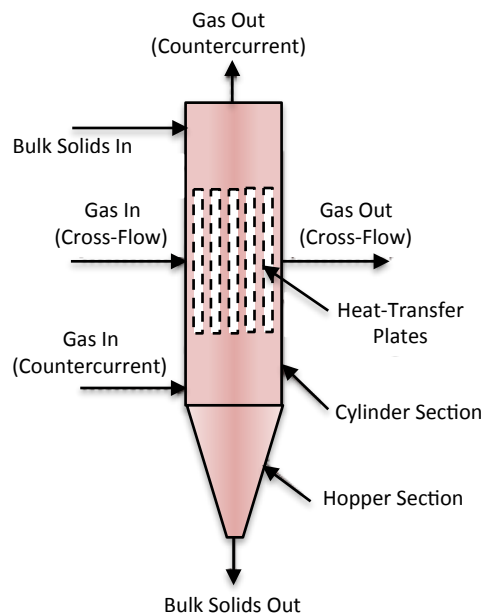


## Process vessels

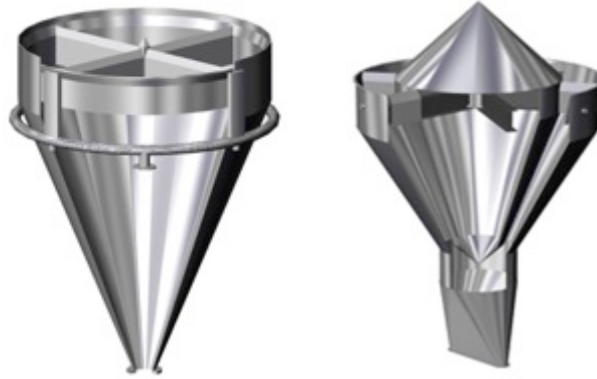
Chemical engineers who understand the fundamentals of bulk solids handling should be adept at designing moving bed processors. Essentially, moving-bed process vessels are hoppers, bins, or silos that have been modified to allow processing of a bulk solid, *e.g.*, heating or cooling, drying, purging, conditioning, or accommodating a chemical reaction. Frequently a gas is injected either countercurrent or perpendicular to the flow of bulk solid. The gas may be used to remove volatiles or by-products of chemical reactions or it may be a reactant itself. A schematic of a process vessel with plenty of bells and whistles is shown in Figure 8.9.



**Figure 8.9. Process vessel schematic.**

The key to the performance of a moving bed process vessel is uniform solids and gas flow. For the solid phase, the usual features – mass flow, sufficiently sized outlet are desired. If the process requires injection of a gas, for example, to remove volatile compounds or provide direct heat transfer, the gas must flow uniformly and in a manner that does not cause channeling or other bed instabilities.

The gas can be either counter-flow or cross-flow. In a counter-flow system, the gas feed system must prevent high gas velocities since localized fluidization will cause channeling. Therefore, nozzles or perforated plates should not be used. Two examples of properly-designed gas distributors, in which the gas is injected into the moving solids bed via an annulus and a set of crossbeams located near the intersection of the cylinder and hopper sections, are shown in Figure 8.10 [Mehos, *Chem. Engr.*116, 5, 34 (2009)].



**Figure 8.10. Gas distributors with crossbeams.**

When gas flows countercurrent to the flow of solids, the gas velocity must be low enough to prevent fluidization in the cylindrical section of the processor. A rule of thumb is that the vessel's cross-sectional area at the level the gas is introduced should be large enough to keep the superficial gas velocity less than approximately one-third the bulk material's minimum fluidization velocity.

The gas pressure profile is determined by adding a pressure gradient term to the differential form of the Janssen equation (Equation 3.5) and applying Darcy's law (Equation 4.19) to evaluate the pressure gradient:

$$\frac{d\sigma_v}{dz} + \frac{k \tan \phi'}{R_H} \sigma_v = \rho_b g + \frac{dP}{dz} \quad (8.5)$$

$$\frac{dP}{dz} = - \frac{u_s \rho_b g}{K} \quad (8.6)$$

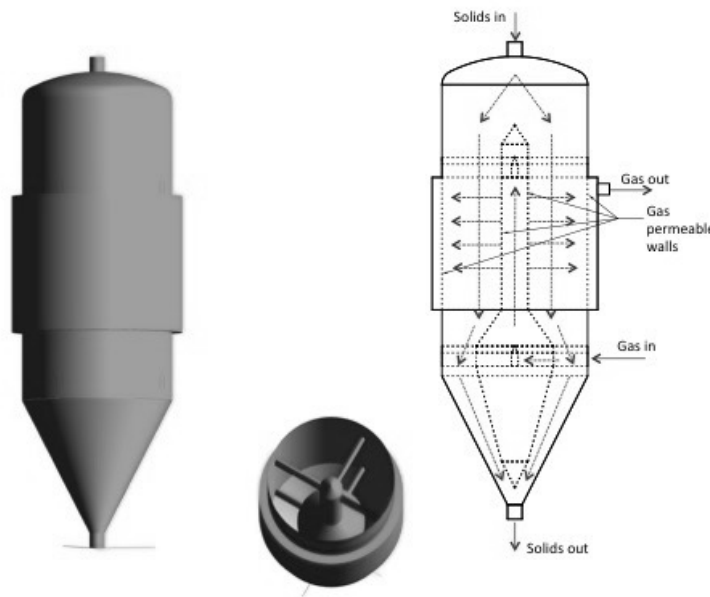
where  $\sigma_v$  is the solids stress,  $k$  is the Janssen coefficient,  $\phi'$  is the wall friction angle,  $\rho_b$  is the bulk density,  $g$  is gravitation due to gravity,  $P$  is the gas pressure,  $K$  is the permeability,  $u_s$  is the gas slip velocity, and  $z$  is the distance from the top of the solids bed. These equations must be solved numerically using a known value of the solids stress (generally equal to zero at the top of the bed) and the gas pressure (not necessarily zero at the top of the column) since both the bulk density and the permeability are functions of solids stress. Because the gas density changes with pressure, the slip velocity will also change within the column. Equations 8.5 and 8.6 can be used to determine the required gas pressure at the inlet of the processor and the solids stress at that level. It is important to ensure that the solids stress is sufficiently greater than zero at that local.

If an annulus and crossbeams are used for gas injection, they should be sized to ensure that the solids stress on the components are non-zero. It is best to have Jenike & Johanson size these components.

If the gas flow rate is too low, a driving force for mass transfer will not exist in part of the column. The minimum gas rate can be determined from a mass balance in which the concentration of the volatile species in the gas leaving the top of the column is in equilibrium with the incoming solids.

This is analogous to specifying a high enough gas rate to avoid pinching in a liquid stripping column. The gas velocity should not be so high that excessive entrainment of fines will occur.

Cross-flow designs are preferred if the required gas flow rate is high because the pressure drop will be lower. Cross-flow processors are fabricated with permeable walls, such as those manufactured by Young Industries (Muncy, Pennsylvania) through which the gas enters and exits the processing vessel perpendicular to the flow of solids. Moving bed cross-flow processors having a circular cylinder section are designed with two (or more) permeable annuli. Gas is typically fed into a permeable inner cylinder, travels through a bed of solids that are flowing inside the annulus, and then exits through an outer permeable wall. Figure 8.11 is a schematic of a radial gas flow moving bed processor (see <http://jenike.com/13778-2/>).



For cross-flow designs, the gas velocity must be low enough to prevent cavities or pinning. A cavity can develop if the pressure gradient that develops when gas is injected into the bed causes a gap to form between the bulk solid and the wall from which the gas is introduced. If a cavity forms, gas will flow preferably upward rather than across the bed. Introducing solids through a rotary valve may reduce cavity formation.

Pinning can occur on the opposite wall. Pinning happens when the friction between the bulk solid and the permeable wall through which the gas exits is high enough to prevent the particles from flowing downward along the wall. A periodic pulse of reverse air can be used to prevent material from building on the exit walls.

Moving bed processors generally have residence time requirements. The residence time of a bulk solid in a process vessel is related to its feed rate by

$$t = \frac{z\rho_b A}{\dot{m}_s} \quad (8.7)$$

where  $t$  is the time in the processor,  $\dot{m}_s$  is the solids mass flow rate,  $z$  is the distance traveled from the top of the column,  $A$  is its cross-sectional area, and  $\rho_b$  is the bulk density of the solids. The product  $Az$  is equal to the volume of the moving bed in the cylinder. For some applications, the volume of the hopper section should be included in the residence time calculations.

### Purge columns and gravity dryers

In a purge column or gravity dryer, the mass transfer driving force must be known. The driving force is equal to the difference between the volatiles content of the solid particles and that which is in equilibrium with the bulk gas. Phase equilibrium data are therefore needed to design purge vessels and gravity dryers. Usually, determining the phase equilibria is much less challenging than gathering kinetics information.

Kinetics within solid particles are frequently described by Fick's law. Fick's second law for spherical particles is given by

$$\frac{\partial x}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( D_{eff} r^2 \frac{\partial x}{\partial r} \right) \quad (8.8)$$

where  $x$  is the mass fraction of the volatile component in the solid,  $D_{eff}$  is the effective diffusion coefficient of the volatile species in the solid particle, and  $r$  is the radial coordinate. Often, the effective diffusivity is expressed as the product of the molecular diffusivity, which is usually known, and what's called the porosity-tortuosity ratio, which is rarely known and cannot be even estimated with confidence. It's best just to determine the effective diffusivity by experiment.

Initially, the mass fraction of the volatile component is equal to  $x_{init}$ , *i.e.*,

$$x(r, 0) = x_{init} \quad (8.9)$$

Boundary conditions are:

$$\frac{\partial x(0, t)}{\partial r} = 0 \quad (8.10)$$

$$x(r_o, t) = x_\infty \quad (8.11)$$

where  $x_\infty$  is the mass fraction of the volatile component in the solid in equilibrium with the bulk gas. Equation 8.10 describes symmetry at the center of the particle. The mass fraction at the solid surface is only equal to  $x_\infty$  if there is no resistance to mass transfer in the gas phase, which is not always the case. If the gas-phase resistance cannot be ignored, Equation 8.12 can be used to describe the boundary condition at the surface:

$$-D_{eff} \frac{\partial [x(r_o, t)]}{\partial r} = k_x (x - x_\infty) \quad (8.12)$$

where  $k_x$  is the convective mass transfer coefficient. In principle, expressions for mass transfer in the gas phase should be based on a gas-phase driving force, but for convenience, the difference in solids mass fractions is often used. If a linear relationship exists, *i.e.*,  $y = mx$ , where  $m$  is the slope

of the equilibrium line and  $y$  is the mass fraction of the volatile species in the gas phase (a.k.a. Hank's Law, or Henry's Law if we are more formal), then

$$k_y(y - y_\infty) = k_x(mx - mx_\infty) \quad (8.13)$$

and  $k_x = mk_y$ , where  $k_y$  is the mass transfer coefficient based on the gas phase driving force ( $y - y_\infty$ ).

Whether or not gas-phase resistance is important can be gleaned from the Biot number **Bi**, which reveals the relative contributions of the resistances to mass transfer due to diffusion in the solid particle and convection in the gas phase. The Biot number is a dimensionless group given by

$$\mathbf{Bi} = \frac{k_x r_o}{D_{eff}} \quad (8.14)$$

A Biot number significantly greater than 1 signifies that mass transfer is limited by diffusion in the solid phase. Low values, *i.e.*, Biot numbers less than approximately 0.1, indicate that the rate is limited by convection in the gas phase. For systems having small Biot numbers, the concentration of the diffusant species will be nearly constant and the kinetics can be described by

$$\frac{d\bar{x}}{dt} = -k'(\bar{x} - x_\infty) \quad (8.15)$$

where  $\bar{x}$  is the mean volatiles content (mass fraction) of the particle, and

$$k' = \frac{3k_x}{r_o} \quad (8.16)$$

The  $3/r_o$  factor arises from a surface area per unit volume calculation. Analytical expressions for the solution to the diffusion equation for **Bi** appreciably greater than 1 or less than 0.1 respectively are:

$$\frac{\bar{x} - x_\infty}{x_{init} - x_\infty} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-n^2 \pi^2 D_{eff} t}{r_o^2}\right) \quad \mathbf{Bi} \gg 1 \quad (8.17)$$

and

$$\frac{\bar{x} - x_\infty}{x_{init} - x_\infty} = \exp(-k't) \quad \mathbf{Bi} < 0.1 \quad (8.18)$$

For the dreaded scenario in which the Biot number is neither very large nor very small, the following approximate solution can be used:

$$\frac{\bar{x}(t) - x_\infty}{x_{init} - x_\infty} = \frac{3A_1}{\lambda_1^3} (\sin \lambda_1 - \lambda_1 \cos \lambda_1) \exp\left(-\lambda_1^2 \frac{D_{eff} t}{r_o^2}\right) \quad (8.19)$$

where

$$A_1 = \frac{4 \sin(\lambda_1) - \lambda_1 \cos(\lambda_1)}{2\lambda_1 - \sin(2\lambda_1)} \quad (8.20)$$

and  $\lambda_1$  is the first eigenvalue, which for spheres is the root of the equation

$$1 - \frac{\lambda_1}{\tan \lambda_1} = \mathbf{Bi} \quad (8.21)$$

Equation 8.19 is the truncated form of an infinite series solution to the diffusion equation with a mass transfer type boundary condition. It holds for residence times greater than *ca.*  $0.2r_o^2/D_{eff}$ .

In a purge column, the surface volatiles content is not constant but instead varies with position inside the cylinder. Hence, Equations 8.17 through 8.21 *cannot* be applied to moving beds. However, the equations can be used to regress the parameters  $D_{eff}$ ,  $k'$ , and  $k_x$  from batch stripping data, which can be collected by passing a gas stream through a compact bed of powder and measuring its volatiles content over time. The Sauter mean particle size should be used to calculate  $r_o$ . The tests should be conducted over a range of bulk densities to match the expected range of densities in the column.

Figures 8.12 through 8.14 illustrate how the parameters are determined by regressing batch stripping data. When data are plotted on a semi-logarithmic scale, regression of the linear portion of the data will yield a line that intersects the vertical axis at  $6/\pi^2$  if mass transfer is limited by diffusion, 1 if mass transfer is limited by convection in the gas phase, and a value greater than  $6/\pi^2$  and less than 1 if resistances due to diffusion and convection are both significant. Hence, inspection of the intercept allows insight to which mass transfer resistances dominate.

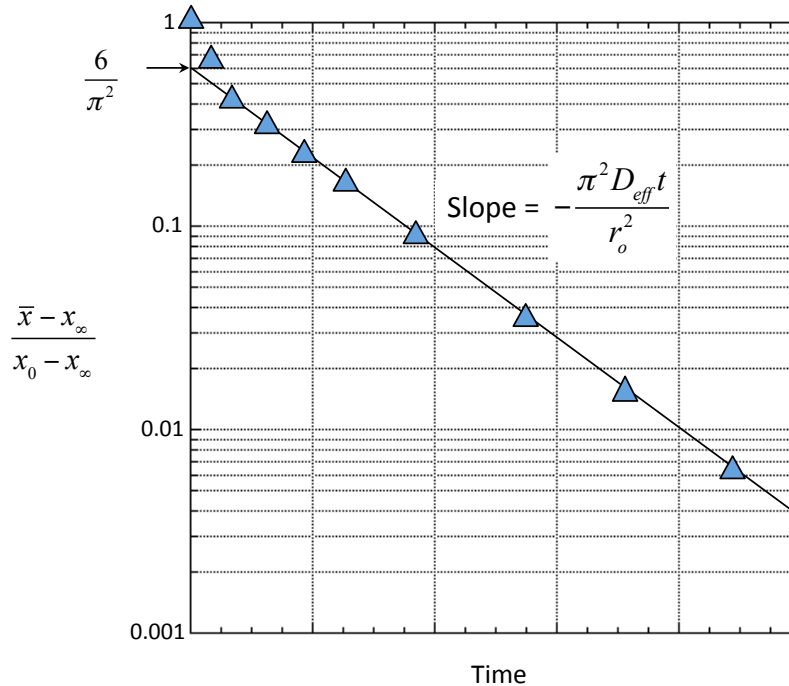


Figure 8.12. Typical batch devolatilization data when Biot Number  $\gg 1$ .

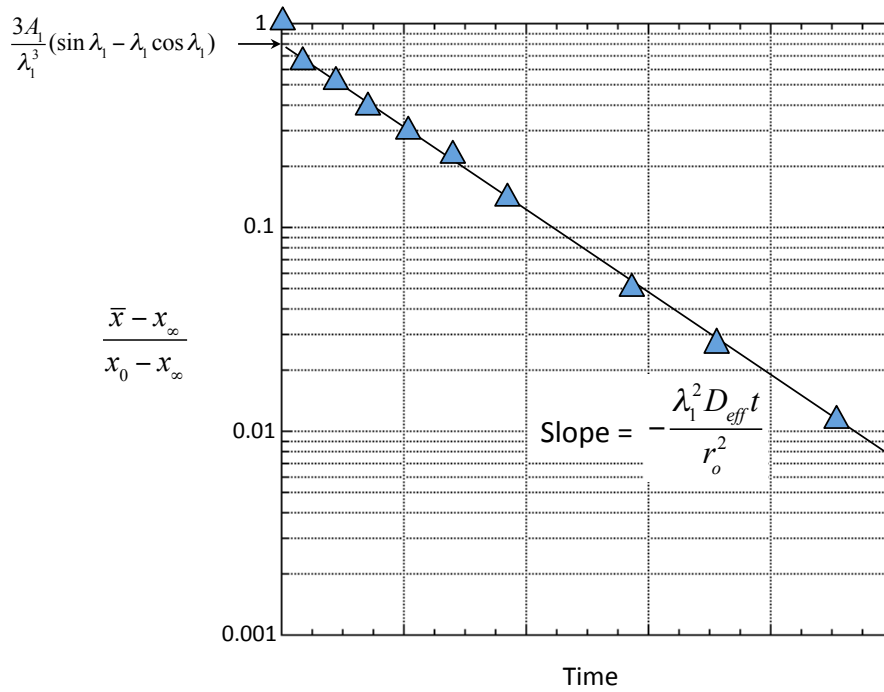


Figure 8.13. Typical batch devolatilization data when Biot Number  $> 0.1$  and  $< 1$ .

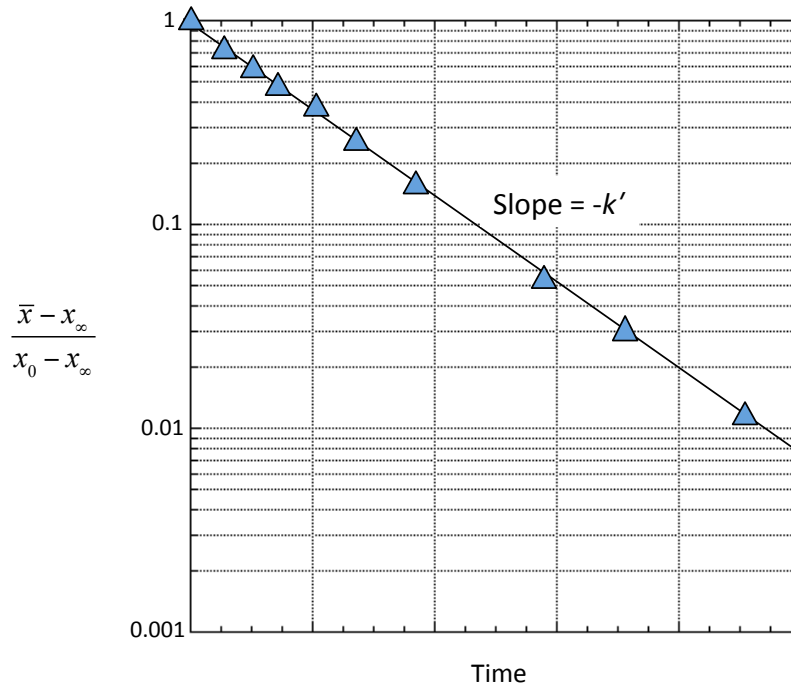


Figure 8.14. Typical batch devolatilization data when Biot Number  $< 0.1$ .

The parameters obtained by regression of batch data can then be used to model continuous columns. Once the kinetics parameters have been determined, the transfer equations are solved numerically using a mass balance to track the volatiles in the gas stream. The column is partitioned, each segment having gas and solids streams entering from or exiting to adjacent segments. Unless  $\mathbf{Bi} < 0.1$ , the diffusion equation is integrated numerically over the residence time of each segment to determine the concentration profile of the particles leaving the segment, and a material balance is used to determine the volatiles content of the gas entering the segment. The solids concentration profile is then used as the initial condition for solving the diffusion equation for the next segment. The required column height or total residence time is determined iteratively until the volatiles content of the solids leaving the column is equal to the target.

Note that the above analysis assumes spherical particles, which is often not the case. Solids fed into a process vessel can have a variety of shapes, and engineering judgment must be used to assess the results of analyses that assume a spherical geometry. Other shapes can be assumed, but a characteristic length or diameter may not be immediately apparent. Given the choice between waterboarding and calculating the volume and area of an ellipsoid, enemy combatants in Gitmo would probably chose the former. In addition, the characteristic radius may be that of a collection of particles. For this reason, it is often convenient to use the term  $D_{eff}/r^2$  as a lumped term.

When the Biot number is less than 1, a purge column can be designed by methods analogous to those used to design packed columns for mass transfer between gases and liquids. The column height  $Z$  is equal to the height of a transfer unit  $H_s$  times the number of transfer units  $N_s$ :

$$Z = H_s N_s \quad (8.19)$$

The height of a transfer unit is calculated from

$$H_s = \frac{\dot{m}_s}{\rho_b g k_x a_s A_x} \quad (8.20)$$

where  $A_x$  is the cross-sectional area of the column and  $a_s$  is the specific surface area of the bulk solid (*i.e.*, the surface area per unit volume of the solids bed). For spherical particles, the specific surface area is given by

$$a_s = \frac{3(1-\varepsilon)}{r_o} \quad (8.21)$$

where  $\varepsilon$  is the void fraction of the solids bed. Average values of  $\varepsilon$  and  $k_x$  are used.

The number of transfer units  $N_s$  is given by

$$N_s = \int_{x_{in}}^{x_{out}} \frac{d\bar{x}}{x^* - \bar{x}} \quad (8.22)$$

where  $x^*$  is the mass fraction of the volatile compound in the solid phase that is in equilibrium with bulk gas. The subscripts *in* and *out* denote the top and the bottom of the column, respectively.



If the gas fed into a purge column is free of volatiles, as is typical, and the phase equilibrium relationship is linear, the number of transfer units can be calculated from

$$N_s = \frac{\ln \left[ \left( \frac{\bar{x}_{in}}{\bar{x}_{out}} \right) (1 - \mathcal{A}) + \mathcal{A} \right]}{(1 - \mathcal{A})} \quad (8.23)$$

where the absorption factor  $\mathcal{A}$  is given by

$$\mathcal{A} = \frac{\dot{m}_s}{m\dot{m}_g} \quad (8.24)$$

where  $\dot{m}_g$  is the gas mass flow rate.

The analysis may feel nostalgic for chemical engineers who have designed strippers or absorbers. For purge columns, the stream flowing downwards is a bulk solid rather than a liquid, and the column cross-sectional area is set by bed stability rather than hydraulic considerations. For both liquids and solids, the gas requirement is set by phase equilibria.

The analysis above applies only to purge columns where trace amounts of volatiles are removed from the solids. For moving bed dryers where considerable drying is required, both heat and mass transfer must be considered, which can make the analysis quite challenging.

In general, drying initially proceeds at a constant rate, but once the moisture content reaches a critical value, the drying rate begins to decline. This critical moisture content is a function of the wet bulb temperature of the drying gas if the gas is air.

A much simpler method to model drying kinetics is a semi-empirical approach in which the constant rate period is described by a convective heat transfer model and an empirical fudge factor is applied when the moisture content of the solid falls below its critical value [Satija, "A Scale-up Study of Nozzle Spray Dryers", *Drying Techn.*, 5, 1, 63 (1987).]:

$$\Delta H^{lv} \rho_b \frac{dX}{dt} = -h a_{sv} (T - T_{wb}) \cdot f \quad (8.25)$$

where  $\Delta H^{lv}$  is the latent heat of vaporization,  $X$  is the moisture content (dry basis),  $T$  is the temperature of the drying gas,  $T_{wb}$  is its wet bulb temperature, and  $f$  is a function defined as:

$$f = 1 \text{ for } X \geq X_{eq} \quad (8.26)$$

$$f = \left( \frac{X - X_{eq}}{X_{cr} - X_{eq}} \right)^q \text{ for } X > X_{cr} \quad (8.27)$$

where  $X_{eq}$  and  $X_{cr}$  are the equilibrium and critical moisture contents, respectively, and  $q$  is an empirical parameter. The parameters  $X_{cr}$  and  $q$  are determined from batch drying tests. The

equilibrium moisture content  $X_{eq}$  is determined by exposing a sample of dry bulk material to an environment with a controlled relative humidity and measuring its moisture uptake or from moisture desorption isotherm data.

### Moving bed heat exchangers

The analysis of direct contact moving bed dryers, in which a gas is injected into a moving bed of solids to change the streams' temperatures, is similar to purge columns except that heat transfer is modeled instead of mass transfer. The Biot number for heat transfer is

$$\mathbf{Bi} = \frac{hr_o}{k} \quad (8.28)$$

where  $h$  is the heat transfer coefficient, and  $k$  is the thermal conductivity of the particle.

If  $\mathbf{Bi} < 0.1$ , which is often the case, the solid particle temperature profile is nearly uniform, and volume requirements for direct contact bulk solids heat exchangers can be readily determined. For countercurrent heat exchangers, a gas rate that gives a suitable approach temperature, *i.e.*, the difference between the temperatures of the solids entering and the gas leaving the column, is specified. The volume  $V$  needed to provide the required heat transfer can then be calculated from {Mehos, G., "Operating Direct Contact Heat Exchangers", *Chem. Engr.*, 110, 11, 58 (2014)}:

$$\ln \frac{\bar{T}_{gout} - \bar{T}_{sin}}{\bar{T}_{gin} - \bar{T}_{sout}} = -ha_s \left( \frac{1}{\dot{m}_g C_{Pg}} - \frac{1}{\dot{m}_s C_{Ps}} \right) V \quad (8.29)$$

where  $C_{Pg}$  is the specific heat of the gas,  $\bar{T}_{gin}$  and  $\bar{T}_{gout}$  are the average inlet and outlet gas temperatures, respectively, and  $\bar{T}_{sin}$  and  $\bar{T}_{sout}$  are the average solids inlet and outlet temperatures, respectively.

A rather excruciating analytical expression is available [Almendros-Ibáñez *et al.*, *App. Therm. Engr.*, 31, 1200 (2011)] that can be used to calculate the temperature profile of the solids leaving the cooler:

$$\frac{T_s - T_{sin}}{T_{gin} - T_{sin}} = 1 - \exp \left( - \frac{A_z H h a_s}{\dot{m}_s C_{Ps}} - \frac{A_x x h a_s}{\dot{m}_g C_{Pg}} \right) \sum_{j=0}^{\infty} \frac{\left( \frac{A_x x h a_s}{\dot{m}_g C_{Pg}} \right)^j}{j!} \sum_{k=0}^j \frac{\left( \frac{A_z H h a_s}{\dot{m}_s C_{Ps}} \right)^k}{k!} \quad (8.29)$$

where  $A_x$  and  $A_z$  are the side and plan cross-sectional areas, respectively,  $H$  is the height of the heat transfer section of the cylinder, and  $x$  is the horizontal distance from the gas entry.

An indirect contact moving bed bulk solids heat exchanger usually consists of a rectangular cylinder section containing plate-and-frame heat-transfer plates above a mass flow hopper. Manufacturers include Solex Thermal and Mosman. If the heat exchanger acts as a cooler, a sweeping gas is sometimes introduced into the bed to prevent condensation. Condensation can lead to material adhering onto the plates and plugging up the heat exchanger.

An improvised version of Fourier's second law is used to describe heat transfer in an indirect contact bulk solids heat exchanger:

$$\frac{\dot{m}_{sb} C_{Ps}}{A_{zb}} \frac{\partial T_s}{\partial z} = k_{eff} \frac{\partial^2 T_s}{\partial x^2} \quad (8.30)$$

with boundary conditions

$$T_s(x, 0) = T_{sin} \quad (8.31)$$

$$T_s\left(\frac{b}{2}, z\right) = T_w \quad (8.32)$$

$$\frac{\partial [T(0, z)]}{\partial x} = 0 \quad (8.33)$$

where  $\dot{m}_{sb}$  is the mass flow rate between adjacent plates,  $A_{zb}$  is the plan cross-sectional area between adjacent plates,  $T_s$  is the solids bed temperature,  $T_w$  is the wall temperature,  $k_{eff}$  is the effective thermal conductivity of the bulk material,  $x$  is the distance from the centerline between adjacent plates,  $b$  is the plate spacing, and  $z$  is the vertical distance from the top of the heat exchanger. Note that the thermal conductivity used in the analysis is an effective conductivity. Be wary of mixing rules that some investigators assume. It is best to measure thermal conductivity directly. The specific heat can be assumed to be that of the pure solid since the thermal mass of the gas in the voids of the bulk material is paltry.

Because the wall temperature is variable, the system of equations must be solved numerically to determine the height of the heat exchanger that gives the desired solids exit temperature. The fluid side heat transfer coefficient must be known, and the calculated height depends on the width, spacing, required duty, and number of heat transfer plates.

The temperature of the bulk solids exiting the heat transfer plates will not be uniform as it will have a parabola-like profile. The temperature leaving the hopper section will be much more uniform, however, as the solids will equilibrate during the time spent in the section.

### Moving bed reactors

Moving bed reactors are reactors in which a bulk solid is continuously fed into the top of column and removed from the bottom. A gas is added such that it flows either co-current, countercurrent, or radially through a moving bed of solids. Often, the solids are used as a catalyst.

If the reaction is exothermic, heat transfer plates positioned radially can be used. The hopper section beneath the reactor must be designed for mass flow to prevent the formation of stagnant regions.

Fixed bed reactors are more common than moving beds, especially for catalytic reactors. A fluid is passed either axially or radially through the catalytic bed, and once the catalyst has become spent or fouled, the reactor is shut down, and its contents are replaced with fresh catalyst.