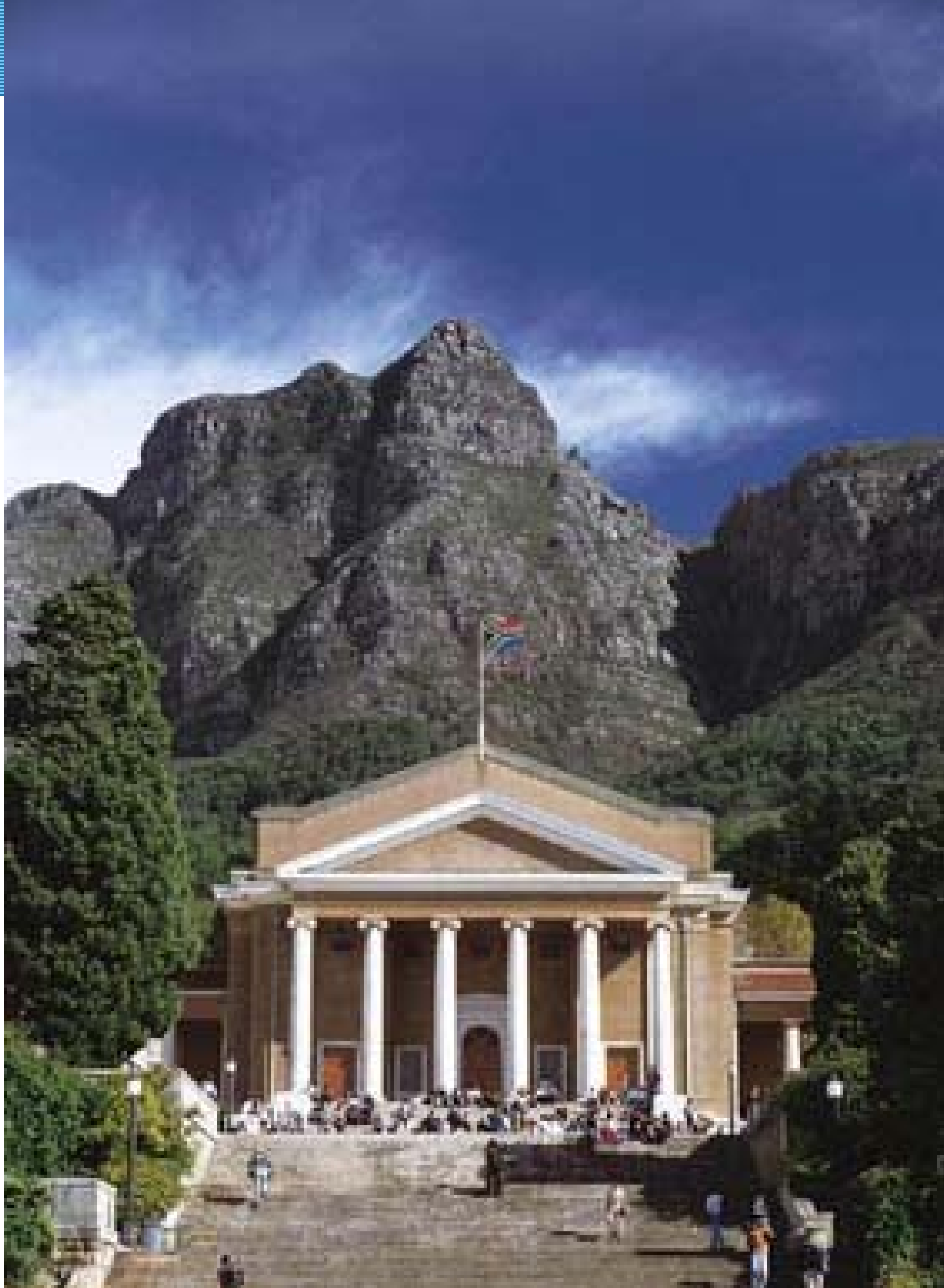
UNIVERSITY OF CAPE TOWN

Centre for Catalysis Research

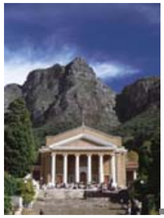
Department of Chemical Engineering
University of Cape Town • Rondebosch 7701
South Africa



Residence time distribution in real reactors

Linda H. Callanan
Eric van Steen

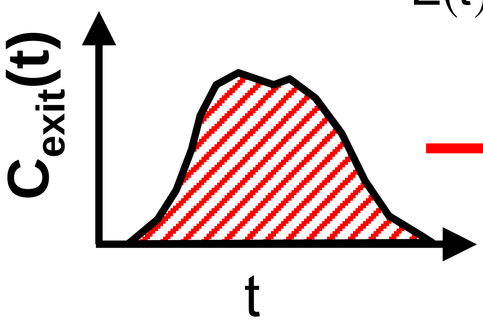
1. Recap on RTD and conversion in real reactors
2. Dispersion model
3. Tank-in-series model
4. Compartment model



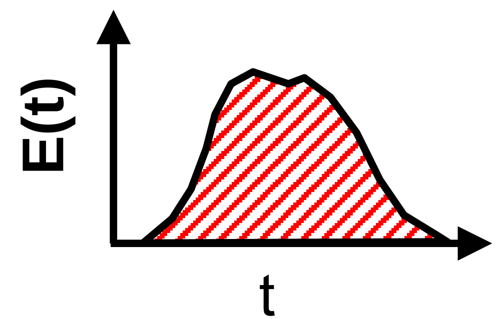
Residence Time Distribution (RTD)

Determined by introducing a *non-reactive*, *non-adsorbing* tracer into the feed and measuring the concentration of the tracer in the exit line.

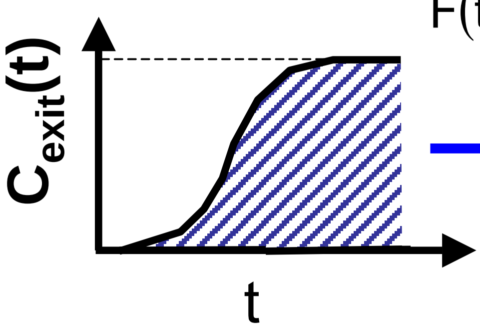
Pulse input



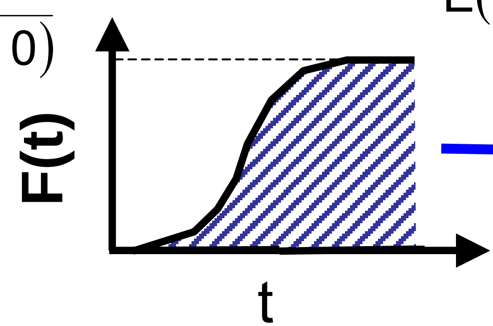
$$E(t) = \frac{C(t)}{\int_{t=0}^{t=\infty} C(t)\cdot dt}$$



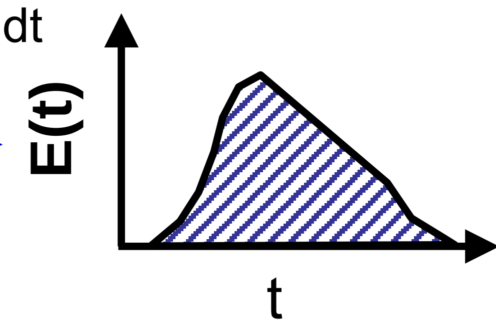
Step input

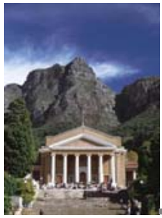


$$F(t) = \frac{C(t)}{C_{inlet}(t>0)}$$



$$E(t) = \frac{d(F(t))}{dt}$$





Evaluation of Residence Time Distributions (RTD)

Consistence check

Pulse input $$\int_{t=0}^{t=\infty} C \cdot dt = \frac{n_{injected}}{v_{fluid}}$$

Step input $$C(t=\infty) = C_{inlet}$$

Mean Residence time

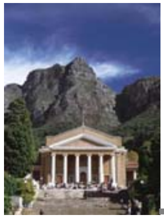
The mean or average residence time: $$t_m = \int_{t=0}^{t=\infty} t \cdot E \cdot dt$$

The mean residence time should be equal to the space time: $$\boxed{t_m \overset{?}{=} \tau = \frac{V}{v}}$$

Variance

Spread in the residence time distribution is commonly measured by the variance:

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

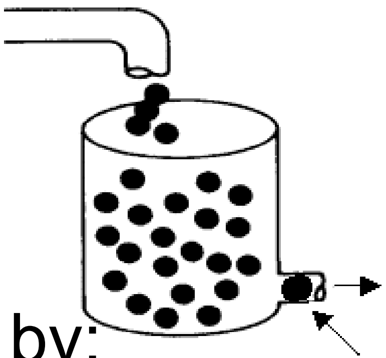


Conversion in real reactors - Segregation Model

The fluid → consisting of non-interacting elements

Each exit stream is thought to consist of elements having spent various times in the reactor.

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



The exit concentration of the reactant is given by:

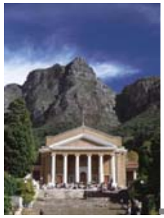
$$\boxed{\overline{C_A} = \int_{t=0}^{t=\infty} C_{A,\text{element}} \cdot E \cdot dt}$$

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

Assumptions:

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

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



Determination of conversion from E-curve

The residence time distribution in a reactor has been determined and the E(t) data have been determined as shown below:

Time t, min	0	5	10	15	20	25	30	35
E, min^{-1}	0	0.03	0.05	0.05	0.04	0.02	0.01	0

The reactor is to be used for a liquid phase decomposition. The rate of reaction is 1^{st} order with respect to the reactant ($k = 0.1$ min^{-1}). Determine:

1. The mean residence time
2. The conversion, which would have been obtained if the reactor is an ideal PFR/CSTR
3. The conversion obtained in this reactor according the segregation model

Determination of mean residence time from E-curve

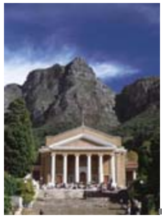
Mean residence time:

$$t_m = \int_{t=0}^{t=\infty} t \cdot E \cdot dt$$

t, min	0	5	10	15	20	25	30	35
E, min^{-1}	0	0.03	0.05	0.05	0.04	0.02	0.01	0
$t \cdot E$	0	0.15	0.50	0.75	0.80	0.50	0.30	0
Integral		0.375	1.625	3.125	3.875	3.25	2.00	0.75

$$\frac{1}{2} \cdot \left((E \cdot t)_2 + (E \cdot t)_1\right) \cdot (t_2 - t_1)$$

<u>Mean residence time:</u> 15 min



Determination of conversion in ideal reactors

PFR:

$$\frac{dX}{dV} = \frac{-r_A}{F_{A,0}} = \frac{-r_A}{v \cdot C_{A,0}} \qquad \frac{dX}{d\tau} = \frac{-r_A}{C_{A,0}}$$

1st order reaction:

$$\frac{dX}{d\tau} = \frac{-r_A}{C_{A,0}} = \frac{k \cdot C_A}{C_{A,0}} = k \cdot (1 - X)$$

$$-\ln(1 - X) = k \cdot \tau$$

$$\boxed{X = 1 - e^{-k \cdot \tau}}$$

Conversion in ideal PFR: **77.8 %**

CSTR

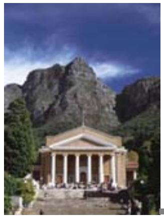
$$\frac{X}{V} = \frac{-r_A}{F_{A,0}} = \frac{-r_A}{v \cdot C_{A,0}} \qquad \frac{X}{\tau} = \frac{-r_A}{C_{A,0}}$$

1st order reaction:

$$\frac{X}{\tau} = \frac{-r_A}{C_{A,0}} = \frac{k \cdot C_A}{C_{A,0}} = k \cdot (1 - X)$$

$$\boxed{X = \frac{k \cdot \tau}{1 + k \cdot \tau}}$$

Conversion in ideal CSTR: **60 %**



Conversion using segregation model

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

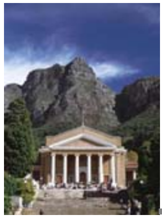
The concentration of the reactant in each element depends on the time it spent in the reactor. Each element can be seen as a batch-type reactor.

$$C_{A,element} = C_{A,0} \cdot e^{-k \cdot t}$$

The average concentration of the reactant in the exit stream is given by:

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

$$X = 1 - \frac{\overline{C}_A}{C_{A,0}} = 1 - \int_{t=0}^{t=\infty} e^{-k \cdot t} \cdot E \cdot dt$$



Conversion using segregation model

t, min	0	5	10	15	20	25	30	35
E, min^{-1}	0	0.03	0.05	0.05	0.04	0.02	0.01	0
$e^{-k \cdot t} \cdot E$	0	0.018	0.018	0.011	0.005	0.002	0.000	0
Integral		0.045	0.091	0.074	0.041	0.018	0.005	0.001

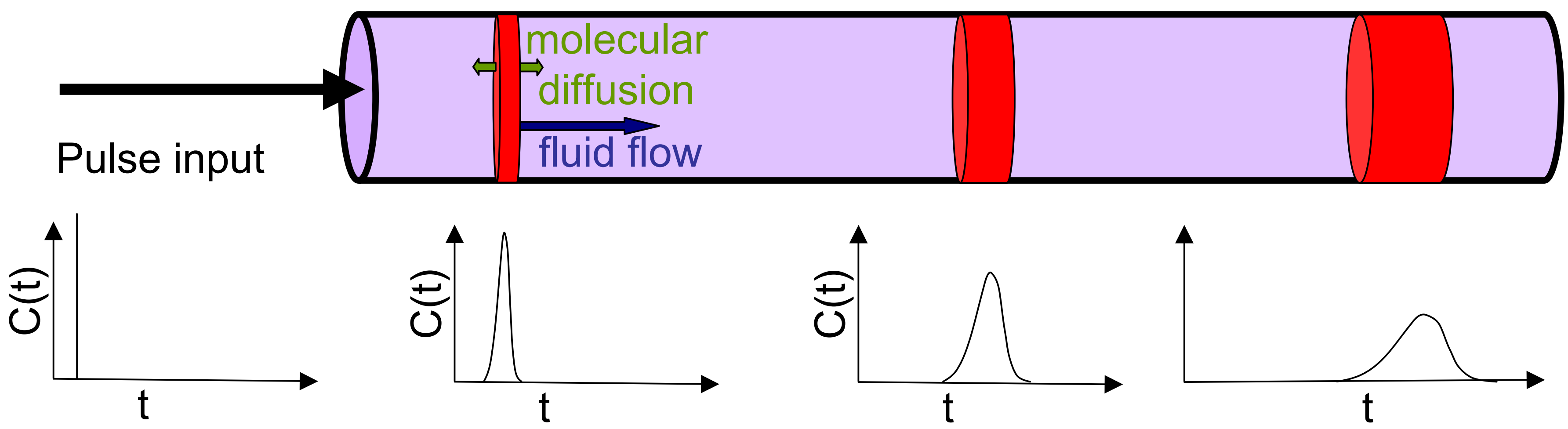
$$\frac{1}{2}\cdot\left(\left(e^{-k\cdot t_2}\cdot E\right)_2+\left(e^{-k\cdot t_1}\cdot E\right)_1\right)\cdot\left(t_2-t_1\right)$$

$X = 1 - \Sigma_{integral}$

Comparison of conversions:

PFR	**77.8%**
CSTR	**60.0%**
Segregation model	**72.4%**

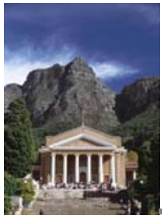
Dispersion model



Flux of inert tracer: $$F_T = \underbrace{-D \cdot A_c \cdot \frac{dC_T}{dz}}_{\text{dispersion}} + \underbrace{u \cdot A_c \cdot C_T}_{\text{convection}}$$

Mole balance on inert tracer: $$-\frac{\partial F_T}{\partial z} = A_c \cdot \frac{\partial C_T}{\partial t}$$

F_T: molar flux of tracer
D: diffusion coefficient for tracer
A_c: cross sectional area of tube
z: length
u: linear velocity



Development of dispersion model

Mole balance on inert tracer: $$D \cdot \frac{\partial^2 C_T}{\partial z^2} - u \cdot \frac{\partial C_T}{\partial z} = \frac{\partial C_T}{\partial t}$$

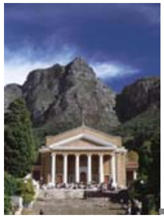
Introducing a dimensionless time: $$\theta = t/\tau = t \cdot u/L \qquad dt = \frac{L}{u} \cdot d\theta$$

a dimensionless length: $$\lambda = z/L \qquad dz = L \cdot d\lambda$$

$$dz^2 = 2 \cdot z \cdot dz = 2 \cdot L^2 \cdot \lambda \cdot d\lambda = L^2 \cdot d\lambda^2$$

Substituting dimensionless numbers in mole balance on inert tracer:

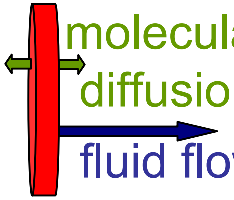
$$\frac{D}{u \cdot L} \cdot \frac{\partial^2 C_T}{\partial \lambda^2} - \frac{\partial C_T}{\partial \lambda} = \frac{\partial C_T}{\partial \theta}$$



Development of dispersion model

$$\frac{D}{u \cdot L} \cdot \frac{\partial^2 C_T}{\partial \lambda^2} - \frac{\partial C_T}{\partial \lambda} = \frac{\partial C_T}{\partial \theta}$$

Bodenstein number *Bo* $Bo = \frac{u \cdot L}{D}$ (also called Pe_r)



Characteristic rate of diffusion: $\frac{D}{L}$

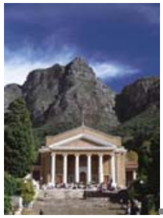
Characteristic rate of convective flow: u

Ratio of rate of convective transport relative to rate of transport by diffusion

Convective transport large ($Bo \rightarrow \infty$) PFR-behaviour
Transport by diffusion (($Bo \rightarrow 0$) mixing by diffusion → CSTR-behaviour

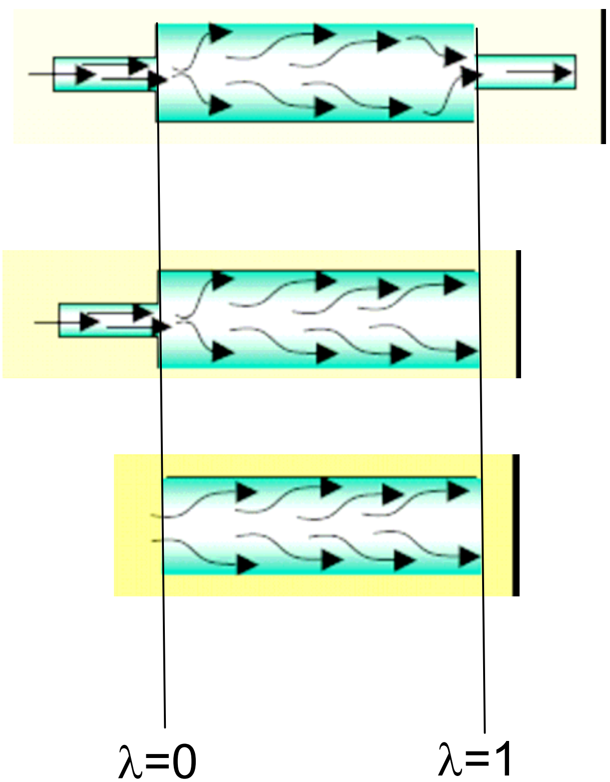
For constant conditions (temperature/pressure, etc.),
Bo increases with increasing L (length of reactor)

Long reactors, B0 → ∞ approaching plug flow behaviour!



Development of dispersion model

$$\frac{1}{Bo}\cdot\frac{\partial^2 C_T}{\partial\lambda^2}-\frac{\partial C_T}{\partial\lambda}=\frac{\partial C_T}{\partial\theta}$$



Closed system (discontinuity in *Bo* at λ=0 and λ=1)

$$\bar{t}=\tau \qquad \sigma^2=\bar{t}^2\cdot\left(\frac{2}{Bo}-\frac{2}{Bo^2}\cdot\left(1-e^{-Bo}\right)\right)$$

Closed-open system (discontinuity in *Bo* at λ=0)

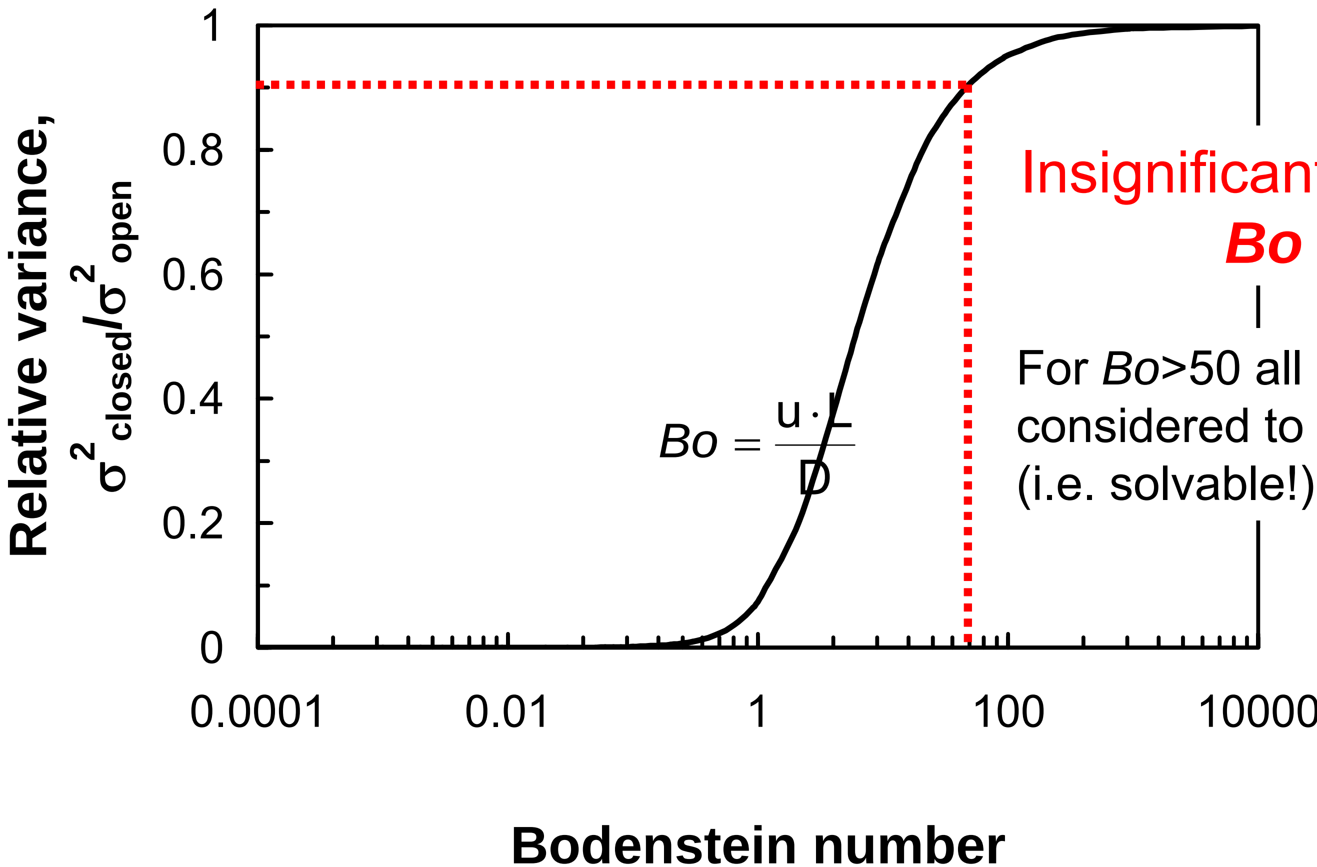
$$\bar{t}=\tau\cdot(1+Bo) \qquad \sigma^2=\bar{t}^2\cdot\left(\frac{2}{Bo}+\frac{3}{Bo^3}\right)$$

Open system

$$E=\frac{1}{2}\cdot\sqrt{\frac{Bo}{\pi\cdot\theta}}\cdot e^{\frac{-\left(1-\theta^2\right)Bo}{4\cdot\theta}}$$

$$\bar{t}=\tau \qquad \sigma^2=\bar{t}^2\cdot\left(\frac{2}{Bo}+\frac{8}{Bo^2}\right)$$

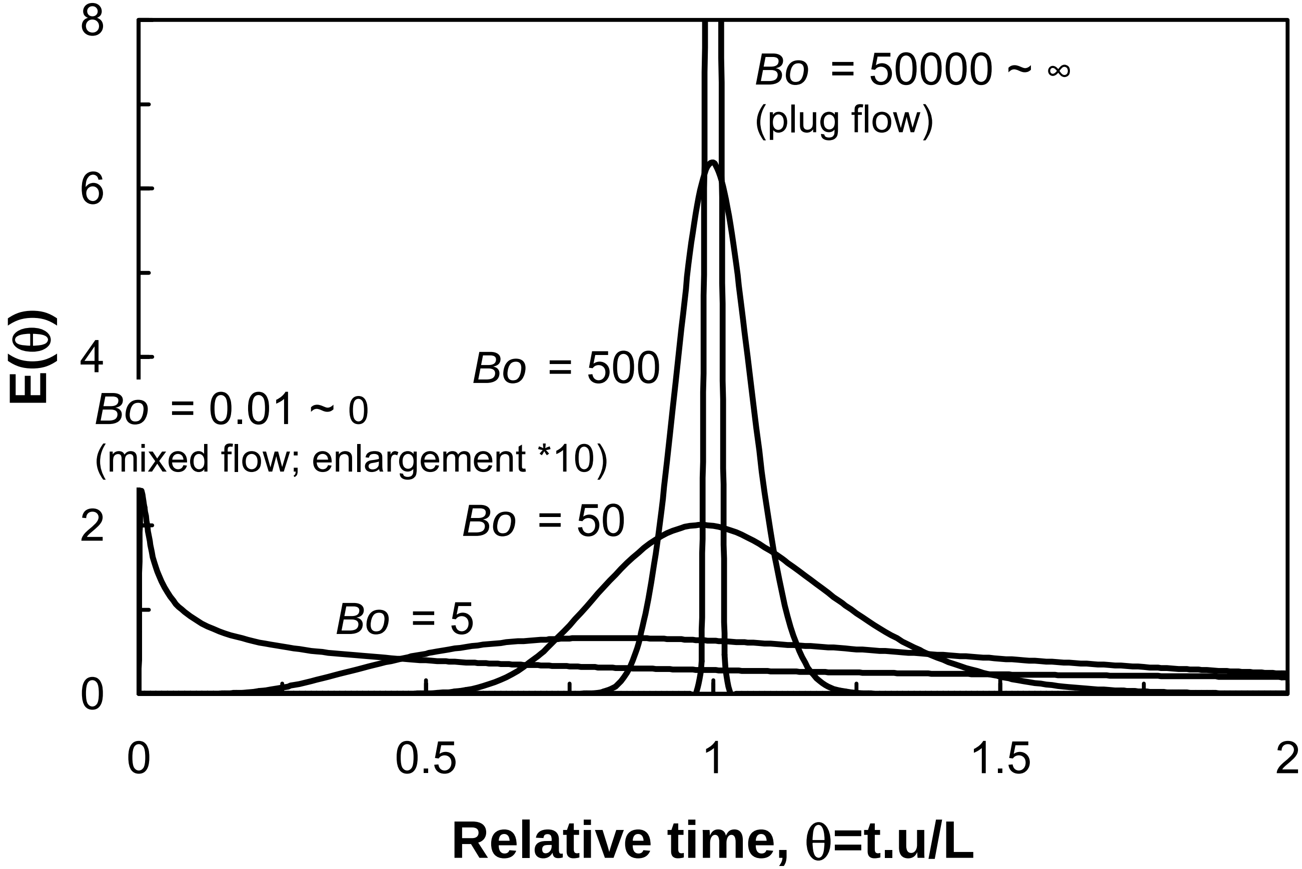
Dispersion model
comparison open and closed systems

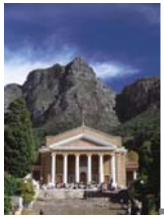


Insignificant change for ***Bo* >50**

For *Bo*>50 all systems can be considered to be open systems (i.e. solvable!)

Dispersion model
open systems





Determination of *Bo* from E-curve

The residence time distribution in a reactor has been determined and the E(t) data have been determined as shown below:

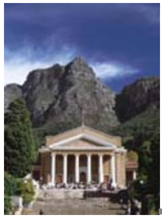
Time t, min	0	5	10	15	20	25	30	35
E, min^{-1}	0	0.03	0.05	0.05	0.04	0.02	0.01	0

Average residence time: 15 min

Variance: $\sigma^2 = \int_0^\infty (t - t_m)^2 \cdot E \cdot dt = 47.5 \cdot min^2$

Assuming an open system: $\sigma^2 = \bar{t}^2 \cdot \left(\frac{2}{Bo} + \frac{8}{Bo^2} \right)$ *Bo* = 12.5

Assuming a closed system: $\sigma^2 = \bar{t}^2 \cdot \left(\frac{2}{Bo} - \frac{2}{Bo^2} \cdot \left(1 - e^{-Bo}\right) \right)$ *Bo* = 8.3



Conversion and dispersion model (1st order rxn – Closed system)

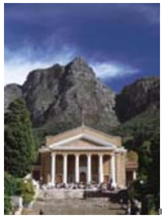
Damköhler number: $$Da = k \cdot C_{A0}^{n-1} \cdot \tau$$

1st order reactions: $$Da = k \cdot \tau$$

Solving the mole balance of species A in the reactor (closed system) (second order differential equation) :

$$1 - X = \frac{C_{A,L}}{C_{A0}} = \frac{4 \cdot q \cdot e^{\frac{Bo}{2}}}{(1+q)^2 \cdot e^{\frac{Bo \cdot q}{2}} - (1-q)^2 \cdot e^{\frac{-Bo \cdot q}{2}}}$$

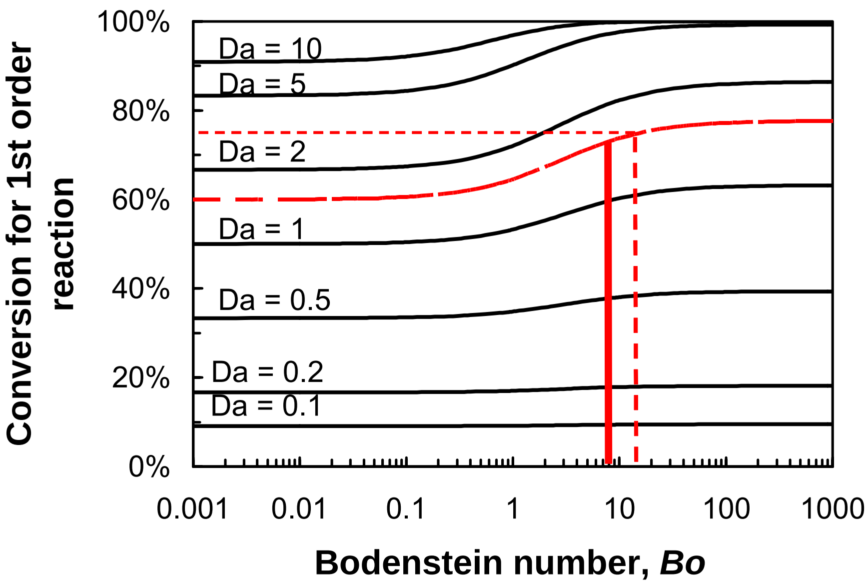
$$q = \sqrt{1 + \frac{4 \cdot Da}{Bo}}$$



Conversion and dispersion model (1st order rxn – Closed system)

The reactor (average residence time: 15 min) is to be used for a liquid phase decomposition. The rate of reaction is 1st order with respect to the reactant ($k = 0.1\ \text{min}^{-1}$).

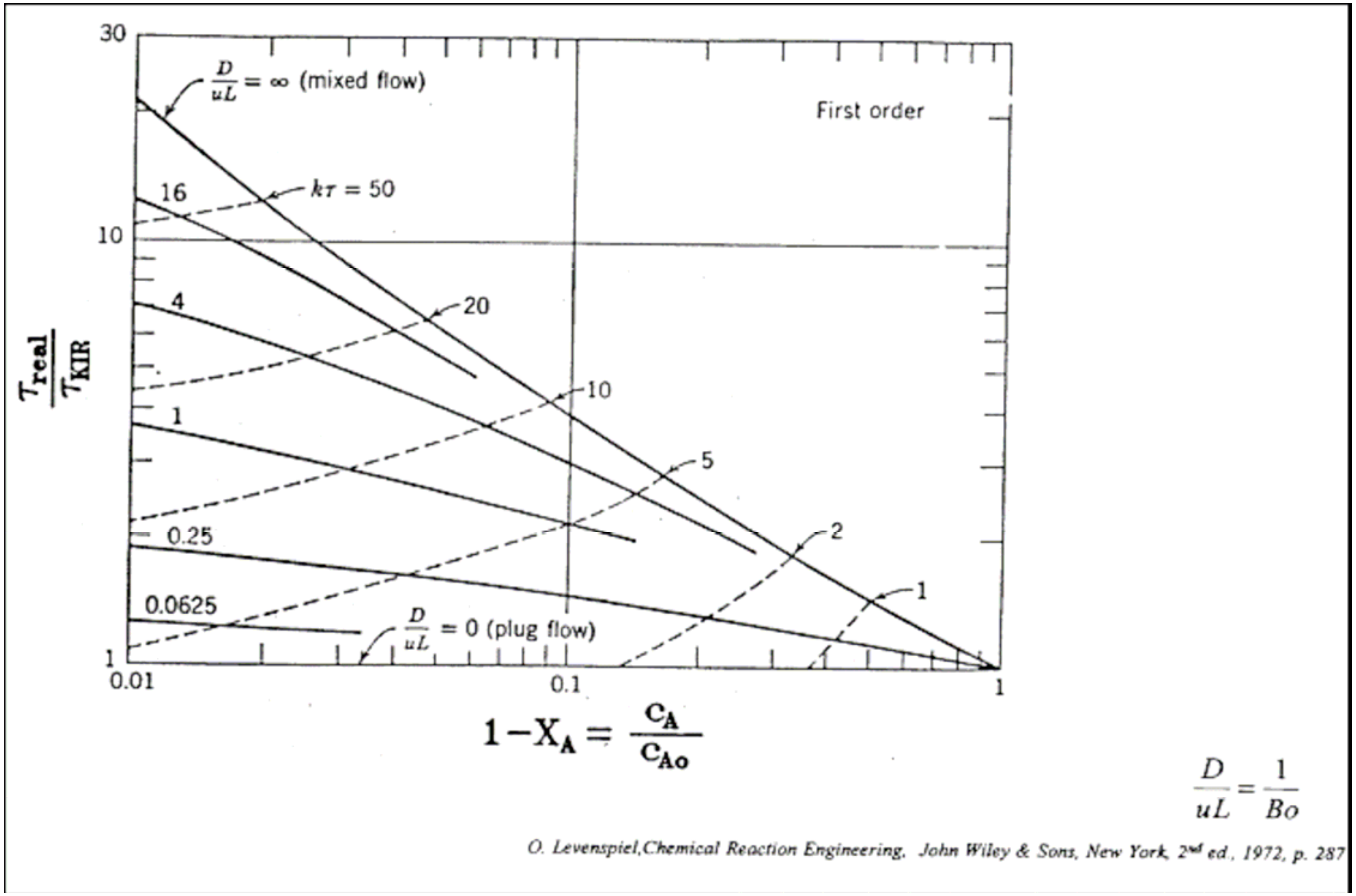
$Da = 1.5$ ($Bo_{\text{closed system}} = 8.3$)



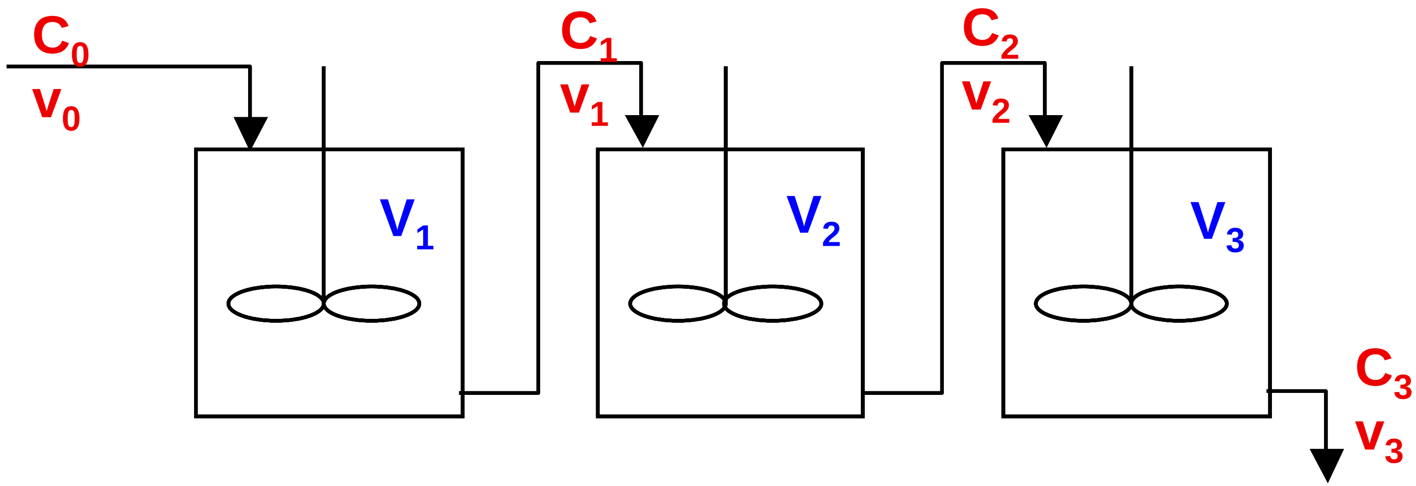
Comparison of conversions:

PFR	77.8%
CSTR	60.0%
Segregation model	72.4%
Dispersion model	**73.2%**

Conversion and Dispersion model (1st order rxn)



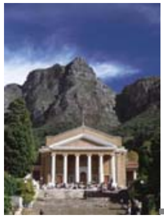
Tank-in-series model



Reactor is assumed to contain n equally sized CSTRs in series
(PFR can be viewed as an infinite number of CSTRs in series)

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

$$\sigma^2 = \frac{\tau^2}{n}$$



Determination of number of CSTRs in series from E-curve

The residence time distribution in a reactor has been determined and the E(t) data have been determined as shown below:

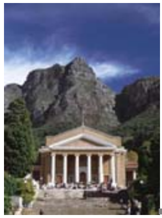
Time t, min	0	5	10	15	20	25	30	35
E, min^{-1}	0	0.03	0.05	0.05	0.04	0.02	0.01	0

Average residence time: 15 min

Variance: $\sigma^2 = \int_0^\infty (t - t_m)^2 \cdot E \cdot dt = 47.5 \cdot min^2$

Assuming tank in series model: $\sigma^2 = \frac{\tau^2}{n}$

n = 4.7



Conversion from tank-in-series model

Performance equation CSTR: $\tau_i = \frac{C_0 \cdot (X_i - X_{i-1})}{-r_i}$

For 1st order reaction: $\tau_i = \frac{C_{i-1} - C_i}{k \cdot C_i}$

$$\frac{C_i}{C_{i-1}} = \frac{1}{1 + k \cdot \tau_i}$$

$$\boxed{1 - X = \frac{C_i}{C_0} = \frac{1}{(1 + k \cdot \tau_i)^n} = \frac{1}{\left(1 + k \cdot \frac{\tau}{n}\right)^n}}$$

Assuming tank in series model (n = 4.7; τ_i = 15/4.7 = 3.16 min; $k \cdot \tau_i$ = 0.3) → X= 72.8%

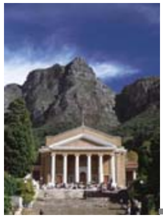
<u>Comparison of conversions:</u>

PFR	77.8%
CSTR	60.0%
Segregation model	72.4%
Dispersion model	73.2%
Tank-in-series model	**72.8%**

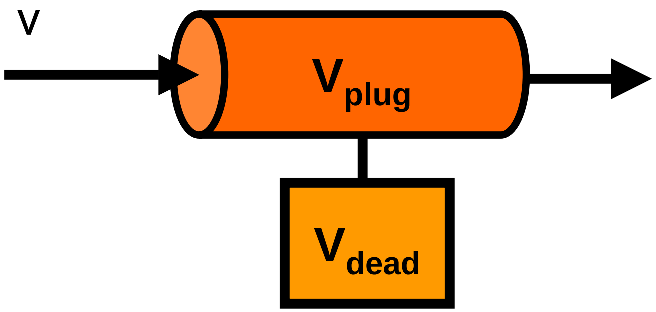
Compartment models

Considering the actual reactor as a set of ideal set-ups:

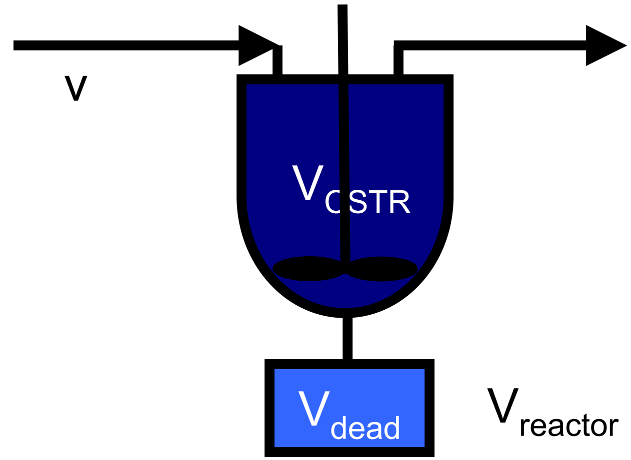
1. Ideal reactor(s) with dead volume
2. Ideal reactor(s) with by-pass
3. Ideal reactor(s) in parallel
4. Ideal reactors in series (tank-in-series model)
5. Combinations of dead volume, bypassing, ideal reactors in series/parallel



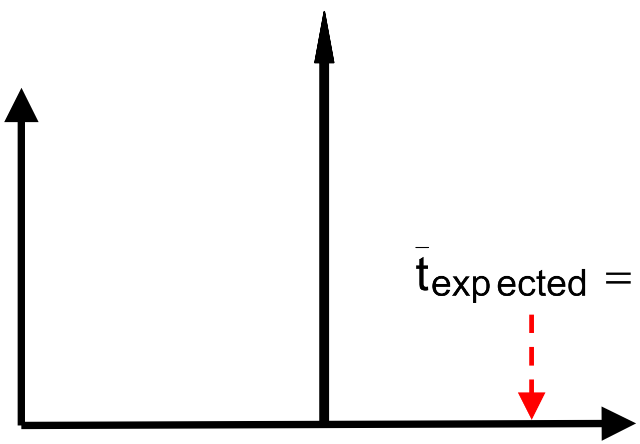
Compartment models
Ideal reactors with dead volume



$$V_{reactor} = V_{plug} + V_{dead}$$

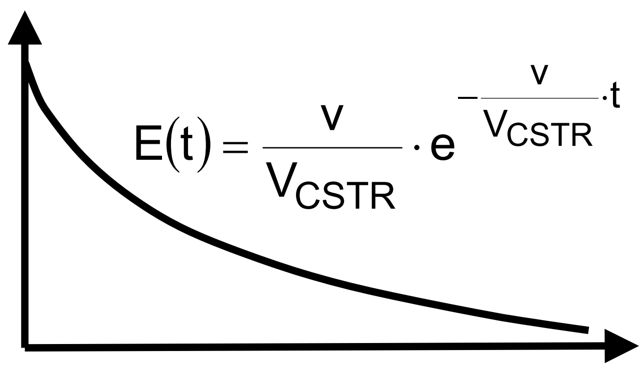


$$V_{reactor} = V_{CSTR} + V_{dead}$$

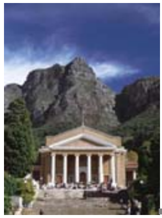


$$\bar{t}_{expected} = \frac{V_{reactor}}{v}$$

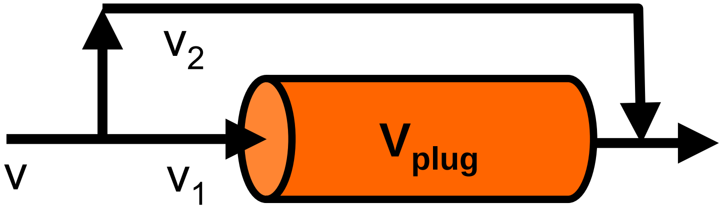
$$\bar{t} = \frac{V_{plug}}{v}$$

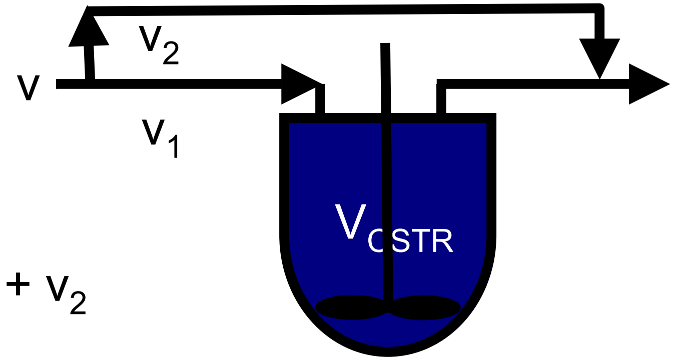


$$E(t) = \frac{v}{V_{CSTR}} \cdot e^{-\frac{v}{V_{CSTR}} \cdot t}$$

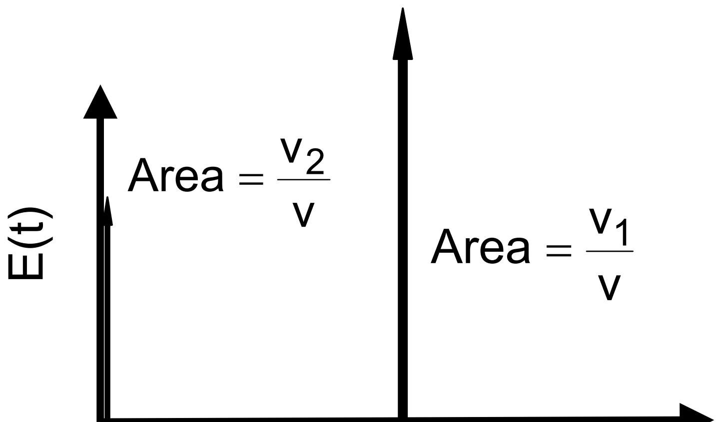


Compartment models
Ideal reactors with bypassing

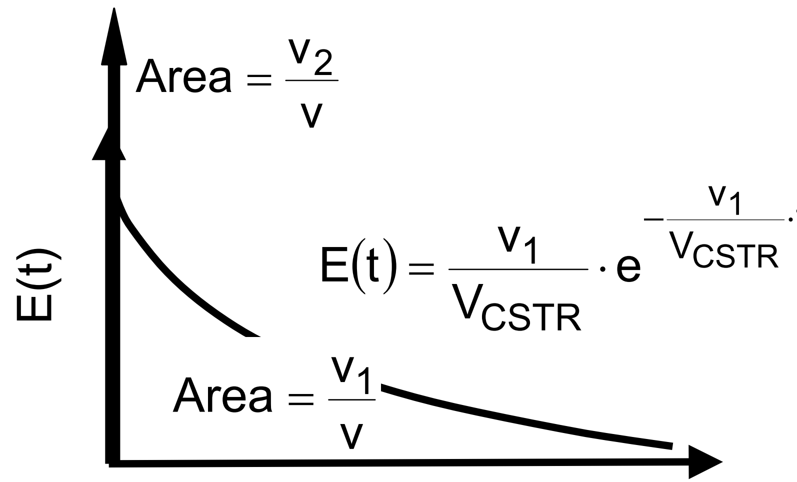




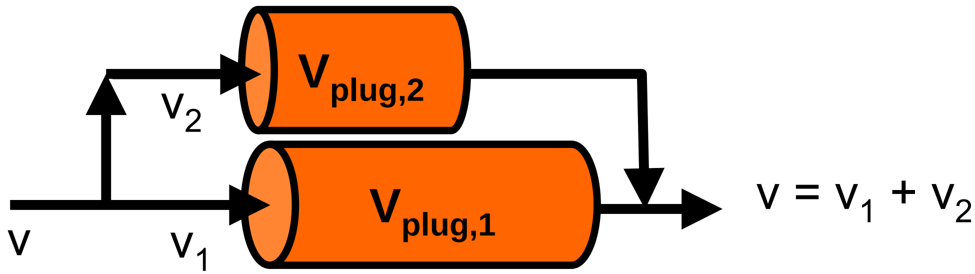
$v = v_1 + v_2$

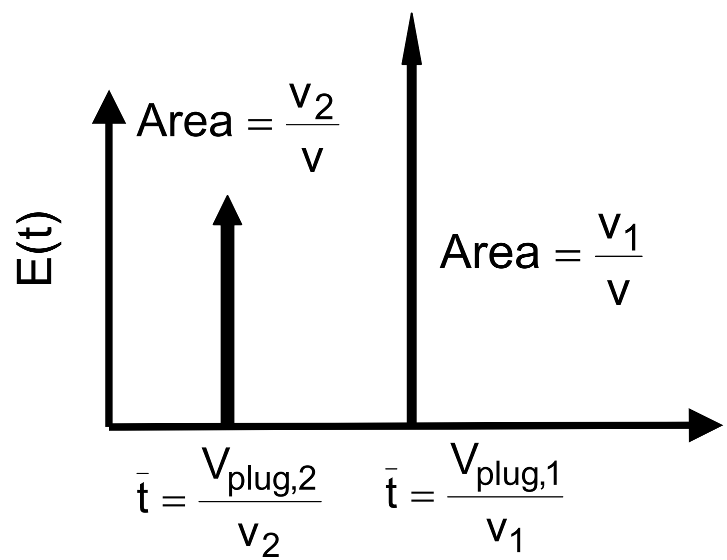


$\bar{t} = \frac{V_{plug}}{v_1}$

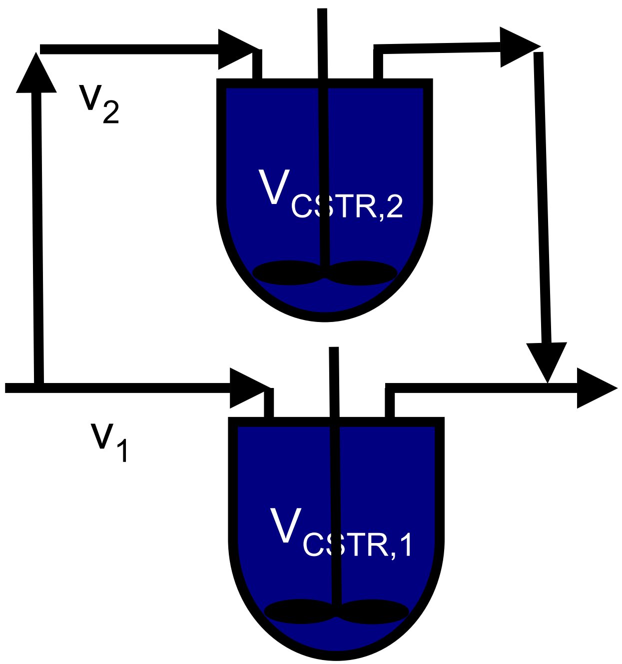


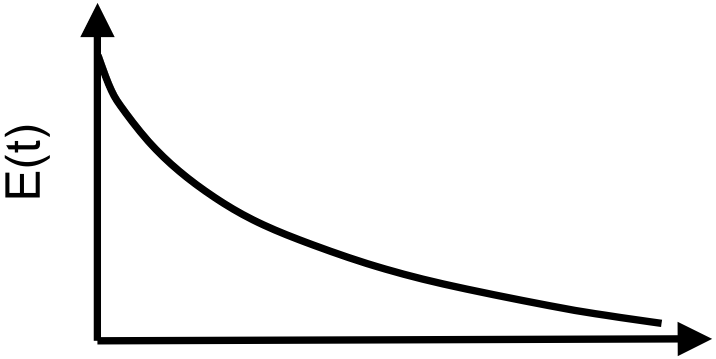
Compartment models
ideal PFRs in parallel



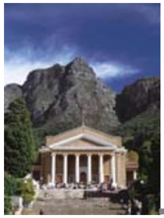


Compartment models
ideal CSTRs in parallel (1)

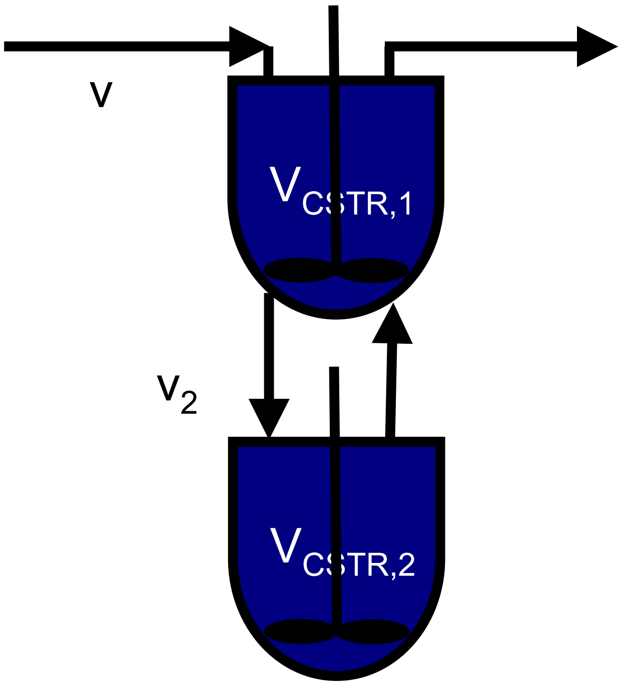


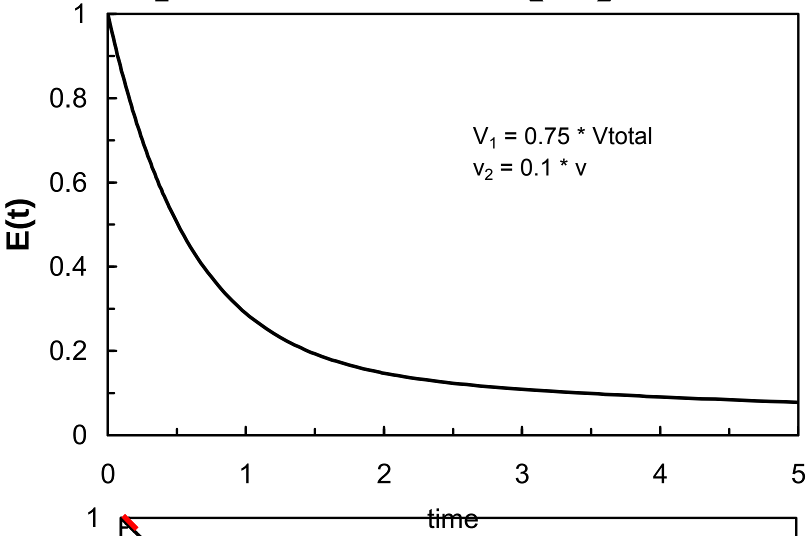


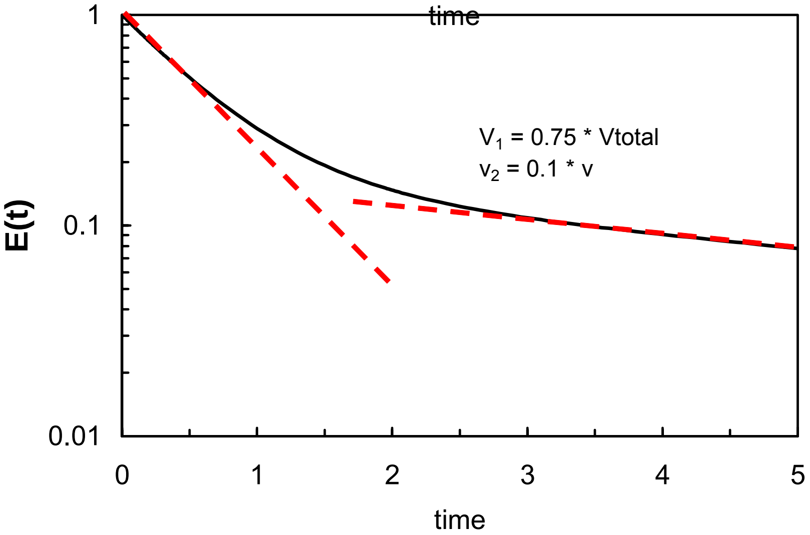
$$E(t) = \frac{v_1}{V_{CSTR,1}} \cdot e^{-\frac{v_1}{V_{CSTR,1}} \cdot t} + \frac{v_2}{V_{CSTR,2}} \cdot e^{-\frac{v_2}{V_{CSTR,2}} \cdot t}$$



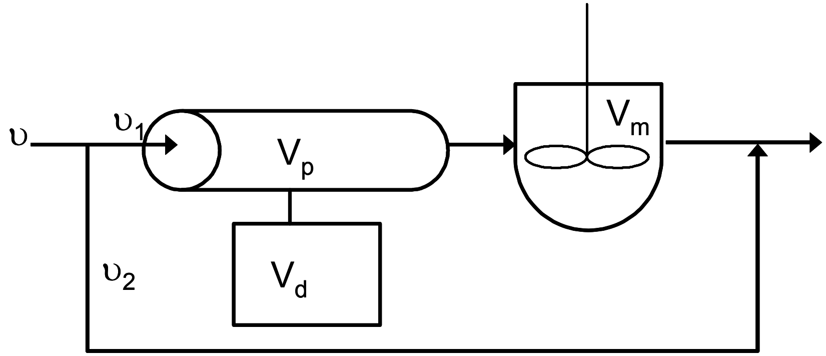
Compartment models ideal CSTRs in parallel (2)

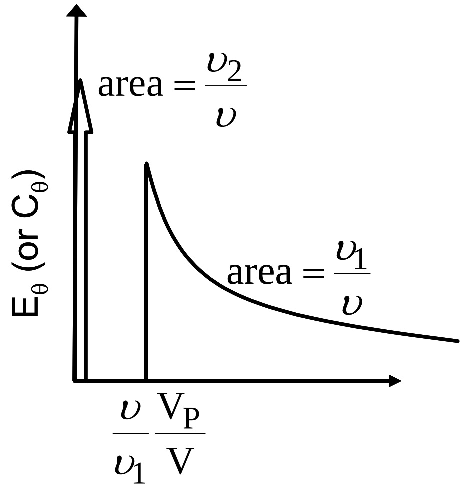






Compartment models combination of models





What is the “best” model

Dispersion model:

Gives insight in the design phase to anticipate non-ideal behaviour and the consequences

Compartment model

“Visualizes” the origin of possible non-ideal behaviour:

- by-passing
- dead volume
- mixing zones