

# Mixing Effects in Chemical Reactors—V —Micromixing and the Segregated Flow Model

M. P. Duduković

Department of Chemical Engineering  
Washington University  
St. Louis, Missouri

and

R. M. Felder

Department of Chemical Engineering  
North Carolina State University  
Raleigh, North Carolina

## OBJECTIVES

At the completion of this module, the student should be able to:

1. Define the concepts of earliness and lateness of mixing, macrofluid and microfluid, segregation, macromixing, and micromixing; and recognize the roles of these concepts in the behavior of chemical reactors.
2. Define the segregated flow model, and calculate conversions based on the model for any residence time distribution and kinetic scheme.
3. State whether the conversion calculated assuming segregated flow represents an upper bound, a lower bound, or an exact

estimate of the conversion that can be achieved in a reactor with a given residence time distribution.

## PREREQUISITE MATHEMATICAL SKILL

1. Differential and integral Calculus.

## PREREQUISITE ENGINEERING AND SCIENCE SKILLS

1. Kinetic rate laws and design equations for ideal plug flow and stirred tank reactors. Residence time distributions (Module E4.7); mixing in chemical reactors (Modules E4.4, E4.5).

We have seen that the behavior of real chemical reactors may resemble neither ideal plug flow nor perfect mixing. Tracer tests can tell us whether a reactor flow pattern may be approximated as one or another of these ideal types (Module E4.4); if it cannot, the parameters of an appropriate model for nonideal flow, such as the dispersion model or tanks-in-series model (Modules E4.5 and E4.6) may be determined from the tracer response, and the model may then be used to predict reactor performance.

There is nothing unique about a model determined in this manner, however. *While every real system has a*

*unique residence time distribution (Module E4.7), a given residence time distribution may correspond to many different systems, and hence may be reproduced by many alternative models.*

Several questions arise in this regard.

1. Can two reactive systems have the same residence time distribution, and yet yield different reactant conversions or product selectivities?
2. If the answer to the first question is yes (it is), what besides the RTD affects the reactor performance for a given reaction and rate law?
3. If the residence time distribution for a reactor is

known, can the reactor performance be predicted directly without having recourse to a model such as those mentioned in the first paragraph? If so, how?

4. For a given residence time distribution, how much variation exists between the possible values of reactant conversion?

We will propose answers to each of these questions in this module.

### EARLINESS OF MIXING

Let us consider an ideal plug flow reactor and a perfect mixer with equal volumes in series. See Figure 1. A second-order reaction  $A \rightarrow R$ ,  $k = 10 \text{ L/mol} \cdot \text{min}$ , is carried out in this system. The question is, does the order of the reactors make any difference in the conversion obtained?

Let us suppose that someone performed a tracer impulse response measurement on each of the two possible reactor arrangements. The results, yielding the residence time density function, which are shown in Figure 2, would be identical.

$$E(t) = 0, t < \bar{t}/2$$

$$= \frac{2}{\bar{t}} \exp\left[-\frac{2(t - \bar{t}/2)}{\bar{t}}\right], t \geq \bar{t}/2 \quad (1)$$

where  $\bar{t}$  is the total mean residence time in the two reactors. If the system performance were determined entirely by the residence time distribution, the order of the two reactors would obviously make no difference; yet, the order does make a difference. Let  $\bar{t}/2 = 0.5 \text{ min}$ , and  $C_{A0} = 1.0 \text{ mol/L}$ .

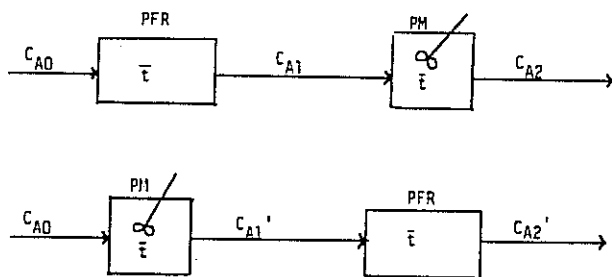


Figure 1. Two combinations of an ideal PFR and a perfect mixer in series yielding the same residence time density function.

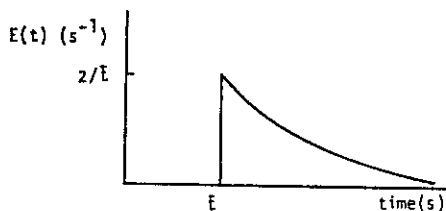


Figure 2. Residence time density function for an ideal PFR and a perfect mixer in series.

### PFR-CSTR:

The design equation for the plug flow section is:

$$\tau = \bar{t}_{\text{PFR}} = \frac{\bar{t}}{2}$$

$$= \int_{C_{A1}}^{C_{A0}} \frac{dC_A}{kC_A^2} = \frac{1}{k} \left[ \frac{1}{C_{A1}} - \frac{1}{C_{A0}} \right] \quad (2)$$

and that for the perfect mixer is:

$$\tau = \bar{t}_{\text{CSTR}} = \frac{\bar{t}}{2} = \frac{C_{A1} - C_{A2}}{kC_{A2}^2} \quad (3)$$

From these two equations, the intermediate concentration  $C_{A1}$  and the final reactant concentration  $C_{A2}$  can be readily calculated:

$$C_{A1} = \frac{2C_{A0}}{2 + k\bar{t}C_{A0}} = \frac{1}{2 + 10} = 0.1667 \text{ (mol/L)} \quad (4)$$

$$C_{A2} = \frac{-1 + \sqrt{1 + 2k\bar{t}C_{A1}}}{k\bar{t}} = \frac{-1 + \sqrt{1 + 20 \times 0.1667}}{10}$$

$$= 0.1082 \text{ (mol/L)} \quad (5)$$

(Verify these equations.) The final conversion is:

$$x_A = 1 - \frac{C_{A2}}{C_{A0}} = 0.892$$

### CSTR-PFR:

The design equations are

$$\tau = \frac{\bar{t}}{2} = \frac{C_{A0} - C'_{A1}}{kC'_{A1}{}^2} \quad (7)$$

$$\tau = \frac{\bar{t}}{2} = \int_{C_{A2}'}^{C_{A1}'} \frac{dC_A}{kC_A^2} \quad (8)$$

The intermediate and final concentrations are:

$$C'_{A1} = \frac{-1 + \sqrt{1 + 2k\bar{t}C_{A0}}}{k\bar{t}} = \frac{-1 + \sqrt{1 + 20}}{10} = 0.3582 \text{ (mol/L)} \quad (9)$$

$$C'_{A2} = \frac{C'_{A1}}{1 + k\left(\frac{\bar{t}}{2}\right)C'_{A1}} = \frac{0.3582}{1 + 5 \times 0.3582} = 0.1283 \text{ (mol/L)} \quad (10)$$

The final conversion is

$$x'_A = 1 - \frac{C'_{A2}}{C_{A0}} = 0.872 \neq 0.892 \quad (11)$$

Let us consider the differences between the configurations that might have led to the different conversions. A second-order reaction is favored by a high reactant concentration; for example, doubling  $C_A$  quadruples the rate. In a plug flow reactor the concentration decreases gradually from its maximum value, whereas in a CSTR the decrease is abrupt. Placing the PFR first in the sequence keeps the

concentration as high as possible for as long as possible, and so yields a higher conversion than the reverse placement.

Viewed another way, in an ideal PFR all fluid elements age at the same rate. In the PFR-CSTR arrangement, mixing between fluid elements of different ages is therefore delayed as long as possible, while in the CSTR-PFR arrangement, elements entering the system are immediately mixed with other elements of different ages. The result just obtained suggests, at least for a second-order reaction, that *the reactor performance is affected both by the age distribution at the outlet and by the earliness or lateness of the mixing required to achieve this distribution.*

Later, this result will be generalized to show that for a given residence time distribution, early mixing increases conversion for reaction orders less than one, has no effect on first-order reactions, and decreases conversion for reaction orders greater than one. It may also be shown that earliness of mixing has an even greater effect on product distributions in multiple reaction systems than on reactant conversion in a single reaction.

## STATES OF AGGREGATION AND MICROMIXING

This and previous modules have referred rather casually to "fluid elements," without ever really saying what was meant. Let us now define a fluid element, or "clump," as a group of molecules small enough to occupy no more than a microscopic volume (a "point") in the reactor, but large enough for the concept of reactant concentration to be meaningful. As a rough estimate, a clump may be considered to contain  $10^{10}$  molecules, give or take five orders of magnitude.

Two extreme states of aggregation of a process fluid are represented schematically in Figure 3, and are referred to as macrofluid and microfluid. In a macrofluid, molecules move together in clumps; the clumps are distributed in residence times, but all molecules within a clump have the same age. In a microfluid, the clumps are dispersed; all molecules move independently of one another, regardless of age.

A real process fluid is generally neither a macrofluid nor a microfluid, but may approach one or the other of these extremes. For example, in a spray tower the liquid may be considered a macrofluid and the gas a microfluid, and vice versa in a bubble tower. Viscous elastomers are much more likely to behave as macrofluids than gases and low viscosity liquids.

In general, however, the state of aggregation of a

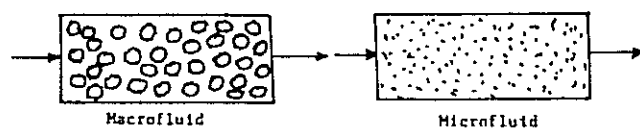


Figure 3. States of aggregation of a process fluid.

fluid depends on various physical properties, the apparatus in which the operation takes place, the force fields to which the fluid is subjected, and the residence time in the process unit. The aggregative state may be guessed at using intuition and perhaps turbulence and mixing theory, but it cannot be predicted with certainty.

The residence time distribution in a reactor is in a sense a measure of the degree to which fluid elements (clumps) mix: in an ideal plug flow reactor no mixing occurs, while in a perfect mixer there is uniformity among elements of different ages. It has also been seen, however, that mixing on another level occurs, namely, between molecules in different fluid elements. The terms *macromixing* and *micromixing* are used to denote these two mixing modes. Another term is the *segregation* of a system, meaning the extent to which micromixing is negligible. Saying that a fluid is completely segregated is the same as saying that it is a macrofluid.

Two conceptual models have been developed to describe the extreme cases of segregation.

### Segregated flow model

The process fluid behaves as a macrofluid. Some clumps exit early, others late, as required by the residence time distribution, but the molecules in each clump are surrounded only by molecules of the same age at all times. Mixing of molecules of different ages occurs as late as possible, that is, at the reactor exit where the outflow is formed.

### Maximum mixedness model

The molecules of the feed immediately upon entering mix and become associated with the molecules in whose company they will eventually leave the reactor.

Mixing that falls short of complete segregation is referred to as *partially segregated flow*. Figures 4a and 4b illustrate segregated and partially segregated flow. The system is viewed as being able to accommodate 4 fluid clumps of four subelements apiece. At fixed time increments, 3 clumps leave the system and 3 new clumps enter in their place. Between increments the subelements may mix to form new clumps with distributed ages.

Figures 4a and 4b show the ages of all fluid subelements in the system and in the exiting fluid when the system is at steady state. The age of a subelement in the reactor is the time that has elapsed

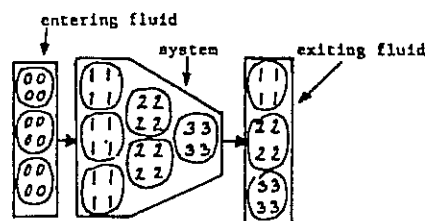


Figure 4a. Segregated flow.

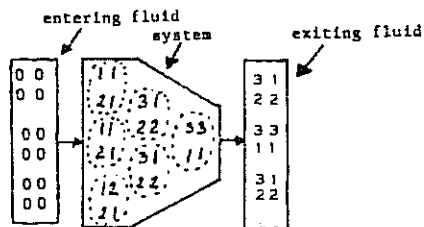


Figure 4b. Partially segregated flow.

since the subelement entered the reactor, and the exit age (residence time) in the effluent fluid is the time the subelement spent in the reactor. An age of one for a subelement in the system indicates an age less than one time period in the system, while age 2 indicates an age greater than or equal to one but less than two periods, and age 3 indicates an age larger than or equal to two but less than three periods. In the effluent fluid age one indicates a residence time equal to or greater than one period but less than two, and exit age 2 and 3 are defined in the same manner. Note that the residence time distribution is the same for both models in Figure 4: a third of the emerging molecules have ages of one, a third have ages of 2, and one third have ages of 3.

In segregated flow the fluid behaves as if the boundaries of each clump were impermeable. The fluid is completely segregated by age, and no mixing between elements of various ages occurs until the exit is reached. If reaction were taking place, each of the clumps would behave like a batch reactor, with the reaction time being equal to the residence time of the clump.

In Figure 4b, the dashed lines may be viewed as permeable boundaries. In every time period the boundaries break, and the contents are mixed with the incoming fluid to form new loose clusters.

Procedures have been derived to predict the performance of a reactor in the extremes of segregated flow and maximum mixedness, and it has also been shown that these two models provide the bounds for conversion that can be achieved for a single  $n$ th-order reaction and a specified residence time distribution. The maximum mixedness formula is difficult to implement, generally requiring the numerical solution of a differential equation (3), and will not be discussed further. The next section illustrates the application of the segregated flow model to reactor analysis.

## SEGREGATED FLOW MODEL

Consider a segregated flow reactor with a known residence time distribution, in which a reaction  $A \rightarrow R$  with a rate of disappearance of  $A$  given by  $[-r_A(C_A)]$ ,  $r_A(C_A)$  takes place. See Figure 5. Since the fluid flows in clumps and is completely segregated by age, each clump behaves like a batch reactor. For a constant density fluid, one can calculate the reactant concentration in every clump from:

$$-\left(\frac{dC_A}{dt}\right)_{\text{clump}} = r_A(C_{A,\text{clump}}) \quad (12)$$

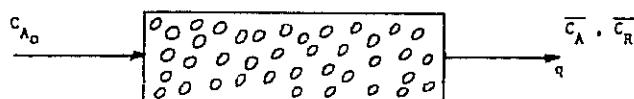


Figure 5. Reactor with segregated flow.

which may be integrated to yield:

$$\int_{C_{A0}}^{C_{A,\text{clump}}} \frac{dC_A}{r_A(C_A)} = t \quad (13)$$

From Equation 13,  $C_{A,\text{clump}}$  can be determined explicitly as a function of time for all  $n$ th-order reactions, and for other rate laws an implicit relationship may be obtained. The mean concentration in the outflow can be found as follows:

$$\begin{aligned} & \left( \begin{array}{l} \text{mean concentration} \\ \text{of reactant in} \\ \text{exit stream} \end{array} \right) \\ &= \bar{C}_A = \lim_{\Delta t \rightarrow 0} \sum_{\text{all elements of exit stream}} \left( \begin{array}{l} \text{concentration} \\ \text{of reactant} \\ \text{remaining in} \\ \text{an element} \\ \text{(clump) of age} \\ \text{between } t \text{ and } (t + \Delta t) \end{array} \right) \\ & \cdot \left( \begin{array}{l} \text{fraction of} \\ \text{exit stream} \\ \text{which is of} \\ \text{age between} \\ t \text{ and } (t + \Delta t) \end{array} \right) \end{aligned}$$

Using Equation 12 for the reactant concentration remaining in an element that has been in the reactor for a time  $t$ , and recalling that by definition,  $E(t)dt$  = the fraction of the exit stream with ages between  $t$  and  $(t + dt)$ , one obtains

$$\bar{C}_A = \int_0^{\infty} C_{A,\text{clump}}(t)E(t)dt \quad (14)$$

The reactant conversion is  $x_A = 1 - \bar{C}_A/C_{A0}$ , so that

$$1 - x_A = \int_0^{\infty} \left( \frac{\bar{C}_A}{C_{A0}} \right)_{\text{clump}} E(t)dt \quad (15)$$

### Example 1:

A first-order reaction ( $k = 2 \text{ min}^{-1}$ ) is carried out in a flow reactor with the following residence time distribution:

$$\begin{aligned} E(t) &= 0 \text{ when } t < 1 \text{ min} \\ &= \exp(1-t) \text{ when } t \geq 1 \text{ min} \end{aligned}$$

Estimate the fractional conversion using the segregated flow model.

**Solution:**

For a first-order reaction,

$$\left(\frac{C_A}{C_{A0}}\right)_{\text{clump}} = \exp(-kt) = \exp(-2t)$$

From Equation 15,

$$\begin{aligned} 1 - x_A &= \int_0^{\infty} \left(\frac{C_A}{C_{A0}}\right)_{\text{clump}} E(t) dt \\ &= \int_0^{\infty} \exp(1-3t) dt \\ &= -\frac{1}{3} \exp(1-3t) \Big|_0^{\infty} = 0.0451 \end{aligned}$$

Therefore,

$$x_A = 0.955$$

**Example 2:**

An impulse tracer test produced the exit age density function presented in Table 1, for a reactor in which a first-order reaction with rate constant  $k = 0.1 \text{ min}^{-1}$  is taking place. Find the reactant conversion at the same operating conditions at which the tracer test was performed.

**Solution:**

Let us first verify that  $E(t)$  is properly normalized, using Simpson's rule to perform the integration.

$$\begin{aligned} \int_0^{\infty} E(t) dt &\approx \frac{\Delta t}{3} [E_1 + 4[E_2 + E_4 + \dots + E_{2n}] \\ &\quad + 2[E_3 + \dots + E_{2n-1} \dots] + E_{2n}] \\ &= \frac{5}{3} \{0.0 + 4[0.03 + 0.05 + 0.02 + 0.002] \\ &\quad + 2[0.050 + 0.040 + 0.010] + 0.0\} \\ &= 1.0 \end{aligned}$$

The table can now be extended; see Table 2.

Then from Equation 15,

$$1 - x_A = \int_0^{\infty} e^{-kt} E(t) dt \xrightarrow{\text{Simpson's rule}} 0.288$$

or

$$x_A = 0.712$$

The mean residence time in the reactor is

$$\bar{t} = \int_0^{\infty} t E(t) dt \xrightarrow{\text{Simpson's rule}} 15.13 \text{ min}$$

If ideal plug flow is assumed for the reactor,

$$1 - x_A = e^{-k\bar{t}} = e^{-1.513} = 0.220 \Rightarrow x_{A\text{PFR}} = 0.780$$

and if perfect mixing is assumed

$$1 - x_A = \frac{1}{1 + k\bar{t}} = \frac{1}{1 + 1.513} = 0.398 \Rightarrow x_{A\text{CSTR}} = 0.602$$

As expected the conversion based on the actual residence time distribution lies between these two extremes.

**Example 3:**

Evaluate the conversion for a second-order reaction with rate constant  $k = 10 \text{ L/mol} \cdot \text{min}$  in a reactor with the residence time distribution of a perfect mixer, assuming segregated flow. The feed reactant concentration is  $C_{A0} = 1 \text{ (mol/L)}$  and the mean residence time is  $\bar{t} = 1 \text{ min}$ . Then compare the calculated conversion with that which would be achieved if the reactor contents behaved as a microfluid.

**Solution:**

The residence time density function

$$E(t) = \frac{1}{\bar{t}} e^{-t/\bar{t}} = e^{-t}$$

The clump concentration is

$$\left(\frac{C_A}{C_{A0}}\right)_{\text{clump}} = \frac{1}{1 + ktC_{A0}} = \frac{1}{1 + 10t}$$

**Table 1.**

$t$ (min)	0	5	10	15	20	25	30	35	40
$E(t)$ ( $\text{min}^{-1}$ )	0	0.030	0.050	0.050	0.040	0.020	0.010	0.002	0

**Table 2.**

$t$ (min)	0	5	10	15	20	25	30	35	40
$E(t)$ ( $\text{min}^{-1}$ )	0	0.030	0.050	0.050	0.040	0.020	0.010	0.002	0
$e^{-kt}$	1	0.606	0.368	0.223	0.135	0.082	0.050	0.030	0.018
$e^{-kt} E(t)$	0	0.0182	0.0184	0.0112	0.0054	0.0016	0.0005	0.00006	0
$tE(t)$	0	0.15	0.5	0.75	0.8	0.5	0.3	0	0

The segregated flow model. Equation 15, predicts

$$1 - x_A = \int_0^x \frac{1}{1 + ktC_{A0}} \frac{1}{\bar{t}} e^{-t/\bar{t}} dt = \int_0^x \frac{e^{-t/\bar{t}}}{1 + 10t} dt$$

$$= 0.1e^{0.1} \int_1^x \frac{e^{-0.1x}}{x} dx$$

This integral may be evaluated in terms of a tabulated function called the exponential integral (see Homework Problem 3) or it may be integrated numerically. The result is

$$1 - x_A = 0.201 \Rightarrow x_A = 0.799$$

Recall that when the earliness and lateness of mixing was discussed at the beginning of this module, it was shown that late mixing favors higher conversions for second-order reactions. One would suspect, since segregated flow implies the latest possible mixing, that conversion in a segregated perfect mixer is higher than in the one in which a microfluid is ideally mixed. The familiar design equation for an ideal CSTR,

$$\bar{t} = \frac{C_{A0} - C_A}{-r_A(C_A)}$$

presumes that the fluid in the tank is completely homogeneous in composition, that is, a microfluid. Substituting a second-order rate law for  $-r_A$  in this equation eventually yields:

$$1 - x_A = \frac{(1 + 4k\bar{t}C_{A0})^{1/2} - 1}{2k\bar{t}C_{A0}}$$

If,

$$k = 10 \text{ (L/mol} \cdot \text{min)}$$

$$\bar{t} = 1 \text{ (min)}$$

$$C_{A0} = 1 \text{ (mol/L)}$$

then,

$$1 - x_A = 0.270$$

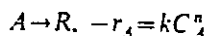
and,

$$x_A = 0.730 < (x_A)_{\text{segregated flow}}$$

Thus, as expected, the conversion in segregated flow is higher than that obtained if the reactor contains a microfluid.

## EFFECT OF MICROMIXING ON CONVERSION

The final result of the last example may be generalized by determining how micromixing affects reactor performance for a reaction of arbitrary order. Let us consider a single reaction



taking place in a flow reactor with an arbitrary residence time distribution. Let us make the following claims:

1. For a first-order reaction (or a series of first-order reactions), micromixing has no effect on the reactor performance. Conversion is thus predicted exactly by the segregated flow model (Equation 15).

2. Micromixing decreases conversion for reaction orders greater than 1, and increases it for orders less than 1. The segregated flow model consequently predicts an upper bound on conversion for  $n > 1$ , and a lower bound for  $n < 1$ .

Let us present a qualitative argument to justify these claims. Figures 6a, b, and c show rate curves for  $n$ th-order reactions and the effects of micromixing on the rate  $-r_A = kC_A^n$  versus  $C_A$  for a)  $n < 1$ , b)  $n = 1$ , c)  $n > 1$ .

Let us consider two fluid elements of equal volumes, one containing A at a concentration  $C_{A1}$ , the other at a concentration  $C_{A2} > C_{A1}$ . If these two elements are not mixed (that is, if flow is segregated), the combined rate of reaction in both elements on a unit volume basis is the average of the rates in each element:

$$-\bar{r}_A = \frac{1}{2} (-r_{A1} + -r_{A2})$$

Graphically,  $-\bar{r}_A$  may be found by drawing a line between  $(C_{A1}, -r_{A1})$  and  $(C_{A2}, -r_{A2})$  on the plot of

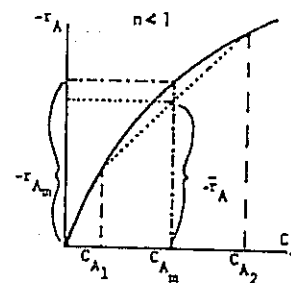


Figure 6a.  $n < 1$ .

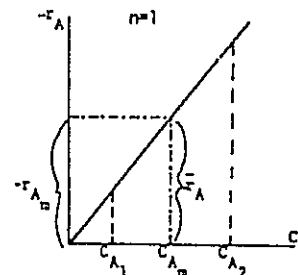


Figure 6b.  $n = 1$ .

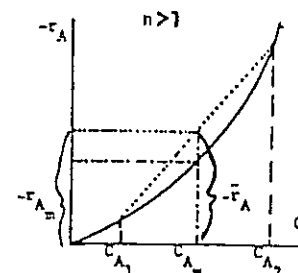


Figure 6c.  $n > 1$ .

$-r_A$  versus  $C_A$ , coming up to this line from the midpoint of  $C_{A1}$  and  $C_{A2}$  on the abscissa, and reading the rate at the intersection (see Figure 6).

Now suppose the elements are mixed completely. The uniform reactant concentration in the combined element is

$$C_{A_m} = \frac{1}{2}(C_{A1} + C_{A2})$$

The rate of reaction  $-r_{A_m}$  is the value of  $-r_A$  corresponding to this concentration; it is found graphically by proceeding vertically from  $C_{A_m}$  to the rate curve, and reading the value of  $-r_A$  at the intersection.

It is clear from Figure 6a that if  $n < 1$ ,  $-\bar{r}_A < -r_{A_m}$ ; that is, mixing of fluid elements of different ages increases the average reaction rate, and hence the conversion. For  $n = 1$  (Figure 6b) mixing of elements of different ages has no effect on the average rate, and for  $n < 1$  (Figure 6c), micromixing decreases conversion ( $-\bar{r}_A < -r_{A_m}$ ). Similar arguments apply for two elements of unequal volumes, and for an arbitrary number of elements.

#### Example 4:

A zero-order reaction  $A \rightarrow R$ ,  $-r_A = 9$  mol/min, is carried out in a perfect mixer. The mean residence time is  $\bar{t} = 1$  min, and the feed enters at  $C_{A0} = 10$  mol/L. Calculate the fractional conversion that will be achieved a) in segregated flow, b) if the reactor contains a microfluid.

#### Solution

a) Segregated flow

$$-r_A = -\frac{dC_A}{dt} = 9 \rightarrow \left( \frac{C_A}{C_{A0}} \right)_{\text{clump}}$$

$$= 1.0 - 0.9t \text{ when } t \leq \frac{10}{9}$$

$$= 0 \text{ when } t > \frac{10}{9}$$

$$E(t) = \frac{1}{\bar{t}} e^{-t/\bar{t}} = e^{-t}$$

$$1 - x_A = \int_0^{\infty} \left( \frac{C_A}{C_{A0}} \right)_{\text{clump}} E(t) dt$$

$$= \int_0^{10/9} (1.0 - 0.9t) e^{-t} dt = 0.396$$

and therefore,

$$x_A = 0.604$$

b) Microfluid

$$\bar{t} = \frac{C_{A0} - C_A}{-r_A}$$

$$1 = \frac{10 - C_A}{9}$$

$$C_A = 1$$

$$x_A = 0.9$$

As expected, conversion in segregated flow is lower (in this case, considerably lower) than that for a microfluid. Regardless of the degree of micromixing in the reactor, the conversion can never be less than 60.4%.

The absence of a micromixing effect for  $n = 1$  should appear reasonable from another point of view. In a first-order reaction, the probability of an individual reactant molecule undergoing transformation in a given time interval is the same, irrespective of its age and the types and ages of the molecules surrounding it. Consequently, the overall conversion achieved depends only on the residence time distribution of the molecules, and not on how they are dispersed within the reactor.

#### NOMENCLATURE

$C_A$	= molar concentration of reactant A
$\bar{C}_A$	= mean molar concentration of A in the outflow
$C_{A,\text{clump}}$	= molar concentration of A in a fluid element (clump)
$C_{A0}$	= feed concentration of A
$E(t)$	= residence time density function
$k$	= reaction rate constant
$n$	= reaction order
$-r_A$	= rate of disappearance of reactant A
$t$	= time
$\bar{t}$	= mean residence time
$x_A$	= fractional conversion of A
$\tau$	= reactor space time

#### LITERATURE CITED

- Levenspiel, O., "Chemical Reaction Engineering," 2nd Edition, Chapter 10. John Wiley & Sons, New York (1972).
- Wen, C. Y., and L. T. Fan, "Models for Flow Systems and Chemical Reactors," Chapter 11. New York, Marcel Dekker (1975).
- Zwietering, T. N., *Chem. Eng. Sci.*, 11, 1(1959).
- Abramowitz, M. and I. A. Stegun, "Handbook of Mathematical Functions," National Bureau of Standards, Washington (1964).

#### STUDY PROBLEMS

- Briefly define the following terms:
  - Clump
  - Macrofluid
  - Microfluid
  - Segregation
  - Macromixing
  - Micromixing
  - Segregated flow model
  - Maximum mixedness model

2. A second-order reaction is carried out in an ideal plug flow reactor. Is the reactor performance affected by whether the fluid behaves as a macrofluid or a microfluid? Explain.
3. A second-order reaction is carried out in a perfect mixer.
  - a) Is the reactor performance affected by whether the fluid behaves as a macrofluid or a microfluid? If so, how is it affected?
  - b) How would the answer change if the reaction was first-order? Half-order?
  - c) Does the usual CSTR material balance equation presume macrofluid or microfluid behavior?
4. An ideal CSTR and an ideal PFR are to be connected in series. How should they be connected (CSTR first, PFR first, or order immaterial) to achieve the highest conversion for an  $n$ th-order reaction with
  - a)  $n = \frac{1}{2}$
  - b)  $n = 1$
  - c)  $n = 3/2$
5. An  $n$ th-order reaction is carried out in a reactor with a nonideal residence time density function  $E(t)$ . Conversion is calculated based on the segregated flow model using Equation 15, but in fact, the reactor is only partially segregated. Is the predicted conversion too high, too low, or correct, for
  - a)  $n = \frac{1}{2}$
  - b)  $n = 1$
  - c)  $n = 3/2$

6. A continuous fluidized bed reactor is used in ore roasting. A large excess of the reactant gas is used, so that its concentration in the reactor is almost constant. The rate of depletion of the solid reactant is given by:

$$\frac{-dC_s}{dt} = f(C_s, C_g)$$

so that

$$(C_s/C_{s0}) = F(t, C_g)$$

for every particle. The mean residence time of the solids in the reactor is  $\bar{t}$ .

- a) What residence time distribution should one assume for the solids if no tracer data are available?
- b) How would the conversion of solids be calculated?

## HOMEWORK PROBLEMS

1. Given below are three residence time density functions. For each one, calculate the mean residence time

$$\bar{t} = \int_0^{\infty} tE(t)dt$$

and the expected reactant conversion  $x_A$ , assuming  
i) segregated flow; ii) ideal plug flow with the same

$\bar{t}$ ; iii) perfect mixing (microfluid) with the same  $\bar{t}$ . When you calculate  $x_A$  based on segregated flow, state whether the calculated value is an upper bound, a lower bound, or an exact estimate of the possible conversions for the given residence time distribution.

- a) For Figure 7.

$$-r_A = 0.1C_A^2 \text{ (mol/L} \cdot \text{min)}$$

$$C_{A0} = 2 \text{ (mol/L)}$$

- b) For Figure 8.

$$-r_A = 2.5C_A$$

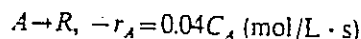
$$C_{A0} = 1 \text{ (mol/L)}$$

- c) For Figure 9.

$$-r_A = 0.5C_A^2 \text{ (mol/L} \cdot \text{min)}$$

$$C_{A0} = 1 \text{ (mol/L)}$$

2. A first-order reaction,



is carried out in an ideal CSTR with a mean residence time of 20 seconds.

- a) How would you expect the conversions for a macrofluid and a microfluid to differ?
- b) Calculate the conversion, assuming segregated flow (Equation 15) and then assuming a

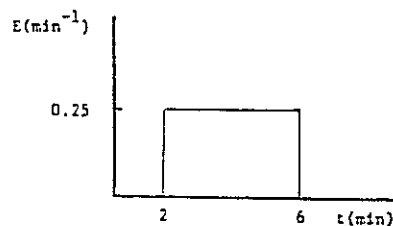


Figure 7.

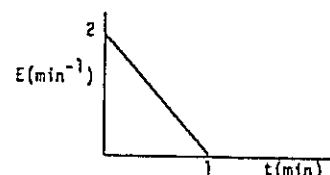


Figure 8.

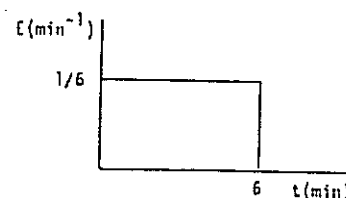
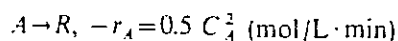


Figure 9.



microfluid (the usual CSTR formula). Verify your prediction of Part (a).

3. A second-order reaction,



is carried out in an ideal CSTR-PFR series combination. The mean residence time in each reactor is 1 minute, and  $C_{A0} = 5 \text{ mol/L}$ .

- Two alternatives are to put the PFR first followed by the CSTR, and vice versa. Would you expect the first alternative to yield a higher conversion, a lower conversion, or the same conversion as the second?
- Calculate the conversions for both arrangements assuming microfluid behavior, and verify your prediction.
- Suppose the segregated flow model were used to predict the conversion. Write the integral formula you would use, making all required substitutions but not evaluating the integral. Then give a range for the possible value of  $x_A$

calculated in this manner (e.g.  $x_A < \underline{\quad}$ , or  $x_A \geq \underline{\quad}$ ).

- Calculate the conversion based on the segregated flow model. Note: values of the exponential integral.

$$E_1(z) = \int_z^\infty \frac{e^{-y}}{y} dy$$

are tabulated in a number of reference handbooks, such as that of Abramowitz and Stegun (4). One such value is  $E_1(1.4) = 0.116219$ .

- A first-order reaction ( $k = 0.1 \text{ min}^{-1}$ ) is carried out in a flow reactor. A tracer response test is used to determine the residence time density function in the reactor, with the results given in Table 3. Verify that the  $E(t)$  curve is normalized. Then calculate the mean residence time and the expected conversion, using Simpson's rule for all required integrations. Finally, calculate the conversion that would be achieved in an ideal PFR and a perfect mixer with the same mean residence time.

Table 3.

$t$ (min)	0	2	4	6	8	10	12	14	16	18
$E(t)$ ( $\text{min}^{-1}$ )	0	0	0.001	0.004	0.013	0.032	0.060	0.088	0.100	0.089
$t$ (min)	20	22	24	26	28	30	32			
$E(t)$ ( $\text{min}^{-1}$ )	0.060	0.032	0.013	0.004	0.002	0	0			

## SOLUTIONS TO THE STUDY PROBLEMS

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1. (a) Clump: a collection of molecules small enough to occupy no more than a microscopic volume in a reactor, but large enough for the concept of concentration to be meaningful.
  - (b) Macrofluid: molecules are organized in coherent clumps. All molecules in a clump have the same age.
  - (c) Microfluid: molecules are randomly dispersed, irrespective of age.
  - (d) Segregation: The tendency of the contents of a reactor to behave as a macrofluid.
  - (e) Macromixing: the phenomenon whereby residence times of clumps are distributed about a mean value.
  - (f) Nicomixing: mixing among molecules of different ages. (Put another way, mixing between macrofluid clumps.)
  - (g) Segregated flow model: the fluid in a flow reactor is assumed to behave as a macrofluid. Each clump functions as a miniature batch reactor. Mixing of molecules of different ages occurs as late as possible.
  - (h) Maximum mixedness model: the fluid in a flow reactor behaves as a microfluid. Mixing of molecules of different ages occurs as early as possible.
2. No Every molecule in an ideal PFR is surrounded by other molecules with the same age, so that all adjacent clumps have the same composition. Whether or not there is exchange between clumps is immaterial.
  3. (a) Yes. Conversion is higher for the macrofluid.
  - (b) 1st - order: No difference.  
½ - order: Conversion is higher for the microfluid.
  - (c) Microfluid.

4. (a) CSTR-PFR  
(b) No difference  
(c) PFR-CSTR
5. (a) Too low  
(b) Correct  
(c) Too high
6. (a)  $E(t) = \frac{1}{\bar{t}} \exp(-t/\bar{t})$   
(b) Use the segregated flow model [Eq. (15)]. Using the usual CSTR equation would be equivalent to assuming that the solids behave as a microfluid, which is certainly not the case.