Chemical reaction engineering

Chapter 16 : Residence time distributions of chemical reactors.

General considerations

→ Models developed so far are for perfectly mixed batch reactor, the plug flow tubular reactor, packed bed reactor, and perfectly mixed continuous tank reactor

→ Real world behavior is often very different from the ideal behavior

⇒ Use residence time distribution to analyze and characterize non-ideal reactors.

→ diagnose problems of reactor operations

→ predict conversion in existing reactor when new chemical reaction is used in the reactor.

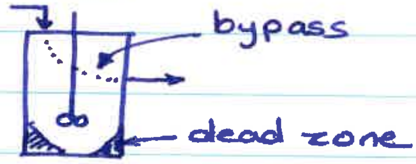
Notes on
Elements of chemical reaction engineering, H. Scott Fogler
- Ranjeet Utikar

Examples of non-ideality

packed bed

- path is not straight
- nonuniform flow

CSTR



- Describing deviation from ideal reactor mixing pattern
  - ⇒ Residence time distribution (RTD)
  - ⇒ quality of mixing
  - ⇒ model used to describe the system

Residence time distribution (RTD) function

- popularized by prof. P.V. Dankwerts.

Residence time : The time atoms have spent in the reactors.

plug flow reactor
ideal batch reactor } atoms spend exactly same time in these two reactors.

CSTR : Feed introduced into a CSTR becomes completely mixed with the material already in the reactor.

⇒ some atoms entering the CSTR leave almost immidiately.

⇒ other atoms remain in the reactor almost forever as all the material recirculates within the reactor and is virtually never removed from the reactor at one time.

⇒ Distribution of residence times can significantly affect reactor performance

- The RTD is a characteristic of the mixing that occurs in the chemical reactor.
- RTD yields distinctive clues to the type of mixing occuring within it and is one of the most informative characteristic of the reactor

Measurement of RTD

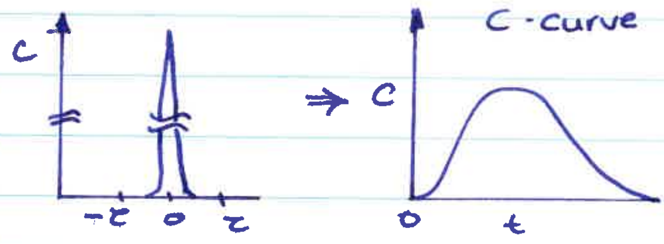
→ determined experimentally
→ Injecting 'tracer' into the reactor at some time $t = 0$ and then measuring the tracer conc. c in the effluent stream as a function of time.

Properties of tracer
- Inert ∴ non-reactive
- easily detectable
- Similar physical properties to the reacting mixture
- completely soluble in reacting mixture
- does not adsorb on reactor walls

— Tracer behavior should mimic the behavior of material flowing in the reactor.

Common tracers : colored dye, radioactive material, inert gases

Pulse input experiment



pulse injection   pulse response

- An amt of tracer N_0 is suddenly injected in one shot into the feed stream

— outlet conc. is measured with time.

- Lets consider single-input and single-output system
- only flow carries the tracer material
- No dispersion
- Increment of time Δt is sufficiently small that conc of tracer $C(t)$ exiting between t and $t+\Delta t$ is essentially same

Amount of tracer material leaving the reactor between t and $(t+\Delta t)$

$$\Delta N = C(t)\, \upsilon\, \Delta t \qquad (1)$$

υ : vol. flow rate

dividing by the total amount of material that was injected

$$\frac{\Delta N}{N_0} = \frac{\upsilon C(t)}{N_0} \Delta t$$

~~fraction of material~~ that has residence time in the reactor betn t and $t+\Delta t$

For pulse injection Let

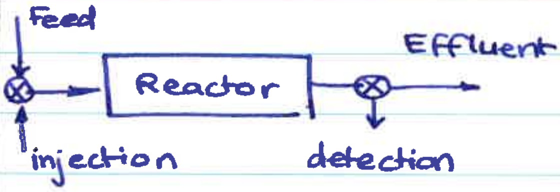
$$E(t) = \frac{\upsilon C(t)}{N_0}$$

... Residence time function

⇓

Function that describes in quantitative manner how much time different fluid elements have spent in the reactor

$$\therefore \frac{\Delta N}{N_0} = E(t)\,\Delta t \quad \text{—} (1)$$



- $E(t)dt$ is the fraction of fluid exiting the reactor that has spent between time t and $t+\Delta t$ inside the reactor.

If N_0 is not known directly, it can be obtained from the outlet conc. measurements by summing up all the amounts. from $0 \rightarrow \infty$

writing 1 in differential form

$$dN = \upsilon C(t)\,dt$$

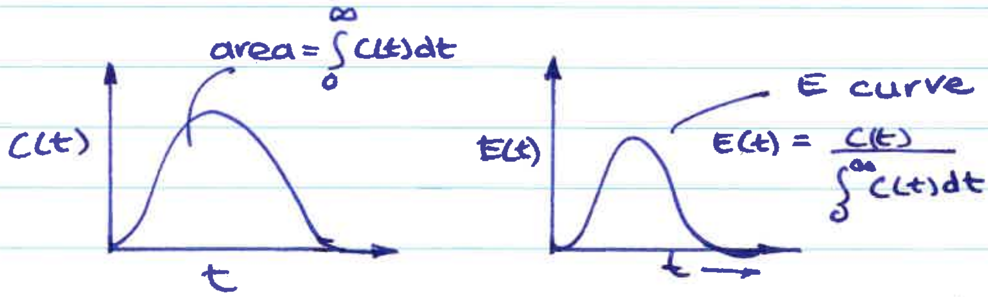
Integrating

$$N_0 = \int_0^\infty \upsilon C(t)\,dt$$

υ is usually constant

$$\therefore \boxed{E(t) = \frac{C(t)}{\int_0^\infty C(t)\,dt}} \quad \text{--- (3)}$$

The E curve is just C curve divided by the area under C curve



$$\boxed{\text{Fraction of material leaving the reactor that has resided in the reactor between } t_1 \text{ \& } t_2 = \int_{t_1}^{t_2} E(t)\,dt} \quad \text{--- (4)}$$

- Fraction of all the material that has resided for a time t in the reactor between $t=0$ and $t=\infty$ is 1.

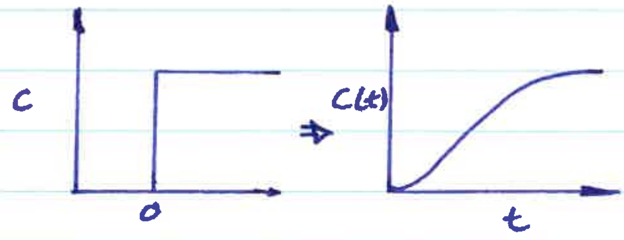
$$\therefore \int_0^\infty E(t)\,dt = 1$$

Difficulties with pulse technique

- Obtaining a reasonable pulse at the reactor entrance
  - Injection time should be very short compared to residence times in various segments of the reactor
  - There must be negligible dispersion between the point of injection and the entrance to the reactor.

↳ If these conditions are achieved, pulse technique is a simple and direct way to obtain RTD

Step tracer experiments



step injection → step response

- Inlet is either perfect pulse input (Dirac delta function)
- or imperfect pulse

$\underbrace{\text{or imperfect pulse}}_{\text{determine } E(t)}$

- Cumulative distribution $(F(t))$ can be determined from step input

Cumulative distribution gives the fraction of material $F(t)$ that has been in the reactor at time t or less.

Consider constant tracer addition to a feed that is initiated at $t=0$

$$C_{out}(t) \begin{cases} = 0 & t<0 \\ = C_0, \text{ const} & t \geq 0 \end{cases}$$

The conc. of tracer in feed is kept at this level until the conc. in effluent is almost same as feed.

As inlet conc. is constant with time, C_0, we can take it out of integral sign

$$C_{out}(t) = C_0 \int_0^t E(t')\,dt'$$

dividing by t_0

$$\left[\frac{C_{out}(t)}{C_0}\right]_{step} = \int_0^t E(t')\,dt' = F(t)$$

$$F(t) = \left[\frac{C_{out}(t)}{C_0}\right]_{step} \quad \text{— } ⑤$$

we differentiate ⑤ to obtain RTD function

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

- Positive step is usually easier to carry out experimentally than the pulse test.

- Total amount of tracer in the feed over the period of test does not have to be known

Drawbacks

- sometimes it may be difficult to maintain const. tracer concentration in the feed.
- Obtaining RTD involves differentiation of the data
  - ↳ on occasions differentiation can lead to large errors.
- Large amount of tracer is required

Other tracer techniques

- Negative step (elution)
- frequency response method
- methods that use inputs other than pulse or step

↳ much more difficult to carry out. and are not encountered often.

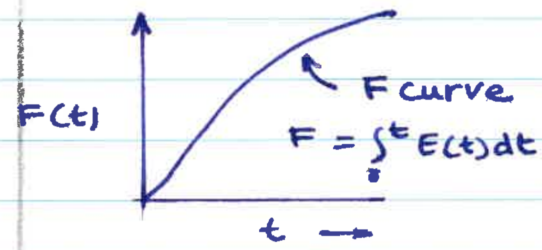
Characteristics of the RTD

$E(t) \Rightarrow$ Exit age distribution function

Integral relationships

$$\int_0^t E(t)\,dt = F(t) =$$ Fraction of effluent that has been in the reactor for less than t

$$\int_t^\infty E(t)\,dt = 1 - F(t) =$$ Fraction of effluent that has been in the reactor for longer than t



- Sometimes F curve is used in the same manner as the RTD in modeling chemical reactors

Mean residence time : First moment of RTD function

$$t_m = \frac{\int_0^\infty t\,E(t)\,dt}{\int_0^\infty E(t)\,dt} = \int_0^\infty t\,E(t)\,dt$$

In absence of dispersion, and for constant volumetric flow rate

$t_m = \tau$ $\nrightarrow$ only for closed systems

$V = v t_m$

Other moments of RTD

Variance (σ^2) : square of std. deviation

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

... magnitude indicates spread of the distribution. Greater $\sigma^2 \rightarrow$ greater spread

Skewness (s^3)

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

... magnitude measures extent that the distribution is skewed in one direction in reference to mean.

$\Rightarrow$ It is common to compare moments instead of comparing entire distribution

Normalized RTD function

- Frequently a normalized function is used instead of $E(t)$

Let $\theta \equiv \frac{t}{\tau}$ ... Number of reactor volumes of fluid based on entrance conditions that have flowed through the reactor in time t

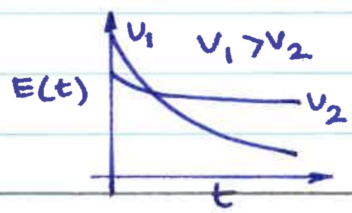
$$E(\theta) = \tau E(t)$$

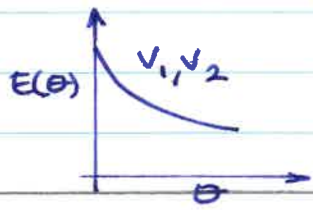
$$\int_0^\infty E(\theta)\, d\theta = 1$$

⇒ The flow performance inside reactors of different sizes can be compared directly.

⇒ If normalized function $E(\theta)$ is used all perfectly mixed CSTRs have numerically the same RTD.

→ If the simple function $E(t)$ is used numerical values of $E(t)$ can differ substantially.





$$E(t) = \frac{1}{\tau} e^{-t/\tau}$$

$$E(\theta) = e^{-\theta}$$

Internal age distribution $I(\alpha)$

A function such that $I(\alpha)\Delta\alpha$ is the fraction of material inside the reactor that has been inside for a period of time between α and $\alpha + \Delta\alpha$

In catalytic reaction using catalyst whose activity decays with time, $I(\alpha)$ is of importance and can be used to model the reactor

$$I(\alpha) = \frac{(1 - F(\alpha))}{\tau}$$

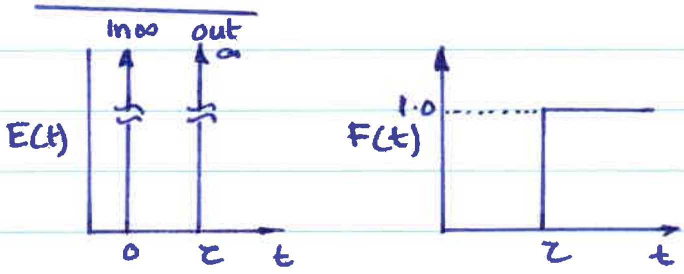
$$E(\alpha) = -\frac{d}{d\alpha}[\tau I(\alpha)]$$

For CSTR

$$I(\alpha) = -\frac{1}{\tau} e^{-\alpha/\tau}$$

RTD in ideal reactors

RTD in batch and plug flow reactor



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

Dirac delta function

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

$$\int_{-\infty}^{\infty} \delta(x)\, dx = 1$$

$$\int_{-\infty}^{\infty} g(x)\, \delta(x-\tau)\, dx = g(\tau)$$

mean residence time

$$t_m = \int_0^{\infty} t\, E(t)\, dt = \int_0^{\infty} t\, \delta(t-\tau)\, dt = \tau$$

$$\sigma^2 = \int_0^{\infty} (t-\tau)^2 \delta(t-\tau)\, dt = 0 \quad \text{... variance}$$

Single CSTR RTD

- Conc. in effluent stream is identical to the conc. throughout the reactor.

Material balance on an inert tracer injected as a pulse at $t=0$

$$\text{In} - \text{out} = \text{Accumulation}$$

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

at $t=0$ $\quad C = C_0$

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

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

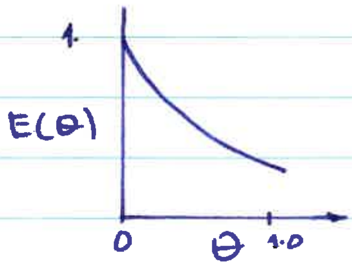
$$E(t) = \frac{e^{-t/\tau}}{\tau}$$

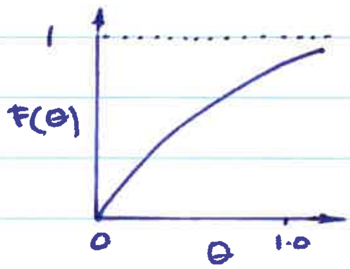
$$E(\Theta) = e^{-\Theta} \qquad \Theta = \frac{t}{\tau}; \; E(\Theta) = \tau E(t)$$

$$F(t) = \int_0^t E(t)dt = \int_0^t \frac{e^{-t/\tau}}{\tau}$$

$$F(t) = 1 - e^{-t/\tau}$$

$$F(\theta) = 1 - e^{-\theta}$$





$$t_m = \int_0^\infty t\,E(t)dt = \int_0^\infty \frac{1}{\tau} e^{-t/\tau} dt = \tau$$

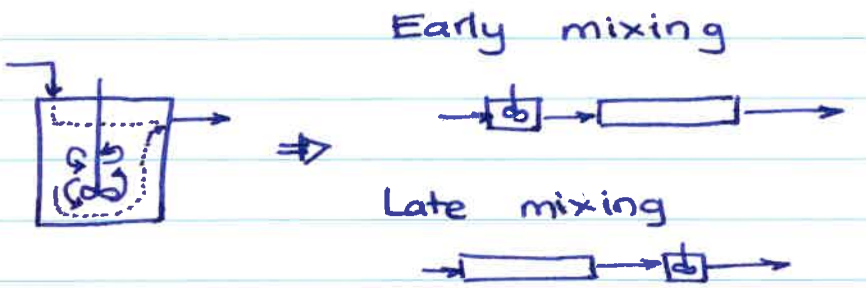
$$\sigma^2 = \int_0^\infty \frac{(t-\tau)^2}{\tau} e^{-t/\tau} dt = \tau^2 \int_0^\infty (x-1)^2 e^{-x} dx = \tau^2$$

$\sigma = \tau$ ... std. deviation is as large as the mean

PFR / CSTR series RTD

- In some stirred tanks there is highly agitated zone in the vicinity of the impeller → CSTR

- Depending on the location of inlet and outlet the reacting mixture may follow a tortuous path either before entering / after leaving the perfectly mixed zone → PFR



Early mixing :
CSTR output conc.

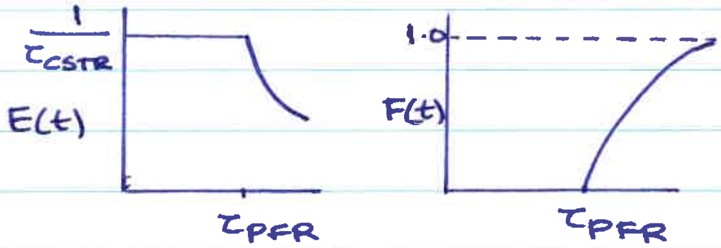
$$C = C_0 e^{-t/\tau_s}$$

τ_s : CSTR mean RT
τ_p : PFR mean RT

This conc. output will be delayed by τ_p at the outlet plug flow section

∴ RTD

$$E(t) = \begin{cases} 0 & t < \tau_p \\ \dfrac{e^{-(t-\tau_p)/\tau_s}}{\tau_s} & t \geq \tau_p \end{cases}$$



Late mixing

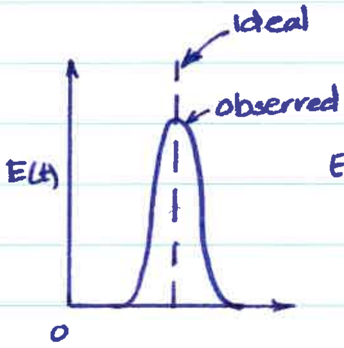
$$E(t) = \begin{cases} 0 & t < \tau_p \\ \dfrac{e^{-(t-\tau_p)/\tau_s}}{\tau_s} & t \geq \tau_p \end{cases}$$

⇒ Exactly same as early mixing

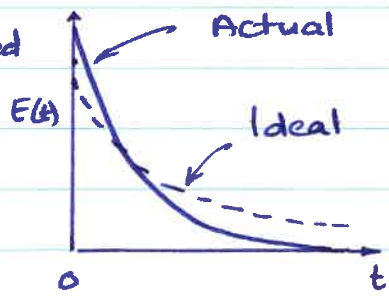
⇏ Even though RTD will be same for both these cases, conversion can be very different

⇏ RTD is not a complete description of the structure for a particular reactor / reactor systems

Diagnostics and troubleshooting

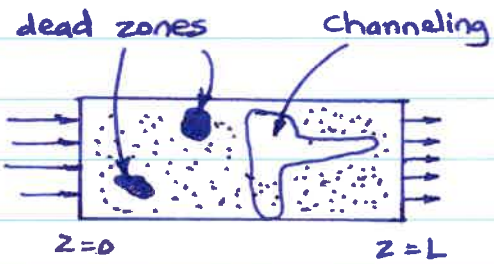


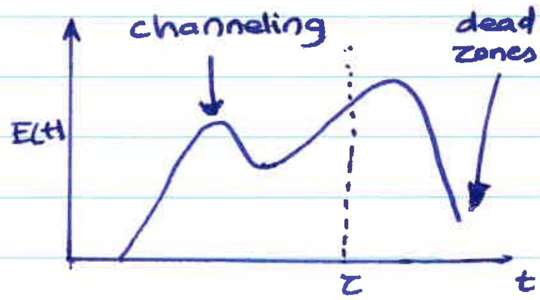
Nearly ideal PFR



Nearly ideal CSTR

Packed bed with dead zone and channeling





Stirred tank