Introduction to Chemical Reactors

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6. Non-ideal reactors

René Bañares-Alcántara
room: 8239
tel: 73-9530
rene.banares@eng.ox.ac.uk

Objectives

- Introduce the concepts of
  - Residence Time Distribution (RTD)
  - mean residence time
  - mean outlet concentration
  - mean conversion
- Apply RTD to calculate the concentration and conversion in the stream exiting a reactor.

Sources for non-ideal reactors

- Metcalfe: Chapter 6
- Schmidt: Chapter 8
- Fogler: Chapters 13 and 14

Motivation

PFR (completely unmixed) and CSTR (completely mixed) reactors are never achieved in practice, however, the behaviour of real reactors can be modelled as a combination of both.

> Interestingly:
> - a PFR can be modelled as an infinite number of CSTR in series
> - a CSTR can be modelled as a PFR with infinite recycle

Any real reactor can be conceptualised as a collection of small elements each one with an associated residence time.

The concentration in each element is a function of its residence time.

RTD (Residence Time Distribution)

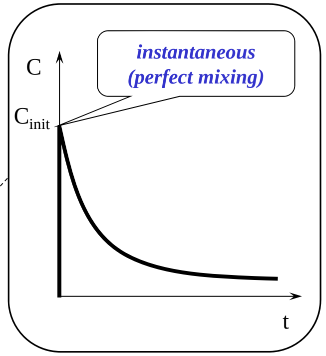
RTD (***Residence Time Distribution***) is the probability of an element of fluid residing in the reactor for a time *t*.

RTDs, denoted ***E(t)***, can be obtained by injecting a tracer at the input stream and then monitoring its concentration in the outlet.

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

normalised

RTD for an ideal CSTR



Introduce N moles of tracer at $t = 0$: $C_{init} = \frac{N}{V}$ — *instantaneous injection*

Non-SS CSTR MB: $V\frac{dC}{dt} = v\left(C_0 - C\right) + v_j r$ — *no reaction*

$\tau\frac{dC}{dt} = -C \qquad \text{BC}: C = C_{init} \ @ \ t = 0$

solution → $C(t) = C_{init}\, e^{-t/\tau}$

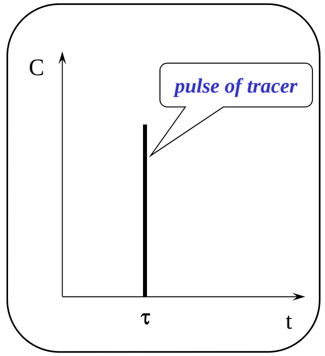
$$E(t) \equiv \frac{C(t)}{\int_0^\infty C(t)\,dt} = \frac{C_{init}\, e^{-t/\tau}}{C_{init}\,\tau} \longrightarrow \boxed{E(t)_{CSTR} = \frac{1}{\tau} e^{-t/\tau}}$$

$$\int_0^\infty C(t)\,dt = \int_0^\infty C_{init}\, e^{-t/\tau} dt = C_{init}\left[-\tau e^{-t/\tau}\right]_0^\infty = C_{init}\,\tau$$

RTD for an ideal PFR

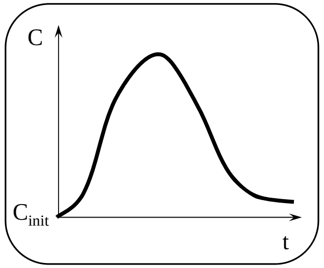
Introduce a pulse of N moles of tracer at $t = 0$.

$$\boxed{E(t)_{PFR} = \delta(t - \tau)}$$

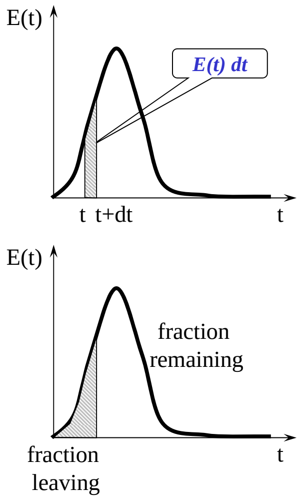


where
$$\delta(t-\tau) = 0 \quad \text{for} \quad t \neq \tau$$
$$\delta(t-\tau) \neq 0 \quad \text{for} \quad t = \tau$$
$$\int \delta(t-\tau)\,dt = 1$$

RTD for a non-ideal reactor



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



$E(t)\,dt$: fraction of effluent with a residence time between t and $(t+dt)$

Mean residence time ($\bar{t}$)

$\bar{t}$ is the time-weighted average over all residence times:

$$\boxed{\bar{t} = \int_0^\infty t\,E(t)\,dt}$$

for ideal reactors:

$$\bar{t}_{CSTR} = \int_0^\infty t\left[\frac{1}{\tau} e^{-t/\tau}\right] dt = \left[-t\, e^{-t/\tau}\right]_0^\infty + \int_0^\infty e^{-t/\tau} dt = \tau$$

by parts

$$\bar{t}_{PFR} = \int_0^\infty t\,\delta(t-\tau)\,dt = \tau$$

δ(t-τ) is zero for all times except t = τ

as expected!

Average values

In fact, the average value of any variable $f(t)$ is:

$$\overline{f} \equiv \int_0^\infty f(t)\cdot E(t)\,dt$$

The ***mean outlet concentration*** of reactant:

$$\overline{C_A} \equiv \int_0^\infty C_A(t)E(t)\,dt$$

The ***mean conversion*** in a non-ideal reactor:

$$\overline{X} \equiv \int_0^\infty X(t)\cdot E(t)\,dt$$

Mean conversion ($\bar{X}$)

If we treat each fluid element in the reactor as a well-mixed batch reactor (for a first order reaction A → B):

$$C_A = C_{A0}\exp[-kt] \quad \rightarrow \quad \frac{C_A}{C_{A0}} = 1 - X = \exp[-kt] \quad \rightarrow \quad X = 1 - \exp[-kt]$$

for ideal reactors:

$$\overline{X}_{CSTR} = \int_0^\infty \left(1-e^{-kt}\right)\left[\frac{1}{\tau}e^{-t/\tau}\right]dt = \left[\frac{1}{\tau}(-\tau)e^{-t/\tau}\right]_0^\infty - \frac{1}{\tau}\int_0^\infty e^{-kt-\frac{t}{\tau}}dt = \frac{k\tau}{1+k\tau}$$

by parts

$$\overline{X}_{PFR} = \int_0^\infty \left(1-e^{-kt}\right)\cdot\delta(t-\tau)\,dt = 1-e^{-k\tau}$$

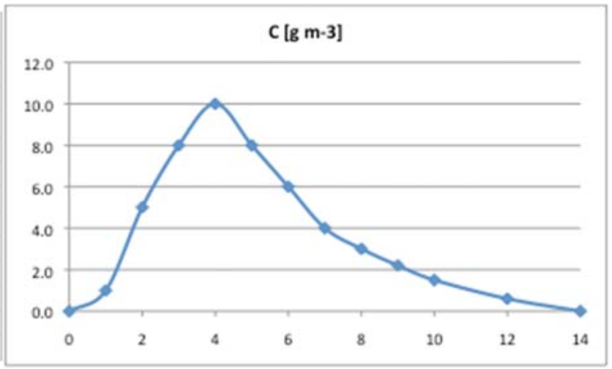
δ(t-τ) is zero for all times except t = τ

again, as expected!

Example: C(t) curve for tracers (Example 13-1 in Fogler)

A tracer is injected as a pulse to a reactor and the effluent concentration is measured:

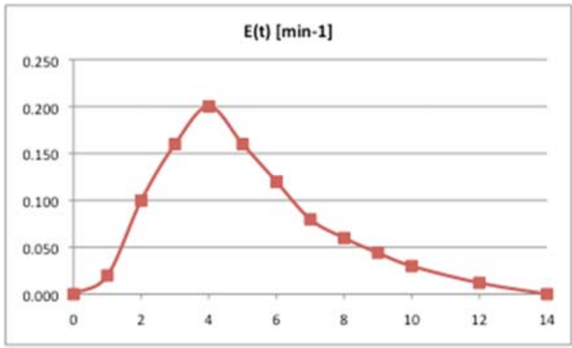
t [min]	C [g m-3]
0	0.0
1	1.0
2	5.0
3	8.0
4	10.0
5	8.0
6	6.0
7	4.0
8	3.0
9	2.2
10	1.5
12	0.6
14	0.0



Example: E(t) curve for tracers

$$E(t) \equiv \frac{C(t)}{\int_0^\infty C(t)\,dt} = \frac{C(t)}{50.033}$$ (the integral is evaluated numerically using Simpson´s rule)

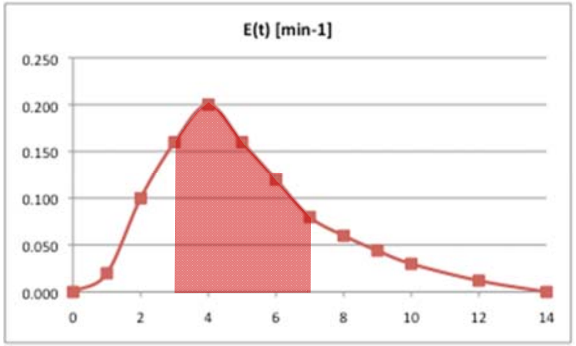
t [min]	E(t) [min-1]
0	0.000
1	0.020
2	0.100
3	0.160
4	0.200
5	0.160
6	0.120
7	0.080
8	0.060
9	0.044
10	0.030
12	0.012
14	0.000



Example: fraction of material with a given residence time

What is the fraction of the material that has spent between 3 and 7 minutes in the reactor?

t [min]	E(t) [min-1]
0	0.000
1	0.020
2	0.100
3	0.160
4	0.200
5	0.160
6	0.120
7	0.080
8	0.060
9	0.044
10	0.030
12	0.012
14	0.000



$$\int_3^7 E(t)\,dt = \frac{1}{3}\left[0.16 + 4(0.2) + 2(0.16) + 4(0.12) + 0.08\right] = 0.61$$

(Example: numerical integration)

For N+1 points (N even):

$$\int_{X_0}^{X_N} f(X)\,dX = \frac{h}{3}\left[f_0 + 4f_1 + 2f_2 + 4f_3 + 2f_4 + \ldots + 4f_{N-1} + f_N\right]$$

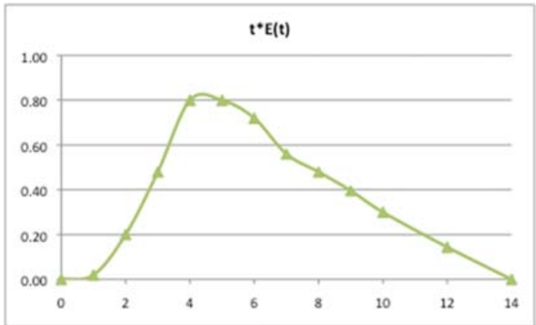
where $h = \dfrac{X_N - X_0}{N}$

Example: mean residence time for tracers

$$\bar{t} = \int_0^\infty tE(t)\,dt = 5.155\,\text{min}$$

(t_{mean} is the mean residence time; it is also evaluated using Simpson´s rule)

t [min]	E(t) [min-1]	t*E(t)
0	0,000	0,00
1	0,020	0,02
2	0,100	0,20
3	0,160	0,48
4	0,200	0,80
5	0,160	0,80
6	0,120	0,72
7	0,080	0,56
8	0,060	0,48
9	0,044	0,40
10	0,030	0,30
12	0,012	0,14
14	0,000	0,00



Laminar flow tubular reactors

If a reactor has mixed flow, $E(t)$ will be between the limits of a perfectly mixed (CSTR) and unmixed (PFR) reactors.

In a PFR:

- if u is low → Re < 2100 → laminar flow (no radial or axial mixing)
- if u is high → Re > 2100 → turbulent flow (axial dispersion)

For laminar flow, the velocity profile is:

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

$$U_{max} = 2\bar{u}$$

$$\bar{u} = \frac{v}{A}$$

Laminar flow tubular reactors

$$E(t) \equiv \frac{\text{fraction of total fluid passing between } r \text{ and } (r+dr)}{\text{total fluid passing through the reactor}}$$

$$= \frac{\int_0^r (2\pi r) u(r)\, dr}{\int_0^R (2\pi r) u(r)\, dr} = \frac{\int_0^r (2\pi r) u(r)\, dr}{v} = \frac{\tau}{2t^3}$$

(complete derivation @ Fogler, 3rd ed., Section 13.4.3)

So, the RTD for a laminar flow tubular reactor is:

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

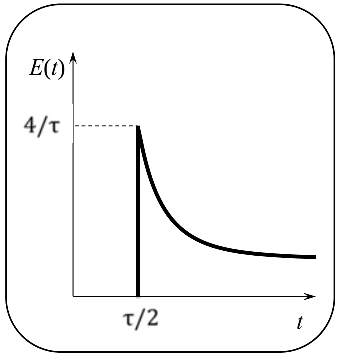
Laminar flow tubular reactors: average conversion

Note that the minimum time that a fraction of fluid spends in the reactor (t_{min}) is:

$$t_{min} = \frac{L}{U_{max}} = \frac{L}{2\bar{u}}\left(\frac{\pi R^2}{\pi R^2}\right) = \frac{V}{2v} = \frac{\tau}{2}$$

So, $E(t) = 0 \qquad t < \frac{\tau}{2}$

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



Laminar flow tubular reactors: average conversion

Since $\boxed{\bar{X} \equiv \int_0^\infty X(t) \cdot E(t)\, dt}$

$$\bar{X}_{\text{laminar flow PFR}} = \int_{\frac{\tau}{2}}^\infty X(t) \cdot E(t)\, dt = \int_{\frac{\tau}{2}}^\infty (1 - \exp[-kt]) \cdot \frac{\tau^2}{2t^3} dt$$

and, comparing the conversion of a laminar flow PFR vs a PFR for 1st and 2nd order kinetics:

$$\frac{\bar{X}_{\text{laminar flow PFR}}}{\bar{X}_{\text{PFR}}} = \frac{\int_{\frac{\tau}{2}}^\infty (1 - \exp[-kt]) \cdot \frac{\tau^2}{2t^3} dt}{1 - \exp[-k\tau]} \quad \begin{cases} > 0.88 \text{ (worst case)} \\ = 1.0 \text{ (best case)} \end{cases}$$

… PFR assumption are a good approximation!

Non-ideal reactors

We treat each fluid element in the reactor as a well-mixed batch reactor.

For a batch reactor (with a 1st order, irreversible reaction A → B):

design equation: $\frac{dC_A}{dt} = \nu_j r = -kC_A \quad \overset{\text{soln}}{\Rightarrow} \quad C_A = C_{A0} e^{-kt}$

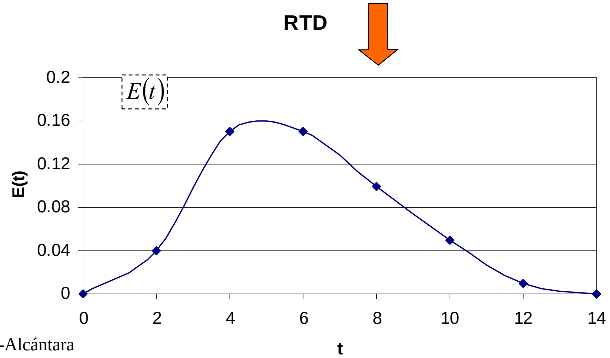
$$\boxed{\bar{C}_A = \int_0^\infty C_A(t) E(t)\, dt = C_{A0} \int_0^\infty e^{-kt} E(t)\, dt}$$

Non-ideal reactors: example (1) (6.2 Metcalfe)

Input data:

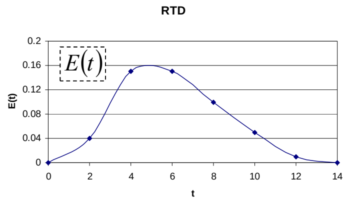
- first order, liquid phase reaction A $\rightarrow$ B, $\boldsymbol{r} = k\,C_A$, $k = 0.307\ s^{-1}$
- $E(t)$ vs. t

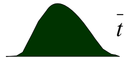
t [s]	0	2	4	6	8	10	12	14
E [s^{-1}]	0.00	0.04	0.15	0.15	0.10	0.05	0.01	0.00



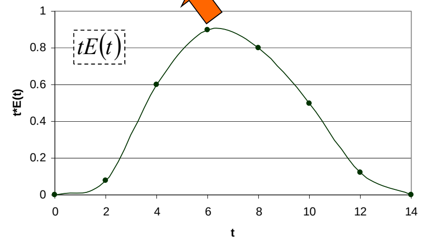
Non-ideal reactors: example (2) (6.2 Metcalfe)

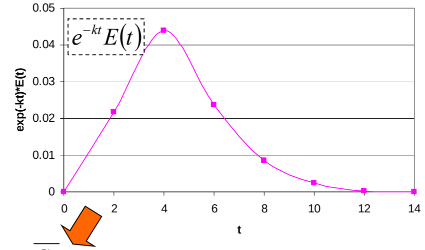
Input data:

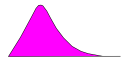




$$\bar{t} = \int_0^\infty tE(t)\,dt = 6.0$$







$$\frac{\overline{C_A}}{C_{A0}} = 1 - X_A = \int_0^\infty e^{-kt} E(t)\,dt = 0.201$$

Non-ideal reactors: example (3) (6.2 Metcalfe)

Solution:

$$X_{A,non-ideal} = 1 - 0.201 = 0.799$$

$$\bar{t}_{non-ideal} = 6\ s$$

mean residence time

Compare with CSTR and PFR:

- CSTR $\quad \dfrac{C_A}{C_{A0}} = \dfrac{1}{1+k\tau} \Rightarrow X_{A,CSTR} = 1 - \dfrac{1}{1+k\tau} = \dfrac{k\tau}{1+k\tau} = 0.65$

$$X_A = 1 - \frac{C_A}{C_{A0}} \quad ; \quad \tau = 6\ s$$

- PFR $\quad \dfrac{C_A}{C_{A0}} = \exp[-k\tau] \Rightarrow X_{A,PFR} = 1 - \exp[-k\tau] = 0.84$

Some *RTDs* for non-ideal reactors (Fig 8-1, Schmidt)