Advanced Reactor Design

Week 4

One Parameters Models for Nonideal Reactors

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Introduction

- This presentation covers models for nonideal reactors with a focus on residence time distribution (RTD) and reactor flow behavior.

Topics to be Addressed

- - Residence Time Distribution (RTD)
- - Nonideal Flow Patterns
- - Models for Mixing
- - Calculation of Exit Conversion
- - Reactor Performance Assessment

Objectives

- - Understand the principles of nonideal flow in reactors
- - Learn how to use RTD for analyzing reactor performance
- - Apply mathematical models for mixing and conversion calculation
- - Compare different reactor modeling approaches

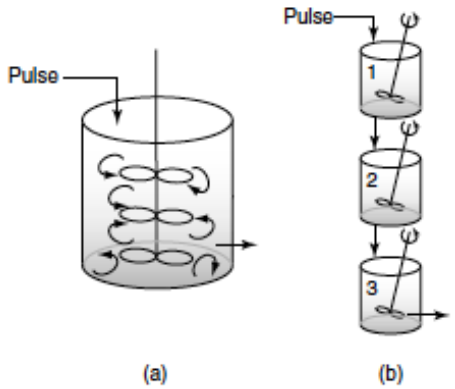
Some Guidelines for Developing Models

- The overall goal is to use the following equation
  - RTD Data + Model + Kinetics = Predictions
- The model must be mathematically tractable
- The model must realistically describe the characteristics of the non-ideal reactor
- The model should not have more than two adjustable parameters

A PROCEDURE FOR CHOOSING A MODEL TO PREDICT THE OUTLET CONCENTRATION AND CONVERSION

1. Look at the reactor
   A. Where are the inlet and outlet streams to and from the reactors? (Is by-passing a possibility?)
   B. Look at the mixing system. How many impellers are there? (Could there be multiple mixing zones in the reactor?)
   C. Look at the configuration. (Is internal recirculation possible? Is the packing of the catalyst particles loose so channeling could occur?)
2. Look at the tracer data
   A. Plot the E(t) and F(t) curves.
   B. Plot and analyze the shapes of the E(Θ) and F(Θ) curves. Is the shape of the curve such that the curve or parts of the curve can be fit by an ideal reactor model? Does the curve have a long tail suggesting a stagnant zone? Does the curve have an early spike indicating bypassing?
   C. Calculate the mean residence time, tm, and variance, σ^2. How does the tm determined from the RTD data compare with τ as measured with a yardstick and flow meter? How large is the variance; is it larger or smaller than τ^2?
3. Choose a model or perhaps two or three models
4. Use the tracer data to determine the model parameters (e.g., n, D_a, v_b)
5. Use the CRE algorithm in Chapter 5. Calculate the exit concentrations and conversion for the model system you have selected

The RTD will be analyzed from a tracer pulse injected into the first reactor of three equally sized CSTRs in series



Generalizing this method to a series of n CSTRs gives the RTD for n CSTRs in series, E(t):

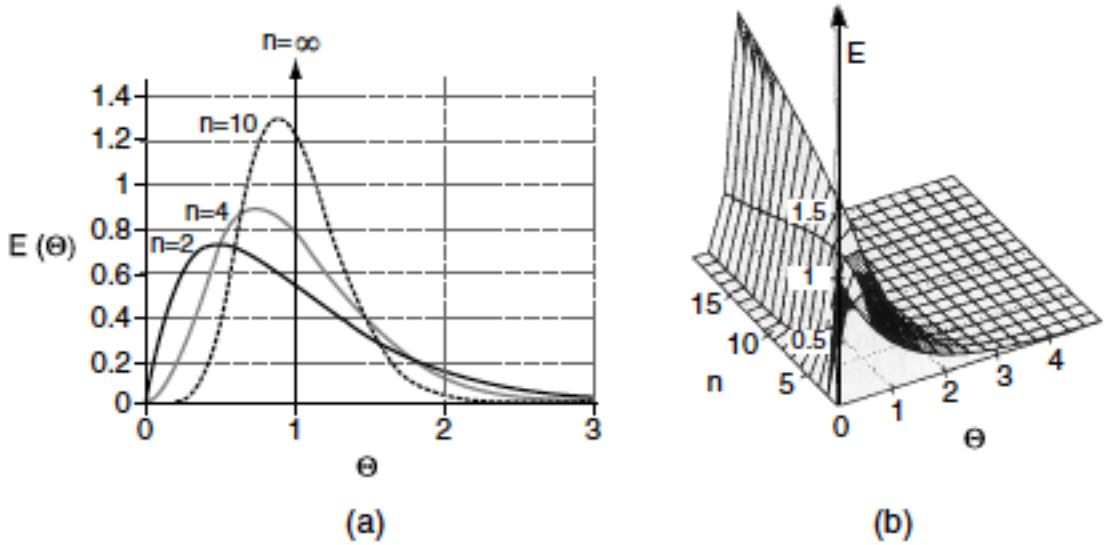
$$E(t) = \frac{t^{n-1}}{(n-1)!\tau_i^n} e^{-t/\tau_i} \qquad (18\text{-}4)$$

$$E(\Theta) = \tau E(t) = \frac{n(n\Theta)^{n-1}}{(n-1)!} e^{-n\Theta} \qquad (18\text{-}5)$$

Tanks-in-series response to a pulse tracer input for different numbers of tanks

$$\sigma_\Theta^2 = \int_0^\infty \Theta^2 E(\Theta)\, d\Theta - 1 \qquad (18\text{-}8)$$

$$\sigma_\Theta^2 = \frac{1}{n} \qquad (18\text{-}9)$$



The number of tanks in series is

$$n = \frac{1}{\sigma_\Theta^2} = \frac{\tau^2}{\sigma^2} \qquad (18\text{-}11)$$

Calculating Conversion for the T-I-S Model

If the reaction is first order, we can use the equation below to calculate the conversion

$$X = 1 - \frac{1}{(1 + \tau_i k)^n} \qquad (5\text{-}15)$$

where

$$\tau_i = \frac{V}{v_0 n}$$

Tanks-in-Series versus Segregation for a First-Order Reaction

$$\boxed{X_{\text{T-I-S}} = X_{\text{seg}} = X_{\text{mm}}} \qquad (18\text{-}12)$$

The molar flow rate of tracer (FT) by both convection and dispersion is:

$$F_T = \left[-D_a \frac{\partial C_T}{\partial z} + UC_T \right] A_c \qquad (14\text{-}14)$$

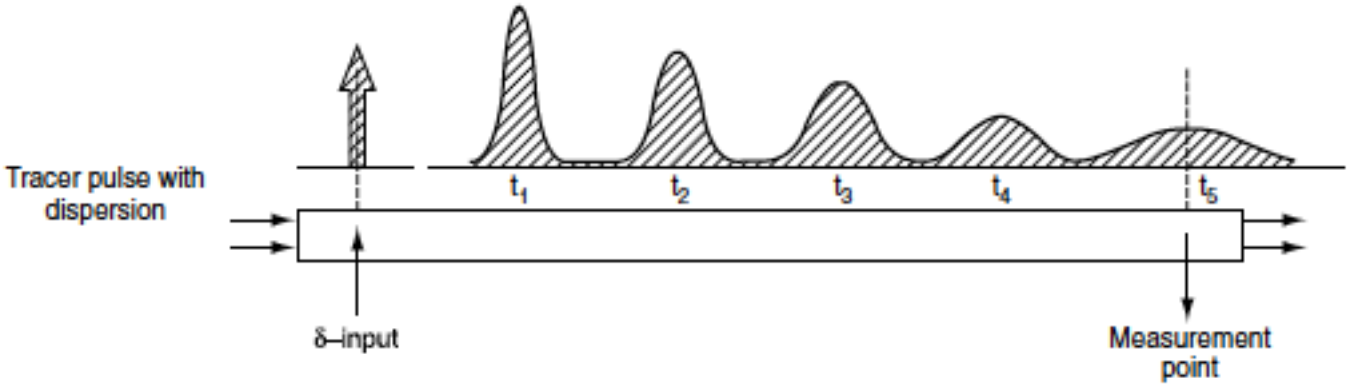


Figure 18-5 Dispersion in a tubular reactor. (Levenspiel, O., *Chemical Reaction Engineering*, 2nd ed. Copyright © 1972 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. All rights reserved.)

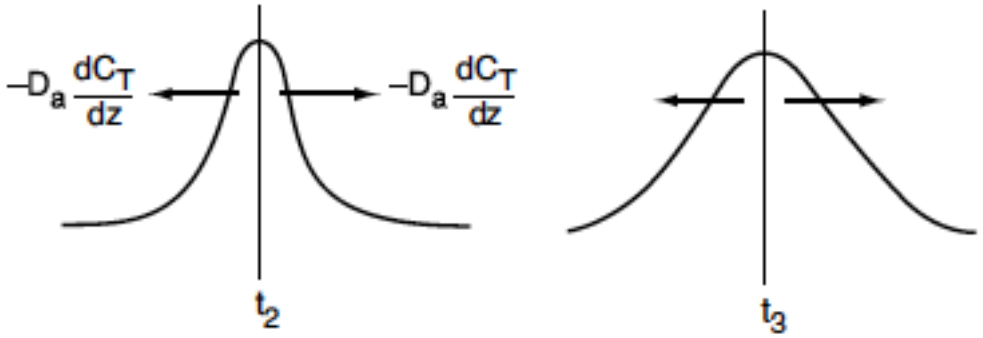


Figure 18-6 Symmetric concentration gradients causing the spreading by dispersion of a pulse input.

$$D_a \frac{\partial^2 C_T}{\partial z^2} - \frac{\partial (UC_T)}{\partial z} = \frac{\partial C_T}{\partial t} \tag{18-14}$$

Flow, Reaction, and Dispersion

$$D_a \frac{d^2 C_A}{dz^2} - U \frac{dC_A}{dz} + r_A = 0 \qquad (14\text{-}16)$$

Rearranging Equation (14-16) we obtain

$$\frac{D_a}{U} \frac{d^2 C_A}{dz^2} - \frac{dC_A}{dz} + \frac{r_A}{U} = 0 \qquad (18\text{-}15)$$

$$\frac{D_a}{U} \frac{d^2 C_A}{dz^2} - \frac{dC_A}{dz} - \frac{kC_A}{U} = 0 \qquad (18\text{-}16)$$

by letting $\psi = C_A / C_{A0}$ and $\lambda = z/L$

$$\frac{1}{Pe_r} \frac{d^2 \psi}{d\lambda^2} - \frac{d\psi}{d\lambda} - Da_1 \cdot \psi = 0 \qquad (18\text{-}17)$$

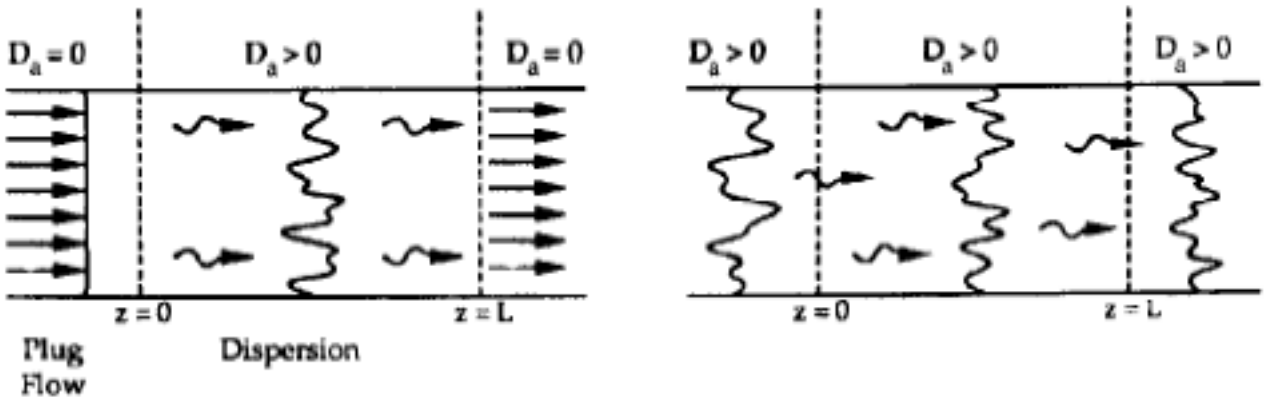
The quantity Da_1 appearing in Equation (18-17) is called the *Damköhler number* for a first-order conversion and physically represents the ratio

$$Da_1 = \frac{\text{Rate of consumption of A by reaction}}{\text{Rate of transport of A by convection}} = k\tau \qquad (18\text{-}18)$$

The other dimensionless term is the *Peclet number, Pe*,

$$Pe_r = \frac{\text{Rate of transport by convection}}{\text{Rate of transport by diffusion or dispersion}} = \frac{Ul}{D_a} \qquad (18\text{-}19)$$

Boundary Conditions



(a) Closed-closed vessel

(b) Open-open vessel

At z = 0

$$F_A(0^-) = F_A(0^+)$$

Substituting for F_A yields

$$UA_cC_A(0^-) = -A_cD_a\left(\frac{dC_A}{dz}\right)_{z=0^+} + UA_cC_A(0^+)$$

Solving for the entering concentration $C_A(0–) = C_{A0}$

$$C_{A0} = \frac{-D_a}{U}\left(\frac{dC_A}{dz}\right)_{z=0^+} + C_A(0^+) \qquad (18\text{-}20)$$

At the exit to the reaction section, the concentration is continuous, and there is no gradient in tracer concentration.

At $z = L$:

$$C_A(L^-) = C_A(L^+)$$
$$\frac{dC_A}{dz} = 0 \qquad (18\text{-}21)$$

Open-Open System

For an open-open system, there is continuity of flux at the boundaries at

At z = 0

$$F_A(0-) = F_A(0+)$$

$$\boxed{-D_a \frac{\partial C_A}{\partial z}\Big)_{z=0^-} + UC_A(0^-) = -D_a \frac{\partial C_A}{\partial z}\Big)_{z=0^+} + UC_A(0^+)} \qquad (18\text{-}22)$$

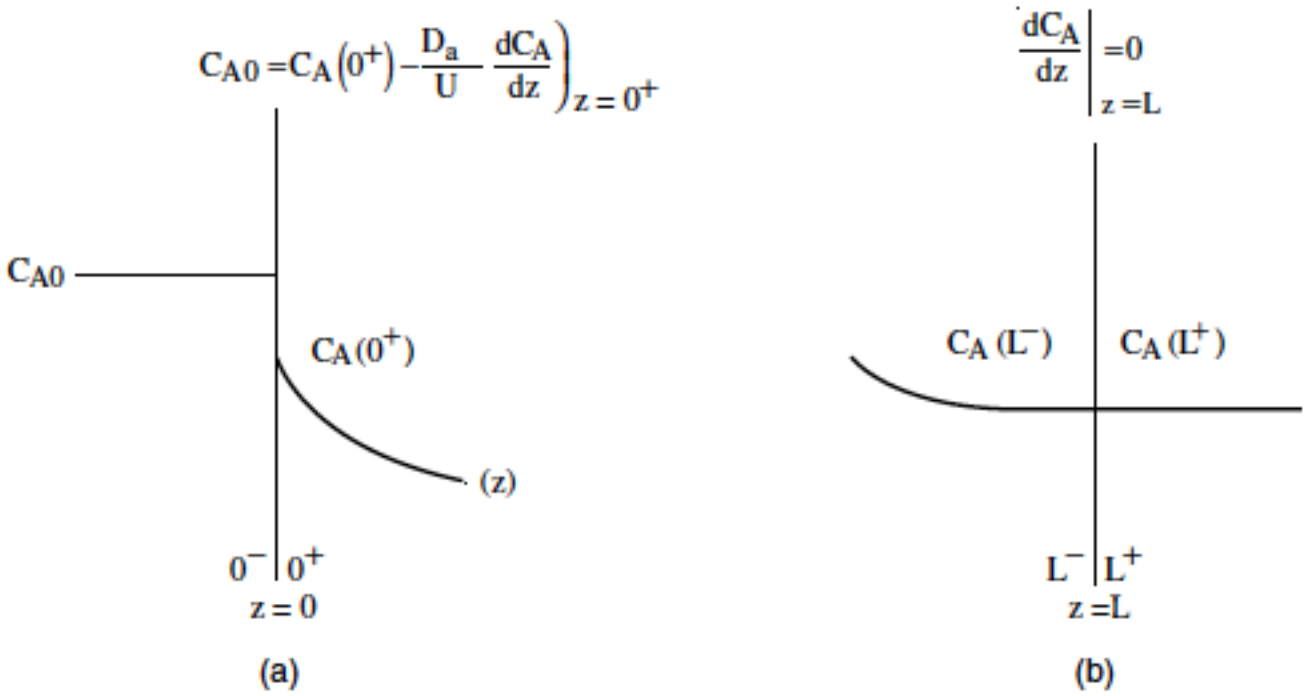


Figure 18-8 Schematic of Danckwerts boundary conditions: (a) entrance; (b) exit.

At z = L, we have continuity of concentration and

$$\boxed{\frac{dC_A}{dz} = 0} \qquad (18\text{-}23)$$

Back to the Solution for a Closed-Closed System

We now shall solve the dispersion reaction balance for a first-order reaction

$$\frac{1}{Pe_r}\frac{d^2\psi}{d\lambda^2} - \frac{d\psi}{d\lambda} - Da_I\psi = 0 \qquad (18\text{-}17)$$

For the closed-closed system, the Danckwerts boundary conditions in dimensionless form are

$$\text{At } \lambda = 0 \text{ then } 1 = -\frac{1}{Pe_r}\frac{d\psi}{d\lambda}\bigg)_{\lambda=0^+} + \psi(0^+) \qquad (18\text{-}24)$$

$$\text{At } \lambda = 1 \text{ then } \frac{d\psi}{d\lambda} = 0 \qquad (18\text{-}25)$$

At the end of the reactor, where $\lambda = 1$, the solution to the top equation is

$$\psi_L = \frac{C_{AL}}{C_{A0}} = 1 - X$$

$$= \frac{4q\exp(Pe_r/2)}{(1+q)^2 \exp(Pe_r q/2) - (1-q)^2 \exp(-Pe_r q/2)} \qquad (18\text{-}26)$$

where $q = \sqrt{1 + 4Da_I/\mathrm{Pe}_r}$

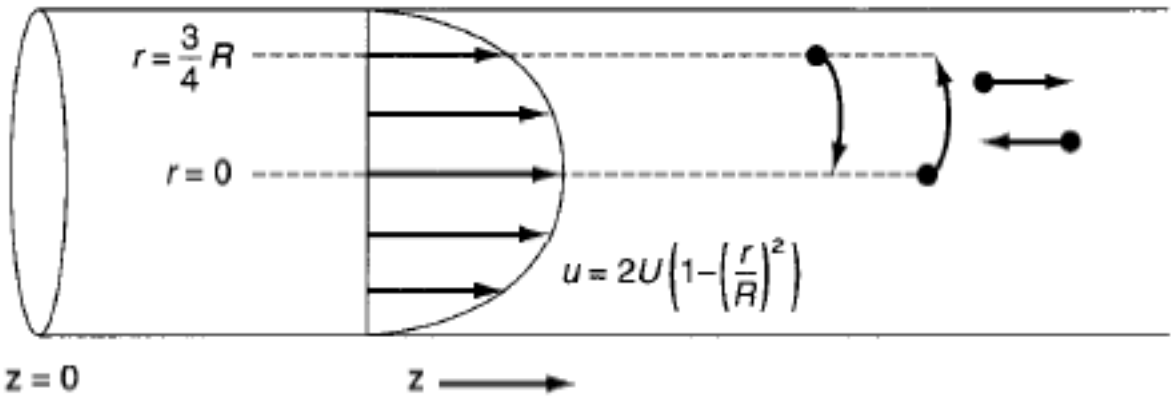
$$X = 1 - \frac{4q \exp(Pe_r/2)}{(1+q)^2 \exp(Pe_r q/2) - (1-q)^2 \exp(-Pe_r q/2)} \qquad (18\text{-}27)$$

Finding D_a and the Peclet Number

There are three ways we can use to find D_a and hence P_{er}

1. Laminar flow with radial and axial molecular diffusion theory
2. Correlations from the literature for pipes and packed beds
3. Experimental tracer data

Dispersion in a Tubular Reactor with Laminar Flow



$$\frac{\partial c}{\partial t} + u(r)\frac{\partial c}{\partial z} = D_{AB}\left\{\frac{1}{r}\frac{\partial [r(\partial c/\partial r)]}{\partial r} + \frac{\partial^2 c}{\partial z^2}\right\} \qquad (18\text{-}28)$$

$$\bar{C}(z,t) = \frac{1}{\pi R^2}\int_0^R c(r,z,t)2\pi r\,dr \qquad (18\text{-}31)$$

$$\frac{\partial \bar{C}}{\partial t} + U\frac{\partial \bar{C}}{\partial z^*} = D^*\frac{\partial^2 \bar{C}}{\partial z^{*2}} \qquad (18\text{-}32)$$

Where D* is the Aris-Taylor dispersion coefficient

$$\boxed{D^* = D_{AB} + \frac{U^2R^2}{48D_{AB}}} \qquad (18\text{-}33)$$

That is, for laminar flow in a pipe

$$D_a \equiv D^*$$

Correlations for D_a

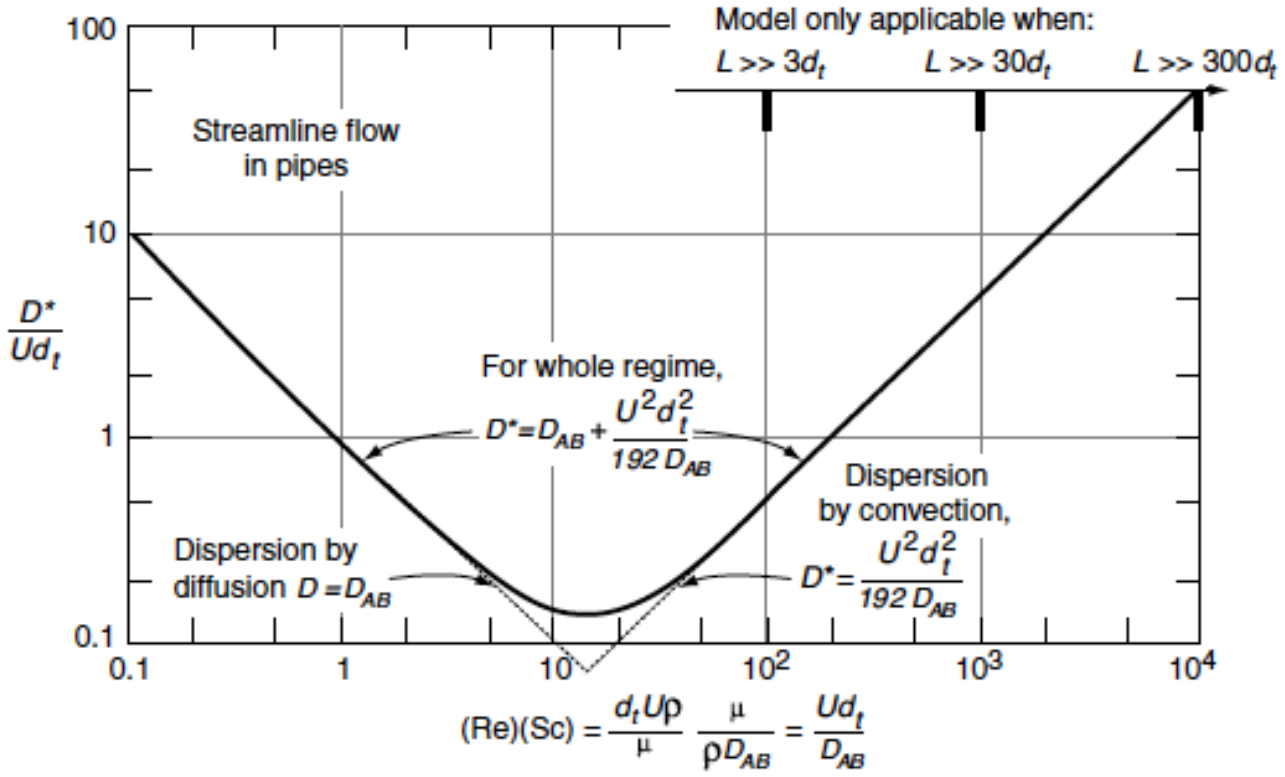


Figure 18-10 Correlation for dispersion for streamline flow in pipes. (Levenspiel, O., *Chemical Reaction Engineering*, 2nd ed. Copyright © 1972 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. All rights reserved.) [Note: $D \equiv D_a$]

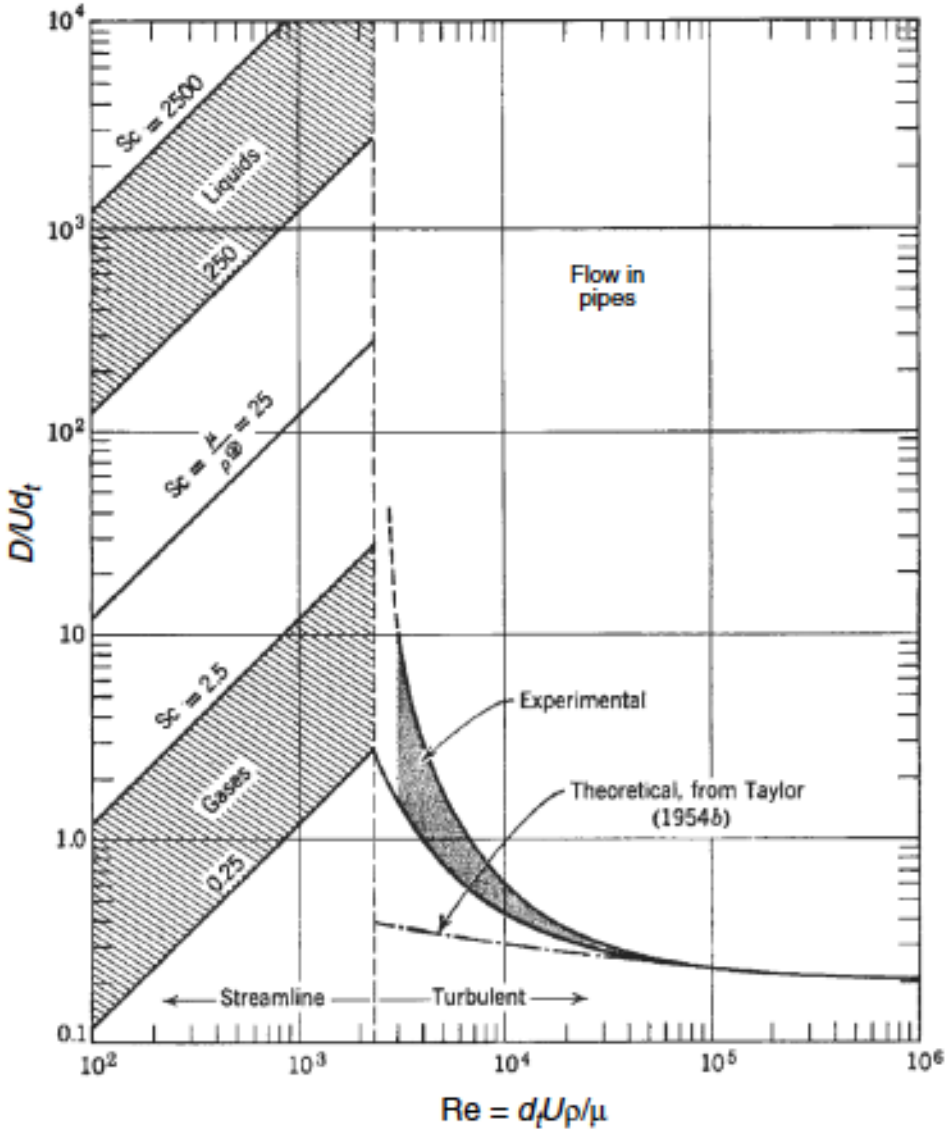


Figure 18-11 Correlation for dispersion of fluids flowing in pipes. (Levenspiel, O., *Chemical Reaction Engineering*, 2nd ed. Copyright © 1972 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. All rights reserved.) [*Note*: $D \equiv D_a$]

Dispersion in Packed Beds

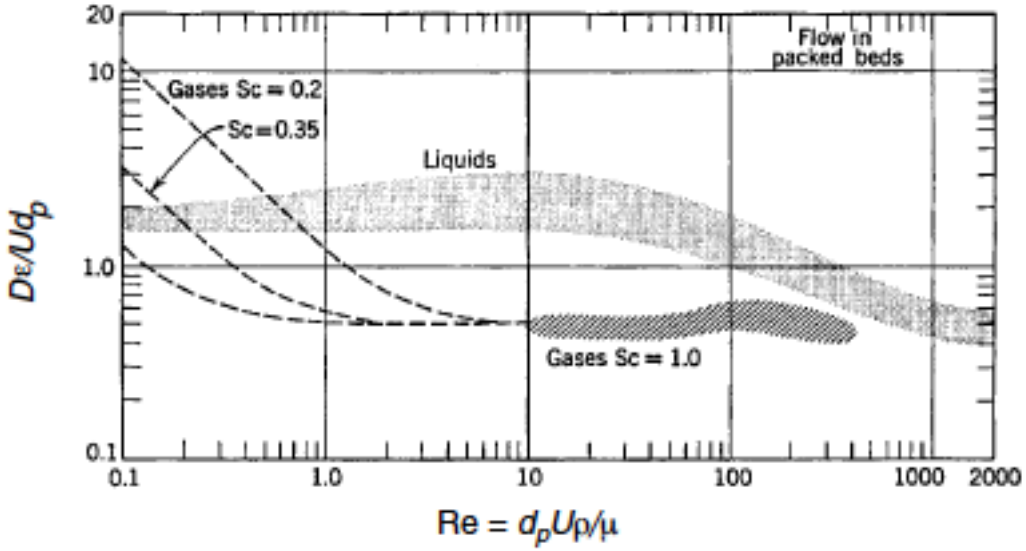


Figure 18-12 Experimental findings on dispersion of fluids flowing with mean axial velocity u in packed beds. (Levenspiel. O., *Chemical Reaction Engineering*, 2nd ed. Copyright © 1972 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. All rights reserved.) [*Note*: $D \equiv D_a$]

Experimental Determination of D_a

$$D_a \frac{\partial^2 C_T}{\partial z^2} - \frac{\partial (U C_T)}{\partial z} = \frac{\partial C_T}{\partial t} \qquad (18\text{-}13)$$

The Unsteady-State Tracer Balance

$$\boxed{\frac{1}{Pe_r} \frac{\partial^2 \psi}{\partial \lambda^2} - \frac{\partial \psi}{\partial \lambda} = \frac{\partial \psi}{\partial \Theta}} \qquad (18\text{-}34)$$

Solution for a Closed-Closed System

In dimensionless form, the Danckwerts boundary conditions are

$$\text{At } \lambda = 0: \qquad \left(-\frac{1}{Pe_r} \frac{\partial \psi}{\partial \lambda}\right)_{\lambda = 0^+} + \psi(0^+) = \frac{C_T(0^-, t)}{C_{T0}} = 1 \qquad (18\text{-}36)$$

$$\text{At } \lambda = 1: \qquad \frac{\partial \psi}{\partial \lambda} = 0 \qquad (18\text{-}37)$$

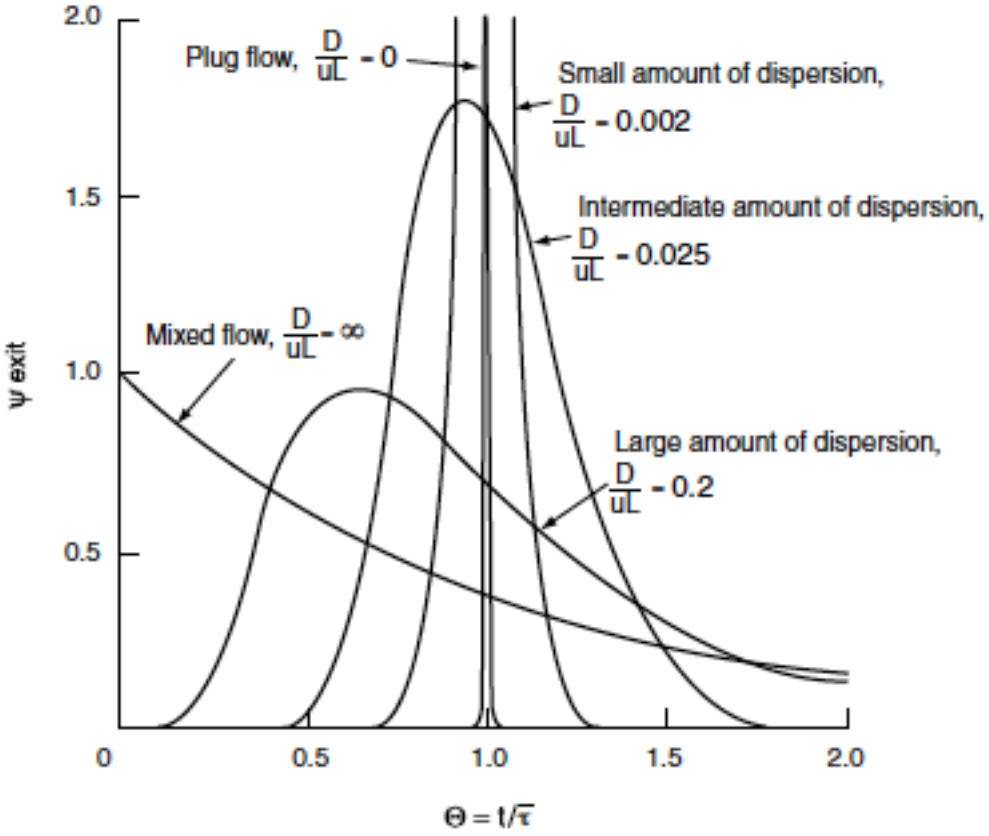


Figure 18-13 *C*-curves in closed vessels for various extents of back-mixing as predicted by the dispersion model. (Levenspiel, O., *Chemical Reaction Engineering*, 2nd ed. Copyright © 1972 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. All rights reserved.) [*Note*: $D \equiv D_a$][10]

$$\frac{\sigma^2}{t_m^2} = \frac{2}{Pe_r} - \frac{2}{Pe_r^2}\left(1 - e^{-Pe_r}\right) \tag{18-39}$$

For long tubes (Per > 100) in which the concentration gradient at ± ∞ will be zero, the solution to the Unsteady-State Tracer balance at the exit is[11]

$$\psi(1,\Theta) = \frac{C_T(L,t)}{C_{T0}} = \frac{1}{2\sqrt{\pi\Theta/Pe_r}} \exp\left[\frac{-(1-\Theta)^2}{4\Theta/Pe_r}\right] \qquad (18\text{-}44)$$

The mean residence time for an open-open system is

$$t_m = \left(1 + \frac{2}{Pe_r}\right)\tau \qquad (18\text{-}45)$$

$$\frac{\sigma^2}{\tau^2} = \frac{2}{Pe_r} + \frac{8}{Pe_r^2} \qquad (18\text{-}46)$$

[11] W. Jost, Diffusion in Solids, Liquids and Gases (New York: Academic Press, 1960), pp. 17, 47.

We now consider two cases for which we can use previous equations to determine the system parameters:

Case 1. The space time τ is known. That is, V and v_0 are measured independently. Here, we can determine the Peclet number by determining t_m and σ^2 from the concentration–time data and then use Equation (18-46) to calculate P_{er}. We can also calculate t_m and then use Equation (18-45) as a check, but this is usually less accurate.

Case 2. The space time τ is unknown. This situation arises when there are dead or stagnant pockets that exist in the reactor along with the dispersion effects. To analyze this situation, we first calculate mean residence time, t_m, and the variance, σ^2, from the data as in case 1. Then, we use Equation (18-45) to eliminate τ^2 from Equation (18-46) to arrive at

$$\frac{\sigma^2}{t_m^2} = \frac{2Pe_r + 8}{Pe_r^2 + 4Pe_r + 4} \qquad (18\text{-}47)$$

We now can solve for the Peclet number in terms of our experimentally determined variables σ^2 and t_m . Knowing P_{er}, we can solve Equation (18-45) for τ, and hence V. The dead volume is the difference between the measured volume (i.e., with a yardstick) and the effective volume calculated from the RTD.

Two-Parameter Models—Modeling Real Reactors with Combinations of Ideal Reactors

Real CSTR Modeled Using Bypassing and Dead Space

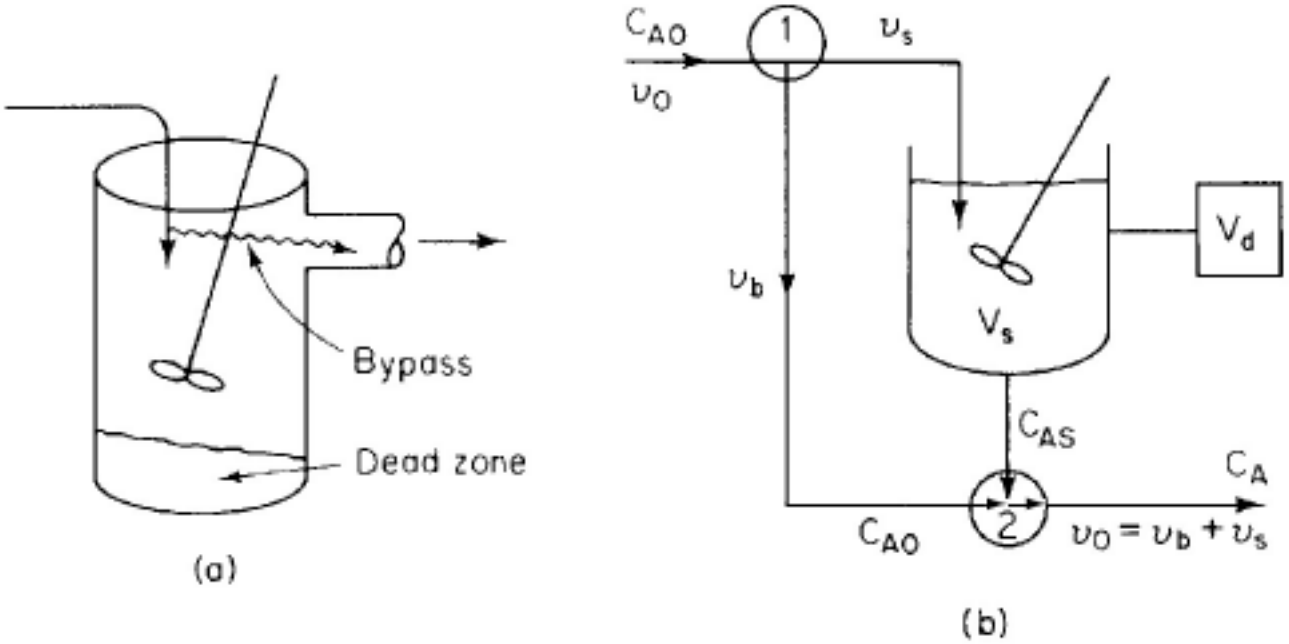


Figure 18-14 (a) Real system; (b) model system.

Solving the Model System for C_A and X

We shall calculate the conversion for this model for the first-order reaction

$$A \longrightarrow B$$

The bypass stream and effluent stream from the reaction volume are mixed at the junction point 2. From a balance on species A around this point

$$[In]=[Out]$$

$$[C_{A0}v_b + C_{as}v_s]=[C_A\,(v_b+v_s)] \qquad (18\text{-}57)$$

Let $\alpha = V_s / V$ and $\beta = v_b / v_0$, then

$$C_A = \beta C_{A0} + (1 - \beta) C_{As} \tag{18-58}$$

For a first-order reaction, a mole balance on V_s gives

$$v_s C_{A0} - v_s C_{As} - k C_{As} V_s = 0 \tag{18-59}$$

or, in terms of α and β

$$C_{As} = \frac{C_{A0}(1-\beta) v_0}{(1-\beta) v_0 + \alpha V k} \tag{18-60}$$

Substituting Equation (18-60) into (18-58) gives the effluent concentration of species A:

$$\frac{C_A}{C_{A0}} = 1 - X = \beta + \frac{(1-\beta)^2}{(1-\beta) + \alpha \tau k} \tag{18-61}$$

Using a Tracer to Determine the Model Parameters in a CSTR-with-Dead-Space-and-Bypass Model

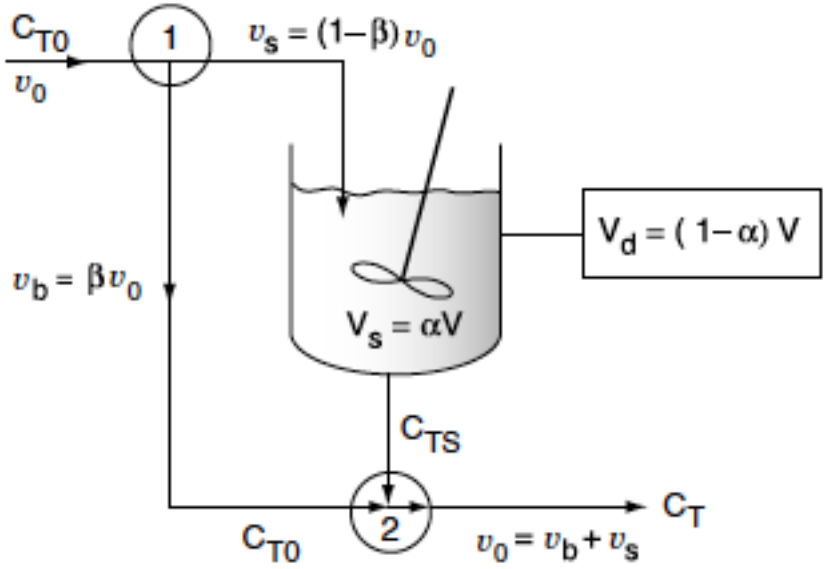


Figure 18-15 Model system: CSTR with dead volume and bypassing.

$$v_s C_{T0} - v_s C_{Ts} = \frac{dN_{Ts}}{dt} = V_s \frac{dC_{Ts}}{dt} \qquad (18\text{-}62)$$

The conditions for the positive-step input are

At $t < 0$, $C_T = 0$
At $t \geq 0$, $C_T = C_{T0}$

A balance around junction point 2 gives

$$C_T = \frac{v_b C_{T0} + C_{Ts} v_s}{v_0} \qquad (18\text{-}63)$$

As before

$$V_s = \alpha V$$

$$v_b = \beta v$$

$$\tau = \frac{V}{v_0}$$

Integrating Equation (18-62) and substituting in terms of α and β

$$\frac{C_T}{C_{T0}} = 1 - (1-\beta)\exp\left[-\frac{1-\beta}{\alpha}\left(\frac{t}{\tau}\right)\right] \qquad (18\text{-}64)$$

Combining Equations (18-63) and (18-64), the effluent tracer concentration is

$$\frac{C_{Ts}}{C_{T0}} = 1 - \exp\left[-\frac{1-\beta}{\alpha}\left(\frac{t}{\tau}\right)\right] \qquad (18\text{-}65)$$

$$\boxed{\ln\frac{C_{T0}}{C_{T0}-C_T} = \ln\frac{1}{1-\beta} + \left(\frac{1-\beta}{\alpha}\right)\frac{t}{\tau}} \qquad (18\text{-}66)$$

Other Models

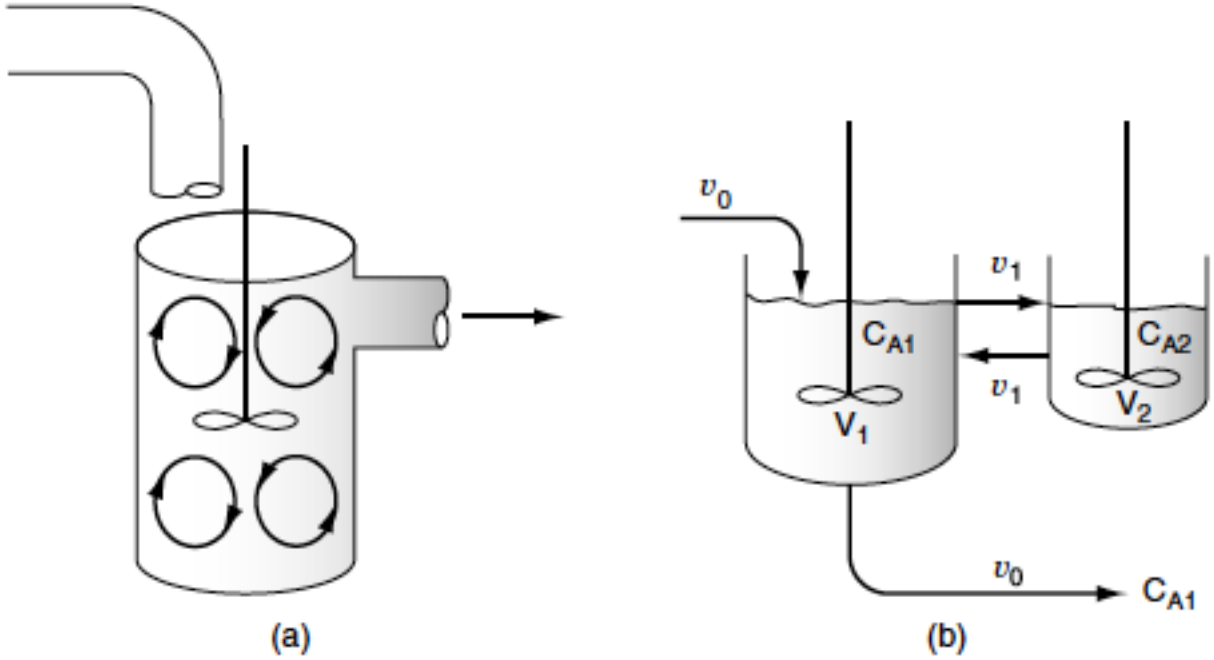


Figure 18-16 (a) Real reaction system; (b) model reaction system.

Solving the Model System for C_A and X

Let β represent that fraction of the total flow that is exchanged between reactors 1 and 2; that is,

$$v_1 = \beta v_0$$

and let α represent that fraction of the total volume, V, occupied by the highly agitated region:

$$V_1 = \alpha V$$

Then

$$V_2 = (1 - \alpha)V$$

The space time is

$$\tau = \frac{V}{v_0}$$

$$C_{A1} = \frac{C_{A0}}{1 + \beta + \alpha\tau k - \{\beta^2/[\beta + (1-\alpha)\tau k]\}} \qquad (18\text{-}67)$$

and

$$\boxed{X = 1 - \frac{C_{A1}}{C_{A0}} = \frac{(\beta + \alpha\tau k)[\beta + (1-\alpha)\tau k] - \beta^2}{(1 + \beta + \alpha\tau k)[\beta + (1-\alpha)\tau k] - \beta^2}} \qquad (18\text{-}68)$$

Using a Tracer to Determine the Model Parameters in a CSTR with an Exchange Volume

The problem now is to evaluate the parameters α and β using the RTD data. A mole balance on a tracer pulse injected at t = 0 for each of the tanks is

Accumulation = Rate in - Rate out

Reactor 1:
$$V_1 \frac{dC_{T1}}{dt} = v_1 C_{T2} - (v_0 C_{T1} + v_1 C_{T1}) \qquad (18\text{-}67)$$

Reactor 2:
$$V_2 \frac{dC_{T2}}{dt} = v_1 C_{T1} - v_1 C_{T2} \qquad (18\text{-}68)$$

$$\tau\alpha \frac{dC_{T1}}{dt} = \beta C_{T2} - (1+\beta) C_{T1} \qquad (18\text{-}71)$$

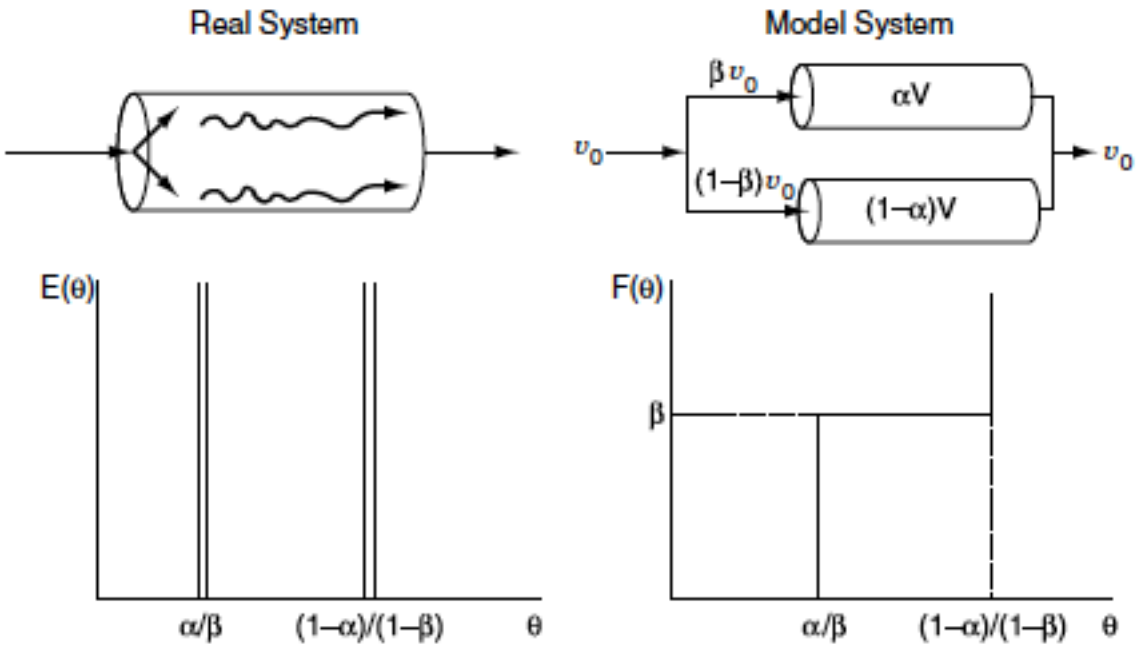
$$\tau(1-\alpha) \frac{dC_{T2}}{dt} = \beta C_{T1} - \beta C_{T2} \qquad (18\text{-}72)$$

$$\left(\frac{C_{T1}}{C_{T10}}\right)_{\text{pulse}} = \frac{(\alpha m_1 + \beta + 1) e^{m_2 t/\tau} - (\alpha m_2 + \beta + 1) e^{m_1 t/\tau}}{\alpha (m_1 - m_2)} \qquad (18\text{-}73)$$

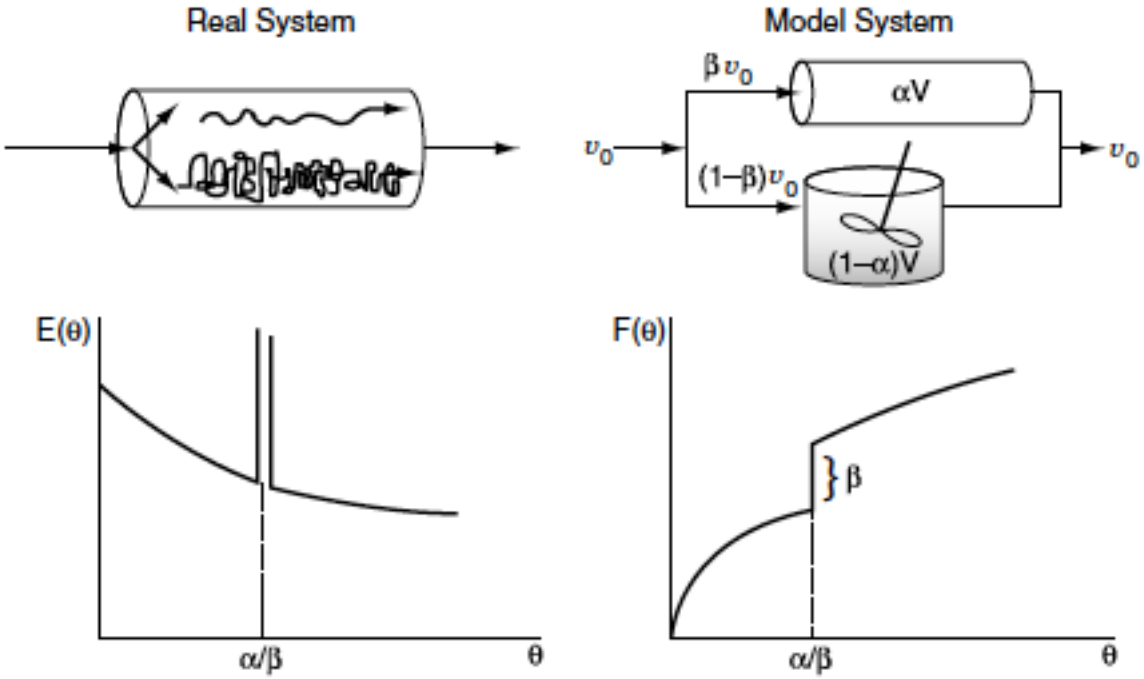
where

$$m_1,\ m_2 = \left[\frac{1-\alpha+\beta}{2\alpha(1-\alpha)}\right]\left[-1 \pm \sqrt{1 - \frac{4\alpha\beta(1-\alpha)}{(1-\alpha+\beta^2)}}\right]$$

Other Models of Nonideal Reactors Using CSTRs and PFRs



Combinations of ideal reactors used to model real tubular reactors: two ideal PFRs in parallel



Combinations of ideal reactors used to model real tubular reactors: ideal PFR and ideal CSTR in parallel

Summary

1. The models for predicting conversion from RTD data are:
   A. Zero adjustable parameters
      i. Segregation model
      ii. Maximum mixedness model
   B. One adjustable parameter
      i. Tanks-in-series model
      ii. Dispersion model
   C. Two adjustable parameters: real reactor modeled as combinations of ideal reactors
2. Tanks-in-series model: Use RTD data to estimate the number of tanks in series,

$$n = \frac{\tau^2}{\sigma^2} \qquad \text{(S18-1)}$$

For a first-order reaction

$$X = 1 - \frac{1}{(1 + \tau_i k)^n}$$

3. Dispersion model: For a first-order reaction, use the Danckwerts boundary conditions

$$X = 1 - \frac{4q \exp(Pe_r/2)}{(1+q)^2 \exp(Pe_r q/2) - (1-q)^2 \exp(-Pe_r q/2)} \qquad \text{(S18-2)}$$

where

$$q = \sqrt{1 + \frac{4Da_1}{Pe_r}} \qquad \text{(S18-3)}$$

$$Da_1 = \tau k \qquad \text{(S18-4)}$$

For a first-order reaction

$$Pe_r = \frac{UL}{D_a} \qquad Pe_f = \frac{Ud_p}{D_a \phi} \qquad \text{(S18-5)}$$

4. Determine Da

A For laminar flow, the dispersion coefficient is

$$D^* = D_{AB} + \frac{U^2 R^2}{48 D_{AB}} \qquad \text{(S18-6)}$$

B Correlations. Use Figures 18-10 through 18-12.

C Experiment in RTD analysis to find t_m and σ^2.

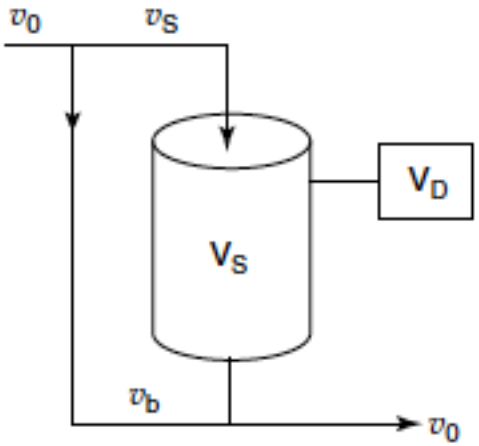
For a closed-closed system, use Equation (S18-6) to calculate Per from the RTD data

$$\frac{\sigma^2}{\tau^2} = \frac{2}{Pe_r} - \frac{2}{Pe_r^2}\left(1 - e^{-Pe_r}\right) \qquad \text{(S18-7)}$$

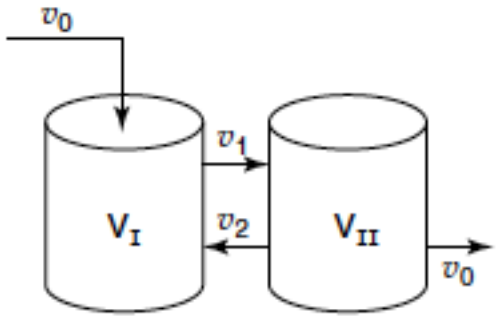
For an open-open system, use

$$\boxed{\frac{\sigma^2}{t_m^2} = \frac{2Pe_\tau + 8}{Pe_\tau^2 + 4Pe_\tau + 4}} \qquad \text{(18-47)}$$

5. If a real reactor is modeled as a combination of ideal reactors, the model should have at most two parameters



CSTR with bypass and dead volume



Two CSTRs with interchange

6. The RTD is used to extract model parameters.
7. Comparison of conversions for a PFR and CSTR with the zero-parameter and two-parameter models. X_{seg} symbolizes the conversion obtained from the segregation model and X_{mm} is that from the maxi-mum mixedness model for reaction orders greater than one.

$$X_{PFR} > X_{seg} > X_{mm} > X_{CSTR}$$

$$X_{PFR} > X_{model} \quad \text{with } X_{model} < X_{CSTR} \quad \text{or} \quad X_{model} > X_{CSTR}$$

Cautions: For rate laws with unusual concentration functionalities or for nonisothermal operation, these bounds may not be accurate for certain types of rate laws.

Summary

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- This presentation discussed nonideal reactor flow, RTD, and the application of models for reactor design and performance assessment.