Non-ideal reactors – from the RTD curves to conversions

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❑ **Non-ideal reactors**

❑ **Construction of C(t) and E(t)**

❑ **Convolution integral and the Step-input**

❑ t_m **and** τ **and other moments**

❑ **RTD of PFR/PBR and CSTR**

❑ **RTD of LFR**

Knowledge of the E(t) (or other) curves for a real reactor can provide insights into the reactors functioning

▶ Let the volume of the CSTR be V and mean residence time be τ

▶ The E(t) curve for this CSTR is given by the equation: $E(t) = \frac{1}{\tau}\exp(-t/\tau)$

▶ With only dead-volume, V_1, $then$: $V = V_{CSTR-D} + V_1$

▶ *Thus,* $\tau_{CSTR-D} < \tau$ (v_o is the same!)

▶ Thus, $E(t)$ will decay more rapidly and start from a larger value

▶ The $E(t)$ curve for an ideal CSTR with bypass can also be rationalized. There will be a bump in the exponential decay!
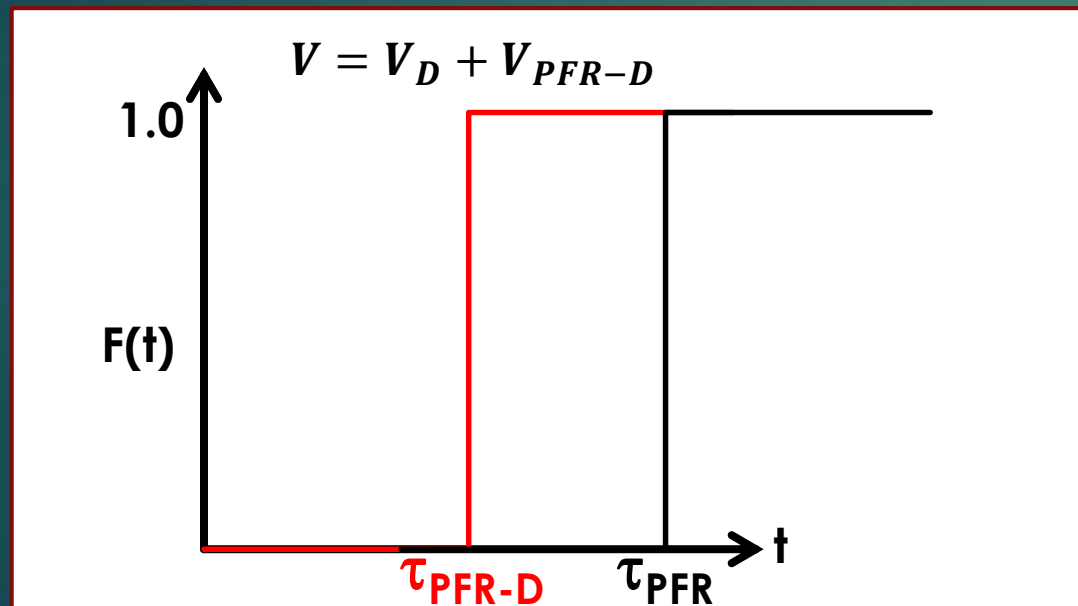
Deadzone (no mixing)

A real CSTR

$(1/\tau_{CSTR-D})$ **exp**$(-t/\tau_{CSTR-D})$

$(1/\tau)$ **exp**$(-t/\tau)$

E(t)
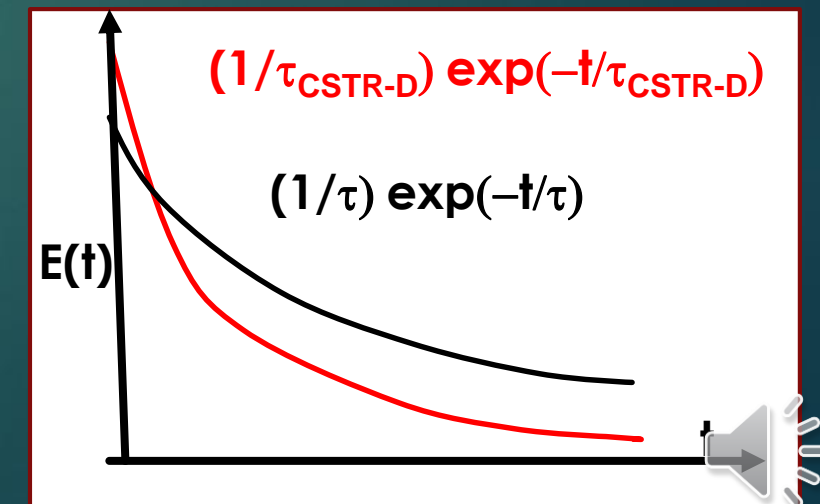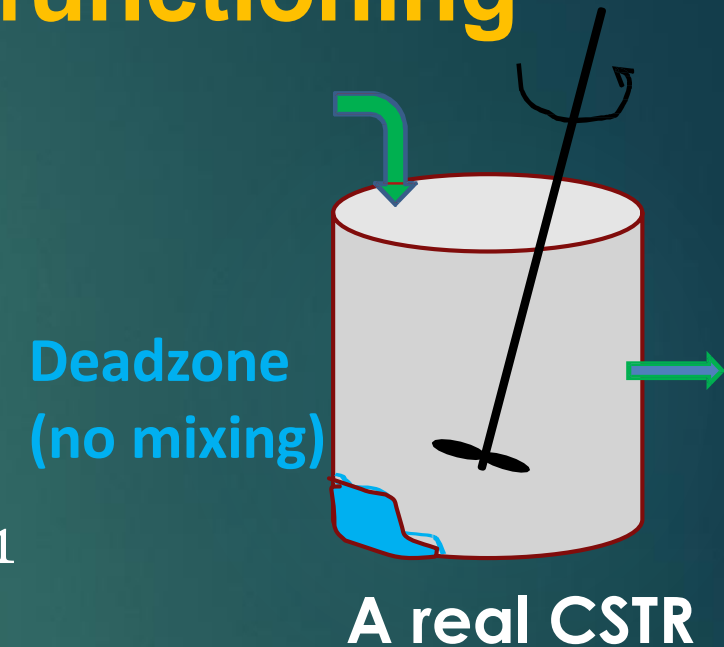
PFR with non-ideal flows

PFR with dead-volume

▶ With dead-volume V_D then with similar logic as before
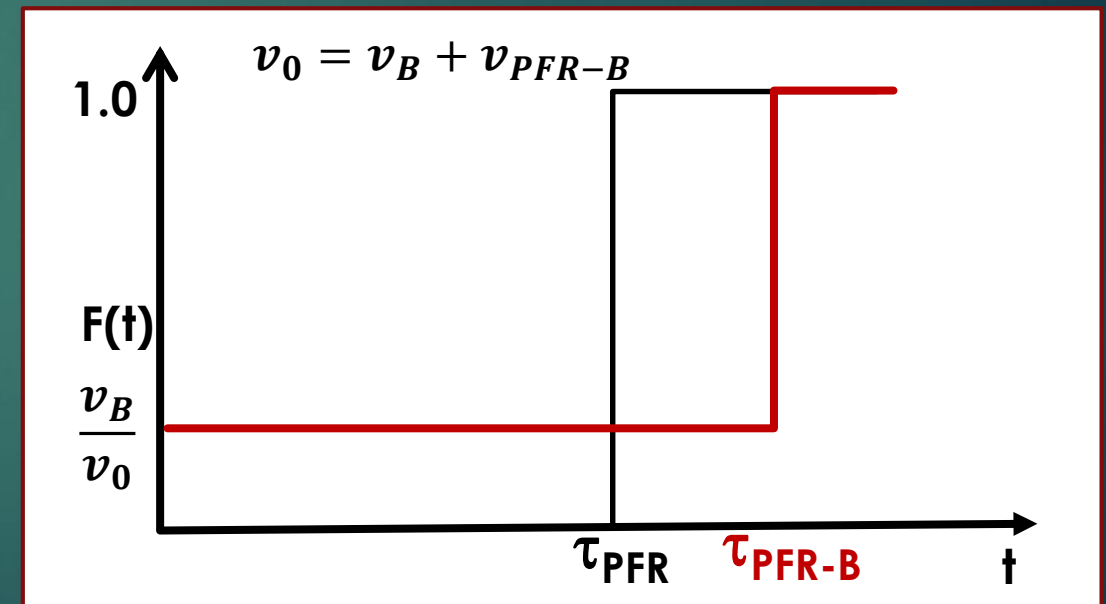
$\tau_{PFR-D} < \tau_{PFR}$ and the F(t) curves are shown

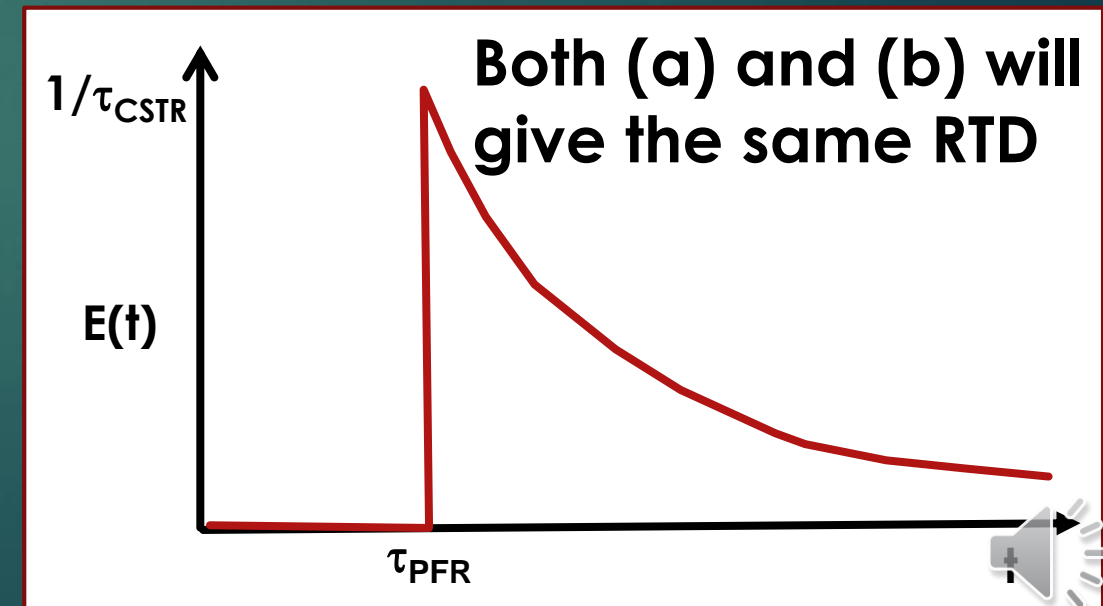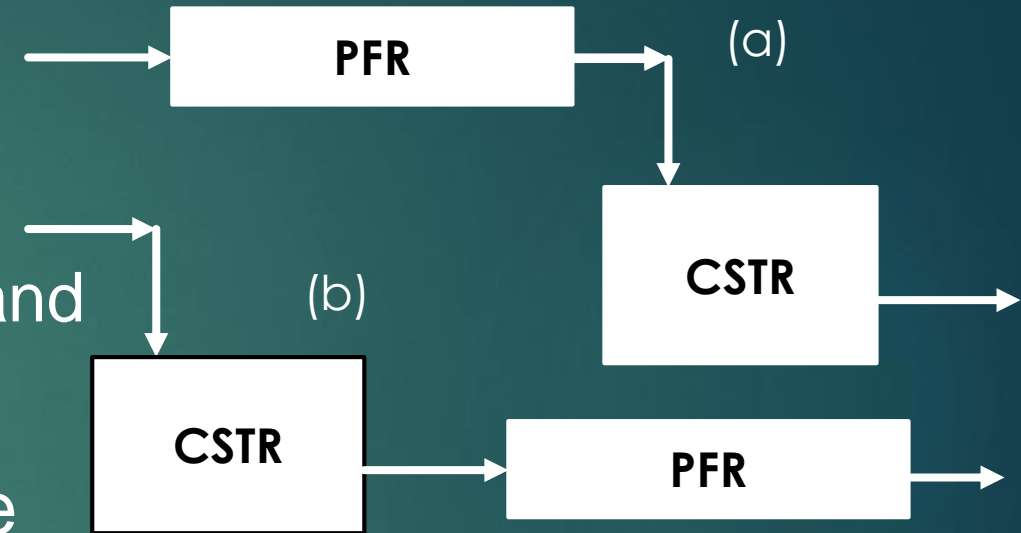

▶ How would the E(t) curve look like?

PFR with bypass

▶ With bypass-volumetric flow v_1 then some of v_o has been diverted to bypass and $\tau_{PFR-B} > \tau_{PFR}$ and the F(t) curves are shown

Reactor combinations and effects of (micro/macro) mixing

▶ Let us look at a combination of ideal reactors in series:

- (a) ideal PFR followed by an ideal CSTR and
- (b) ideal CSTR followed by an ideal PFR

▶ The residence time τ_{TPR} and τ_{CSTR} are the same

▶ The E(t) curve after the above reactor combinations are shown

▶ RTD given by: $E(t) = 0$ for t $< \tau_{PFR}$ and

$$E(t) = \frac{\exp\left(-\frac{(t-\tau_{PFR})}{\tau_{CSTR}}\right)}{\tau_{CSTR}} \text{ for t} \geq \tau_{PFR}$$

PFR (a)

CSTR

(b)

CSTR

PFR

Both (a) and (b) will give the same RTD

$1/\tau_{CSTR}$

E(t)

τ_{PFR}

Conversions for a 2nd order reaction in the combination of reactors

- Reaction $A \rightarrow products$, where $-r_A = kC_A^2$
  - Conversion would depend on $\tau_{CSTR}, \tau_{PFR}, k$ and C_{A0}
  - Assume all $\tau_{CSTR}, \tau_{PFR}, k$ and C_{A0} are equal to 1.0
- $CSTR \rightarrow PFR$ combo
  - $X_{CSTR} = 0.382$ and $X_{CSTR \rightarrow PFR} = 0.618$
- $PFR \rightarrow CSTR$ combo
  - $X_{PFR} = 0.5$ and $X_{PFR \rightarrow CSTR} = 0.634$
- Though the RTD is the same (previous overhead) the conversions are not!

RTD is unique for a particular reactor – not a complete description

- We see that for CSTR-PFR and PFR-CSTR combinations the conversions are not the same

  - For CSTR-PFR we have early mixing and then segregated flow, and for PFR-CSTR we have segregated flow and then late mixing

- RTD tells us how long fluid elements spend in the reactor

  - Not sufficient to determine performance of the reactor (e.g., conversion) and more information required

  - For first order reactions RTD is sufficient since only the time a fluid element spends in the reactor is required, and mixing (conc.) is not important

Models are required to describe quality of mixing or degree of segregation

▶ Models can then be used along with RTD and known kinetics to predict conversions

  ○ RTD + Model + kinetics $\Rightarrow$ exit X and C_A

▶ Five main models used

  ○ Zero adjustable parameters: (a) Segregation & (b) Maximum mixedness

  ○ One adjustable parameter: (a) Tank-in-series & (b) Dispersion

▶ Two adjustable parameter

Segregation model (little batch reactors!)

▶ In an CSTR, the entering fluid elements are distributed immediately and evenly throughout the reacting mixture

▶ Fluid elements of different ages mix completely → ideal CSTR

▶ Fluid elements of different ages do not mix at all then element completely segregated → non-ideal CSTR
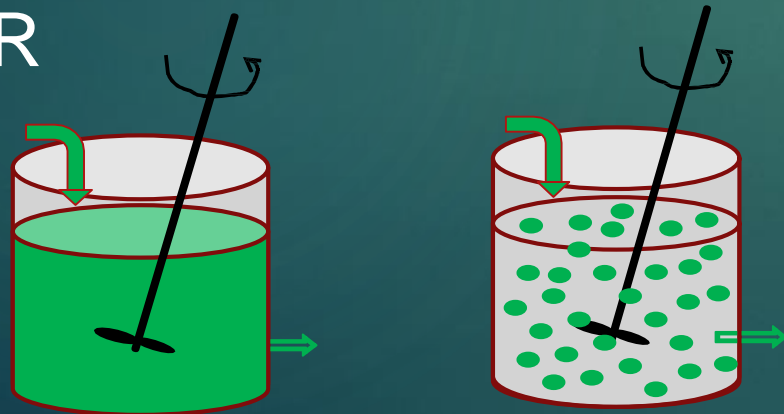
▶ In a PFR the segregated model can also be conceptualized

▶ After spending the required time in the reactor, given by the $E(t)$ curve, the fluid element is removed and mixed with the other stream

v_0 v_0
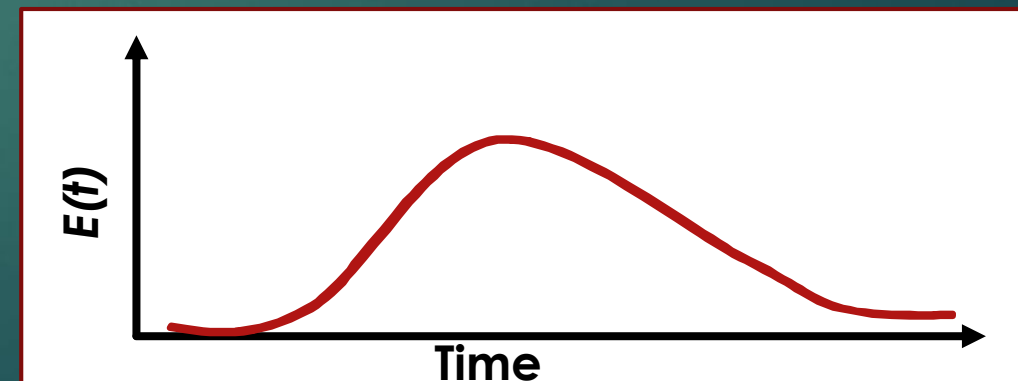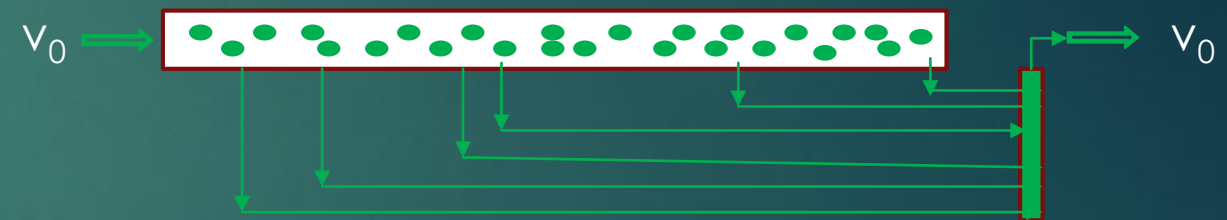
Reaction time is the time spent by each globule in the reaction environment

▶ Time spent is given by the RTD of the particular reactor

▶ Mean conversion at exit is average of the conversions of all exiting globules

▶ That is:

$$
\begin{bmatrix} \text{Mean conversion of} \\ \text{those fluid elements} \\ \text{spending between} \\ \text{t and t + dt in} \\ \text{the reactor} \end{bmatrix} = \begin{bmatrix} \text{Conversion achieved} \\ \text{in a fluid element after} \\ \text{spending a time t in} \\ \text{the reactor} \end{bmatrix} \times \begin{bmatrix} \text{Fraction of fluid elements} \\ \text{that spend between t and} \\ \text{t + dt in the reactor} \end{bmatrix}
$$

▶ Then: $d\bar{X} = X(t) * E(t)dt$ and summing over all globules

$$
\bar{X} = \int_0^\infty X(t).E(t).dt
$$

▶ Thus, knowledge of RTD + rate law + model (segregated flow) the conversion can be calculated

Application of the segregated model

▶ RTD + kinetics + Model → conversion

▶ 1st order reaction: $A \rightarrow products$

▶ Batch reactor: $\frac{dN_A}{dt} = r_A V \rightarrow N_{A0} \frac{dX}{dt} = -r_A V = kC_A V = kN_A = kN_{A0}(1-X)$

$$\frac{dX}{dt} = k(1-X)$$

$$X(t) = 1 - \exp(-kt)$$

▶ Mean conversion for a reactor with RTD of E(t) : $\bar{X} = \int_0^\infty X(t)E(t)dt$

▶ Thus, $\bar{X} = \int_0^\infty X(t)E(t)dt = \int_0^\infty [1 - \exp(-kt)]E(t)dt$ and

$$\bar{X} = 1 - \int_0^\infty \exp(-kt)E(t)dt$$

▶ Above equation can be applied for a 1st order reaction occurring in a reactor of known $E(t)$

Segregated model applied to a PFR and CSTR

▶ For a PFR: $E(t) = \delta(t - \tau)$

▶ Substituting, $\bar{X} = 1 - \int_0^\infty \exp(-kt)E(t)dt = 1 - \int_0^\infty \exp(-kt)\delta(t - \tau)dt$

$$\bar{X} = 1 - \exp(-k\tau)$$

▶ For a PFR and a 1st order reaction: $\frac{dX}{d\tau} = k(1 - X) \implies X = 1 - \exp(-k\tau)$

▶ Conversions using segregated model and MB equation for PFR are identical

▶ For a CSTR: $E(t) = \frac{1}{\tau}\exp(-t/\tau)$, and $\bar{X} = 1 - \int_0^\infty \exp(-kt)]\frac{1}{\tau}\exp(-t/\tau)dt$

▶ $\bar{X} = 1 - \int_0^\infty \frac{1}{\tau}\exp\left[-t\left(\frac{1}{\tau} + k\right)\right]dt = 1 + \frac{1}{\left(\frac{1}{\tau}+k\right)}\frac{1}{\tau}\exp\left[-t\left(\frac{1}{\tau} + k\right)\right]_0^\infty = 1 - \frac{1}{(1+k\tau)}$

$$\bar{X} = \frac{k\tau}{(1 + k\tau)} \quad same \ as \ that \ of \ CSTR$$

▶ Conversions based on segregated model and MB equation are identical

Segregated model applied to a LFR

▶ The RTD function for a LFR is given by:

$$E(t) = 0 \ for \ t < \frac{\tau}{2}$$

$$E(t) = \frac{\tau^2}{2t^3} \ for \ t \geq \frac{\tau}{2}$$

▶ Thus, $\bar{X} = 1 - \int_0^\infty \exp(-kt)E(t)dt = 1 - \int_{\tau/2}^\infty \exp(-kt)\frac{\tau^2}{2t^3} dt$ (Hilder's approx.)

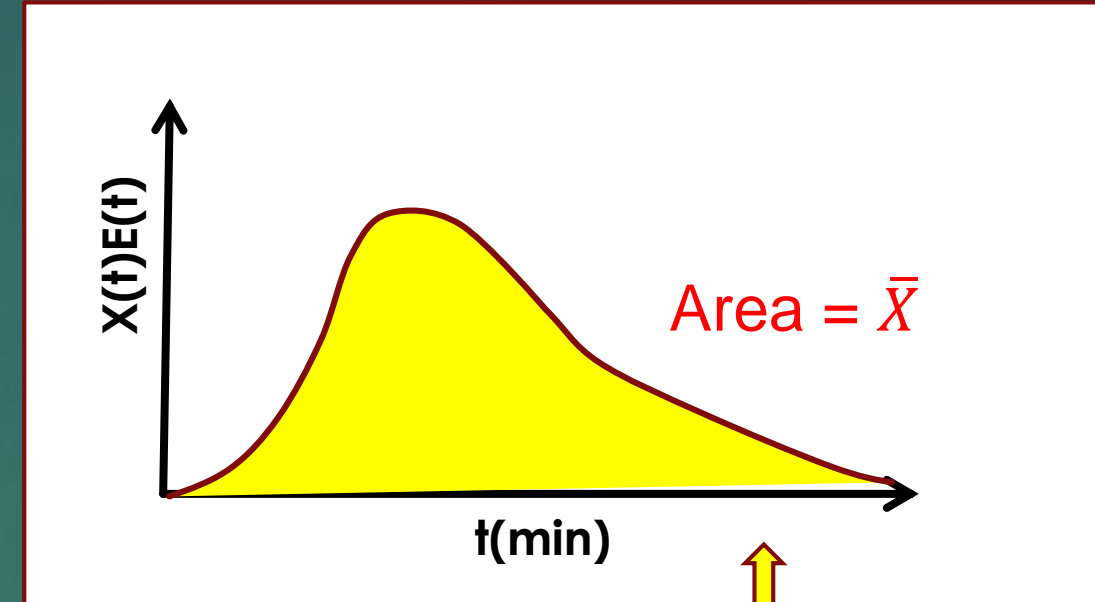$$\bar{X} = \frac{(4+Da)e^{0.5Da} + Da - 4}{(4+Da)e^{0.5Da} + Da}, where \ Da = k\tau$$
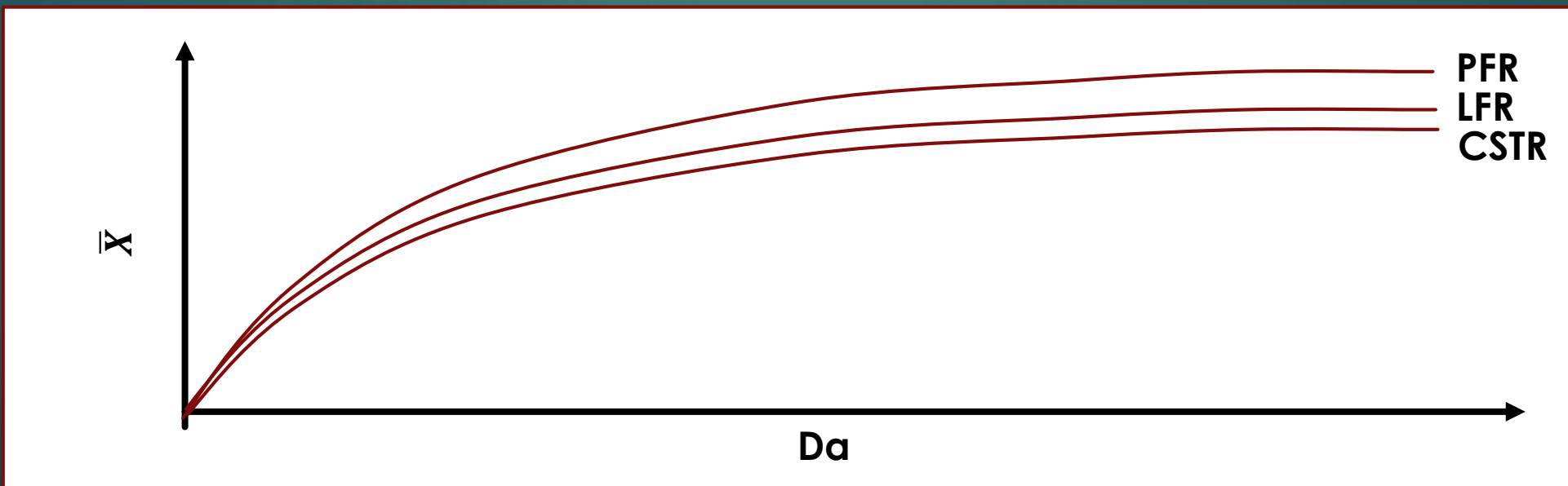
For an experimentally obtained RTD curve

▶ Experimentally determined *E(t)* curve from *C(t)*

E(t) curve: E(t) vs t(min)

X(t)E(t) vs t(min), Area = $\bar{X}$
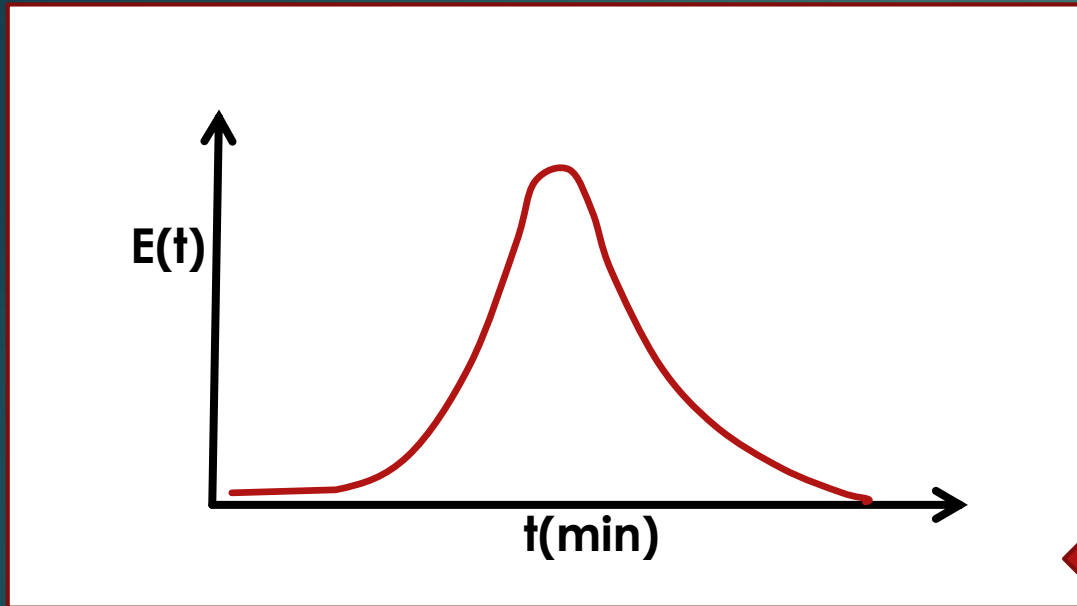
▶ *X(t)* determined for a batch reactor for specified kinetics

t (min)	C(t)	E(t) min^{-1}	X(t)	X(t).E(t) min^{-1}
0	0	0	0	0
1	1	0.02	0.095	0.0019
2	5	0.10	0.181	0.0180
And so on				