

A First Course on Kinetics and Reaction Engineering

Unit 33. Axial Dispersion Model

Overview

In the plug flow reactor model, concentration only varies in the axial direction, and the sole causes of that variation are convection and reaction. Unit 33 describes axial dispersion models where a diffusion-like phenomenon in the z direction is added to the model. In real reactors, axial diffusion is almost never significant. Nonetheless, the axial dispersion model can still be useful because in effect, it can add a variable amount of back-mixing to a PFR. As such, axial dispersion models sometimes offer an accurate description of a tubular reactor that does not fully conform to the assumptions of an ideal PFR.

Learning Objectives

Upon completion of this unit, you should be able to define, in words, the following terms:

- axial dispersion
- dispersion coefficient
- superficial velocity

Upon completion of this unit, you should be able to write the defining equation for the following quantities:

- Danckwerts boundary conditions

Upon completion of this unit, you should be able to perform the following specific tasks and be able to recognize when they are needed and apply them correctly in the course of a more complex analysis:

- explain the physical meaning of the Danckwerts boundary conditions
- explain the difference between a diffusion coefficient and a dispersion coefficient
- formulate mole balance equations for a tubular reactor that include axial dispersion, solve the resulting set of equations and use the results to perform a specified reaction engineering task

Information

When we studied reaction kinetics in Part II of this course, we examined two different kinds of models for reaction rates: empirical models and theory-based models. We found that empirical models can be highly accurate even though they do not have any basis in theory. When our focus shifted to reactor models in Part III, we only considered theory-based models. That is, the ideal reactors models were developed using mathematical models for actual physical phenomena such as fluid flow and heat conduction. We did not examine any models for reactors that were empirical in nature. In this unit we will add a term to the plug flow reactor model that is difficult to justify on a theoretical basis. Nonetheless, models that include this added term sometimes can be more accurate than the models we have considered prior to this point.

The term we are going to add is called an axial dispersion term, and at first glance, it appears that it does have a theoretical significance. In order to add an axial dispersion term, it is easiest to use a plug flow reactor model that is written in terms of the linear velocity and concentrations instead of molar flow rates. For reasons to be discussed presently, the symbol u_s will be used to represent the linear velocity of

the fluid. Since we are still limiting consideration to plug flow, at any one axial position, z , in the reactor, u_s is oriented in the z direction and has a magnitude equal to the volumetric flow rate at that axial position divided by the cross sectional area of the tube as expressed in equation (33.1), where A represents the cross-sectional area inside the tube and D represents the inside diameter of the tube.

$$u_s|_z = \frac{\dot{V}|_z}{A} = \frac{4\dot{V}|_z}{\pi D^2} \quad (33.1)$$

An astute reader might question the velocity calculated using equation (33.1) because it assumes that the full cross-sectional area of the tube is available for the fluid to flow through. If the reactor is packed with solid catalyst particles, then in reality, most of the cross-sectional area of the tube will be blocked by the solid catalyst. The fluid can only flow through the spaces between the solid particles. Put differently, only a fraction of the total cross-sectional area is available for fluid flow, and consequently, the linear velocity in the spaces between the particles will be much larger than the value calculated using equation (33.1). This is illustrated in Figure 33.1; it is also the reason why the subscript s is included in the variable u_s . The s stands for “superficial,” in recognition of the fact that it does not necessarily equal the actual velocity in the z -direction.

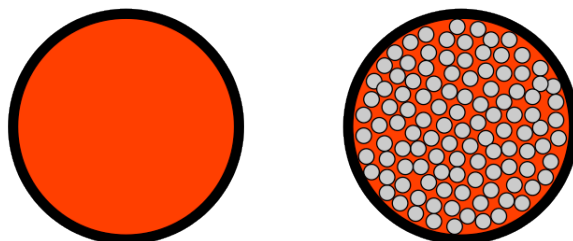


Figure 33.1. Two views down the centerline of a tube are shown here. In the calculation of the superficial velocity using equation (33.1) it is assumed that the entire cross-sectional area of the tube is available for fluid flow as shown by the red area in the left view. In reality, solid catalyst particles (gray circles) might block much of the tube cross-sectional area so that a much smaller area is actually available for fluid flow as shown in red in the right view.

In this unit, if the reactor contains packing, we will use a pseudo-homogeneous fluid model. That is, if the reactor contains a packed bed, we will treat it as if it is a homogeneous fluid and not a bed of solid particles with fluid flowing between them. Doing this requires that the rate expression is also normalized using a pseudo-homogeneous fluid model. With this definition of superficial velocity and the assumption of a pseudo-homogeneous fluid, the molar flow rate of species i at axial position z can be expressed in terms of the superficial velocity and the concentration as shown in equation (33.2). Substituting this expression into the steady state PFR mole balance, equation (33.3), gives the equivalent steady state PFR mole balance in terms of the superficial velocity and concentration, equation (33.4).

$$\dot{n}_i(z) = \dot{V}(z)C_i(z) = \frac{\pi D^2}{4}u_s(z)C_i(z) \quad (33.2)$$

$$\frac{d\dot{n}_i}{dz} = \frac{\pi D^2}{4} \sum_{\substack{j=all \\ reactions}} v_{i,j} r_j \quad (33.3)$$

$$\frac{d}{dz}(u_s C_i) = \sum_{\substack{j=all \\ reactions}} v_{i,j} r_j \quad (33.4)$$

Now we can add that dispersion term. It is likely that mixing in the axial direction is caused by variations in the axial component of the fluid velocity caused by turbulence or flow through bed packing. The formulation of a reactor model that theoretically accounts for variations in the axial flow velocity is a challenging problem. For this reason, a much more common approach is to attribute axial mixing to a diffusion-like process. Specifically, the plug flow reactor design equation is modified to include a term that looks like it represents diffusion in the axial direction. This can be seen in equation (33.5) where the term containing the second derivative of the concentration has the appearance of a term representing a diffusive flux in the z direction. While it looks like a diffusion term, the constant, D_{ax} , in equation (33.5) is not a diffusion coefficient; instead it is called a dispersion coefficient. Unlike a diffusion coefficient, the dispersion coefficient appearing in equation (33.5) is the same for every species, i . There is an equivalent energy balance equation where axial thermal mixing is introduced by adding a conduction-like term with an effective axial thermal conductivity to the PFR energy balance equation. In this unit we will limit our consideration to isothermal reactors, and the energy balance will not be presented.

$$-D_{ax} \frac{d^2 C_i}{dz^2} + \frac{d}{dz}(u_s C_i) = \sum_{\substack{j=all \\ reactions}} v_{i,j} r_j \quad (33.5)$$

The value of the dispersion coefficient can sometimes be found from engineering correlations. The most common correlations show the axial Peclet number, Pe_{ax} , defined in equation (33.6) as a function of the Reynolds number. The reciprocal of the axial Peclet number is sometimes called the dispersion number. In either case, the velocity, u , in equation (33.6) is typically equal to the axial velocity, the interstitial axial velocity or the superficial velocity, depending upon the particular geometry of the system, and the length, l , is typically either the length of the reactor or the characteristic dimension of the bed packing, again depending upon the particular system for which the correlation has been developed.

$$Pe_{ax} = \frac{ul}{D_{ax}} \quad (33.6)$$

In order to solve equation (33.5), assuming an appropriate value of the dispersion coefficient is available, one needs two boundary conditions. You should recall that each ideal PFR mole balance design equation was a first order differential equation and to solve it one needed a single initial condition, namely the value of the molar flow rate at $z = 0$. Here, because the equation is second order, two boundary conditions are needed, and since equation (33.5) does not use the molar flow rate as the dependent variable, the ideal PFR initial condition cannot be used directly as one of those two boundary

conditions. In fact, there are a few different ways of specifying the boundary conditions for equation (33.5), and each way has its own merits and issues. The “Danckwerts boundary conditions” given in equations (33.7) and (33.8) are one very commonly used set of boundary conditions for equation (33.5).

$$\text{at } z = 0; \quad u_s C_i(z=0) - D_{ax} \left. \frac{dC_i}{dz} \right|_{z=0} = u_s C_{i,feed} \quad (33.7)$$

$$\text{at } z = L; \quad \left. \frac{dC_i}{dz} \right|_{z=L} = 0 \quad (33.8)$$

The first boundary condition, equation (33.7), recognizes that as soon as the feed enters the reactor, it will be diluted by axial mixing. This is similar to what happens in a CSTR where the feed is immediately diluted upon entering the reactor. To account for this, it requires that the flow of A upstream of the reactor entrance (where no mixing has occurred) must be equal to the net flow of A (due to convection and mixing) at the inlet to the reactor. The second boundary condition, equation (33.8) simply requires that the concentration stops changing at the point where the flow leaves the reactor.

The axial dispersion model, equation (33.5) with the Danckwerts boundary conditions represents what is known as a mixed boundary value problem. Its solution requires a different approach than we have used when solving ideal batch, transient CSTR and steady-state PFR design equations. In those cases, the differential equations were of the initial value type (all of the boundary conditions were specified at the point where the independent variable, typically t or z , was equal to zero). The numerical solution of mixed boundary ordinary differential equations is discussed in Supplemental Unit S6, which also provides MATLAB template files that can be used when solving these types of equations. Many other mathematics software packages also provide routines to perform this type numerical solution.

Finally, it is worth noting that in packed bed reactors operating at industrial scale flow velocities, axial dispersion rarely affects the conversion in the reactor if the reactor is longer than about 50 times the diameter of the catalyst particles it contains. Nonetheless, the axial dispersion model has been thoroughly examined in the reaction engineering literature. One interesting consequence of including axial dispersion in the model is the appearance of multiple steady states, similar to those possible in a CSTR.

It is also possible to use the axial dispersion model empirically. That is, if a reactor cannot be modeled accurately as an ideal PFR, one can attempt to model the reactor using equation (33.5). In this case, the dispersion coefficient is treated as an adjustable parameter. Its value is adjusted so that the resulting axial dispersion model gives the best possible agreement between the outlet concentrations predicted by the model and the actual reactor outlet concentrations. One way to choose a value for the dispersion coefficient in this situation is to derive the age function according to a transient version of equation (33.5) and fit it to the actual age function measured experimentally using a tracer stimulus and response (see Unit 11).

When the axial dispersion model is used in this empirical manner, it is revealing to note that when the dispersion coefficient is equal to zero, the axial dispersion model simplifies to the plug flow reactor model. When the dispersion coefficient becomes very, very large, the behavior predicted by the axial

dispersion model approaches the behavior of a CSTR. Thus, when used empirically to model a reactor, varying the dispersion coefficient allows the axial dispersion model to predict performance that is intermediate between a PFR and a CSTR.