

8. Characteristics of continuous and batch crystallizers

8.1 Continuous MSMPR crystallizer

- What change of crystal size is expected if the mean residence time is varied?

Assemble the characteristic equations representing some properties.

$$\bar{L}_D = 3G\tau$$

$$M_T = 6\rho_{cry}\alpha BG^3\tau^4$$

$$B = K_R M_T G^i$$

where

$$B = k_b M_T \Delta C^b$$

$$G = k_g \Delta C^g$$

$$K_R = k_b / k_g^i$$

$$i = b/g$$

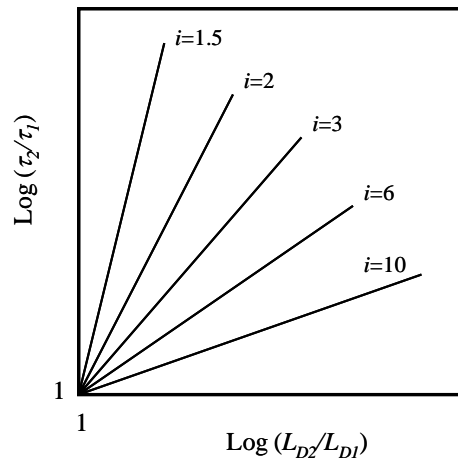
From assembly of above equations,

$$\tau = \frac{\bar{L}_D}{3} \left[\frac{2\rho_{cry}\alpha K_R \bar{L}_D^4}{27} \right]^{1/(i-1)}$$

That is,

$$\tau \propto \bar{L}_D^{(i+3)/(i-1)} \quad \text{if } i \neq 1$$

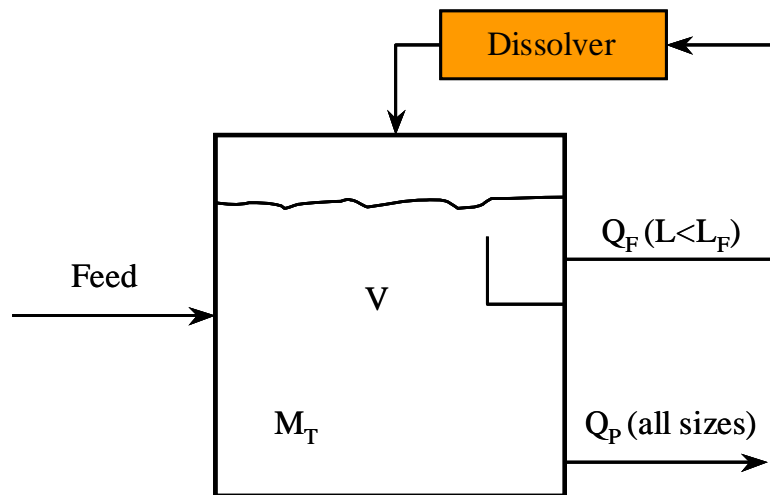
$$\bar{L}_D = \left[\frac{27}{2\rho_{cry}\alpha K_R} \right]^{1/4} \quad \text{if } i = 1$$



8.2 Size-dependent removal rates

Mean residence time of crystals depending on their size.

- *Fine removal*



Producing the same production rate with the fewer crystals of larger average size.

The mean residence time of fines (τ_F) and of the product (τ_P)

$$\tau_F = \frac{v}{Q_F + Q_P} \quad (L < L_F)$$

$$\tau_P = \frac{V}{Q_P} \quad (L > L_F)$$

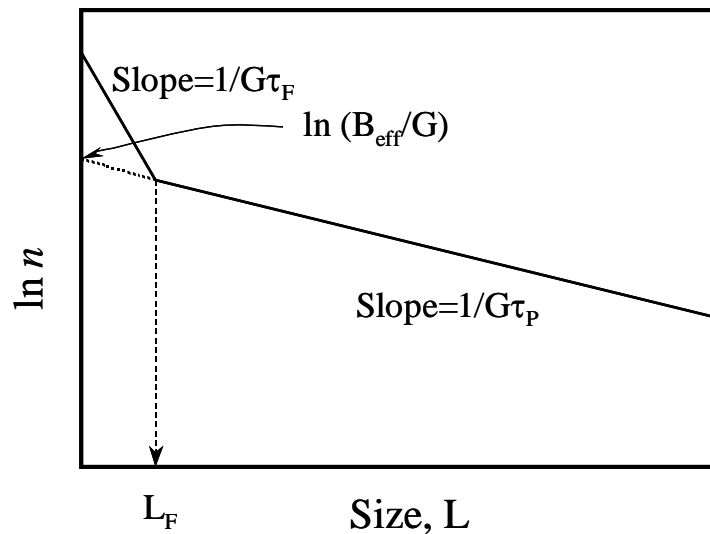
Then, the population density distribution of crystals

$$n = n^0 \exp\left(-\frac{L}{G\tau_F}\right) \quad \text{for } L < L_F$$

$$n = n^0 \exp\left(-\frac{L_F}{G\tau_F}\right) \exp\left(-\frac{L}{G\tau_P}\right) \quad \text{for } L > L_F \text{ if } L_F \ll \bar{L}_D$$

Thereby, the effective birth rate can be defined as

$$B_{eff} = Gn^0 \exp\left(-\frac{L_F}{G\tau_F}\right)$$



As analogously in Eq. (8.1),

$$\tau = \frac{f \bar{L}_D}{3} \left[\frac{2\rho_{cry} \alpha K_R \bar{L}_D^4}{27} \right]^{1/(i-1)}$$

where

$$f = \left[\exp\left[-\frac{3L_F \tau_P}{L_D \tau_F}\right] \right]^{1/(i-1)}$$

Typical parameter values for the fine removal system are

$$\tau_P/\tau_F=10, \quad L_F/L_D=0.1, \quad i=3, \quad \text{then } \underline{f=0.22}$$

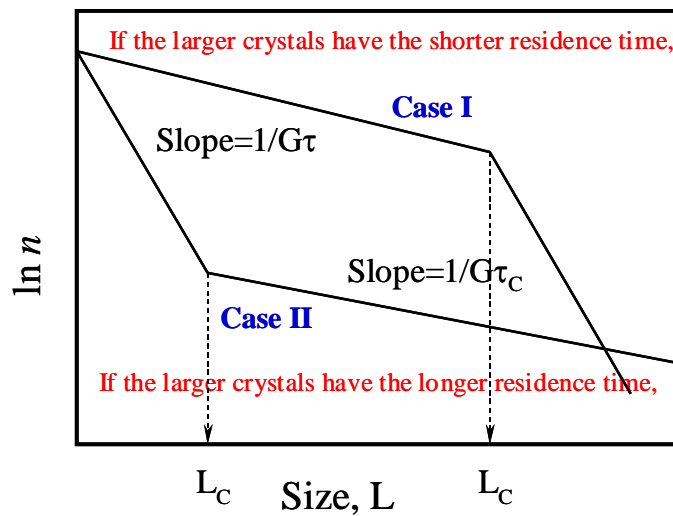
Advantage of the system

- greater operating flexibility

Disadvantage of the system

- greater encrustation on the crystallizer wall
- higher possibility of instability
- more energy cost for fine dissolution

- Classified product removal



Case I

- smaller mean crystal size than one in normal crystallizer
- narrow crystal size distribution
- low number of crystals in product
- high population of small crystals in crystallizer
- low supersaturation level in crystallizer → low growth rate
combining with fine removal system

Case II

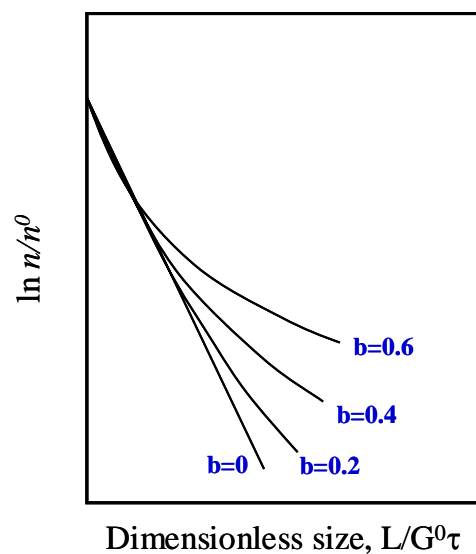
- larger mean crystal size than one in normal crystallizer
- wide crystal size distribution
- leading to unstable operating conditions.

8.3 Other factors influencing crystal size distribution

- Size-dependent growth rate

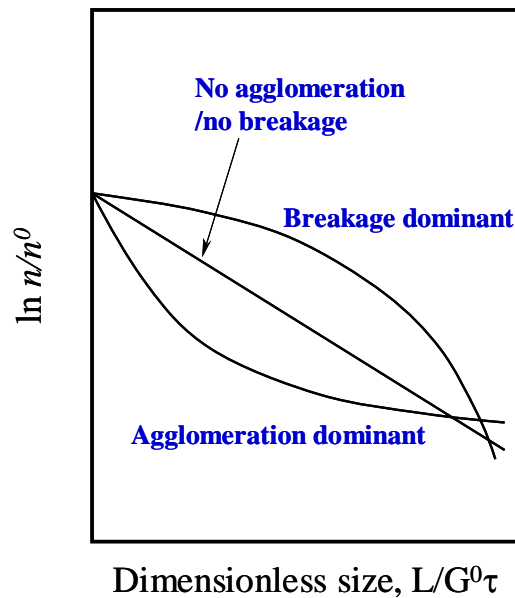
The small crystals have the lower growth rate than the large crystals.

$$G = G_0[1 + \gamma L]^b \quad \text{for } b < 1$$



- Agglomeration and breakage

In general, the agglomeration is occurring in the smaller size range whereas the breakage does in the larger size range.



8.4 Dynamics and stability of continuous crystallizer

- unsteady state MSMPR crystallizer

$$\frac{\partial n}{\partial t} + G \frac{\partial n}{\partial L} = -\frac{n}{\tau}$$

Instability is originated from interaction between the inherent kinetics of crystallizing system and the residence time distribution function.

Typical cases of instability

- when the nucleation mechanism is changed from secondary to primary in either way.
- low frequency cycling combined with a fine removal system.

8.5 Batch crystallizer

- for low production rate of specialty, agro- and pharmaceutical chemicals
- simple and flexible system
- low capital investment
- multi-purpose process (reactor, crystallizer, mixer, blender handling many products)

Typical type of crystallization

- cooling crystallization
- evaporation crystallization
- drowning-out (salting-out) crystallization
- reaction crystallization

Operation variables

- batch time
- supersaturation rate
- addition of seed crystals
- agitation type and level
- feeding mode and rate etc.

- *The mass balance*

$$\frac{dM}{dt} + \frac{dVc}{dt} = 0$$

where M is the amount of crystals in suspension, V is the solution volume and c is the concentration of solute in solution.

(1) In cooling crystallization with assumption of c approximately equal to c_{eq} , the mass balance is rearranged as,

$$\frac{dM}{dt} + V\left(\frac{dc_{eq}}{d\theta} \frac{d\theta}{dt}\right) = 0$$

where

$$\frac{dc_{eq}}{d\theta} = \text{slope of solubility curve}$$

$$\frac{d\theta}{dt} = \text{cooling rate}$$

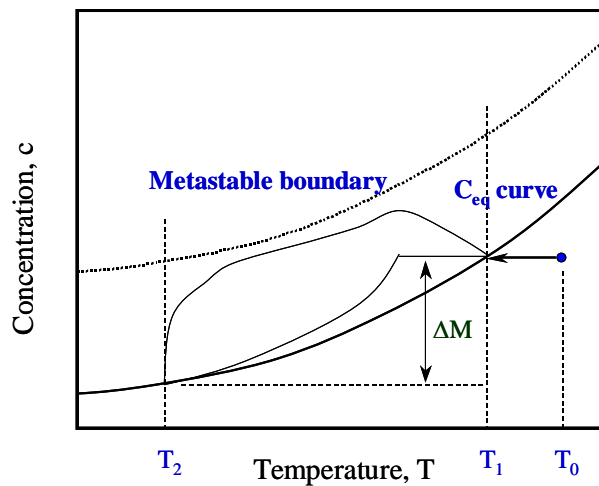
(2) In evaporation crystallization with assumption of c approximately equal to c_{eq} , the mass balance is rearranged as,

$$\frac{dM}{dt} + c_{eq} \frac{dV}{dt} = 0$$

where

$$\frac{dV}{dt} = \text{evaporation rate}$$

- Supersaturation control and seeding



$$\frac{L_p}{L_s} = \left[\frac{M_p}{M_s} \right]^{1/3}$$

L_s and L_p : crystals sizes of seed and product, respectively

M_s and M_p : masses of seed and product, respectively

- Cooling crystallization

Natural cooling : constant temperature and constant flow rate of cooling water.

$$\frac{\theta - \theta_0}{\theta_i - \theta_0} = \exp(-t / \tau_B)$$

where θ_i and θ_0 are the initial and final temperatures, respectively, and τ_B is the batch time constant defined as,

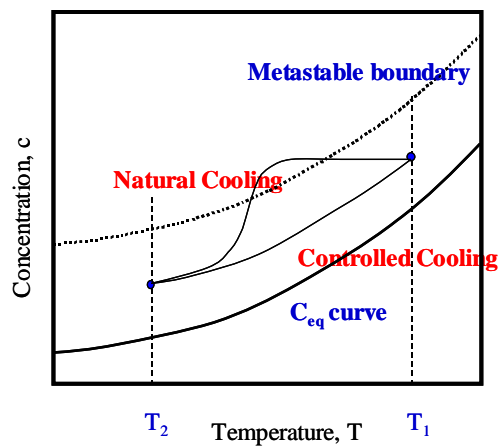
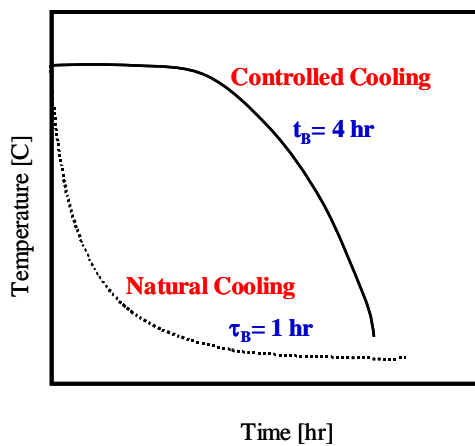
$$\tau_B = \frac{M_S C_P}{U A_B}$$

where U is overall heat transfer coefficient, A_B is the heat transfer area, M_S is the mass of solution and C_P is the heat capacity of the solution.

Controlled cooling : for constant supersaturation

$$\frac{\theta_i - \theta}{\theta_i - \theta_0} = (t / t_B)^4 \quad \text{for unseeded system}$$

$$\frac{\theta_i - \theta}{\theta_i - \theta_0} = (t / t_B)^3 \quad \text{for seeded system}$$



- Other crystallization method

Similarly, in evaporation crystallization the evaporation rate should be very low at the first of the batch and gradually increase as a greater crystal surface is developed.

Also, in drowning-out crystallization the anti-solvent should be slowly added and gradually increase in the course of the batch.

- The population balance for batch crystallization

$$\frac{\partial n}{\partial t} + \frac{\partial nG}{\partial L} = 0$$

Kinetic data are required to solve the balance equation.

- Practical operating factors in batch crystallization

Minimum stirring speed (N_{js}) to suspend the crystals of specific size L .

$$N_{js} = S[\nu^{0.1} L^{0.2} X^{0.15} D^{-0.85} (g\Delta\rho / \rho_l)^{0.45}]$$

ν is the kinetic viscosity of the solution, X is the fraction of solid in the vessel, D is the stirrer diameter, g is the gravity, ρ_l is the liquid density and $\Delta\rho$ is the density difference between crystal and solution. S is the dimensionless constant depending on the vessel geometry.

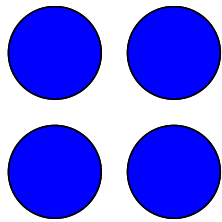
9. Crystals in formulated products

9.1 Crystals as active products

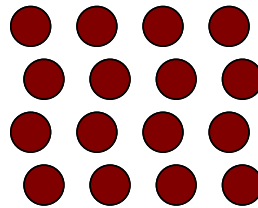
Pharmaceutical drug of active ingredients :

$$\frac{dm}{dt} = \frac{DA}{h}(c_{eq} - c)$$

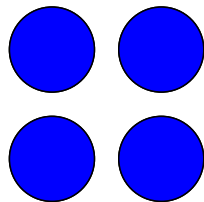
where dm/dt is the dissolution rate, D is the diffusivity, A is the surface area, h is the diffusion layer thickness, and c_{eq} and c are the solute concentration at equilibrium and bulk, respectively.



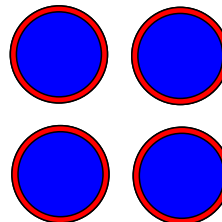
Low surface area
Slow dissolution



High surface area
Fast dissolution



Low diffusion resistance
High dissolution

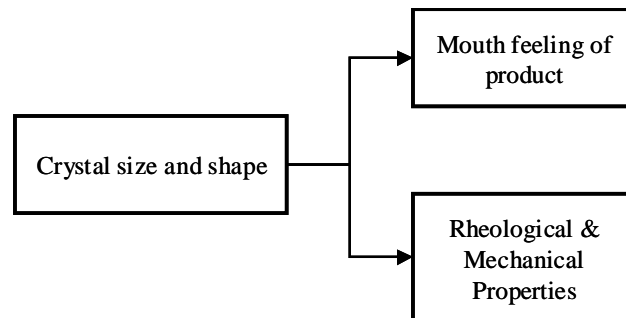


High diffusion resistance
Slow dissolution

9.2 Crystals as property controllers

Margarine and chocolate : triglyceride crystal

Ice cream : water ice crystals



9.3 Crystals causing problems

Ostwald ripening : Crystal size increase, surface area decrease

Phase transformation : Ammonium nitrate

9.4 Crystallization controllers as products

Crystallization inhibitor to paraffins in middle distillate fuels: copolymer of ethylene and vinylacetate.

Scale inhibitor : organic phosphate and carboxylate