Advanced Rxn Engineering / Session 11

1. For particles of a single size, plug flow of solids, and uniform gas composition → contact time for a given conversion can be obtained from eqs. derived earlier and reported in table I

2. For mixtures of particles of different but unchanging size, plug flow of solids, uniform gas composition
   - → size distribution can be represented as a continuous or discrete distribution
   - → let $F \triangleq$ volumetric (or mass) feed rate of solids
   - → $F(R_i) \triangleq$ feed rate of material of size R_i

     $$F \triangleq \sum_{R_i=0}^{R_m} F(R_i) \quad , \quad R_0 = \text{smallest particle size}, \quad R_m = \text{largest particle size}$$
   - → suppose the contact time in PFR is t_p.
   - → using the appropriate conversion-time eq. reported in table I for the situation at hand, we can obtain the fractional conversion $X_B(R_i)$ for any size of particle R_i
   - → we have then:

     $$\begin{pmatrix}\text{mean value for}\\ \text{the fraction of}\\ B \text{ unconverted}\end{pmatrix} = \sum_{\text{all sizes}} \begin{pmatrix}\text{fraction of reactant}\\ B \text{ unconverted in}\\ \text{particles of size } R_i\end{pmatrix}\begin{pmatrix}\text{fraction of feed}\\ \text{which is of size } R_i\end{pmatrix}$$

     $$\Rightarrow 1-\bar{X}_B = \sum_{(R_{i=0})=(R_{t_p=\tau})}^{R_m} [1-X_B(R_i)]\,\frac{F(R_i)}{F} \quad , \text{ if } 0 \leqslant X_B(R_i) \leqslant 1$$

- Ex. 01
  - → Solid feed size distribution (30% 50 μm – 40% 100 μm – 30% 200 μm)
  - → under operating condition in a moving belt with crosscurrent flow of gas, the time for complete conversion for the three particle size is 5, 10, 20 minutes. (τ_{50}, τ_{100}, τ_{200})
  - → what is the conversion for a residence time of 8 min ?
  - → we can see that $\tau \propto R \Rightarrow$ chemical rxn controls $\Rightarrow t/\tau = 1-(1-X_B)^{1/3} \Rightarrow 1-X_B = (1-t/\tau)^3$
  - → $1-X_B(R_i) = [1-\frac{t_p}{\tau(R_i)}]^3 \Rightarrow 1-\bar{X}_B = \sum_{R_{i=0}}^{R_m} [1-X_B(R_i)].\frac{F(R_i)}{F}$
  - → $t_p = 8$, for $\tau_{50} = 5$, conversion is complete and it does not contribute to above summation
  - → $1-\bar{X}_B = (1-\frac{8}{10})^3 \cdot (0.4) + (1-\frac{8}{20})^3 (0.3) = 0.0032 + 0.0648 = 0.068 \Rightarrow \bar{X}_B = 0.932$

3. Mixed flow of particles of a single unchanging size, uniform gas comp. (i.e. a fluidized bed reactor)
   - → CSTR: the length of stay is not the same for all particles and hence, we must calculate a mean conversion.
   - → treatment of solids as a macrofluid.
   - → recall exit size distribution for a CSTR: $E(t) = \frac{1}{\bar{t}} \cdot \exp(-t/\bar{t})$

     $\bar{t} \triangleq$ mean residence time

     $$1-\bar{X}_B = \int_0^\infty (1-X_B) \cdot E(t)\,dt$$
   - → If τ is the time required for single size solid particles to be completely converted, then all particles remaining in the reactor for a time greater than τ would be completely converted. Hence,

     $$1-\bar{X}_B = \int_0^{\tau} (1-X_B)\,\frac{\exp(-t/\bar{t})}{\bar{t}} \qquad (a)$$
   - → we need to substitute for $(1-X_B)$ using the appropriate relationship as governed by the rate controlling step
     - → If film resistance controls: $1-X_B = 1-t/\tau$
     - → " Chemical rxn " " : $1-X_B = (1-t/\tau)^3$
     - → " ash " " : $\frac{t}{\tau} = 1-3(1-X_B)^{2/3} + 2(1-X_B)$

⇒ film resistance controlling: $\bar{X}_B = \frac{\bar{t}}{\tau}(1-\exp(-\frac{\tau}{\bar{t}}))$, $1-\bar{X}_B = \frac{1}{2}\frac{\tau}{\bar{t}} - \frac{1}{3!}(\frac{\tau}{\bar{t}})^2 + \frac{1}{4!}(\frac{\tau}{\bar{t}})^3 - \ldots$

chemical rxn " : $\bar{X}_B = 3\frac{\bar{t}}{\tau} - 6(\frac{\bar{t}}{\tau})^2 + 6(\frac{\bar{t}}{\tau})^3 \cdot \cancel{(\frac{\tau}{\bar{t}})^3}(1-\exp(-\frac{\tau}{\bar{t}}))$, $1-\bar{X}_B = \frac{1}{4}\cdot\frac{\tau}{\bar{t}} - \frac{1}{20}\cdot(\frac{\tau}{\bar{t}})^2 + \frac{1}{120}(\frac{\tau}{\bar{t}})^3 - \ldots$

ash resistance controlling : $1-\bar{X}_B = \frac{1}{5}\cdot\frac{\tau}{\bar{t}} - \frac{19}{420}(\frac{\tau}{\bar{t}})^2 + \frac{41}{4620}(\frac{\tau}{\bar{t}})^3 - 0.00149(\frac{\tau}{\bar{t}})^4 + \ldots$

- Ex.02
  - $\tau \propto R^{1.5}$ for roasting of pyrrhotide (iron sulfide) where a hard product is formed.
  - uniform feed with particles for which $\tau = 20^{min}$
  - mean residence time, $\bar{t} = 60^{min}$
  - what is the fractional conversion
  - since hard ash is formed film resistance can be ruled out as the rate controlling step.
  - for chemical rxn controlling : $\tau \propto R$
  - for ash resistance " : $\tau \propto R^2$
  - both resistances contribute to the process, each going a lower and upper bound for conversion :
  - for chemical rxn: $1-\bar{X}_B = \frac{1}{4}(\frac{20}{60}) - \frac{1}{20}(\frac{20}{60})^2 + \frac{1}{120}(\frac{20}{60})^3 - \dots = 0.078$
  - for ash resistance: $1-\bar{X}_B = \frac{1}{5}(\frac{20}{60}) - \frac{19}{420}(\frac{20}{60})^2 + \frac{41}{4620}(\frac{20}{60})^3 - \dots = 0.062$
  - on average: $1-\bar{X}_B = 0.07 \Rightarrow \bar{X}_B = 0.93 = 93\%$

4. Mixed flow of a size mixture of particles of unchanging size, uniform gas composition
   - same as case 3 that the feed has a distribution of particles sizes.
   - since the particle size is unchanging, the particle size distribution inside the reactor is similar to that of the feed: $\frac{F(R_i)}{F} = \frac{W(R_i)}{W}$
   - where
     - $W(R_i)$ is quantity of particles of radius R_i inside the reactor.
     - W " " " solids inside the reactor.
   - $\bar{t} = \frac{W}{F}$
   - for particles of size R_i in a CSTR: $1-\bar{X}_B(R_i) = \int_0^{\tau(R_i)} [1 - X_B(R_i)] \frac{\exp(-t/\bar{t})}{\bar{t}} dt$ (a)
     (gives average conversion of particles of size R_i)
   - for a feed consisting of different particle size, the mean value for fraction of B unconverted is (gives overall average of all particle sizes): $1-\bar{\bar{X}}_B = \sum_{R_i=0}^{R_m} [1-\bar{X}_B(R_i)] \frac{F(R_i)}{F}$ (b)
   - given the rate controling step, we have the following case:

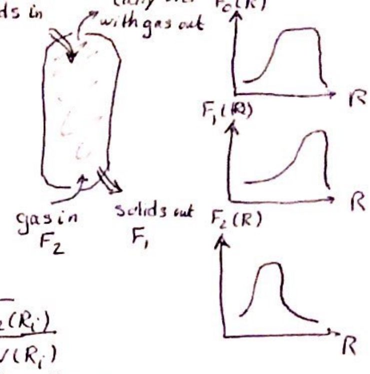
- film resistance controls: $1-\bar{\bar{X}}_B = \sum_{R_i=0}^{R_m} \left[\frac{1}{2!}\frac{\tau(R_i)}{\bar{t}} - \frac{1}{3!}\left(\frac{\tau(R_i)}{\bar{t}}\right)^2 + \frac{1}{4!}\left(\frac{\tau(R_i)}{\bar{t}}\right)^3 - \dots\right] \frac{F(R_i)}{F}$
- chemical rxn " : $1-\bar{\bar{X}}_B = \sum_{R_i=0}^{R_m} \left[\frac{1}{4}\frac{\tau(R_i)}{\bar{t}} - \frac{1}{20}\left(\frac{\tau(R_i)}{\bar{t}}\right)^2 + \frac{1}{120}\left(\frac{\tau(R_i)}{\bar{t}}\right)^3 - \dots\right] \frac{F(R_i)}{F}$
- Ash resistance " : $1-\bar{\bar{X}}_B = \sum_{R_i=0}^{R_m} \left[\frac{1}{5}\frac{\tau(R_i)}{\bar{t}} - \frac{19}{420}\left(\frac{\tau(R_i)}{\bar{t}}\right)^2 + \frac{41}{4620}\left(\frac{\tau(R_i)}{\bar{t}}\right)^3 - \dots\right] \frac{F(R_i)}{F}$

- Ex.03
  - size distribution of feed:
  - spherical particles of unchanging size, constant gas composition
  - Fluidized bed reactor, D = 4", L = 4'
  - feedrate = 1 kg/min , $W_{\text{solids in bed}} = 10$ kg
  - $\bar{t} = \frac{10 \text{ kg}}{1 \text{ kg/min}} = 10$ min
  - $\tau(R_i) \propto R_i \Rightarrow$ Chemical rxn in RCS
  - $1-\bar{\bar{X}}_B = [\frac{1}{4}(\frac{5}{10}) - \frac{1}{20}(\frac{5}{10})^2 + \frac{1}{100}(\frac{5}{10})^3 - \dots](0.3) + [\frac{1}{4}(\frac{10}{10}) - \frac{1}{20}(\frac{10}{10})^2 + \frac{1}{120}(\frac{10}{10})^3 - \dots](0.4)$

$+ [\frac{1}{4}(\frac{20}{10}) - \frac{1}{20}(\frac{20}{10})^2 + \frac{1}{100}(\frac{20}{10})^3 - \dots](0.3) = 0.227 \Rightarrow \bar{X}_B = 77.3\%$

R_i (μm)	$\frac{F(R_i)}{F}$	$\tau(R_i)$ (min)
50	0.3	5
100	0.4	10
200	0.3	20

5. Fluidized Bed with Entrainment of solids



→ Carry over of fines in the gas stream leaving the reactor.

→ This would shift the size distribution inside reactor towards larger particles

→ $F_0 = F_1 + F_2$, $F_0(R_i) = F_1(R_i) + F_2(R_i)$

$$\Rightarrow \frac{F_1(R_i)}{F_1} = \frac{W_1(R_i)}{W_k}$$

→ Hence, mean residence time would be different for different sized particles: $\bar{t}(R_i) = \dfrac{W(R_i)}{F_0(R_i)} = \dfrac{W(R_i)}{F_1(R_i) + F_2(R_i)} = \dfrac{1}{\frac{F_1}{W} + \frac{F_2(R_i)}{W(R_i)}}$

→ once we have the mean residence time for each particle size, $\bar{t}(R_i)$, then the mean conversion of particles of size R_i can be obtained: $1-\bar{X}_B(R_i) = \int_0^{\tau(R_i)} [1 - X_B(R_i)] \cdot \dfrac{\exp(-t/\bar{t}(R_i))}{\bar{t}(R_i)} dt$

→ and for a feed consisting of a size mixture : $1-\bar{\bar{X}}_B = \sum_{R_i=0}^{R_m} (1-\bar{X}_B(R_i)) \dfrac{F_0(R_i)}{F_0}$

→ and for various situations we have:

- film diffusion controlling : $1-\bar{\bar{X}}_B = \sum_{R_i=0}^{R_m} \left[\frac{1}{2!} \cdot \frac{\tau(R_i)}{\bar{t}(R_i)} - \frac{1}{3!}\left(\frac{\tau(R_i)}{\bar{t}(R_i)}\right)^2 + \cdots\right] \frac{F_0(R_i)}{F_0}$
- chemical rxn " : $1-\bar{\bar{X}}_B = \sum_{R_i=0}^{R_m} \left[\frac{1}{4} \frac{\tau(R_i)}{\bar{t}(R_i)} - \frac{1}{20}\left(\frac{\tau(R_i)}{\bar{t}(R_i)}\right)^2 + \cdots\right] \frac{F_0(R_i)}{F_0}$
- ash diffusion " : $1-\bar{\bar{X}}_B = \sum_{R_i=0}^{R_m} \left[\frac{1}{5} \frac{\tau(R_i)}{\bar{t}(R_i)} - \frac{19}{420}\left(\frac{\tau(R_i)}{\bar{t}(R_i)}\right)^2 + \cdots\right] \frac{F_0(R_i)}{F_0}$

→ to use the above eqs. we need to know $\bar{t}(R_i)$; $\bar{t}(R_i) = \dfrac{1}{\frac{F_1}{W} + \frac{F_2(R_i)}{W(R_i)}}$

- which requires independent information on the flow split and size distribution in the two exit streams

→ Elutriation velocity rate constant, k

→ $\dfrac{dN_p}{dt} = kN_p$, $N_p \triangleq$ Number of particles in the bed.

→ $k \propto \dfrac{(\text{gas velocity})^4}{(\text{bed height}) \cdot (\text{particle size})^{2 \text{ or } 3}}$

→ $k(R_i) = \dfrac{\text{rate of carry over of particles of size } R_i}{\text{weight of such particles present in the bed}} = \dfrac{F_2(R_i)}{W(R_i)}$

→ $\bar{t}(R_i) = \dfrac{1}{\frac{F_1}{W} + k(R_i)} = \dfrac{W(R_i)}{F_0(R_i)} \Rightarrow F_1(R_i) = \dfrac{F_1}{W} \cdot W(R_i)$

$\dfrac{F_1(R_i)}{F_1} = \dfrac{W(R_i)}{W} \Rightarrow F_1(R_i) = \dfrac{F_1}{W} \cdot \dfrac{F_0(R_i)}{\frac{F_1}{W} + k(R_i)}$

$$\Rightarrow F_1(R_i) = \frac{F_0(R_i)}{1 + \frac{W}{F_1} \cdot k(R_i)}$$

→ $F_1 = \sum F_1(R_i) = \sum \dfrac{F_0(R_i)}{1 + \frac{W}{F_1} \cdot k(R_i)} = F_1$

→ the above expression can be used to obtain F_1 by trial and error and once F_1 is obtained: $\bar{t}(R_i) = \dfrac{1}{\frac{F_1}{W} + k(R_i)}$

- Ex. 04 → Fluidized Bed, $F_0 = 1^{kg/min}$, $W = 10^{kg}$, $k = \dfrac{500}{R_i^2}$, Particle Size Distribution

R_i	$F_0(R_i)/F_0$	$F_0(R_i)$	$\tau(R_i)$	$k(R_i) = \frac{500}{R_i^2}$
50	0.3	0.3	5	0.2
100	0.4	0.4	10	0.05
200	0.3	0.3	20	0.0125

→

F_1 (guess)	$F_1(R_1)$	$F_1(R_2)$	$F_1(R_3)$	$\sum F_1(R_i)$
0.4	0.05	0.1778	0.2286	0.4564
0.6	0.0692	0.2182	0.2483	0.5357
0.5	0.06	0.2	0.24	0.5

$F_1 = 0.5 \Rightarrow \bar{t}_1 = 4^{min}, \bar{t}_2 = 10^{min}, \bar{t}_3 = 16^{min}$

$1 - \bar{\bar{X}}_B = 0.233$