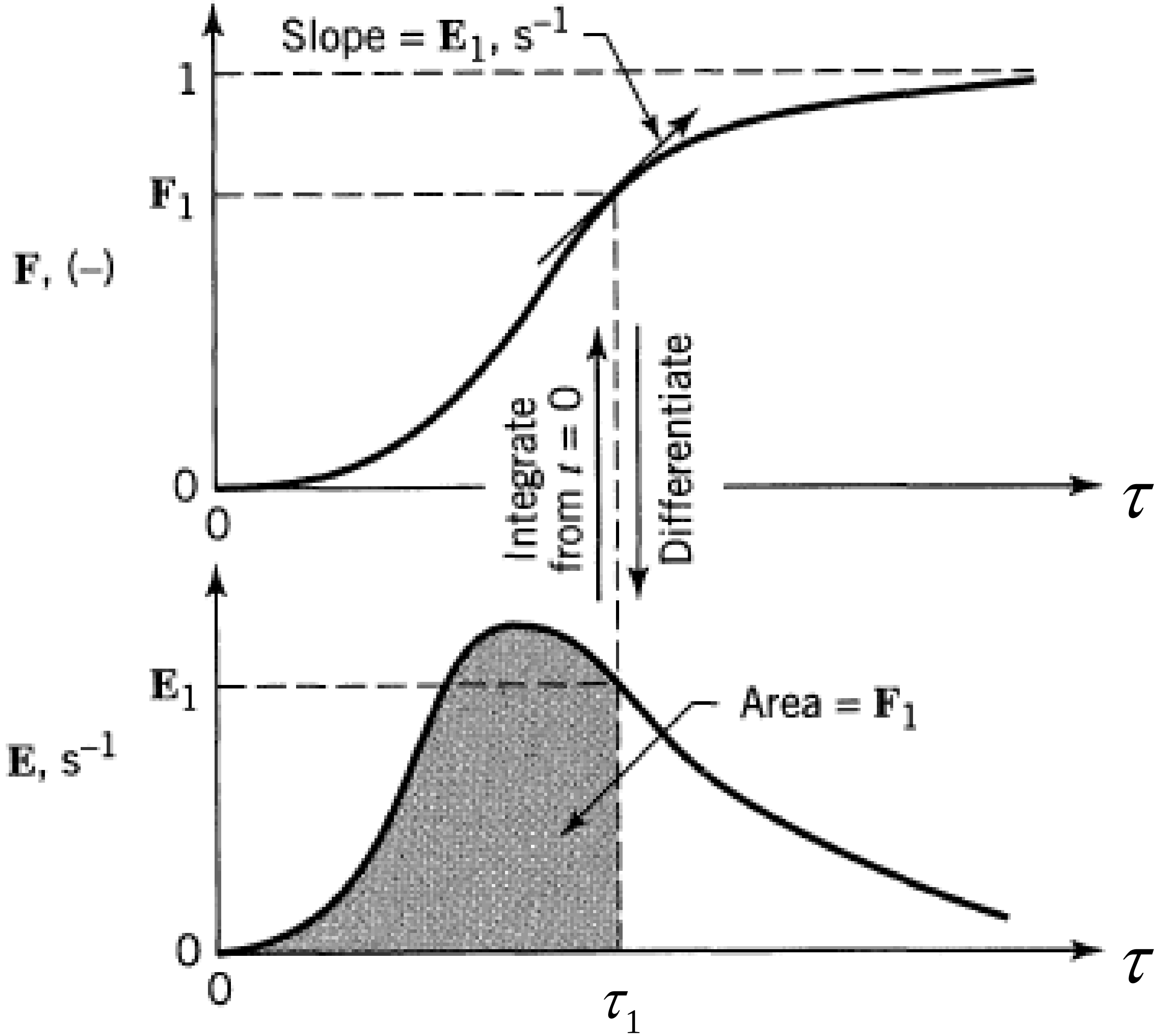
E(τ) **– The fraction of fluid of the effluent stream which has been in the reactor in time interval (τ ; τ +dτ)**

$$E(\tau) = \frac{dF}{d\tau}$$

$$E_{CSTR}(\tau) = \frac{1}{\bar{\tau}} e^{-\frac{\tau}{\bar{\tau}}}$$

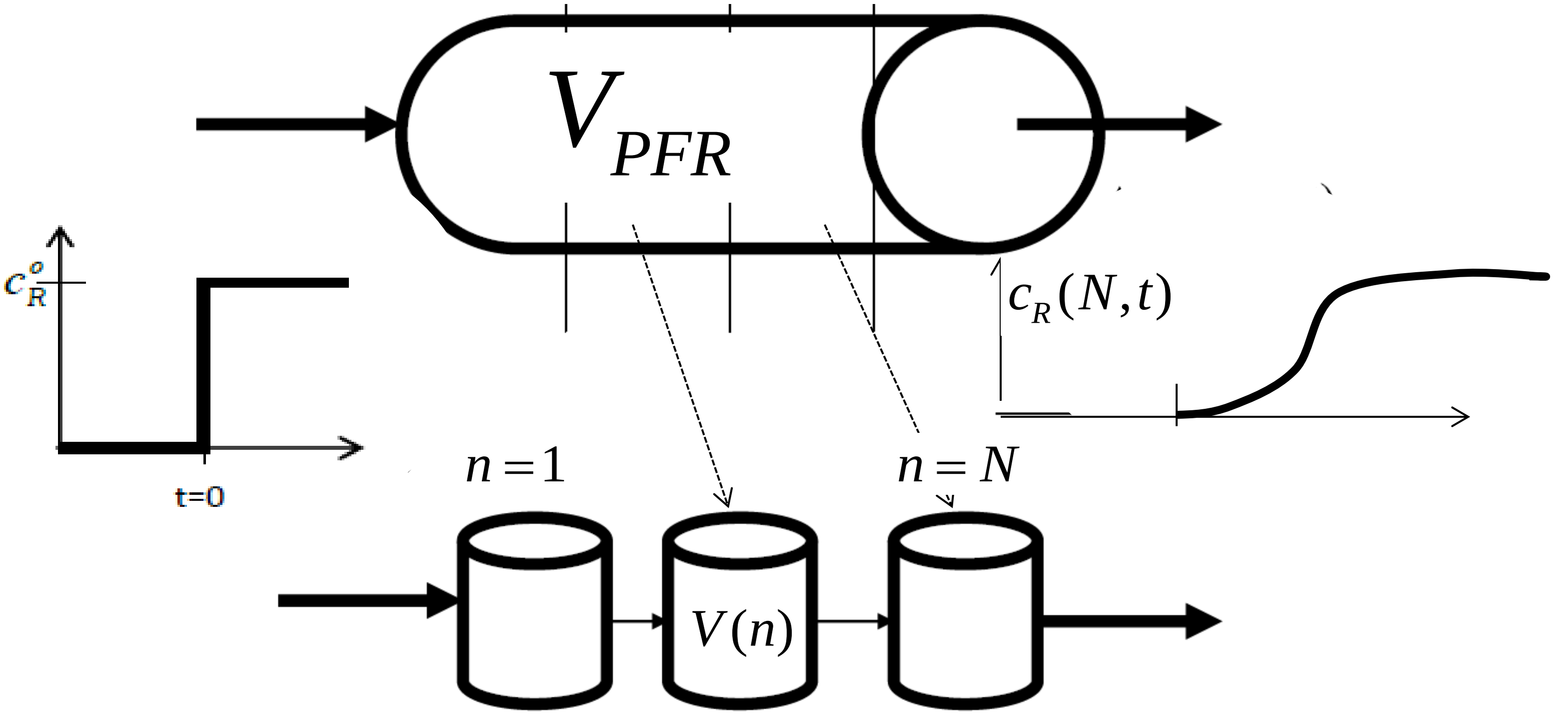
Mean Residence Time

$$\tau_{mean} = \int_0^\infty \tau E(\tau) d\tau = \int_0^\infty \frac{\tau}{\bar{\tau}} e^{-\frac{\tau}{\bar{\tau}}} d\tau = \bar{\tau}$$



Relationship between the *E(τ)* and *F(τ)* functions

Plug flow reactor can be represented by a cascade of small CSTR



$$V(n)=\frac{V_{PFR}}{N},\bar{\tau}(n)=\frac{V(n)}{\dot{V}}=\frac{V_{PFR}}{N\dot{V}}=\frac{\bar{\tau}}{N}$$

$$V(n)\frac{dc_R(n,t)}{dt}=\dot{V}\left(c_R(n-1,t)-c_R(n,t)\right)$$

$$\frac{dc_R(n,t)}{dt}=\frac{N}{\bar{\tau}}\left(c_R(n-1,t)-c_R(n,t)\right)$$

$$n=1,2,\dots N$$

With the initial condition , the solution becomes (integration of linear differential equation by integrating factor):

$$c_R(n,t) = \frac{N}{\bar{\tau}} e^{-\frac{Nt}{\bar{\tau}}} \int_0^t c_R(n-1,y) e^{\frac{Ny}{\bar{\tau}}} dy$$

Calculation of the integral for the first reactor where

$$c_R(n-1,t) = c_R^o = \text{constant}$$

and then for the successive ones yields the final result:

$$\frac{c_R(N,t)}{c_R^o} = F_N(t) = 1 - e^{-\frac{Nt}{\bar{\tau}}} \left[1 + \frac{Nt}{\bar{\tau}} + \frac{1}{2!}\left(\frac{Nt}{\bar{\tau}}\right)^2 + \ldots + \frac{1}{(N-1)!}\left(\frac{Nt}{\bar{\tau}}\right)^{N-1} \right]$$

$$F_N(\tau) = 1 - e^{-\frac{N\tau}{\bar{\tau}}} \sum_{j=1}^{N} \frac{1}{(j-1)!}\left(\frac{N\tau}{\bar{\tau}}\right)^{j-1}$$

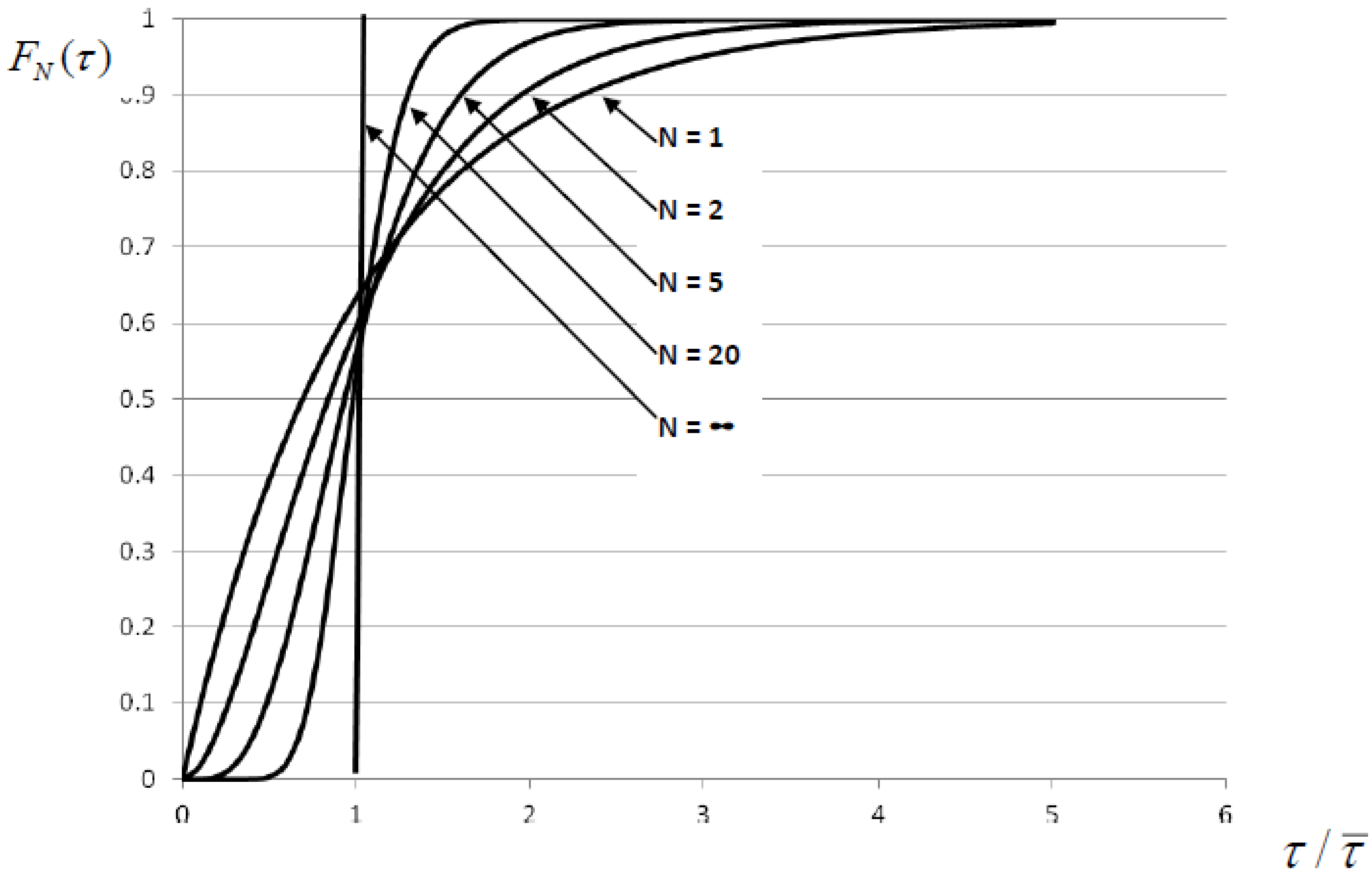


Fig. Cumulative residence time distribution $F_N(\tau)$ curves for several cascades of N equal CSTR reactors.

If the E(τ) function is calculated, we obtain

$$E_N(\tau) = \frac{F_N(\tau)}{d\tau} = \frac{d}{d\tau}\left\{1 - e^{-\frac{N\tau}{\bar{\tau}}}\sum_{j=1}^{N}\frac{1}{(j-1)!}\left(\frac{N\tau}{\bar{\tau}}\right)^{j-1}\right\} =$$

$$= \frac{N}{\bar{\tau}}e^{-\frac{N\tau}{\bar{\tau}}}\sum_{j=1}^{N}\frac{1}{(j-1)!}\left(\frac{N\tau}{\bar{\tau}}\right)^{j-1} - e^{-\frac{N\tau}{\bar{\tau}}}\frac{N}{\bar{\tau}}\sum_{j=2}^{N}\frac{1}{(j-2)!}\left(\frac{N\tau}{\bar{\tau}}\right)^{j-2} =$$

$$= \frac{N}{(N-1)!}\frac{1}{\bar{\tau}}\left(\frac{N\tau}{\bar{\tau}}\right)^{N-1} e^{-\frac{N\tau}{\bar{\tau}}}$$

The last equation is called the Poisson distribution function (see figure below).

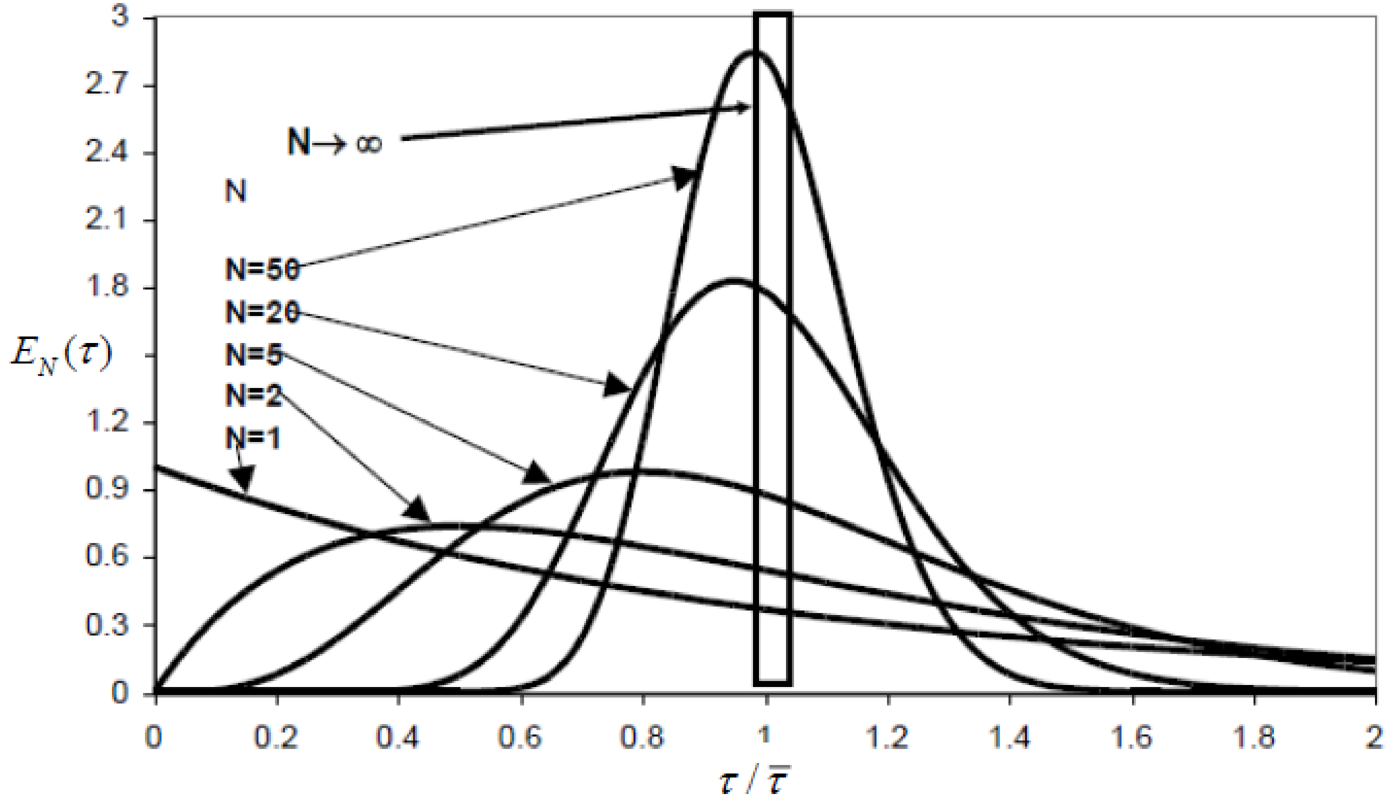


Fig. Residence time distribution *$E_N(\tau)$* curves for several cascades of *N* equal CSTR reactors.

If the slope of the *F(τ)* curves is calculated from *E(τ)* function near the inflection point (i.e. at $\tau = \bar{\tau}$), we find that it is given by

$$E_N(\bar{\tau}) = \frac{N^{N+1}}{N!}\frac{e^{-N}}{\bar{\tau}}$$

Now, according to the Stirling's rule we have for N>5 within error of 2 % (see Annexe 1)

$$N! \cong \sqrt{2N\pi}N^N e^{-N}$$

Introduction of this approximation into the former equation yields:

$$E_N(\bar{\tau}) = \frac{N^{N+1}}{\sqrt{2N\pi}N^N e^{-N}}\frac{e^{-N}}{\bar{\tau}} = \frac{1}{\bar{\tau}}\sqrt{\frac{N}{2\pi}}$$

This result also illustrates the fact that the *F(τ)* curve becomes steeper as N increases.

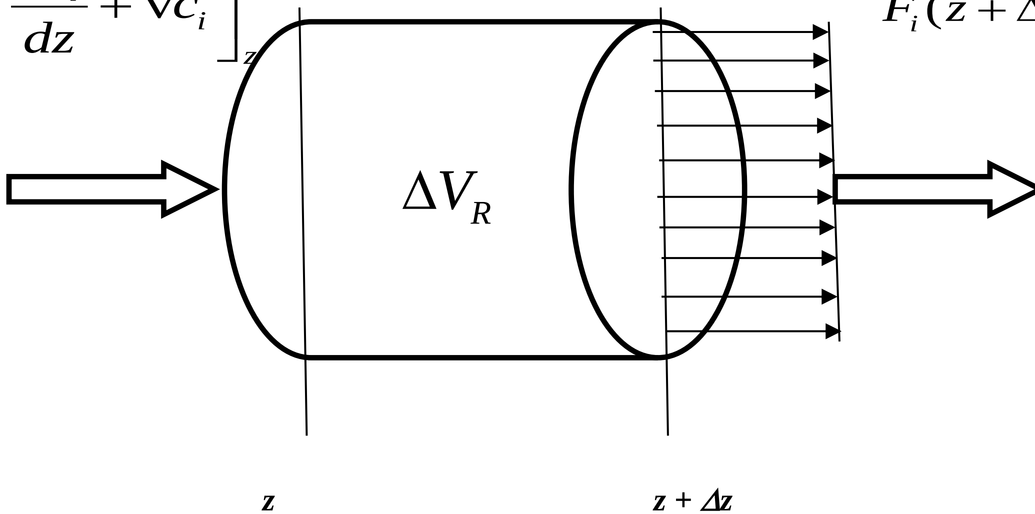
Plug flow reactor can be represented also by a dispersion model

inlet flux of i-th species

$$F_i(z) = S\left[-D_i \frac{dc_i}{dz} + \overline{\mathrm{v}} c_i\right]_z$$

outlet flux of i-th species

$$F_i(z+\Delta z) = S\left[-D_i \frac{dc_i}{dz} + \overline{\mathrm{v}} c_i\right]_{z+\Delta z}$$

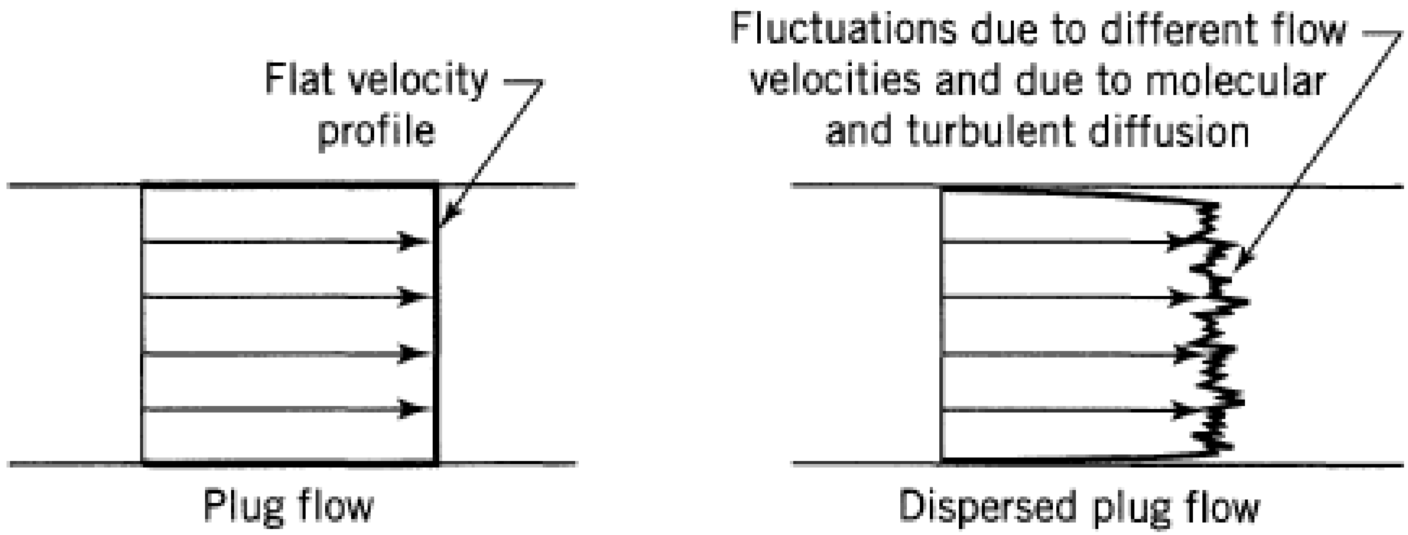


Balance of red component in the volume becomes

$$\frac{\partial c_R}{\partial t} = D_R \frac{\partial^2 c_R}{\partial z^2} - \overline{\mathrm{v}} \frac{\partial c_R}{\partial z}$$

***D**$_R$* **is a " dispersion coefficient " which must be determined experimentally**

Representation of the dispersion (dispersed plug flow) model.



Together with boundary

$$z = 0, -D_R \frac{\partial c_R}{\partial z} + \overline{\mathrm{v}} c_R = \overline{\mathrm{v}} c_R^o$$

$$z = L, D_R \frac{\partial c_R}{\partial z} = 0$$

and initial conditions

$$t = 0, 0 < z \le L, c_R = 0$$

Outlet concentration of red component is given by (see Annexe 2)

$$c_R(L,t) = \frac{c_R^o}{2}\left[1 - \mathrm{erf}\left(\frac{L - \overline{\mathrm{v}}t}{\sqrt{4D_R t}}\right)\right] =$$

$$= \frac{c_R^o}{2}\left[1 - \mathrm{erf}\left(\frac{1 - t/\overline{\tau}}{\sqrt{4t/(Pe.\overline{\tau})}}\right)\right]$$

$$\mathrm{erf}(u) = \frac{2}{\sqrt{\pi}} \int_0^u \exp\left[-y^2\right] dy$$

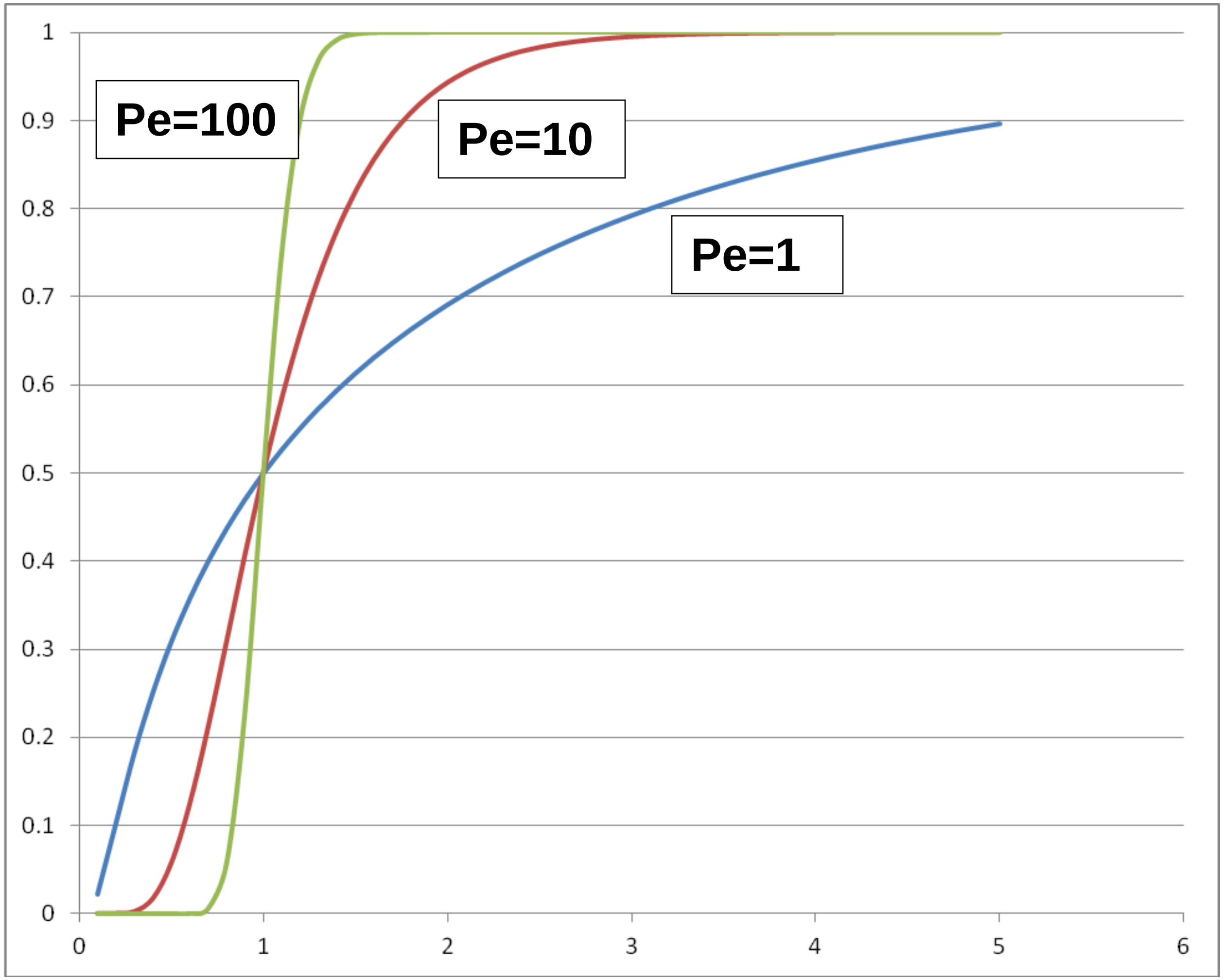
$$\overline{\tau} = \frac{V_R}{\dot{V}} = \frac{L}{\overline{\mathrm{v}}}, Pe = \frac{L\overline{\mathrm{v}}}{D_R}$$

Therefore the cumulative residence time distribution $F_N(\tau)$ curves for PFR with dispersion are given by

$$F_{PFR}(\tau) = \frac{c_R(L,\tau)}{c_R^o} = \frac{1}{2}\left[1 - \mathrm{erf}\left(\frac{1-\tau/\bar{\tau}}{\sqrt{4\tau/(Pe.\bar{\tau})}}\right)\right]$$

$$\bar{\tau} = \frac{V_R}{\dot{V}} = \frac{L}{\bar{\mathrm{v}}}, Pe = \frac{L\bar{\mathrm{v}}}{D_R}$$

$$F_{PFR} = \frac{c_R(L,t)}{c_R^o}$$



$$\frac{t}{\bar{\tau}}$$

Fig. Cumulative residence time distribution *$F_{PFR}(\tau)$* curves for PFR with dispersion

We can differentiate $F_{PFR}(\tau)$ equation to obtain the curve for dispersed plug-flow Residence Time Distribution

$$E_{PFR}(\tau) = \frac{dF_{PFR}(\tau)}{d\tau} = \frac{\sqrt{Pe}}{4\overline{\tau}\sqrt{\pi}}\left(\frac{\overline{\tau}/\tau + 1}{\sqrt{\tau/\overline{\tau}}}\right)\exp\left[-\left(\frac{1-\tau/\overline{\tau}}{\sqrt{4\tau/(Pe.\overline{\tau})}}\right)^2\right] \cong$$

$$\cong \frac{1}{2}\sqrt{\frac{Pe}{\pi\tau\overline{\tau}}}\exp\left[-\left(\frac{1-\tau/\overline{\tau}}{\sqrt{4\tau/(Pe.\overline{\tau})}}\right)^2\right]$$

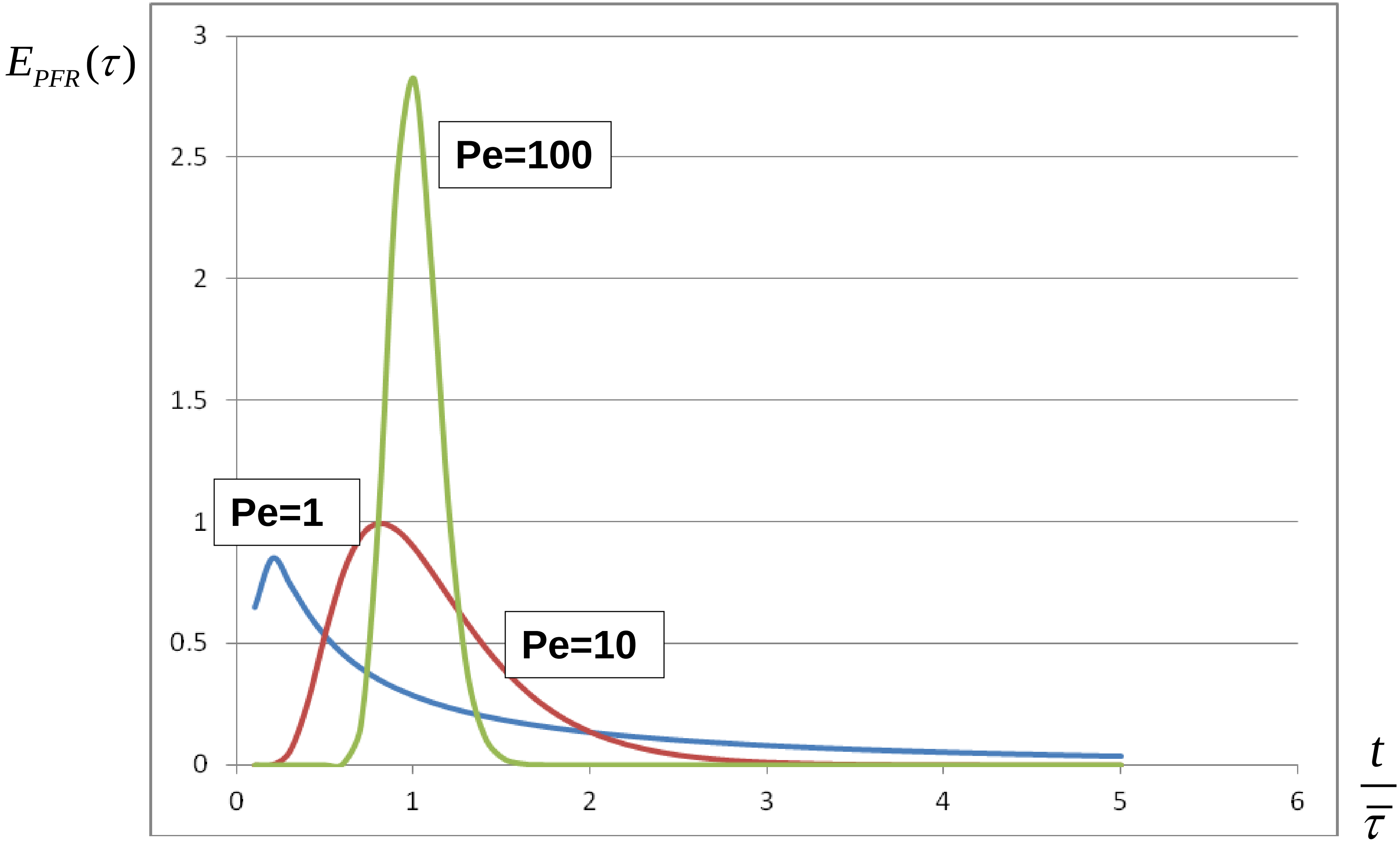
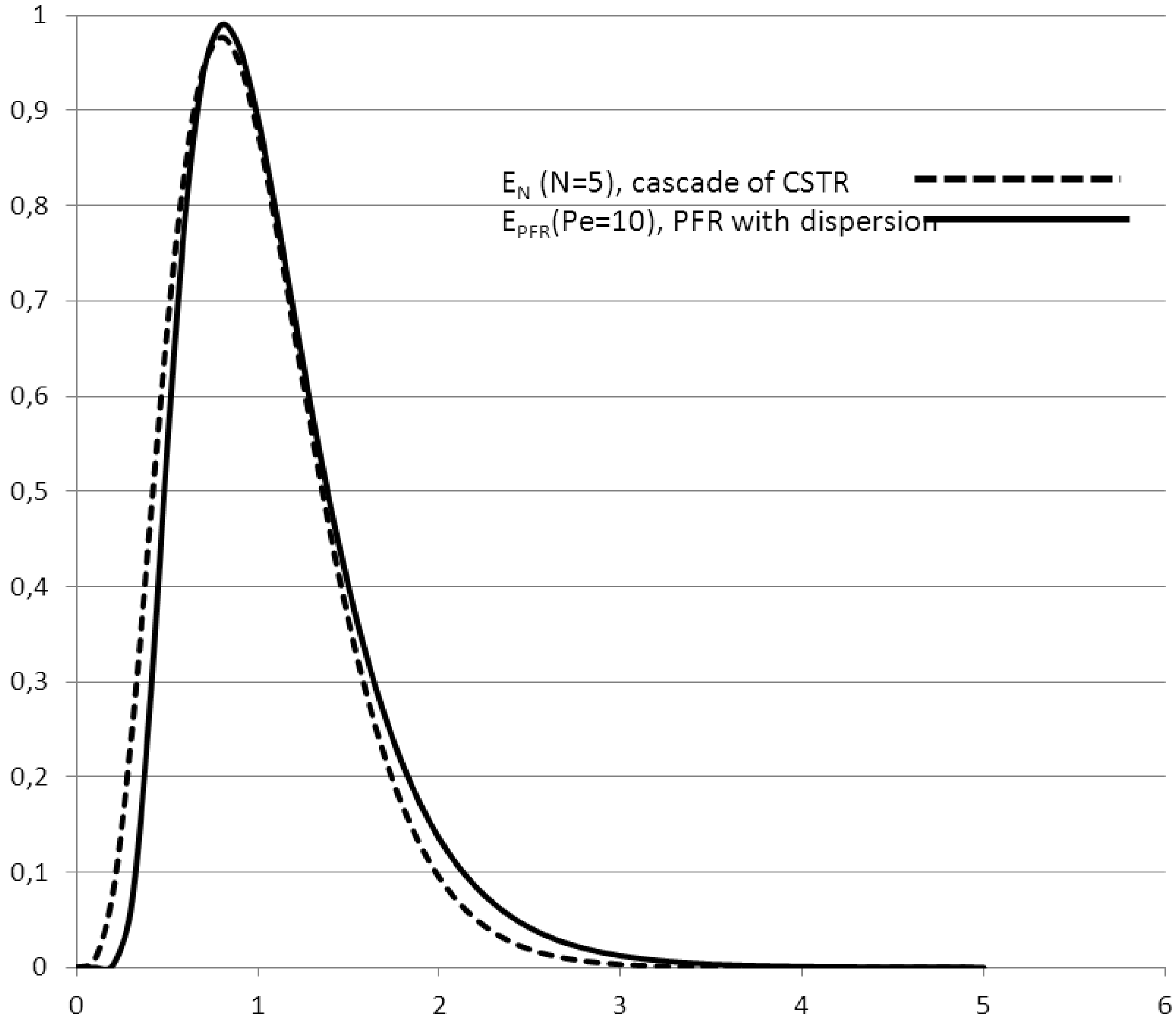


Fig. Residence time distribution $E_{PFR}(\tau)$ curves for PFR with dispersion

Comparison of the cascade and the dispersion models

$$E_{PFR}(\tau)$$
$$E_N(\tau)$$

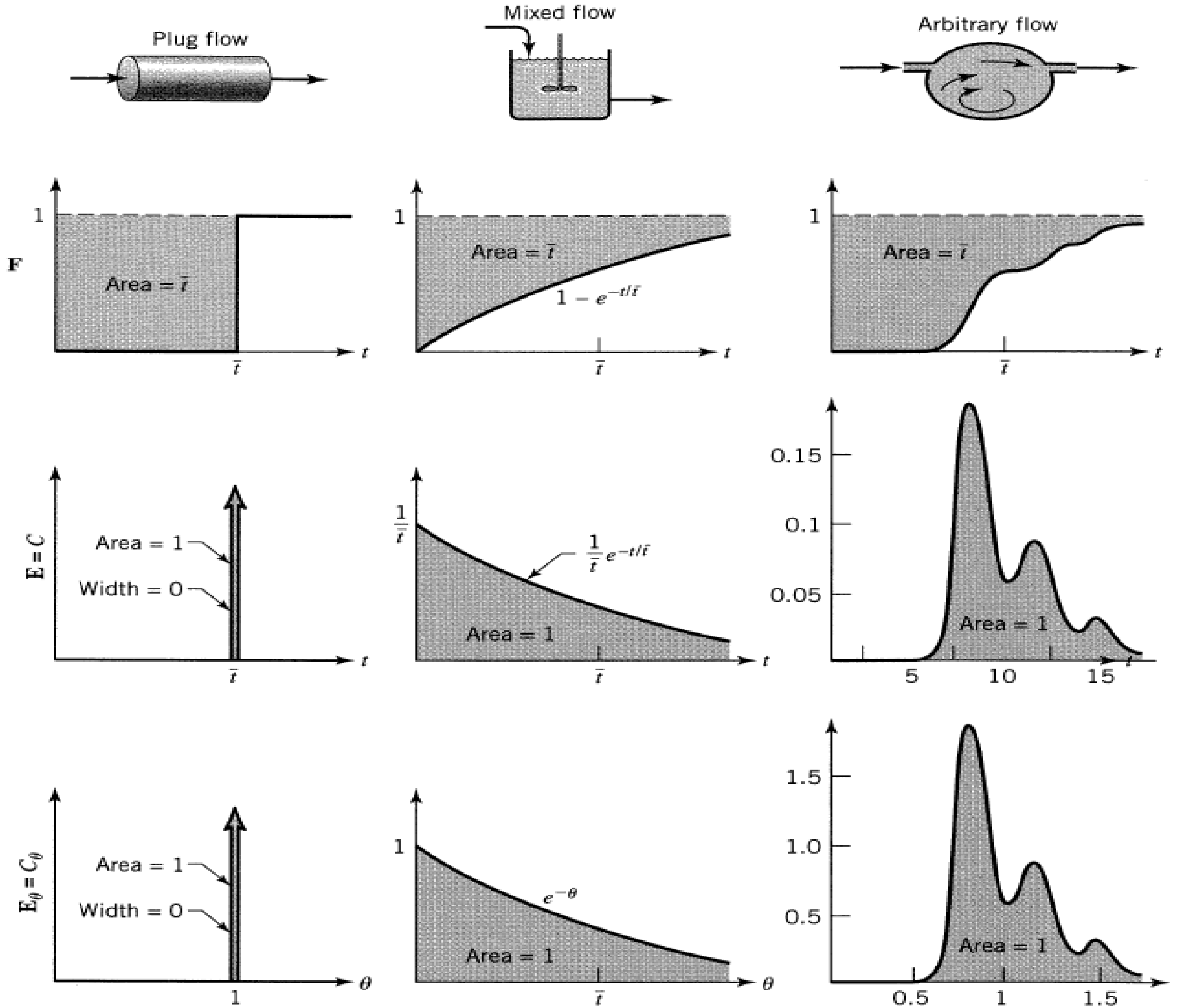


$$\frac{t}{\overline{\tau}}$$

$$E_{PFR}(\overline{\tau}) \cong E_N(\overline{\tau})$$

$$\frac{\sqrt{Pe}}{2\overline{\tau}\sqrt{\pi}} = \frac{1}{\overline{\tau}}\sqrt{\frac{N}{2\pi}}$$

$$\frac{Pe}{2} = N$$


Plug flow
Mixed flow
Arbitrary flow
F
Area = $\bar{t}$
$1 - e^{-t/\bar{t}}$
E = C
Area = 1
Width = 0
$\frac{1}{\bar{t}}e^{-t/\bar{t}}$
0.15
0.1
0.05
5
10
15
$E_\theta = C_\theta$
$e^{-\theta}$
1.5
1.0
0.5
0.5
1
1.5

1-D pseudo homogenous model with axial dispersion

$$\frac{1}{Pe_A}\frac{d^2Y_A}{dx^2} - \frac{dY_A}{dx} - Da_A Y_A = 0$$

$$x = 0 \qquad \frac{1}{Pe_A}\frac{dY_A}{dx} = Y_A - 1$$

$$x = 1 \qquad \frac{dY_A}{dx} = 0$$

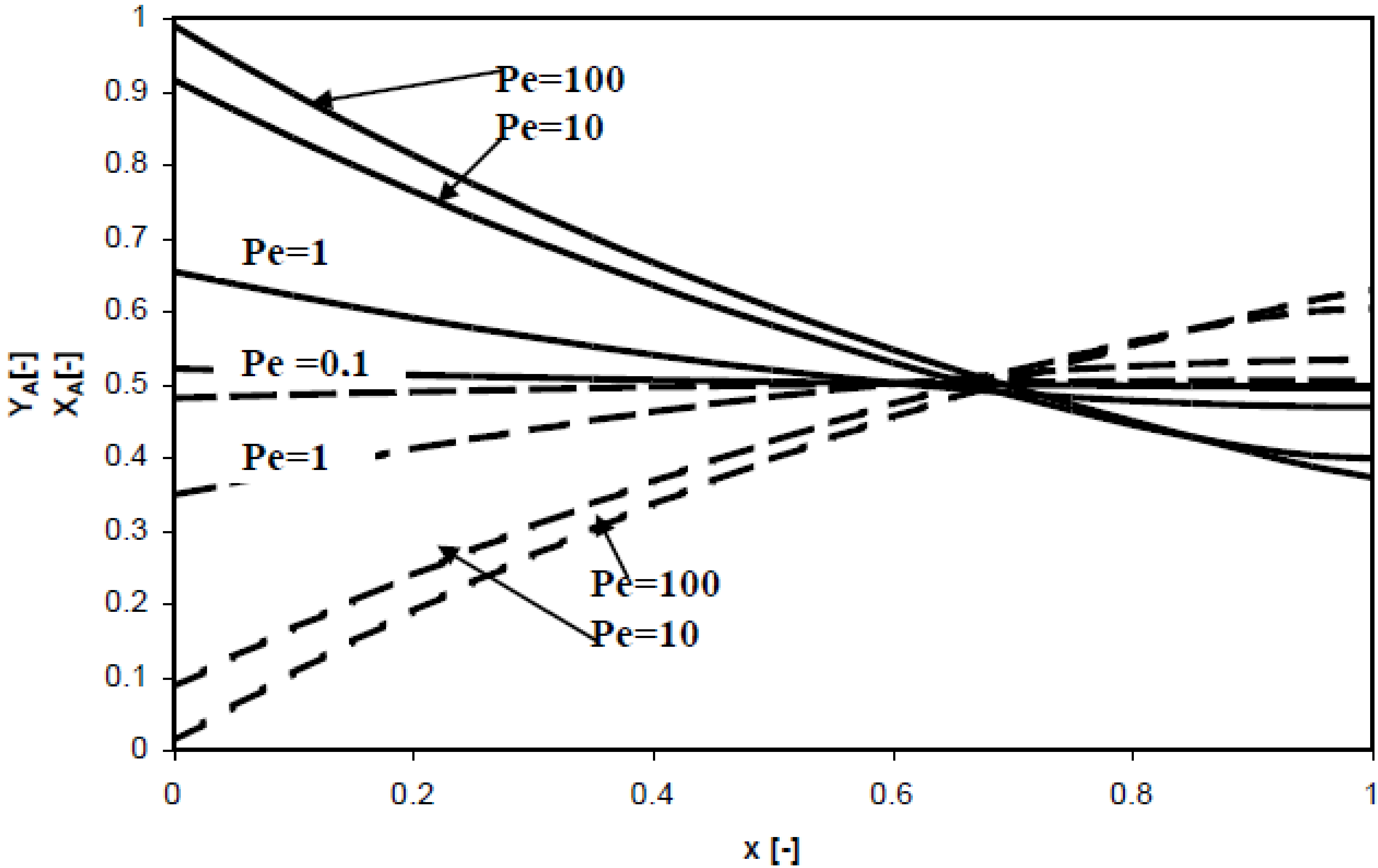
$$x = \frac{z}{L}$$

$$Y_A = \frac{c_A}{c_A^o} \qquad Pe_A = \frac{\bar{\mathrm{v}}L}{D_A} \qquad \mathrm{Da}_A = \frac{kL}{\bar{\mathrm{v}}}$$

To calculate

a) $Y_A(x)$

b) **Conversion(x) = $X_A(x) = 1 - Y_A(x)$ for various values of Pe**



$Y_A(x)$ (solid lines) and $X_A(x)$ (dashed lines) in isothermal reactor with axial dispersion and 1st order kinetics

Thank you for your attention

Annexe 1

Stirling's formula

There exists an approximation due to Stirling (James Stirling, British mathematician (1692-1770)), that is very useful in the evaluation of factorials of large numbers. It can be derived in several ways. For example, the Gamma function is defined by

$$\Gamma(x)=\int_0^\infty t^{x-1}e^{-t}dt$$

If x is replaced by n + 1, a positive integer, $\Gamma(x)$ becomes

$$\Gamma(n+1)=n!=\int_0^\infty t^n e^{-t}dt=\int_0^\infty e^{n\ln t-t}dt$$

The function $e^{n\ln t-t}$ has a sharp maximum at $t = n$ where $p(t)=n\ln t-t$ has maximum, too. We can develop function $p(t)=n\ln t-t$ at $t = n$ using Taylor's series:

$$p(t)=n\ln t-t=p(n)+\frac{p'(n)}{1!}(t-n)+\frac{p''(n)}{2!}(t-n)^2+\frac{p'''(n)}{3!}(t-n)^3+\ldots=$$

$$=n\ln n-n-\frac{1}{2!}\left(\frac{t-n}{\sqrt{n}}\right)^2+\ldots$$

Thus $\Gamma(n+1)$ becomes

$$\Gamma(n+1)=n!\cong\int_0^\infty \exp\left[n\ln(n)-n-\frac{1}{2!}\left(\frac{t-n}{\sqrt{n}}\right)^2\right]dt=n^n e^{-n}\sqrt{2n}\int_{-\sqrt{n/2}}^{\infty}e^{-y^2}dy\cong$$

$$\cong\sqrt{2n\pi}n^n e^{-n}=\sqrt{2n\pi}\left(\frac{n}{e}\right)^n$$

because $\int_{-\sqrt{n/2}}^{\infty}e^{-y^2}dy\cong\sqrt{\pi}$ for large n.

The accuracy of Stirling's formula is confirmed for large n in the table below:

n	n!	Stirling	rel. error, %
2	2	1.919004351	4.049782
10	3628800	3598695.619	0.829596
20	2.4329E+18	2.42279E+18	0.415765
50	3.0414E+64	3.03634E+64	0.166526
100	9.3326E+157	9.3248E+157	0.083298

Annexe 2

Balance of red component in the volume ΔV_R becomes

$$\frac{\partial c_R}{\partial t} = D_R \frac{\partial^2 c_R}{\partial z^2} - \overline{v} \frac{\partial c_R}{\partial z}$$

together with boundary conditions

$$z = 0 : -D_R \frac{\partial c_R}{\partial z} + \overline{v} c_R = \overline{v} c_R^0$$
$$z = L : D_R \frac{\partial c_R}{\partial z} = 0$$

and initial conditions

$$t = 0, 0 < z \leq L, c_R = 0$$

D_R is a " dispersion coefficient " which must be determined experimentally.

Using transformed variables

$$x = x(z,t) = z - \overline{v}t$$
$$\theta = \theta(z,t) = t$$

we obtain

$$\frac{\partial c_R}{\partial t} = \frac{\partial c_R}{\partial \theta}\frac{\partial \theta}{\partial t} + \frac{\partial c_R}{\partial x}\frac{\partial x}{\partial t} = \frac{\partial c_R}{\partial \theta} - \overline{v}\frac{\partial c_R}{\partial x}$$
$$\frac{\partial c_R}{\partial z} = \frac{\partial c_R}{\partial \theta}\frac{\partial \theta}{\partial z} + \frac{\partial c_R}{\partial x}\frac{\partial x}{\partial z} = \frac{\partial c_R}{\partial x}$$
$$\frac{\partial^2 c_R}{\partial z^2} = \frac{\partial^2 c_R}{\partial x^2}$$

$$\frac{\partial c_R}{\partial \theta} = D_R \frac{\partial^2 c_R}{\partial x^2}$$
$$x > 0, \theta = 0, c_R = 0$$
$$x < 0, \theta = 0, c_R = c_R^0$$
$$x \to \infty, \theta > 0, c_R \to 0$$
$$x \to -\infty, \theta > 0, c_R \to c_R^0$$

This equation can be solved by Boltzmann transformation

$$u = \frac{x}{\sqrt{4D_R\theta}}$$

$$\frac{\partial c_R}{\partial \theta} = \frac{dc_R}{du}\frac{\partial u}{\partial \theta} = -\frac{1}{2}\frac{x}{\sqrt{4D_R\theta}}\frac{1}{\theta}\frac{dc_R}{du} = -\frac{1}{2}\frac{u}{\theta}\frac{dc_R}{du}$$

$$\frac{\partial c_R}{\partial x} = \frac{dc_R}{du}\frac{\partial u}{\partial x} = \frac{1}{\sqrt{4D_R\theta}}\frac{dc_R}{du}$$

$$\frac{\partial^2 c_R}{\partial x^2} = \frac{1}{4D_R\theta}\frac{d^2 c_R}{du^2}$$

And we have finally

$$\frac{d^2 c_R}{du^2} + 2u\frac{dc_R}{du} = 0$$

Boundary and initial conditions become

$$u \to -\infty, c_R \to c_R^0$$
$$u \to \infty, c_R \to 0$$

After integrating the last equation we have (taking into account $\int_{-\infty}^{\infty} e^{-y^2} dy = \sqrt{\pi}$)

$$\frac{dc_R}{du} = B_1 \exp\left[-u^2\right]$$

$$c_R(u) - c_R(-\infty) = c_R(u) - c_R^0 = B_1 \int_{-\infty}^{u} \exp\left[-y^2\right] dy$$

$$B_1 = -\frac{c_R^0}{\sqrt{\pi}}$$

$$c_R(u) = c_R^0\left[1 - \frac{1}{\sqrt{\pi}}\int_{-\infty}^{u} \exp\left[-y^2\right] dy\right] =$$

$$= c_R^0\left[1 - \frac{1}{\sqrt{\pi}}\left(\frac{\sqrt{\pi}}{2} + \int_{0}^{u} \exp\left[-y^2\right] dy\right)\right] =$$

$$= \frac{c_R^0}{2}\left[1 - \frac{2}{\sqrt{\pi}}\int_{0}^{u} \exp\left[-y^2\right] dy\right] =$$

$$= \frac{c_R^0}{2}\left[1 - \operatorname{erf}(u)\right]$$

$$\operatorname{erf}(u) = \frac{2}{\sqrt{\pi}}\int_{0}^{u} \exp\left[-y^2\right] dy$$

Substituting original variables we would obtain

$$c_R(z,t) = \frac{c_R^o}{2}\left[1 - \operatorname{erf}\left(\frac{z - \overline{v}t}{\sqrt{4D_R t}}\right)\right] =$$

$$= \frac{c_R^o}{2}\left[1 - \operatorname{erf}\left(\frac{z - \overline{v}t}{\sqrt{4D_R t}}\right)\right] =$$

$$= \frac{c_R^o}{2}\left[1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{z-\overline{v}t}{\sqrt{4D_R t}}} \exp\left[-y^2\right] dy\right]$$

Outlet concentration of red component is given by

$$c_R(L,t) = \frac{c_R^o}{2}\left[1 - \operatorname{erf}\left(\frac{L - \overline{v}t}{\sqrt{4D_R t}}\right)\right] =$$

$$= \frac{c_R^o}{2}\left[1 - \operatorname{erf}\left(\frac{1 - t/\overline{\tau}}{\sqrt{4t/(Pe.\overline{\tau})}}\right)\right]$$

$$\overline{\tau} = \frac{V}{\dot{V}} = \frac{L}{\overline{v}}, Pe = \frac{L\overline{v}}{D_R}$$

where $\overline{\tau}$ is the average residence time and Pe stands for Peclet number.