

## IV. REACTOR MODEL

### 1. Reactors (반응기)

- Reactors : Batch reactors (回分式) vs. Continuous-flow reactors (連續式)
- Completely stirred tank reactor (CSTR or CMF, Completely mixed flow reactor, CFSTR, Continuous flow stirred tank reactor) and Plug-flow reactor

반응기의 종류	그림	설명 또는 응용
회분 반응기 Batch		반응기의 도입 및 배출 흐름이 없다. 액상 내용물은 완전 혼합된다. 가령, 제3장에서 설명한 BOD 시험은 병으로 만든 회분 반응기에서 행한다.
플러그 흐름 반응기 (관형 흐름 반응기) Plug-flow		유체 입자는 도입 될 때와 마찬가지로 순서로 탱크를 거쳐 흘러서 배출된다. 유체 입자는 이론적 체류 시간과 같은 시간 동안 탱크 안에 체류한다. 이러한 형태의 흐름은 길이 대 폭의 비가 큰 긴 탱크에서 볼 수 있는 것으로, 길이 방향에서의 분산은 최소이거나 없다.
연속 흐름 교반 탱크 반응기 (완전 혼합 반응기) CSTR		입자가 탱크 안에 도입되면 즉시 반응기 전체에서 분산되어 완전 혼합이 일어난다. 입자는 그 통계적 모집단에 비례하여 반응기에서 배출된다. 원형 또는 장방형 탱크에서 내용물을 균일하게 연속적으로 재분산시키면 완전 혼합을 이룰 수 있다.
임의의 흐름 반응기 Arbitrary-flow		플러그 흐름과 완전 혼합 사이의 임의의 부분 혼합이 이루어지는 흐름을 임의의 흐름이라 한다.
충전층 반응기 Packed-bed		충전층 반응기는 자갈, 슬랙, 도자기, 플라스틱과 같은 충전 매체를 채운 것이다. 흐름이 완전히 차게 하기도 하고 (혐기성 여상), 간헐적으로 공급하기도 한다 (살수 여상).
유동층 반응기 Fluidized-bed		유동층 반응기는 충전층 반응기와 여러 면에서 비슷하나, 이때는 충전 매체가 유체(공기 또는 물)의 상향 흐름에 의하여 층 전체에 팽창되게 한다. 충전 공급율은 유량을 조절하여 변화시킬 수 있다.



## 1.1 Introduction on Reactor Models

### Batch reactor

- no flow in or out (no transport across the boundary of the reactor)
- Contents are mixed.
- may contain a single or multiple fluids (e.g., air and water)
- Species concentrations within the reactor change with time because of (1) transformation or (2) phase changes across a fluid interface.

### Completely stirred tank reactor (CSTR)

- Generally constant flow rate in and out
- Contents are thoroughly mixed (Perfect mixing assumption).
- Concentration of a species in the effluent is equal to its concentration throughout the reactor.
- The analysis of a CSTR is based on (1) a mass balance on species within the fluid in the reactor accounting for processes, as well as (2) mass transport into and (3) out of the reactor.

### Plug-flow reactor (PFR)

- A tube through which fluid flows
- Assumptions: (1) The tube has constant cross-section at all axial positions, (2) the fluid velocity is uniform over the cross-section of the tube, and (3) no mixing in the axial direction of the tube (mass transport occurs only by advection).
- The analysis of PFR involves (1) considering processes, and (2) advection along the axis of the tube.

(1) Material Balance and (2) Residence Time (or characteristic times) are the most important key concepts for the reactor modeling.



## 1.2 Reactor Material Balances

Material balance equation follows this general form

Accumulation rate = Inflow rate – Outflow rate  $\pm$  Net transformation rate

Net transformation rate : gain “+” and loss “-“

$$\text{Inflow rate} = Q_{\text{in}} \cdot C_{\text{in}}$$

$$\text{Outflow rate} = Q_{\text{out}} \cdot C_{\text{out}}$$

$$\text{Accumulation rate} = \frac{d(C \cdot V)}{dt}$$

where  $Q_{\text{in}}$  = flow rates of fluid in [ $L^3/T$ ];

$Q_{\text{out}}$  = flow rate of fluid out [ $L^3/T$ ];

$C_{\text{in}}$  = concentration of species in the inflow [ $M/L^3$ ] or [ $\text{moles}/L^3$ ];

$C_{\text{out}}$  = concentration of the species in the outflow [ $M/L^3$ ] or [ $\text{moles}/L^3$ ];

$C$  = concentration of the species [ $M/L^3$ ] or [ $\text{moles}/L^3$ ];

$V$  = fluid volume [ $L^3$ ]; and

$T$  = elapsed time [ $T$ ].

For general chemical reactions,

$$\text{Net transformation rate} = r \cdot V$$

where  $r$  = net rate of production of species concentration due to the reaction

$$[M/T, L^3] \text{ or } [\text{moles}/T, L^3].$$

For examples,  $r = -k_0$  (for zero order reaction);

$r = -k_1 \cdot C$  (first order reaction); and

$r = -k_2 \cdot C^2$  (second order reaction).

For flux across fluid interface,

$$\text{Net transformation rate} = J_{\text{gl}} \cdot A$$

where  $J_{\text{gl}}$  = the species flux across the interface area [ $M/L^2$ ] or [ $\text{moles}/L^2$ ]; and

$A$  = interface area [ $L^2$ ].



**Residence time(체류시간),  $\theta$** 

Mean residence time of fluid molecule (hydraulic retention time in the water-based system)

$$\theta = \frac{V}{Q}$$

Sometimes, more than one material balance equation is needed to describe a system.

**1.3 Reactor Models****Batch Reactor**

$$\frac{d(C \cdot V)}{dt} = \text{net transformation rate} = r \cdot V$$

$$\frac{dC}{dt} = r \quad \text{or} \quad \frac{d(C \cdot V)}{dt} = J \cdot A$$



**EXAMPLE 5.A.2** *Species Decay in a Batch Reactor as a Function of Reaction Order*

A species is placed in a batch reactor, where it decays by either a zeroth-, first-, or second-order reaction. Derive equations to describe the change in species concentration and characteristic times in each case. Plot the results.

**SOLUTION** The rates of species decay are given below, where  $C$  represents the species concentration and  $k_i$  the respective rate constants.

$$\text{Zeroth order:} \quad r_0 = -k_0$$

$$\text{First order:} \quad r_1 = -k_1 C$$

$$\text{Second order:} \quad r_2 = -2k_2 C^2$$

In these expressions,  $r_i$  represents the rate of change of species concentration because of the  $i$ th-order reaction. Note that the units of  $k_i$  vary in these three expressions, so that the decay rate ( $r_i$ ) is represented in units of mass (or moles) per volume per time. The governing material-balance equations and initial conditions for the three cases are as follows:

$$\text{Zeroth order:} \quad \frac{d(CV)}{dt} = -r_0 V = -k_0 V \quad C(t=0) = C(0)$$

$$\text{First order:} \quad \frac{d(CV)}{dt} = -r_1 V = -k_1 CV \quad C(t=0) = C(0)$$

$$\text{Second order:} \quad \frac{d(CV)}{dt} = -r_2 V = -2k_2 C^2 V \quad C(t=0) = C(0)$$

Since the batch reactor volumes remain constant throughout the reaction, they cancel from both sides of these equations. The governing equation for the zeroth-order case is valid only for  $C(t) > 0$ . When  $C(t) = 0$ , the reaction rate becomes zero and the concentration remains zero indefinitely.

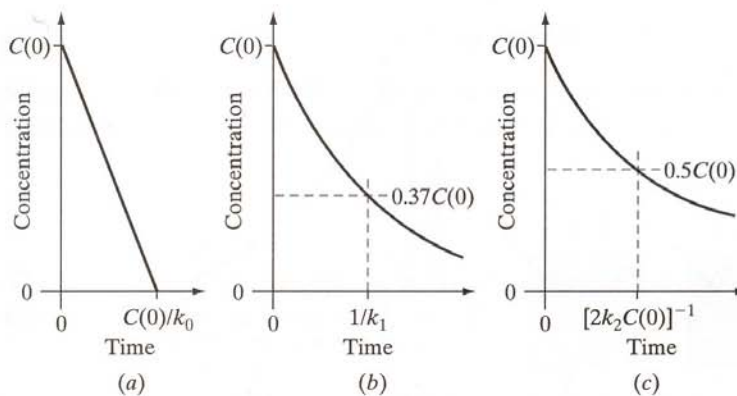
The solutions are obtained by rearranging and directly integrating. The results are presented as equations below and plotted in Figure 5.A.5.



$$\begin{aligned} \text{Zeroth order: } & C(t) = C(0) - k_0 t \quad t \leq C(0)/k_0 \\ & C(t) = 0 \quad t > C(0)/k_0 \\ \text{First order: } & C(t) = C(0) \exp(-k_1 t) \\ \text{Second order: } & C(t) = \frac{C(0)}{1 + 2k_2 t C(0)} \end{aligned}$$

Characteristic times for each case can be calculated by dividing the initial stock by the initial rate of decay as follows:

$$\begin{aligned} \text{Zeroth order: } & \tau_0 \sim \frac{C(0)V}{k_0 V} = \frac{C(0)}{k_0} \\ \text{First order: } & \tau_1 \sim \frac{C(0)V}{k_1 C(0)V} = \frac{1}{k_1} \\ \text{Second order: } & \tau_2 \sim \frac{C(0)V}{2k_2 C(0)^2 V} = \frac{1}{2k_2 C(0)} \end{aligned}$$



**Figure 5.A.5** Change in species concentration as a function of time in a batch reactor in response to (a) zeroth-, (b) first-, and (c) second-order decay. In each case, a characteristic time for the reaction to proceed to completion is indicated on the x-axis.

## CSTR

$$\frac{d(C \cdot V)}{dt} = Q \cdot C_{in} - Q \cdot C + r \cdot V$$

Since  $V = \text{constant}$

$$\frac{dC}{dt\theta} = \frac{1}{V} \cdot (C_{in} - C) + r$$

where  $\theta = V/Q$



If there is no reaction occurred in the reactor (just mixing)

$$\frac{dC}{dt\theta} = \frac{1}{\theta} \cdot (C_{in} - C)$$

$$\int_0^C \frac{dC}{C_{in} - C} = \frac{1}{\theta} \cdot \int_0^t dt$$

$$C = C_{in} \cdot (1 - e^{-t/\theta})$$

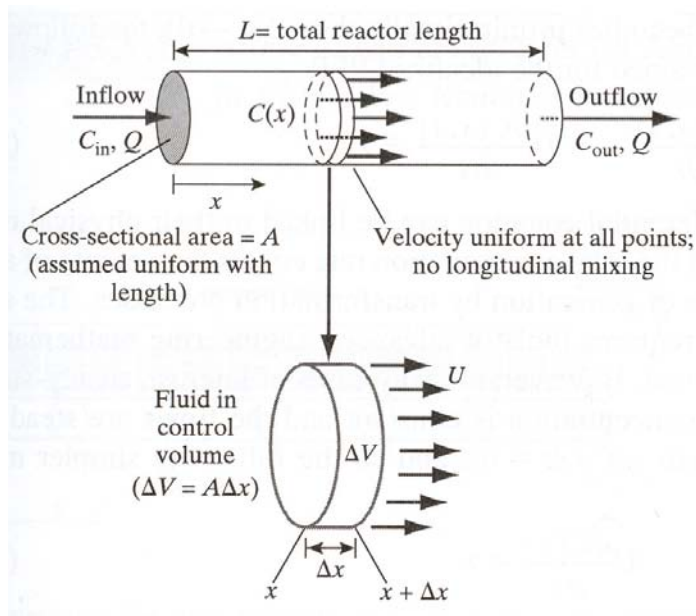
Under steady state conditions ( $dC/dt = 0$ ), a time dependent solution,  $C(t)$  is not required. For example, a zero order reaction

$$\frac{dC}{dt\theta} = 0 = \frac{1}{\theta} \cdot (C_{in} - C) + r$$

$$\frac{1}{\theta} \cdot (C_{in} - C) = k_0$$

$$C = C_{in} - k_0 \cdot \theta$$

## PFR



**Figure 5.A.12** Schematic of an idealized plug-flow reactor and the control volume used for writing a material balance.

$$\frac{\partial(C \cdot \Delta V)}{\partial t} = U \cdot A \cdot C(x, t) - U \cdot A \cdot C(x + \Delta x, t) + r \cdot \Delta V$$

Since  $\Delta V = A \cdot \Delta x$



$$\frac{\partial C(x,t)}{\partial t} = \frac{U \cdot C(x,t) - U \cdot C(x + \Delta x, t)}{\Delta x} + r$$

$$\frac{\partial C(x,t)}{\partial t} = -U \cdot \frac{\partial C(x,t)}{\partial x} + r$$

Under a steady state condition, the concentration is solely a function of position, x.

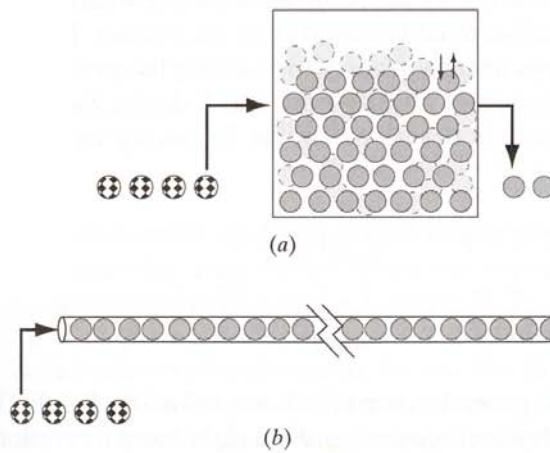
$$\frac{\partial C(x,t)}{\partial t} = 0 \quad \text{and} \quad U \cdot \frac{dC(x)}{dx} = r$$





## Comparison between CSTR and PFR



**EXAMPLE 5.A.1** *Contrasting CMFR and PFR Model Behavior (continued)*


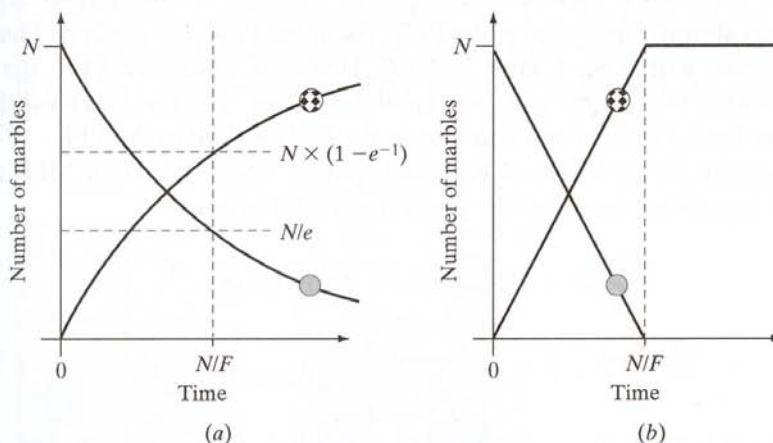
**Figure 5.A.2** System illustrating the fluid flow characteristics of two reactor models: (a) a CMFR and (b) a PFR.

How will the total number of gray and spotted marbles in the two reactors change over time?

**SOLUTION** Although the total number of marbles in each reactor is constant,  $N$ , the numbers of gray and spotted marbles are time dependent and satisfy this “conservation of marbles” equation:

$$N_{\text{gray}}(t) + N_{\text{spotted}}(t) = N$$

The numbers of gray and spotted marbles in each reactor versus time are shown in Figure 5.A.3. First consider the PFR. Each time a spotted marble is added, a gray marble is removed until, finally, the container holds only spotted marbles. Each new marble added to the system spends a fixed amount of time within the PFR, equal to  $N/F$ , before being removed at the outlet. This time is analogous to the mean residence time



**Figure 5.A.3** Expected behavior of (a) the box (CMFR) and (b) the tube (PFR) in response to a change in the design of marbles supplied at the inlet. The vessels each contain  $N$  marbles. Initially, all are gray. Beginning at  $t = 0$ , marbles with a different pattern (spotted) are added to the inlet at rate  $F$ ; marbles are removed from the vessel outlet at this same rate.



**EXAMPLE 5.A.10** Comparing CMFR and PFR Performance

Reactor performance is often characterized by calculating the ratio of the outlet concentration to the inlet concentration under steady-state conditions. Given fixed mean residence times,  $\Theta$ , compare reactor performance for a CMFR and a PFR for contaminants that undergo zeroth-order, first-order, and second-order decay reactions.

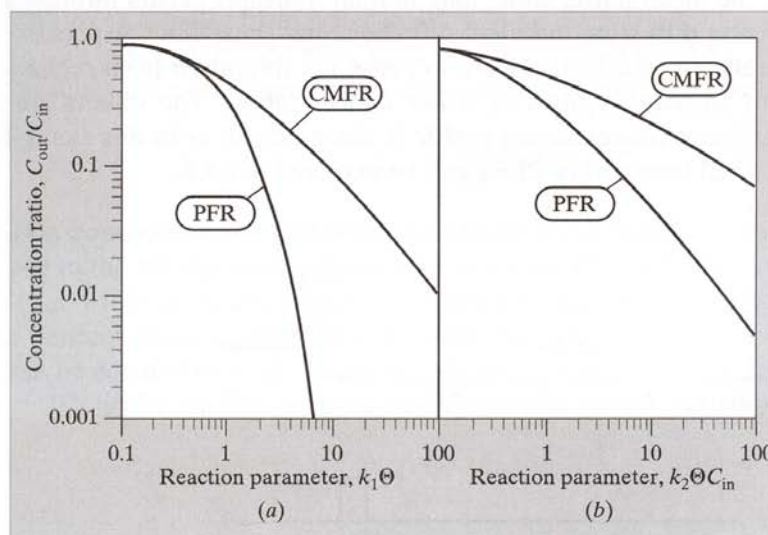
**SOLUTION** Each of the required results has been calculated in Examples 5.A.5 and 5.A.9. The results are summarized in Table 5.A.1 and Figure 5.A.16.

For the case of a zeroth-order reaction, the reactor configuration does not affect performance: The CMFR and the PFR yield the same results. For all positive reaction orders, though, greater conversion is obtained in a PFR than in a CMFR. The difference in performance is negligible if the overall conversion is small ( $C_{\text{out}}/C_{\text{in}} \sim 1$ ), but the difference becomes progressively greater as conversion increases ( $C_{\text{out}}/C_{\text{in}} \rightarrow 0$ ).

**Table 5.A.1** Comparison of the Steady-State Performance of CMFRs and PFRs

Reaction order	$r$	$C_{\text{out}}/C_{\text{in}}$	
		CMFR	PFR
Zeroth <sup>a</sup>	$-k_0$	$1 - \frac{k_0\Theta}{C_{\text{in}}}$	$1 - \frac{k_0\Theta}{C_{\text{in}}}$
First	$-k_1C$	$\frac{1}{1 + k_1\Theta}$	$\exp(-k_1\Theta)$
Second	$-2k_2C^2$	$\frac{(8k_2\Theta C_{\text{in}} + 1)^{1/2} - 1}{4k_2\Theta C_{\text{in}}}$	$\frac{1}{1 + 2k_2\Theta C_{\text{in}}}$

<sup>a</sup>Expressions are valid provided that  $k_0\Theta \leq C_{\text{in}}$ ; otherwise,  $C_{\text{out}} = 0$ .



**Figure 5.A.16** Steady-state reactor performance, comparing the outlet to inlet concentration ratio for a CMFR and a PFR for a species decaying by a homogeneous reaction of (a) first order or (b) second order.

