# Chapter 13 The Dispersion Model

- 13.1 Axial Dispersion
- Suppose an ideal pulse of tracer is introduced into the fluid entering a vessel. The pulse spreads as it passes through the vessel, and to characterize the spreading according to this model, we assume a <u>diffusion-like process</u> to distinguish it from molecular diffusion.



Figure 13.1 The spreading of tracer according to the dispersion model.

Define dispersion coefficient D [m<sup>2</sup>/s] and a dimensionless group D/(uL) for describing the dispersion.

To characterize dispersion, two variables should be measured Mean time of passage  $\bar{t}$  and variance  $\sigma^2$ 

$$\bar{t} = \frac{\int_{0}^{\infty} tCdt}{\int_{0}^{\infty} Cdt} \cong \frac{\sum t_{i}C_{i}\Delta t_{i}}{\sum C_{i}\Delta t_{i}} \quad [time]$$

$$\sigma^{2} = \frac{\int_{0}^{\infty} (t-\bar{t})^{2}Cdt}{\int_{0}^{\infty} Cdt} = \frac{\int_{0}^{\infty} t^{2}Cdt}{\int_{0}^{\infty} Cdt} - \bar{t}^{2} \quad [time^{2}]$$

$$\sigma^{2} \cong \frac{\sum (t_{i}-\bar{t})^{2}C_{i}\Delta t_{i}}{\sum C_{i}\Delta t_{i}} = \frac{\sum t_{i}^{2}C_{i}\Delta t_{i}}{\sum C_{i}\Delta t_{i}} - \bar{t}^{2} \quad [time^{2}]$$

## The variance



Figure 13.2

• Consider plug flow of a fluid, on top of which is superimposed some degree of backmixing, the magnitude of which is independent of position within the vessel.



Figure 13.3 Representation of the dispersion (dispersed plug flow) model.

• For molecular diffusion, the Fick's law

$$\frac{\partial C}{\partial t} = \mathscr{D}\frac{\partial^2 C}{\partial x^2}$$

• For dispersion model

$$\frac{\partial c}{\partial t} = \mathbf{D} \frac{\partial^2 c}{\partial x^2}$$

D: dispersion coefficient

• In dimensionless form:  $z = (ut + x)/L \qquad \theta = t/\bar{t} = tu/L$ and  $C = c/C_0 \qquad \frac{\partial C}{\partial \theta} = \left(\frac{D}{uL}\right)\frac{\partial^2 C}{\partial z^2} - \frac{\partial C}{\partial z}$ 

# • For small extents of dispersion, D/uL<0.01 $\frac{\partial C}{\partial \theta} = \left(\frac{D}{uL}\right) \frac{\partial^2 C}{\partial z^2} - \frac{\partial C}{\partial z} \text{ can be solved}$

$$E_{\theta} = \bar{t}E = \frac{1}{\sqrt{4\pi(D/uL)}} \exp\left(-\frac{(1-\theta)^2}{4(D/uL)}\right)$$
$$E_t = \sqrt{\frac{u^3}{4\pi DL}} \exp\left(-\frac{(L-ut)^2}{4DL/u}\right)$$

$$\overline{t}_E = \frac{V}{v} = \frac{L}{u} \text{ or } \overline{\theta}_E = 1$$

$$\sigma_{\theta}^{2} = \frac{\sigma_{t}^{2}}{\bar{t}^{2}} = 2\frac{D}{uL} \text{ or } \sigma_{t}^{2} = \sigma_{\theta}^{2} \left(\frac{L}{u}\right)^{2} = 2\frac{DL}{u^{3}} \quad \sigma_{t} = \bar{t}\sqrt{2\frac{D}{uL}}$$



Gaussian curve or Normal curve

**Figure 13.4** Relationship between D/uL and the dimensionless  $E_{\theta}$  curve for small extents of dispersion, Eq. 7.

- D/uL is the only parameter of this curve.
- If we know D/uL, we can draw a curve, on the contrary, we can get D/uL by the experimental curve.



Figure 13.5 Illustration of additivity of means and of variances of the E curves of vessels  $a, b, \ldots, n$ .

From 
$$\sigma^2 = 2 \frac{DL}{u^3} \Rightarrow \sigma^2 \propto L$$

• The additivity of variances

$$\bar{t}_{overall} = \bar{t}_a + \bar{t}_b + \dots = \frac{V_a}{v} + \frac{V_b}{v} + \dots = \left(\frac{L}{u}\right)_a + \left(\frac{L}{u}\right)_b + \dots$$
$$\sigma_{overall}^2 = \sigma_a^2 + \sigma_b^2 + \dots = 2\left(\frac{DL}{u^3}\right)_a + 2\left(\frac{DL}{u^3}\right)_b + \dots$$

## Therefore



Figure 13.6 Increase in variance is the same in both cases, or  $\sigma^2 = \sigma_{out}^2 - \sigma_{in}^2 = \Delta \sigma^2$ .

# Large deviation from plug flow, D/uL>0.01

## Boundary condition





- Closed vessel
- There is no analytic solution for F and E.

$$\bar{t}_{E} = \bar{t} = \frac{V}{v}$$

$$or\bar{\theta}_{E} = \frac{\bar{t}_{E}}{\bar{t}} = \frac{\bar{t}_{E}v}{V} = 1$$





Figure 13.8 Tracer response curves for closed vessels and large deviations from plug flow.



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Figure 13.9 The open-open vessel boundary condition.

$$E_{\theta o o} = \frac{1}{\sqrt{4\pi \ \theta(D/uL)}} \exp\left(-\frac{(1-\theta)^2}{4\theta(D/uL)}\right) \quad E_{too} = \frac{u}{\sqrt{4\pi Dt}} \exp\left(-\frac{(L-ut)^2}{4Dt}\right)$$
$$\overline{\theta}_{Eoo} = \frac{\overline{t}_{Eoo}}{\overline{t}} = 1 + 2\frac{D}{uL} \quad \overline{t}_{Eoo} = \frac{V}{v} \left(1 + 2\frac{D}{uL}\right) \quad \sigma_{\theta o o}^2 = \frac{\sigma_{too}^2}{\overline{t}^2} = 2\frac{D}{uL} + 8\left(\frac{D}{uL}\right)^2$$

Experimentally determined

## Difference between small and large deviation from plug flow

 $\sigma^2_{\scriptscriptstyle too}$ 

small deviation  

$$E_{\theta} = \frac{1}{\sqrt{4\pi (D/uL)}} \exp\left(-\frac{(1-\theta)^{2}}{4(D/uL)}\right)$$

$$E_{t} = \sqrt{\frac{u^{3}}{4\pi DL}} \exp\left(-\frac{(L-ut)^{2}}{4DL/u}\right)$$

$$\bar{t}_{E} = \frac{V}{v} \qquad \bar{\theta}_{E} = 1$$

$$\sigma_{t}^{2} = 2\frac{DL}{u^{3}} \quad \sigma_{\theta}^{2} = 2\frac{D}{uL}$$

$$large division (open - open condition)$$
$$E_{\theta oo} = \frac{1}{\sqrt{4\pi\theta(D/uL)}} \exp\left(-\frac{(1-\theta)^2}{4\theta(D/uL)}\right)$$
$$E_{too} = \frac{u}{\sqrt{4\pi Dt}} \exp\left(-\frac{(L-ut)^2}{4Dt}\right)$$
$$\bar{t}_{Eoo} = \frac{V}{v} \left(1+2\frac{D}{uL}\right) \quad \bar{\theta}_{Eoo} = 1+2\frac{D}{uL}$$
$$= \bar{t}^2 \left(2\frac{D}{uL}+8\left(\frac{D}{uL}\right)^2\right) \quad \sigma_{\theta oo}^2 = 2\frac{D}{uL}+8\left(\frac{D}{uL}\right)^2$$



**Figure 13.10** Tracer response curves for "open" vessels having large deviations 15 from plug flow.



**Figure 13.4** Relationship between D/uL and the dimensionless  $E_{\theta}$  curve for small extents of dispersion, Eq. 7.

## Step input of tracer

## Small deviation from plug flow D/uL<0.01



Figure 13.11 Step response curves for small deviations from plug flow.



Figure 13.12 Probability plot of a step response signal. From this we find D/uL directly.



Probability Paper for Gaussian (normal) Curve

# Large deviation from plug flow D/uL>0.01



Figure 13.13 Step response curves for large deviations from plug flow in closed vessels.

## Choose a right kind of injection way



Figure 13.14 Sensitivity of the E and F curves for the same flow.



#### EXAMPLE 13.1 D/uL FROM A C<sub>pulse</sub> CURVE

On the assumption that the closed vessel of Example 11.1, Chapter 11, is well represented by the dispersion model, calculate the vessel dispersion number  $\mathbf{D}/uL$ . The C versus t tracer response of this vessel is

t, min  $\begin{vmatrix} 0 & 5 & 10 & 15 & 20 & 25 & 30 & 35 \ C_{pulse}$ , gm/liter  $\begin{vmatrix} 0 & 3 & 5 & 5 & 4 & 2 & 1 & 0 \ \end{vmatrix}$ 

#### **SOLUTION**

Since the C curve for this vessel is broad and unsymmetrical, see Fig. 11.E1, let us guess that dispersion is too large to allow use of the simplification leading to Fig. 13.4. We thus start with the variance matching procedure of Eq. 18. The mean and variance of a continuous distribution measured at a finite number of equidistant locations is given by Eqs. 3 and 4 as

$$\bar{t} = \frac{\sum t_i C_i}{\sum C_i}$$

and

$$\sigma^2 = \frac{\sum t_i^2 C_i}{\sum C_i} - \bar{t}^2 = \frac{\sum t_i^2 C_i}{\sum C_i} - \left[\frac{\sum t_i C_i}{\sum C_i}\right]^2$$

Using the original tracer concentration-time data, we find

$$\sum C_i = 3 + 5 + 5 + 4 + 2 + 1 = 20$$
  
$$\sum t_i C_i = (5 \times 3) + (10 \times 5) + \dots + (30 \times 1) = 300 \text{ min}$$
  
$$\sum t_i^2 C_i = (25 \times 3) + (100 \times 5) + \dots + (900 \times 1) = 5450 \text{ min}^2$$

Therefore

$$\bar{t} = \frac{300}{20} = 15 \min$$
  
 $\sigma^2 = \frac{5450}{20} - \left(\frac{300}{20}\right)^2 = 47.5 \min^2$ 

and

$$\sigma_{\theta}^2 = \frac{\sigma^2}{\bar{t}^2} = \frac{47.5}{(15)^2} = 0.211$$

Now for a closed vessel Eq. 13 relates the variance to D/uL. Thus

$$\sigma_{\theta}^2 = 0.211 = 2 \frac{\mathbf{D}}{uL} - 2\left(\frac{\mathbf{D}}{uL}\right)^2 (1 - e^{-uL/\mathbf{D}})$$

Ignoring the second term on the right, we have as a first approximation

$$\frac{\mathbf{D}}{uL} \cong 0.106$$

Correcting for the term ignored we find by trial and error that

$$\frac{\mathbf{D}}{uL} = \underline{\underbrace{0.120}}$$

Our original guess was correct: This value of D/uL is much beyond the limit where the simple gaussian approximation should be used.



#### D/uL FROM AN F CURVE

von Rosenberg (1956) studied the displacement of benzene by *n*-butyrate in **a** 38 mm diameter packed column 1219 mm long, measuring the fraction of *n*-butyrate in the exit stream by refractive index methods. When graphed, the fraction of *n*-butyrate versus time was found to be S-shaped. This is the **F** curve, and it is shown in Fig. E13.2*a* for von Rosenberg's run at the lowest flow rate, where u = 0.0067 mm/s, which is about 0.5 m/day.

Find the vessel dispersion number of this system.



Figure E13.2a From von Rosenberg (1956).

#### **SOLUTION**

Instead of taking slopes of the **F** curve to give the **E** curve and then determining the spread of this curve, let us use the probability paper method. So, plotting the data on this paper does actually give close to a straight line, as shown in Fig. E13.2b.



Figure E13.2b From Levenspiel and Smith (1957).

To find the variance and D/uL from a probability graph is a simple matter. Just follow the procedure illustrated in Fig. 13.12. Thus Fig. E13.2b shows that



Hence the variance

$$\sigma_{\theta}^2 = (0.0252)^2 = 0.00064$$

and from Eq. 8

$$\frac{\mathbf{D}}{uL} = \frac{\sigma_{\theta}^2}{2} = \underline{0.00032}$$

Note that the value of D/uL is well below 0.01, justifying the use of the gaussian approximation to the tracer curve and this whole procedure.



radioactive tracer is injected directly above the bed, and output signals are recorded by Geiger counters at two levels in the bed 90 cm apart.

The following data apply to a specific experimental run. Bed voidage = 0.4, superficial velocity of fluid (based on an empty tube) = 1.2 cm/sec, and variances of output signals are found to be  $\sigma_1^2 = 39 \sec^2$  and  $\sigma_2^2 = 64 \sec^2$ . Find **D**/*uL*.

#### **SOLUTION**

Bischoff and Levenspiel (1962) have shown that as long as the measurements are taken at least two or three particle diameters into the bed, then the open vessel boundary conditions hold closely. This is the case here because the measurements are made 15 cm into the bed. As a result this experiment corresponds to a one-shot input to an open vessel for which Eq. 12 holds. Thus

$$\Delta \sigma^2 = \sigma_2^2 - \sigma_1^2 = 64 - 39 = 25 \sec^2$$

or in dimensionless form

$$\Delta\sigma_{\theta}^2 = \Delta\sigma^2 \left(\frac{v}{V}\right)^2 = (25 \text{ sec}^2) \left[\frac{1.2 \text{ cm/sec}}{(90 \text{ cm})(0.4)}\right]^2 = \frac{1}{36}$$

from which the dispersion number is

$$\frac{\mathbf{D}}{uL} = \frac{\Delta\sigma_{\theta}^2}{2} = \frac{1}{\underline{72}}$$

• Example--Rotating Packed Bed



13.2 Correlations for axial dispersion

- The matter of D
- D/uL is a product of two terms

 $\frac{D}{uL} = \begin{pmatrix} \text{intensity of} \\ \text{dispersion} \end{pmatrix} \begin{pmatrix} \text{geometric} \\ \text{factor} \end{pmatrix} = \begin{pmatrix} D \\ ud \end{pmatrix} \begin{pmatrix} d \\ L \end{pmatrix}$  $\frac{D}{ud} = f \begin{pmatrix} \text{fluid} \\ \text{properties} \end{pmatrix} \begin{pmatrix} \text{flow} \\ \text{dynamics} \end{pmatrix} = f (\text{Sc, Re})$ 

d is a characteristic length =  $d_{tube}$  or  $d_p$ 



Figure 13.15 Correlation for the dispersion of fluids flowing in pipes, adapted from Levenspiel (1958b).



Figure 13.16 Correlation for dispersion for streamline flow in pipes; prepared from Taylor (1953, 1954a) and Aris (1956).



Figure 13.17 Experimental findings on dispersion of fluids flowing with mean axial velocity u in packed beds; prepared in part from Bischoff (1961).

# 13.3 Chemical reaction and dispersion

• Consider a steady-flow chemical reactor of length which fluid is flowing at a constant velocity u, and in which material is mixed axially with a dispersion coefficient **D**. Let an nth-order reaction be occurring

$$A \rightarrow Products \quad -r_A = kC_A^n$$



**Figure 13.18** Variables for a closed vessel in which reaction and dispersion are occurring.

- For the small element
- input = output + disappearrance by reaction + accumulation entering by bulk flow =  $C_{A,l}uS$
- leaving by bulk flow =  $C_{A,l+\Delta l} uS$
- intering by axial dispersion  $= \frac{dN_A}{dt} = -\left(DS\frac{dC_A}{dl}\right)_l$
- leaving by axial dispersion  $= \frac{dN_A}{dt} = -\left(DS\frac{dC_A}{dl}\right)_{l+\Delta l}$ disappearance by reaction  $= (-r_A)V = (-r_A)S\Delta l$

$$u \frac{C_{A,l+\Delta l} - C_{A,l}}{\Delta l} - D \frac{\left(\frac{dC_A}{dl}\right)_{l+\Delta l} - \left(\frac{dC_A}{dl}\right)_{l}}{\Delta l} + (-r_A) = 0$$

taking  $limit \Delta l \rightarrow 0$ 

$$u\frac{dC_A}{dl} - D\frac{d^2C_A}{dl^2} + kC_A^n = 0$$

Dimensionl ess form

$$\frac{D}{uL}\frac{d^{2}C_{A}}{dz^{2}} - \frac{dC_{A}}{dz} - k\tau C_{A}^{n} = 0$$
  
$$\frac{D}{uL}\frac{d^{2}X_{A}}{dz^{2}} - \frac{dX_{A}}{dz} - k\tau C_{A0}^{n-1}(1 - X_{A})^{n} = 0$$

## Boundary condition

z = l

$$z = 0 \qquad uC_{A0} = uC_{A0}^{+} - D\left(\frac{dC_{A}}{dz}\right)^{+}$$

$$\left(\frac{dC_A}{dz}\right)_{z=1} = 0$$

With above boundary condition, for some specified reaction order

the equation could be solved.



### For first order reaction

$$\frac{C_A}{C_{A0}} = 1 - X_A = \frac{4a \exp\left(\frac{1}{2}\frac{uL}{D}\right)}{\left(1+a\right)^2 \exp\left(\frac{a}{2}\frac{uL}{D}\right) - \left(1-a\right)^2 \exp\left(-\frac{a}{2}\frac{uL}{D}\right)}$$

 $a = \sqrt{1 + 4k\tau(D/uL)}$ For small deviation from plug flow, D/uL is small above equation reduces to

$$\frac{C_A}{C_{A0}} = \exp\left(-k\tau + (k\tau)^2 D/uL\right) \qquad \left(\sigma_\theta^2 = \frac{\sigma_t^2}{\bar{t}^2} = 2\frac{D}{uL}\right)$$

$$= \exp\left(-k\tau + \frac{k^2\sigma^2}{2}\right)$$

(for small deviations from plug flow 
$$a \cong 1$$
  

$$\frac{C_A}{C_{A0}} \cong \exp\left(\left(\frac{1-a}{2}\right)\frac{uL}{D}\right)$$

$$a = \sqrt{1+4k\tau}\frac{D}{ul} \qquad \sqrt{1+x} = 1+\frac{1}{2}x-\frac{1}{8}x^2 \dots$$

$$\sqrt{1+4k\tau}\frac{D}{ul} = 1+\frac{1}{2}4k\tau\frac{D}{ul} - \frac{16}{8}k^2\tau^2\left(\frac{D}{ul}\right)^2$$

$$\frac{1-\sqrt{1+4k\tau}\frac{D}{ul}}{2} = -k\tau\frac{D}{ul} + k^2\tau^2\left(\frac{D}{ul}\right)^2$$

$$\frac{C_A}{C_{A0}} = \exp\left(-k\tau\frac{D}{ul} + k^2\tau^2\left(\frac{D}{ul}\right)^2\right)$$

Compare with plug flow reactor, the size ratio

$$\frac{L}{L_P} = \frac{V}{V_P} = 1 + (k\tau)\frac{D}{uL}$$

for same C<sub>Aout</sub>

$$\frac{C_A}{C_{A0}} = \exp\left(-k\tau + (k\tau)^2 D/uL\right)$$

~

for small deviations from plug flow

$$\frac{C_A}{C_{A0}} = \exp(-k\tau_P) \quad \text{for plug flow}$$

$$-k\tau_P = -k\tau + (k\tau)^2 D/uL = -k\tau(1 - (k\tau)D/uL)$$

$$\frac{\tau}{\tau_P} = \frac{L}{L_P} = \frac{V}{V_P} = \frac{1}{1 - (k\tau)D/uL} \qquad \frac{1}{1 - x} = 1 + x + x^2 + \frac{1}{1 - x}$$

$$\frac{L}{L_P} = \frac{V}{V_P} \cong 1 + (k\tau)D/uL$$

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## The conversion ratio





**Figure 13.19** Comparison of real and plug flow reactors for the first-order  $A \rightarrow$  products, assuming negligible expansion; from Levenspiel and Bischoff (1959, 1961).





$$A + B \rightarrow \text{products}, \quad C_{A0} = C_{B0}$$
  
or...  $2A \rightarrow \text{products}$ 

assuming negligible expansion; from Levenspiel and Bischoff (1959, 1961).

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#### **EXAMPLE 13.4** CONVERSION FROM THE DISPERSION MODEL

Redo Example 11.1 of Chapter 11 assuming that the dispersion model is a good representation of flow in the reactor. Compare the calculated conversion by the two methods and comment.

#### **SOLUTION**

Matching the experimentally found variance with that of the dispersion model, we find from Example 13.1

$$\frac{\mathbf{D}}{uL} = 0.12$$

Conversion in the real reactor is found from Fig. 13.19. Thus moving along the  $k\tau = (0.307)(15) = 4.6$  line from  $C/C_0 = 0.01$  to  $\mathbf{D}/uL = 0.12$ , we find that the fraction of reactant unconverted is approximately

See Example 11.4

$$\frac{C}{C_0} = 0.035$$
, or  $\underline{3.5\%}$ 

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Figure 13.19 Comparison of real and plug flow reactors for the first-order  $A \rightarrow$  products, assuming negligible expansion; from Levenspiel and Bischoff (1959, 1961).

**Comments.** Figure E13.4 shows that except for a long tail the dispersion model curve has for the most part a greater central tendency than the actual curve. On the other hand, the actual curve has more short-lived material leaving the vessel.





Because this contributes most to the reactant remaining unconverted, the finding

$$\left(\frac{C}{C_0}\right)_{\text{actual}} = 4.7\% > \left(\frac{C}{C_0}\right)_{\substack{\text{dispersion}\\\text{model}}} = 3.5\%$$