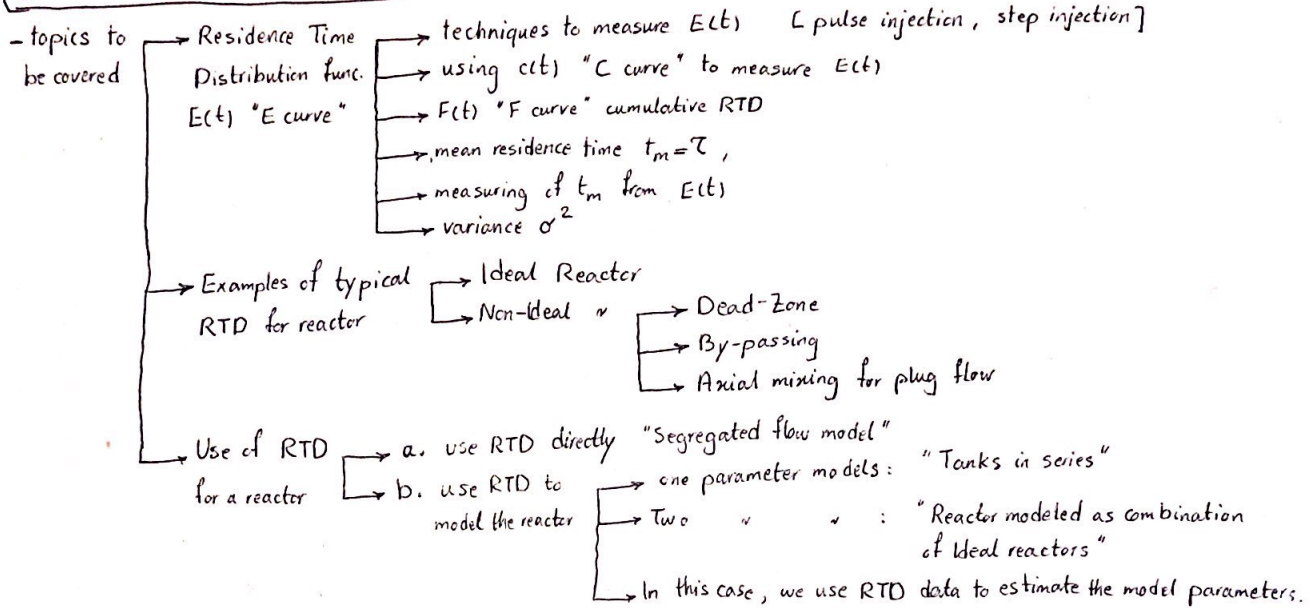


① Non-Ideal Flow - Introduction

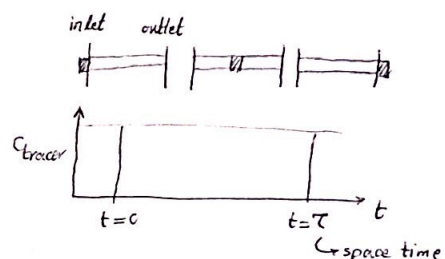


② RTD

- Residence Time  $\rightarrow$  is the time each molecule has spent in a reactor.

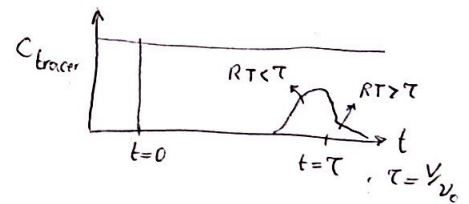
- So far we have considered "ideal reactors"

- for an Ideal PFR "there is no axial mixing" i.e. each molecule spends an identical amount of time in the PFR.
- so if we inject a pulse of a tracer compound, at the inlet of the reactor at  $t=0$ , and measure tracer concentration at outlet:  $\rightarrow$



- In a real tubular reactor

- there is back-mixing and the concentration of tracer at the exit of the reactor can show the following behavior (back-mixing, flow channeling)
- hence, some molecules spend less time in the reactor and some molecules spend more time in the reactor.
- In other words, there is a distribution of residence times



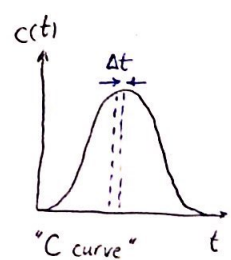
- Now, we are faced with 2 questions

- How can we measure the RTD for a Non-Ideal reactor?
- " " " use RTD to evaluate the performance of the reactor?

2.1 RTD measurement

- Pulse Input Experiments (liquid phase)

- a certain amount of tracer compound,  $N_0$ , is injected at the inlet of reactor at time  $t=0$ ,
- then we monitor the concentration of the tracer at the outlet of the reactor as a function of time,  $c(t)$



Let's choose a small increment of time,  $\Delta t$ , small enough so the concentration of tracer exiting the reactor between  $t$  and  $t+\Delta t$  is constant

$\Delta N =$  the number of moles of tracer compounds leaving the reactor between  $t$  and  $t+\Delta t$

$$= c(t) \cdot v \cdot \Delta t \quad \text{①} \quad v \rightarrow \text{volumetric flowrate of the exit stream.}$$

$=$  number of moles of tracer compound that have spent an amount of time between  $t$  and  $t+\Delta t$  inside the reactor.

$$\frac{\Delta N}{N_0} = \frac{c(t) \cdot v \cdot \Delta t}{N_0} = \text{fraction of material with residence time between } t \text{ and } t+\Delta t$$

We define Residence Time Distribution function,  $E(t)$  as:  $E(t) \triangleq \frac{c(t) \cdot v}{N_0}$  [time<sup>-1</sup>]  $\Rightarrow \frac{\Delta N}{N_0} = E(t) \cdot \Delta t$

$E(t)$  is a function which tells us how much time, different fluid element spend in the reactor.

-  $E(t)$  is a function which tells us how much time, different fluid element spend in the reactor

→ Eq. I in differential form:  $dN = c(t) \cdot v \cdot dt$

→ If  $N_0$  is not known, then we can integrate the above eq.:  $\int_0^{N_0} dN = \int_0^{\infty} c(t) \cdot v \cdot dt \Rightarrow N_0 = \int_0^{\infty} c(t) \cdot v \cdot dt$

$$E(t) = \frac{c(t) \cdot v}{N_0} = \frac{c(t) \cdot v}{\int_0^{\infty} c(t) \cdot v \cdot dt}$$

for constant volumetric flowrate  $\Rightarrow E(t) = \frac{c(t)}{\int_0^{\infty} c(t) \cdot dt}$

→ concentration at any time  
→ area under "c curve"

→ from a "c curve" in a pulse experiment, we can obtain the RTD function,  $E(t)$

- Returning to the definition of  $E(t)$

→  $\frac{\Delta N}{N_0} = E(t) \cdot \Delta t =$  fraction of tracer material with residence time between  $t$  and  $t + \Delta t$

→ If we write in differential form and integrate:

$$\int_0^t E(t) \cdot dt =$$
 fraction of material with residence time between 0 and  $t$ 

$$\int_{t_1}^{t_2} E(t) \cdot dt =$$
 " " " " " " " "  $t_1$  and  $t_2$ 

$$\int_0^{\infty} E(t) \cdot dt =$$
 " " " " " " " " 0 and  $\infty = 1.0$ 

- Ex. 01 → Measuring  $E(t)$  from  $c(t)$

→ Construct the "E curve" or  $E(t)$  for the following tracer study

- Solution of Ex. 01

→  $E(t) = \frac{c(t)}{\int_0^{\infty} c(t) \cdot dt}$  → area under "c curve"

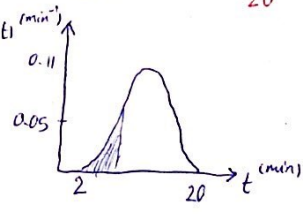
→ the area under the curve can be estimated using a variety of techniques such as trapezoidal, Simpson's  $\frac{1}{3}$  or  $\frac{3}{8}$  rules, & etc.

→ a simple approach:  $\int_0^{\infty} c(t) \cdot dt = \sum_0^{\infty} c(t) \cdot \Delta t$

→  $\int_0^{\infty} E(t) \cdot dt = \sum_0^{\infty} E(t) \cdot \Delta t = \Delta t \sum_0^{\infty} E(t) = (12 \text{ min}) \cdot (5 \text{ min}^{-1}) = 1$

→ fraction of effluent with residence time 0-8 =  $\frac{\text{area under } E(t) \text{ curve between 0 and 8}}{\text{area under } E(t) \text{ curve}}$

time (min)	tracer $C$ (mol/l)	$\Delta t \cdot c(t)$ (mol.min/l)	$E(t) = \frac{c(t)}{\sum c(t) \cdot \Delta t}$
0	0	0	0
2	0	0	0
4	1	2	0.02
6	2	4	0.04
8	4	8	0.08
10	5.5	11	0.11
12	5.5	11	0.11
14	4	8	0.08
16	2	4	0.04
18	1	2	0.02
20	0	0	0
$\infty$	0	0	0
$\sum_0^{\infty} \Delta t \cdot c(t) = 50$			$\sum_0^{\infty} E(t) = 1.0$



→  $E(t)$  same shape as  $c(t)$

**2.2** 2 important properties of the RTD function,  $E(t)$

- Mean Residence time,  $t_m$

- first moment of  $E(t)$
- Its defining eq.:  $t_m = \frac{\int_0^{\infty} t \cdot E(t) \cdot dt}{\int_0^{\infty} E(t) \cdot dt} = \int_0^{\infty} t \cdot E(t) \cdot dt$ ,  $t_m = \tau = \frac{V}{v}$
- average of distribution.

- Variance,  $\sigma^2$

- second moment of  $E(t)$
- Its defining eq.:  $\sigma^2 = \int_0^{\infty} (t - t_m)^2 \cdot E(t) \cdot dt$
- measuring the spread of the distribution

- Ex. 02 → from Ex. 01

→ evaluate  $t_m$  and  $\sigma^2$

- Solution of Ex. 02

→  $t_m = \int_0^{\infty} t \cdot E(t) \cdot dt \approx \sum_0^{\infty} t \cdot E(t) \cdot \Delta t$

→  $\sigma^2 = \int_0^{\infty} (t - t_m)^2 \cdot E(t) \cdot dt \approx \sum_0^{\infty} (t - t_m)^2 \cdot E(t) \cdot \Delta t$

→ for more precise evaluation, we can evaluate the integral using Simpson's rule, etc.

time (min)	$c(t)$ (mol/l)	$t \cdot E(t) \Delta t$	$(t - t_m)^2 \cdot E(t) \Delta t$
0	0	0	0
2	0	0	0
4	1	0.16	1.96
6	2	0.48	2.00
8	4	1.28	1.44
10	5.5	2.20	0.22
12	5.5	2.64	0.22
14	4	2.64	1.44
16	2	1.28	2.00
18	1	0.72	1.96
20	0	0	0
$\sum_0^{\infty} t \cdot E(t) \Delta t = 11$			$\sum_0^{\infty} (t - t_m)^2 \cdot E(t) \Delta t = 11.24$
$\Rightarrow t_m = 11 \text{ min}$			$\Rightarrow \sigma^2 = 11.24 \text{ min}^2$

→  $\sigma = 3.35 \text{ min}$

standard deviation

- Alternative expression for variance,  $\sigma^2$ :

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

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

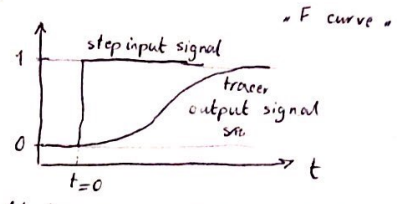
$\underbrace{\int_0^{\infty} t E(t) dt}_{= t_m} \quad \underbrace{\int_0^{\infty} E(t) dt}_{= 1.0}$

$$\sigma^2 = \int_0^{\infty} t^2 E(t) dt - t_m^2 \approx \sum_0^{\infty} t^2 E(t) \Delta t - t_m^2$$

**2.3 Cumulative RTD function,  $F(t)$  + "F curve"**

- For a step input (typically)  $F(t) = \frac{C(t)}{C_0}$ ,  $C_0 \triangleq$  step input of tracer concentration  $C_0$

- It varies between 0 and 1.0
- Construction of F curve from E curve:  $F(t) = \int_0^t E(t) dt$
- " " E " " F "  $E(t) = \frac{dF(t)}{dt}$
- for step input tracer experiments, the F curve can be measured readily by measuring exit concentration.
  - $\frac{C(t)}{C_0}$  would give the E curve
  - $F(t) \triangleq$  fraction of exit stream having residence time between 0 and t

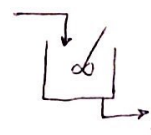


**3 RTD function for Ideal Reactors**

**3.1 Ideal CSTRs**

- Consider the response to a pulse input

- Inject a pulse of tracer into the reactor.
- Note, the  $C$  @ the exit =  $C$  inside the reactor
- Let's do a material balance for the tracer (inert)

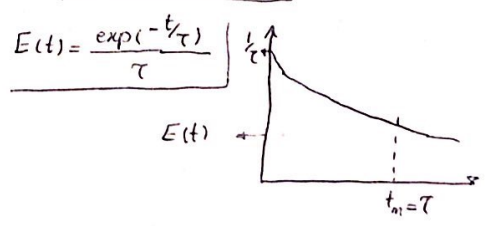


in - out + generation - consumption = accumulation

$$0 - V_0 C_{tracer} + 0 - 0 = V \frac{dC_{tracer}}{dt} \Rightarrow -dt = \frac{V}{V_0} \frac{dC_{tracer}}{C_{tracer}} \Rightarrow dt = -\tau \frac{dC_{tracer}}{C_{tracer}}$$

- Integrating:  $\int_0^t dt = -\tau \int_{C_{tracer,0}}^{C_{tracer}} \frac{dC_{tracer}}{C_{tracer}} \xrightarrow{C_{tracer} \equiv C} t = -\tau \ln \frac{C}{C_0} \Rightarrow C(t) = C_0 \cdot \exp(-t/\tau)$

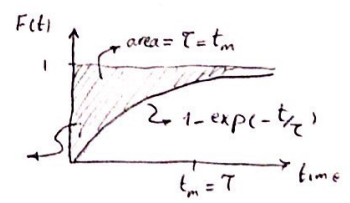
-  $E(t) = \frac{c(t)}{\int_0^{\infty} c(t) dt} = \frac{C_0 \cdot \exp(-t/\tau)}{\int_0^{\infty} C_0 \cdot \exp(-t/\tau) dt} = \frac{\exp(-t/\tau)}{-\tau \cdot \exp(-t/\tau)} \Big|_0^{\infty}$



-  $t_m = \frac{\int_0^{\infty} t \cdot E(t) dt}{\int_0^{\infty} E(t) dt} = \frac{\int_0^{\infty} t \cdot \frac{1}{\tau} \exp(-t/\tau) dt}{1} = \frac{-\tau \cdot \exp(-t/\tau) [t - \tau]}{\tau} \Big|_0^{\infty} = \tau$

-  $F(t) = \int_0^t E(t) dt = \int_0^t \frac{1}{\tau} \exp(-t/\tau) dt = \frac{1}{\tau} (-\tau \cdot \exp(-t/\tau)) \Big|_0^t = 1 - \exp(-t/\tau)$

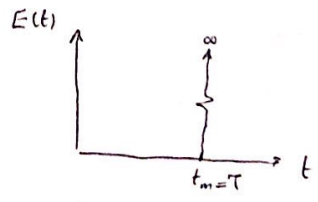
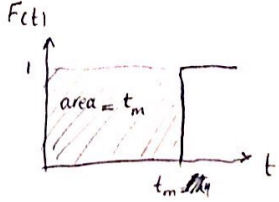
$\Rightarrow F(t) = 1 - \exp(-t/\tau)$  area =  $\int_0^{\infty} (1 - (1 - \exp(-t/\tau))) dt$



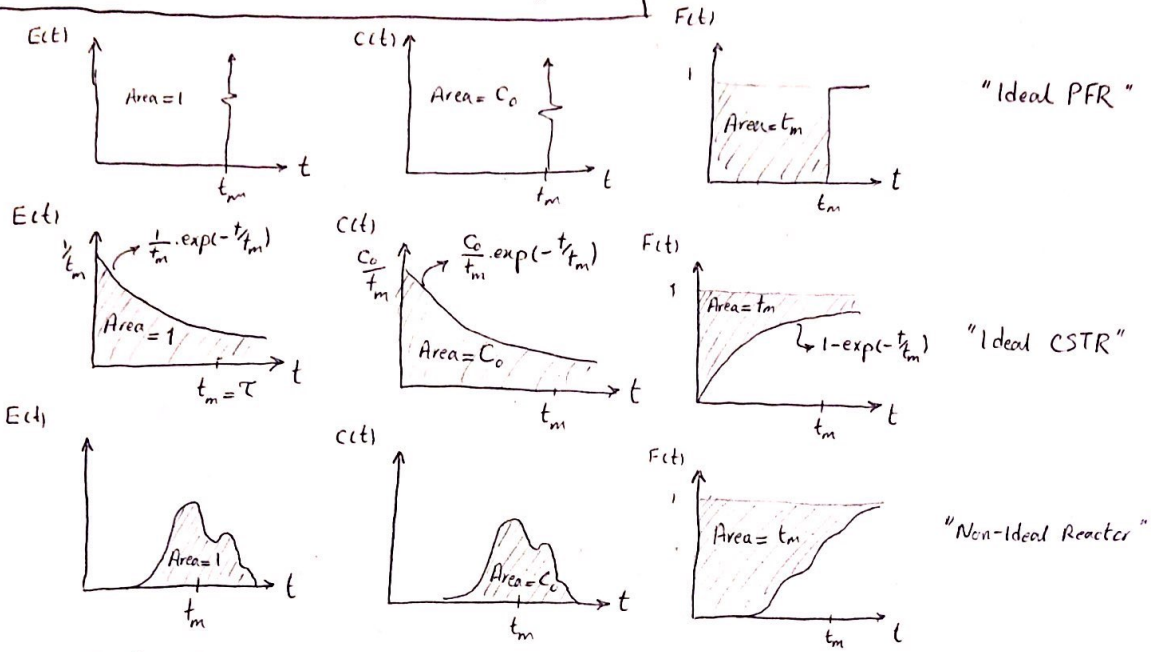
**3.2 Ideal PFRs**

- for a pulse input

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



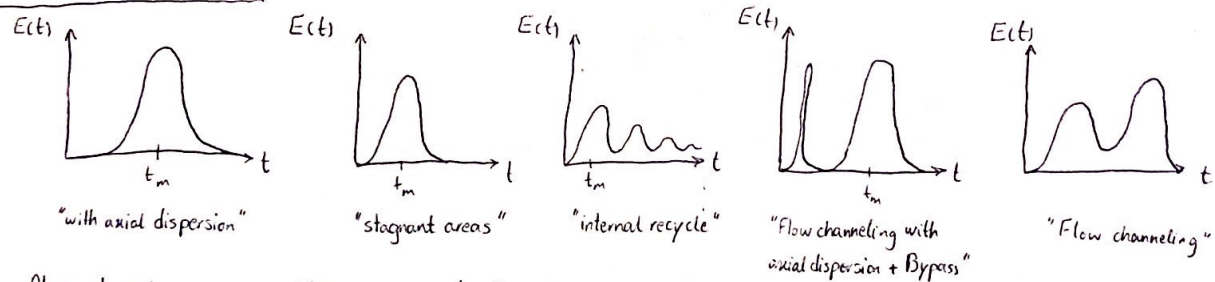
### 3.3 E, C, and F curves for various flows (pulse input of $C_0$ )



- note  $\frac{C}{C_0} (\frac{C}{Q}) = C$   
 - notation used in Levenspiel.  $C$  is normalized dimensionless concentration.  
 -  $C$  curve is the same as  $E$  curve

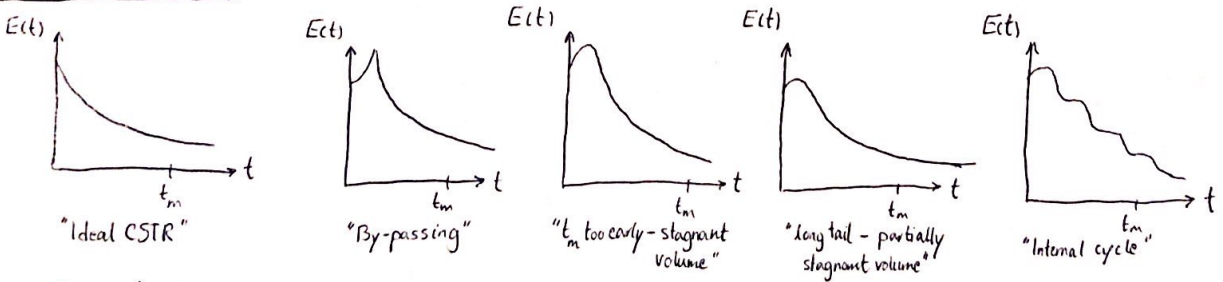
### 4 Qualitative Diagnosis (QD)

#### 4.1 QD for tubular reactors



- Always have to use an appropriate tracer  
 - radioactive, isotope, non-reactive  
 - shouldn't affect the flow pattern  
 - should be non-absorbing in presence of a catalyst.

#### 4.2 QD for CSTRs

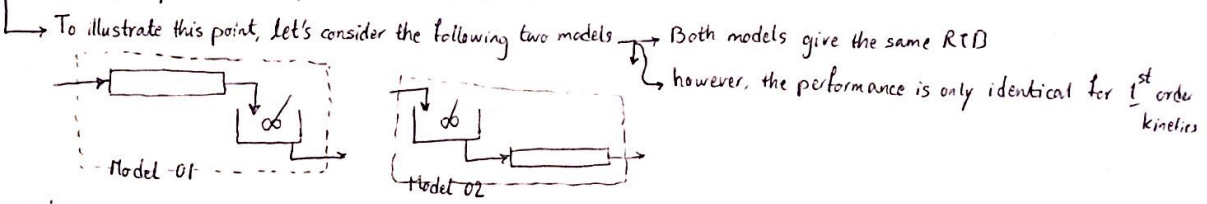


- Tracer Information is used either directly or in conjunction with flow models to predict the performance of real reactors

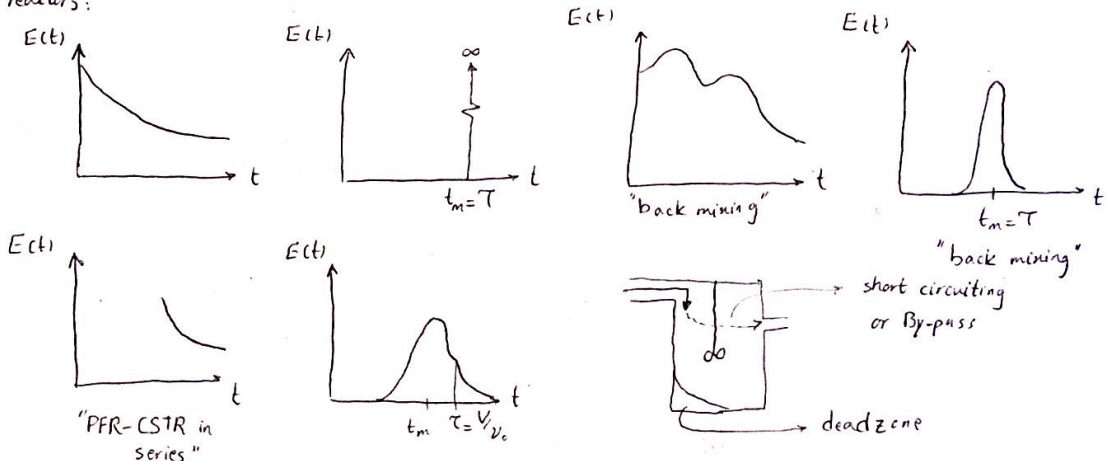
**5 Linear vs. Non-linear system**

- If we have  $1^{st}$  order kinetics, single rxns, reversible rxns, series, and parallel rxns (provided that all rate expressions are first order) then, we can use RTD information directly to obtain conversion (e.g. segregated flow model)

- However, for non-linear systems  
 → RTD information cannot be used directly.  
 → Rather, they are used to evaluate a reactor flow model (e.g. dispersion model, tank-in-series model) which is subsequently used for the performance of the real reactor.



- RTD for real reactors:



- Comments  
 → most reactors do not show ideal flow behavior  
 → RTD for real reactors is much different than RTD for ideal reactors  
 → we can measure Non-Ideal flow characteristic by measuring RTD.