

Fluid-Particle Reaction: Kinetics and Reactor Design

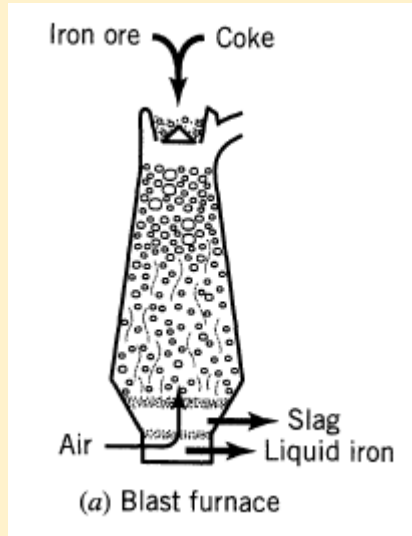
Book: *Chemical Reaction Engineering*, O. Levenspiel, (Chapter 25 and 26), 3rd Edition, Wiley and Sons

Fluid-particle reactor design

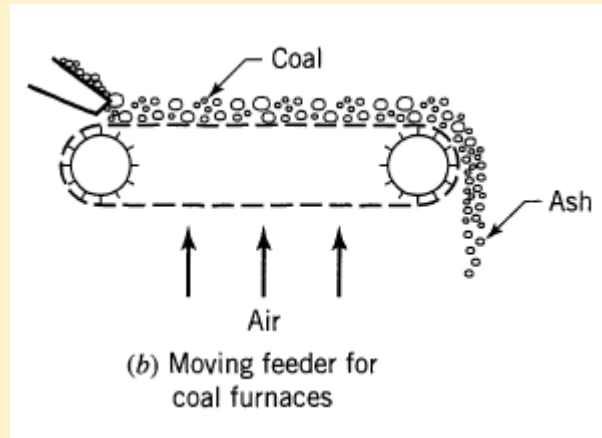
- *Three* factors control the design of a fluid-solid reactor :
 - (a) the ***size distribution of the solids*** being treated
 - (b) the ***flow pattern of solids and fluids in reactor***
 - (c) the ***reaction kinetics for single reactions***
- When the kinetics of the reaction are unknown or complex or the temperature within the system varies greatly from position to position, or products formed forms a blanketing fluid phase, the analysis of the system becomes difficult and solutions need to be provided based on practical experience and innovations
- Here simplified and idealized systems in which the reaction kinetics, flow characteristics and size distribution of solids are known, are analysed to provide an idea as to how such systems are dealt with
- The **contacting pattern** of solid and gas through the reactor may be *plug flow* or *mixed flow*
- For *plug flow*, the compositions change during passage through the reactor. Operations are often non-isothermal
Eg.: counter-current (blast furnace, cement kilns), cross-flow (moving belt feeders for furnaces) co-current flow (polymer driers)
- For *mixed flow*, isothermal conditions are frequently assumed. Eg., fluidized bed
- Apart from these, batch and semi-batch operations are also carried out in certain cases

Fluid-particle reactors

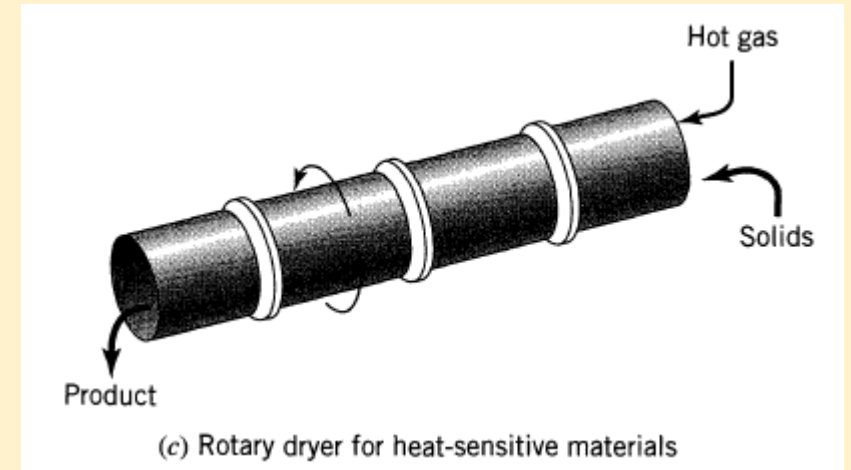
Plug flow



counter-current plug flow

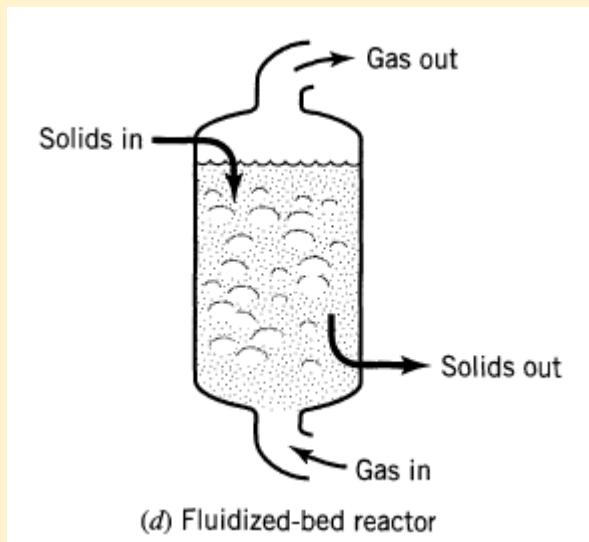


cross-current plug flow

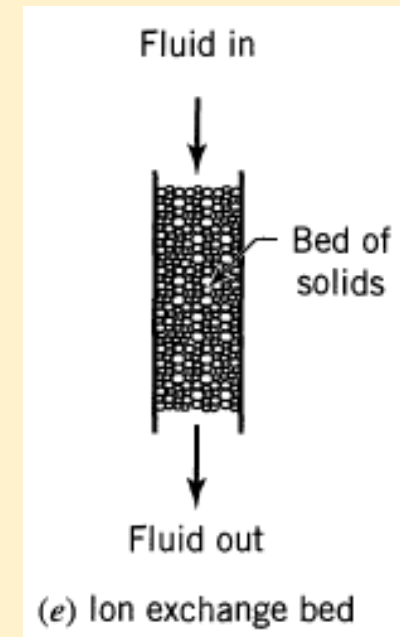


co-current plug flow

Mixed flow



Semi-batch operations



(I) Particles of a single size, plug flow of solids, uniform gas composition

- The reaction time needed for any specific conversion of solid can be found from the expression developed earlier
- For spheres,

For **gas film controls**

$$t = \frac{\rho_B R}{3bk_g C_{Ag}} \left[1 - \left(\frac{r_c}{R} \right)^3 \right] = \frac{\rho_B R}{3bk_g C_{Ag}} X_B$$

For **diffusion through ash controls**,

$$t = \frac{\rho_B R^2}{6bD_e C_{Ag}} \left[1 - 3 \left(\frac{r_c}{R} \right)^2 + 2 \left(\frac{r_c}{R} \right)^3 \right] = \frac{\rho_B R^2}{6bD_e C_{Ag}} \left[1 - 3(1 - X_B)^{2/3} + 2(1 - X_B) \right]$$

For **chemical reaction controls**,

$$t = \frac{\rho_B R}{bk C_{Ag}} \left[1 - \frac{r_c}{R} \right] = \frac{\rho_B R}{bk C_{Ag}} \left[1 - (1 - X_B)^{1/3} \right]$$

- Similar equations are there for particles having other shapes

(II) Mixture of particles of different but unchanging sizes, plug flow of solids, uniform gas composition

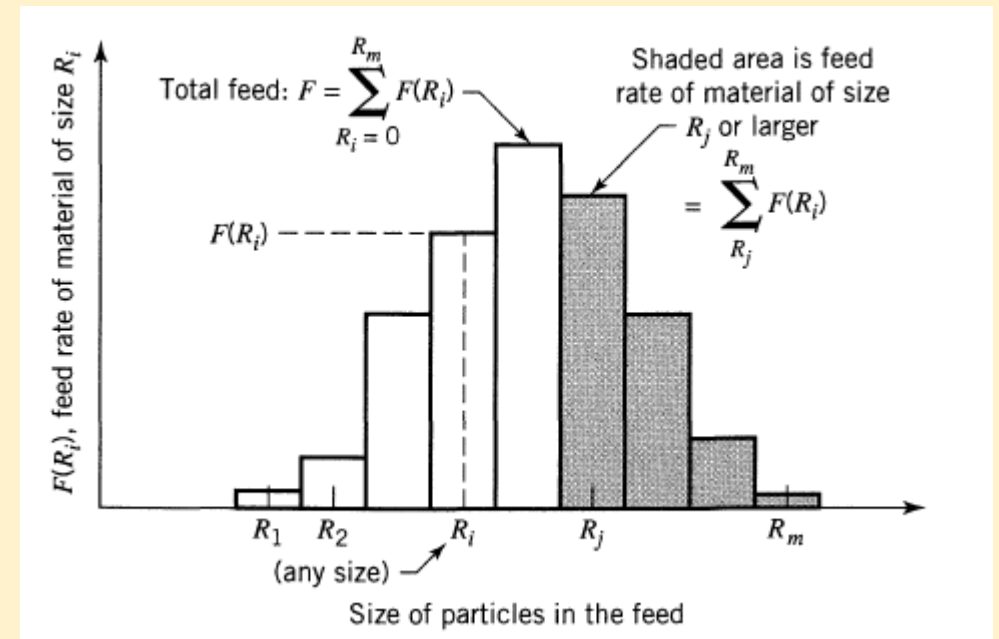
- Let us consider a solid feed consisting of a mixture of different size particles
- The distribution of the sizes may be **continuous or discrete** (usually the case when data obtained from sieve analysis)

F = volumetric feed rate of solid (as the density of the solid may change during reaction) or = mass feed rate of solid (when density change is negligible)

If $F(R_i)$ is the quantity of material of size R_i fed to the reactor,

$$F = \sum_{R_i=0}^{R_m} F(R_i)$$

where F is in cm^3/s or g/s and R_m is the largest particle size in the feed



When in *plug flow*, all solids stay in the reactor for the same length of time t_p

From the value of t_p and the kinetics of whatever resistance controls, the conversion $X_B(R_i)$ for any size of particle R_i can be found

- The mean conversion \bar{X}_B of the solids leaving the reactor can be obtained as

$$\left(\begin{array}{l} \text{mean value for} \\ \text{the fraction of B} \\ \text{unconverted} \end{array} \right) = \sum_{\text{all sizes}} \left(\begin{array}{l} \text{fraction of reactant B} \\ \text{unconverted in particles} \\ \text{of size } R_i \end{array} \right) \left(\begin{array}{l} \text{fraction of feed} \\ \text{of size } R_i \end{array} \right)$$

$$1 - \bar{X}_B = \sum_{R(t_p=\tau)}^{R_m} [1 - X_B(R_i)] \frac{F(R_i)}{F}$$

where $R(t_p = \tau)$ is the radius of the largest particle completely converted in the reactor

- Feed particles smaller than $R(t_p = \tau)$ will be completely reacted as smaller particles require shorter time for complete conversion*
- If the conversion-time equations are applied to such particles, then it is possible to come up with values of $X_B > 1$ which has no physical meaning
- The lower limit of the summation indicates that particles smaller than $R(t_p = \tau)$ are completely converted and do not contribute to the fraction converted, $(1 - X_B)$*

Example

A feed consisting of 30% of 50 μm radius particle, 40% of 100 μm radius particles, 30% of 200 μm radius particles is to be fed continuously onto a moving grate cross current to a flow of reactant gas. The time required for complete conversion of particles are 5, 10 and 20 min, respectively

Find the conversion of solids on the grate for a residence of 8 min in the reactor.

Residence time (t_p) = 8 min

Hence 50 μm particles which have $\tau = 5$ min will be completely converted and should not be taken into consideration for calculations

The flow is plug flow

From the data, we see that $\tau_1 : \tau_2 : \tau_3 = R_1 : R_2 : R_3$

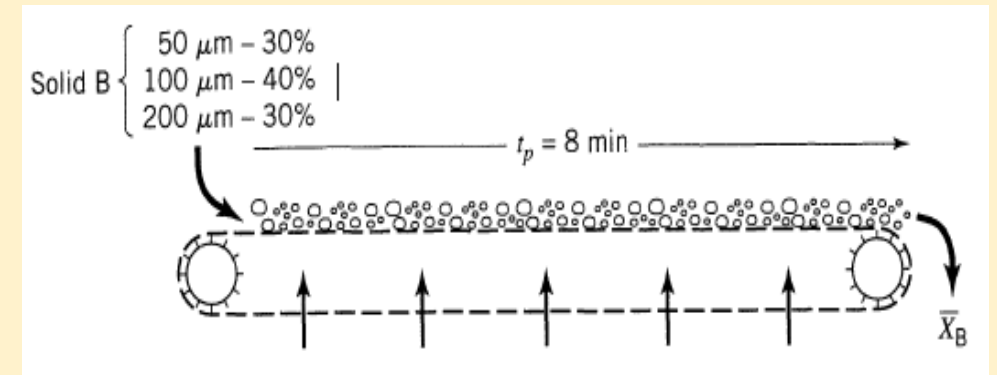
which is the case when **chemical reaction controls**

$$\text{Now, } 1 - \overline{X}_B = [1 - X_B(100 \mu\text{m})] \frac{F(100 \mu\text{m})}{F} + [1 - X_B(200 \mu\text{m})] \frac{F(200 \mu\text{m})}{F}$$

$$\text{For chemical reaction controls, } \frac{t}{\tau} = 1 - (1 - X_B)^{1/3} \quad \therefore \quad (1 - X_B) = \left(1 - \frac{t}{\tau}\right)^3$$

$$\text{or, } 1 - \overline{X}_B = \left[1 - \frac{t}{\tau}(100 \mu\text{m})\right]^3 \frac{F(100 \mu\text{m})}{F} + \left[1 - \frac{t}{\tau}(200 \mu\text{m})\right]^3 \frac{F(200 \mu\text{m})}{F} = \left[1 - \frac{8}{10}\right]^3 \times 0.4 + \left[1 - \frac{8}{20}\right]^3 \times 0.3$$

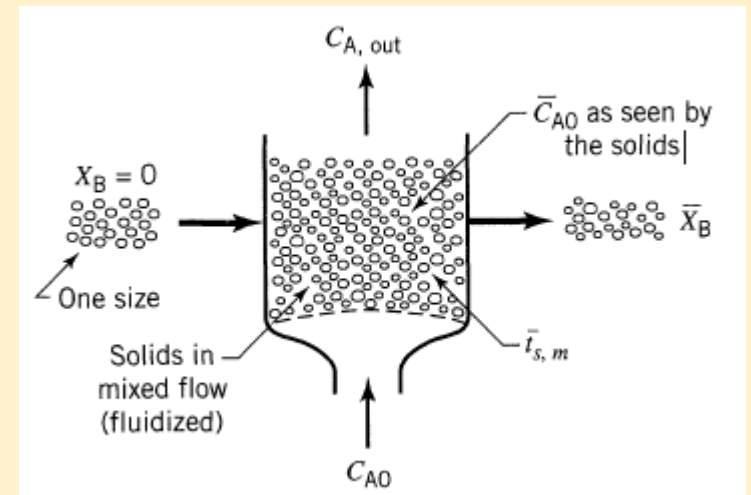
$$1 - \overline{X}_B = 0.0032 + 0.0648 = 0.068 \quad \Rightarrow \quad \overline{X}_B = \mathbf{0.932}$$



(III) Particles of single unchanging size, mixed flow of solids, uniform gas composition

- The flow rate of solid both into and out of the reactor is constant
- The assumption of *uniform gas composition and mixed flow of solids for the model shows that it can be used to represent a fluidized bed reactor*
- The conversion of the particle of a single size will depend on
 - (a) the length of the time spend in the bed and
 - (b) the appropriate controlling resistance

However, the length of stay of all the particles may not be the same and we have a mean conversion \bar{X}_B of the material



$$\left(\begin{array}{l} \text{mean value for} \\ \text{the fraction of B} \\ \text{unconverted} \end{array} \right) = \sum_{\text{particles of all ages}} \left(\begin{array}{l} \text{fraction of reactant B unconverted for} \\ \text{particles staying in the reactor for} \\ \text{time between } t \text{ and } t + dt \end{array} \right) \left(\begin{array}{l} \text{fraction of exit stream which} \\ \text{has stayed in the reactor for} \\ \text{a time between } t + dt \end{array} \right)$$

$$1 - \bar{X}_B = \int_0^{\infty} (1 - X_B) E dt$$

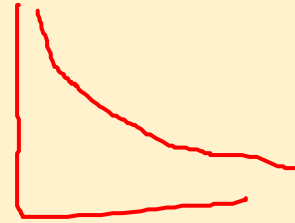
$$\bar{X}_B \leq 1$$

$$1 - \bar{X}_B = \int_0^{\tau} (1 - X_B) E dt$$

where E is the exit age distribution of the solids in the reactor

- For mixed flow of solids with mean residence time of \bar{t} in the reactor

$$E = \frac{1}{\bar{t}} e^{-t/\bar{t}}$$



- Therefore, for mixed flow of single sized solids which is completely converted in time τ , we obtain,

$$1 - \bar{X}_B = \int_0^{\tau} (1 - X_B)_{\text{individual particle}} \left(\frac{1}{\bar{t}} e^{-t/\bar{t}} \right) dt$$

$$\frac{t}{\bar{t}} = X_B$$

This expression is now integrated for various controlling resistances

- For **film resistance controlling**,

$$1 - \bar{X}_B = \int_0^{\tau} \left(1 - \frac{t}{\tau} \right) \left(\frac{1}{\bar{t}} e^{-t/\bar{t}} \right) dt$$

Which on integration by parts gives,

$$\bar{X}_B = \frac{\bar{t}}{\tau} \left(1 - e^{\tau/\bar{t}} \right)$$

Or in the expanded form useful for large $\frac{\bar{t}}{\tau}$ and high conversions,

$$1 - \bar{X}_B = \frac{1}{2} \frac{\tau}{\bar{t}} - \frac{1}{3!} \left(\frac{\tau}{\bar{t}} \right)^2 + \frac{1}{4!} \left(\frac{\tau}{\bar{t}} \right)^3 - \dots$$

- For **chemical reaction controlling**,

$$1 - \bar{X}_B = \int_0^\tau \left(1 - \frac{t}{\tau}\right)^3 \left(\frac{1}{\bar{t}} e^{-t/\bar{t}}\right) dt$$

Which on integration gives,

$$\bar{X}_B = 3 \frac{\bar{t}}{\tau} - 6 \left(\frac{\bar{t}}{\tau}\right)^2 + 6 \left(\frac{\bar{t}}{\tau}\right)^3 \left(1 - e^{\tau/\bar{t}}\right)$$

For large $\frac{\bar{t}}{\tau}$ or for high conversions, the equivalent form is

$$1 - \bar{X}_B = \frac{1}{4} \left(\frac{\tau}{\bar{t}}\right) - \frac{1}{20} \left(\frac{\tau}{\bar{t}}\right)^2 + \frac{1}{120} \left(\frac{\tau}{\bar{t}}\right)^3 - \dots$$

- For **ash layer resistance controlling**,

The expression $\frac{t}{\tau} = 1 - 3(1 - X_B)^{2/3} + 2(1 - X_B)$

Is replaced and the equation integrated to give

$$1 - \bar{X}_B = \frac{1}{5} \left(\frac{\tau}{\bar{t}}\right) - \frac{19}{420} \left(\frac{\tau}{\bar{t}}\right)^2 + \frac{41}{4620} \left(\frac{\tau}{\bar{t}}\right)^3 - 0.00149 \left(\frac{\tau}{\bar{t}}\right)^4 + \dots$$

Example

FeS particles were roasted and the time for complete conversion was related to particle size as $\tau \propto R^{1.5}$. Particles remained as hard solids of unchanging size during reaction. A fluidized bed reactor is used to convert *FeS* ore to the corresponding oxide. The feed is of uniform size, $\tau = 20$ min, with mean residence time, $\bar{t} = 60$ min in the reactor. What fraction of the original sulphide ore remains unconverted?

As hard, solid product is formed during reaction, controlling resistance by film diffusion can be ruled out

For chemical reaction controls, $\tau \propto R$

For diffusion through ash layer controls, $\tau \propto R^2$

As the experimentally found time-particle size dependence is $\tau \propto R^{1.5}$, **it is in between the two values (R and R^2), so we find the answer with both the mechanisms which would give the lower and upper bounds of the conversion**

For chemical reaction controlling,

$$1 - \overline{X_B} = \frac{1}{4} \left(\frac{\tau}{\bar{t}} \right) - \frac{1}{20} \left(\frac{\tau}{\bar{t}} \right)^2 + \frac{1}{120} \left(\frac{\tau}{\bar{t}} \right)^3 - \dots$$

Now, $\frac{\tau}{\bar{t}} = \frac{20}{60} = \frac{1}{3}$

$$1 - \overline{X_B} = \frac{1}{4} \left(\frac{1}{3} \right) - \frac{1}{20} \left(\frac{1}{3} \right)^2 + \frac{1}{120} \left(\frac{1}{3} \right)^3 - \dots = \underline{0.078}$$

For diffusion through ash layer controlling,

$$1 - \overline{X_B} = \frac{1}{5} \left(\frac{\tau}{t} \right) - \frac{19}{420} \left(\frac{\tau}{t} \right)^2 + \frac{41}{4620} \left(\frac{\tau}{t} \right)^3 - 0.00149 \left(\frac{\tau}{t} \right)^4 + \dots$$

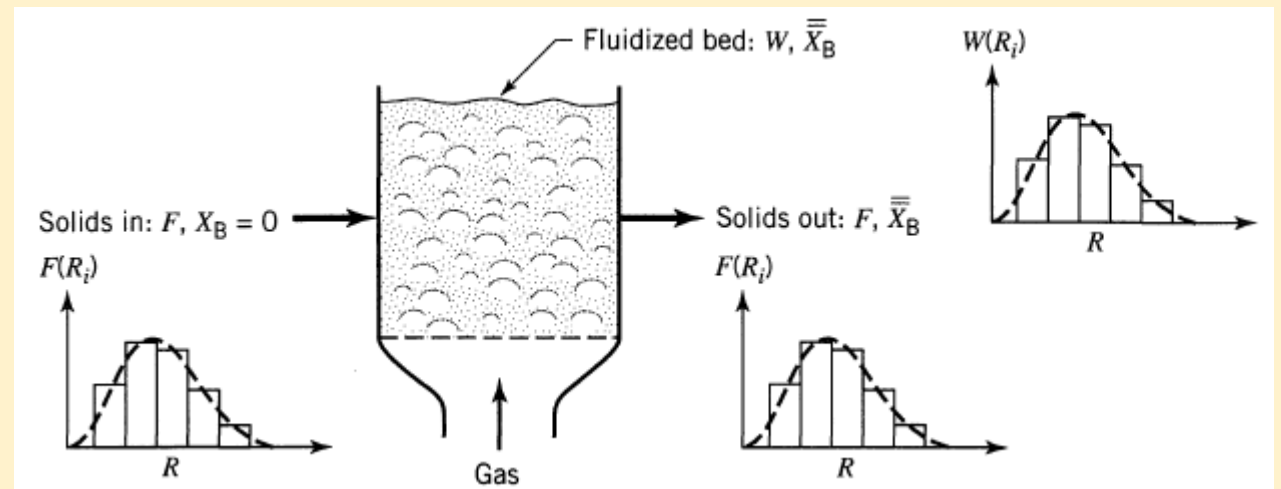
Now, $\frac{\tau}{t} = \frac{20}{60} = \frac{1}{3}$

$$1 - \overline{X_B} = \frac{1}{5} \left(\frac{1}{3} \right) - \frac{19}{420} \left(\frac{1}{3} \right)^2 + \frac{41}{4620} \left(\frac{1}{3} \right)^3 - 0.00149 \left(\frac{1}{3} \right)^4 + \dots = \underline{0.062}$$

∴ fraction of sulphide remaining will be between 6.2% and 7.8% (average 7.0%)

(IV) Mixture of particles of different but unchanging size, mixed flow of solids, uniform gas composition

- Often a range of particle sizes is used as a feed to a mixed flow reactor
- Hence to find the conversion effects due to
 - (a) variation in particle size and
 - (b) variation in time spend by these particles in the reactor must be taken into account



- If W = quantity of material in the reactor and $W(R_i)$ = quantity of material of size R_i in the reactor

$$\frac{F(R_i)}{F} = \frac{W(R_i)}{W}$$

- The mean residence time $\bar{t}(R_i)$ of material of any size R_i is equal to the mean residence time of solid in the bed, or,

$$\bar{t} = \bar{t}(R_i) = \frac{W}{F} = \frac{\text{(weight of all the solids in the reactor)}}{\text{(feed rate of all the solids in the reactor)}}$$

- If $\bar{X}_B(R_i)$ is the mean conversion of particles of size R_i in the bed

$$1 - \bar{X}_B(R_i) = \int_0^{\tau(R_i)} [1 - X_B(R_i)] \left(\frac{1}{\bar{t}} e^{-t/\bar{t}} \right) dt$$

- Overall mean of unconverted B of all particle sizes is

$$\left(\begin{array}{l} \text{mean value for} \\ \text{the fraction of B} \\ \text{unconverted} \end{array} \right) = \sum_{\text{all sizes}} \left(\begin{array}{l} \text{fraction of reactant B} \\ \text{unconverted in particles} \\ \text{of size } R_i \end{array} \right) \left(\begin{array}{l} \text{fraction of exit or entering stream} \\ \text{consisting of particles of size } R_i \end{array} \right)$$

$$1 - \bar{\bar{X}}_B = \sum_{R=0}^{R_m} [1 - \bar{X}_B(R_i)] \frac{F(R_i)}{F}$$

Now,

$$1 - \overline{X}_B(R_i) = \int_0^{\tau(R_i)} [1 - X_B(R_i)] \left(\frac{1}{\bar{t}} e^{-t/\bar{t}} \right) dt$$

$$1 - \overline{\overline{X}}_B = \sum_{R=0}^{R_m} [1 - \overline{X}_B(R_i)] \frac{F(R_i)}{F}$$

- The above two equations are combined and the expressions for different kinetic regimes are used to estimate the conversion
- For **film resistance controlling**,

$$1 - \overline{\overline{X}}_B = \sum_{R=0}^{R_m} \left\{ \frac{1}{2!} \left[\frac{\tau(R_i)}{\bar{t}} \right] - \frac{1}{3!} \left[\frac{\tau(R_i)}{\bar{t}} \right]^2 + \dots \right\} \frac{F(R_i)}{F}$$

- For **chemical reaction controlling**

$$1 - \overline{\overline{X}}_B = \sum_{R=0}^{R_m} \left\{ \frac{1}{4} \left[\frac{\tau(R_i)}{\bar{t}} \right] - \frac{1}{20} \left[\frac{\tau(R_i)}{\bar{t}} \right]^2 + \dots \right\} \frac{F(R_i)}{F}$$

- For **film resistance controlling**,

$$1 - \overline{\overline{X}}_B = \sum_{R=0}^{R_m} \left\{ \frac{1}{5} \left[\frac{\tau(R_i)}{\bar{t}} \right] - \frac{19}{420} \left[\frac{\tau(R_i)}{\bar{t}} \right]^2 + \dots \right\} \frac{F(R_i)}{F}$$

where $\tau(R_i)$ = time for complete reaction of particle of size R_i

Example

A feed consisting of 30% of 50 μm radius particle, 40% of 100 μm radius particles and 30% of 200 μm radius particles is to be reacted in a fluidized bed steady state flow reactor constructed from a 2 m long 20 cm ID pipe. The time required for complete conversion of particles is 5, 10 and 20 min for three sizes of feed, respectively

Find the conversion of solids in the reactor for a feed rate of 1 kg solids/min if the bed contains 10 kg solids.

Since the reactor is a **fluidized bed reactor**, the flow can be considered a **mixed flow**

$$F = 1000 \text{ g/min} \qquad \bar{t} = \frac{W}{F} = \frac{10000}{1000} = 10 \text{ min}$$

$$W = 10000 \text{ g}$$

$$F(50 \mu\text{m}) = 300 \text{ g/min} \quad \text{and} \quad \tau(50 \mu\text{m}) = 5 \text{ min}$$

$$F(100 \mu\text{m}) = 400 \text{ g/min} \quad \text{and} \quad \tau(100 \mu\text{m}) = 10 \text{ min}$$

$$F(200 \mu\text{m}) = 300 \text{ g/min} \quad \text{and} \quad \tau(200 \mu\text{m}) = 20 \text{ min}$$

It can be seen that, $\tau \propto R$. Therefore, chemical reaction is controlling

$$1 - \overline{\overline{X_B}} = \left\{ \frac{1}{4} \left[\frac{5}{10} \right] - \frac{1}{20} \left[\frac{5}{10} \right]^2 + \dots \right\} \frac{300}{1000} + \left\{ \frac{1}{4} \left[\frac{10}{10} \right] - \frac{1}{20} \left[\frac{10}{10} \right]^2 + \dots \right\} \frac{400}{1000} + \left\{ \frac{1}{4} \left[\frac{20}{10} \right] - \frac{1}{20} \left[\frac{20}{10} \right]^2 + \dots \right\} \frac{300}{1000}$$

$$1 - \overline{\overline{X_B}} = \left\{ \frac{1}{8} - \frac{1}{80} + \dots \right\} 0.3 + \left\{ \frac{1}{4} - \frac{1}{20} + \dots \right\} 0.4 + \left\{ \frac{1}{2} - \frac{1}{5} + \dots \right\} 0.3$$

$$1 - \overline{\overline{X_B}} = 0.034 + 0.083 + 0.105 = 0.222 \qquad \Rightarrow \quad \overline{\overline{X_B}} = \mathbf{0.778}$$

Instantaneous Reactions

- When reaction between gas and solid is fast enough so that any volume element of the reactor contains only one or the other of the two reactants, but not both, then the reaction is considered instantaneous
- This occurs in cases such as high temperature combustion of finely divided solids
- For such cases, the performance of the reactor is straightforward and is dependent only on the stoichiometry of the reaction and the kinetics do not enter the picture