REACTOR TECHNOLOGY

1. Introduction

Chemical reactor technology is concerned with the selection, design, and operation of chemical reactors. The principles and methods which are applied to describe reactor operations are commonly known as chemical reaction engineering (CRE).

A chemical reactor is an equipment unit in a chemical process (plant) where chemical transformations (reactions) take place to generate a desirable product at a specified production rate, using a given chemistry. The reactor type (configuration) and its operating conditions are selected to achieve objectives such as maximizing the profit of the process, and minimizing the generation of pollutants, while satisfying several design and operating constraints, such as safety, controllability, availability of raw materials, etc. Usually, the chemical reactor plays a pivotal role in the operation and economics of the entire process since its performance affects most other units in the process such as separation units, utilities, etc.

There are three main requirements that a chemical reactor has to fulfill:

1. Provide appropriate contacting of the reactants.
2. Provide the heat transfer capability required to maintain the specified temperature range.
3. Provide the necessary reaction time for the formation of the desirable product.

In many instances these three requirements are not complimentary, and achieving one of them comes at the expense of another. Chemical reactor technology is concerned with achieving these requirements for a wide range of operating conditions: different reacting phases (liquid, gas, solid); different reaction mechanisms (catalytic, noncatalytic); and different operating temperature and pressure (low temperature for biological reaction, high temperature for many reactions in hydrocarbon processing).

Because of the multitude and diversity of the factors that affect reactor operations, no uniform methodology exits for analyzing and designing chemical reactors. This article provides an overview of the phenomena encountered, the concept and principles used to describe them, and the methods used to analyze and design chemical reactors. The limitations of the current technology are also discussed.

Chemical reactions span over a wide range of applications. For convenience they are classified as homogeneous reactions that occur in a single phase (either liquid or gas) and heterogeneous reactions between reactants in two phases.

Heterogeneous reactions are categorized further as:

1. *Fluid-fluid reactions* are chemical reactions between reactants that are in two immiscible phases (gas-liquid or liquid–liquid). The reaction occurs either at the interface or when one reactant dissolves in the other phase

which also contain the products. In many instances, the overall reaction rate depends on the interface area available, the miscibility of the reactant, and the transfer rates (eg, diffusion) of the reactants to the interface and in the reacting phase.

2. *Noncatalytic gas-solid reactions* eg, combustion of a coal. The reaction occurs on the surface of the solid. The overall reaction rate depends on the surface area available and the rate of transfer of the gaseous reactant to the solid surface.
3. *Catalytic gas-solid reactions* in which the reactants and products are gaseous, but the reaction takes place at the solid surface where a catalytic reagent is present. To facilitate the reaction, a large surface area is required; hence, porous particles are used, and the reaction takes place on the surface of the pores in the interior of the particle. In many instances, the reaction rate is determined by the diffusion rate of reactants into the interior of the pore.
4. *Catalytic gas–liquid–solid reactions* in which reactants are gases and liquids, and the reaction takes place at a solid surface where a catalytic reagent is deposited. Normally, the liquid reactant covers the solid surface and the gaseous reactant is transferred, by diffusion to the catalytic site.

Each of these reaction categories has its features and characteristics which should be described quantitatively.

2. Classification of Reactors

Chemical reactors are commonly classified by the following charateristics: mode of operation (eg, batch, continuous, semibatch); geometric configuration (eg, tubular, agitated tank, radial flow); contacting patterns between phases (eg, packed-bed, fluidized bed, bubble column).

Although not uniformly used in the literature, the following terms are used in this article:

2.1. Batch Reactors. Reactants are charged into a vessel at the beginning of the operation, products are discharged at the end of the operation, and reactions take place over time. The vessel is usually agitated to provide good contacting between the reactants and to create uniform conditions (concentrations and temperature) throughout the vessel (Fig. 1**a**).

2.2. Semibatch Reactor. A tank in which one reactant is charged initially, and another reactant is added continuously during the operation. This mode of operation is used when it is desirable to maintain the injected reactant at low concentration to improve the selectivity to the desirable product, and to supply (or remove) heat (Fig. 1**b**).

2.3. Distillation Reactor. A batch reactor where volatile products are removed continuously from the reactor during the operation (Fig. 1**c**).

2.4. Continuous Reactors (Flow Reactors). A vessel to which reactants are fed continuously and products are withdrawn continuously. The chemical reactions take place over space (the reactor volume), and the residence time of the reacting fluid in the reactor provides the required reaction time.

Common configurations of continuous reactors: tubular reactor (Fig. 2**a**); and continuous stirred tank reactor (Fig. 2**b**); and a cascade of continuous stirred tanks (Fig. 2**c**).

2.5. Multi-Phase Reactors. For multi-phase reactions, the contacting patterns are used as a basis for classifying reactors.

Common configurations include:

1. Packed-bed reactor (Fig. 3**a**) is a vessel filled with catalytic pellets and the reacting fluid passing through the void space between them. Relatively large pellets (eg, larger than 1 cm) are used to avoid excessive pressure drop and higher operating cost. In general, heat-transfer to/from large scale packed-bed reactors is a challenge.
2. Fluidized-bed reactor (Fig. 3**b**) is a vessel filled with fine particles (eg, smaller than 200 micron) that are suspended by the upward flowing fluid. The fluidized bed provides good mixing of the particles, and consequently, a uniform temperature. However, a portion of the fluid passes through the reactor with little contact with the solids.
3. Trickle-bed reactor is a packed-bed reactor where a liquid reactant is fed from the top wetting catalytic pellets and a gas reactant, fed either from the top or the bottom, flows through the void spaces between the pellets. The gaseous reactant must be absorbed and transported across the liquid film to the catalytic sites.
4. Moving bed reactor (Fig. 3**c**).
5. Bubbling column reactor (Fig. 3**d**) and spray reactor (Fig. 3**e**).
6. Others, slurry reactor, kiln reactor (Fig. 3**f**), moving grate reactor (Fig. 3**g**), membrane reactor, etc.

Due to the diverse applications and numerous configurations of chemical reactors, no generic design procedure exists for chemical reactors. Rather, in each case it is necessary to identify the characteristics of the chemical reaction and define the main features that the reactor should provide prior to selecting and designing the reactor.

3. Phenomena and Concepts

The operation of a chemical reactor is affected by a multitude of diverse factors such as the characteristics of the chemical reactions, temperature, pressure, flow conditions, etc. In order to select, design and operate a chemical reactor, it is necessary to identify the phenomena involved, to understand how they affect the reactor operation, and to express these effects mathematically. This section provides a brief review of the phenomena encountered in chemical reactor operations as well as the fundamental and engineering concepts that are used to describe them. Figure 4 shows schematically how various fundamental and engineering concepts are combined in formulating the reactor design equations.

3.1. Stoichiometry. Stoichiometry is an accounting system used to keep track of what species are formed or consumed and to calculate the composition of chemical reactors. Stoichiometry also indicates how many chemical reactions should be considered to determine the species composition and all other state quantities of the reactor, such as, temperature, enthalpy, etc.

In chemical reactor engineering, the term "chemical reaction" is used in four different contexts: (*1*) as a chemical formula; (*2*) as stoichiometric relation between species; (*3*) as a presentation of the pathway of the chemical transformation; and (*4*) as an elementary reaction. It is important to distinguish between these contexts.

The *chemical formula* is essentially the selection of a basis for the calculation of the chemical transformation. A chemical formula represents a given amount of mass. All quantities associated with the chemical transformation (heat of reaction, rate of reaction, etc) are tied to the selected chemical formula. Once the chemical formula is selected, its stoichiometric coefficient can be defined. It is convenient to describe the chemical formula as a homogeneous linear equation by designating the coefficients of the reactants with a minus, and those of the products with a plus. For example, for the chemical formula

$$\mathrm{aA} + \mathrm{bB} \rightarrow \mathrm{cC} + \mathrm{dD},$$

the species' stoichiometric coefficients are: $s_{\mathrm{A}} = (-\mathrm{a})$, $s_{\mathrm{B}} = (-\mathrm{b})$, $s_{\mathrm{C}} = \mathrm{c}$, $s_{\mathrm{D}} = \mathrm{d}$, and, for any other species that does not participate in the reaction the stoichiometric coefficient is zero. One unit of a chemical formula is called an extent, and it is used to express the progress of the reaction.

A *stoichiometric relation* is merely a representation of the proportion between chemical species. To illustrate, consider the chlorination of methane which occurs in four steps:

$$\begin{aligned}
&\text{Reaction 1:}\quad \mathrm{CH_4} + \mathrm{Cl_2} \rightarrow \mathrm{CH_3Cl} + \mathrm{HCl}\\
&\text{Reaction 2:}\quad \mathrm{CH_3Cl} + \mathrm{Cl_2} \rightarrow \mathrm{CH_2Cl_2} + \mathrm{HCl}\\
&\text{Reaction 3:}\quad \mathrm{CH_2Cl_2} + \mathrm{Cl_2} \rightarrow \mathrm{CHCl_3} + \mathrm{HCl}\\
&\text{Reaction 4:}\quad \mathrm{CHCl_3} + \mathrm{Cl_2} \rightarrow \mathrm{CCl_4} + \mathrm{HCl}.
\end{aligned}$$

To relate the trichloromethane to the methane and chlorine, the first three reactions are added to provide the stoichiometric relation

$$\mathrm{CH_4} + 3\,\mathrm{Cl_2} \rightarrow \mathrm{CHCl_3} + 3\,\mathrm{HCl}.$$

Stoichiometric relations are used to determine the yield of the desirable product.

Reaction pathways represent the routes by which the chemical species are formed and consumed. For example, in the methane chlorination above, the four reactions indicate the pathways by which the species are generated, although, in practice, each reaction may involve the formation and destruction of unstable intermediate species (eg, free radicals). The rates of the chemical reactions representing the pathways should be known in order to determine the rate of formation or depletion of the chemical species in the reactor.

An *elementary reaction* is a representation of the interactions between the species. Elementary reactions are used to describe the mechanisms by which species are formed (or depleted) (3,4).

Chemical reactions are also designated as *independent* and *dependent* reactions. A set of independent reactions is a set of chemical reactions that accounts for all the species in the system, and whose stoichiometric coefficients are independent. A dependent reaction is a chemical reaction whose stoichiometric coefficients are obtained by a linear combination of the independent reactions. To understand the role of independent reactions, consider a reversible chemical reaction. From the reaction pathway perspective, there are two chemical reactions, one forward and one backward, yet there is only one independent stoichiometric relation among the species. The stoichiometric coefficients of the backward reactions are the "−1" multiples of the forward reaction. Consider another example, the oxidation of carbon, where the following simultaneous chemical reactions take place:

$$\text{Reaction 1:}\quad C + \tfrac{1}{2}\,O_2 \rightarrow CO$$

$$\text{Reaction 2:}\quad CO + \tfrac{1}{2}\,O_2 \rightarrow CO_2$$

$$\text{Reaction 3:}\quad C + O_2 \rightarrow CO_2.$$

A close examination of these reactions reveals that Reaction 3 is the sum of Reaction 1 and Reaction 2. Hence, there are two independent chemical reactions and one dependent reaction. The relationship between a dependent reaction and the independent reactions (29) is

$$(s_j)_k = \sum_{m}^{n_{ind}} \alpha_{km} \cdot (s_j)_m \qquad j = A, B, \ldots \tag{1}$$

where α_{km} is the multiplier of the m-th independent reaction to obtain the k-th dependent reaction. For the example above, if Reactions 1 and 2 are selected as the independent reaction ($m = 1, 2$) and Reaction 3 as the dependent reaction ($k = 3$), the multipliers are: $\alpha_{31} = 1$ and $\alpha_{32} = 1$.

To determine the species composition (and any other state quantity of the reactor) only a set of the *independent* reactions should be considered. However, to express the species' formation rates, *all* the chemical reactions representing the reaction pathways (both independent and dependent) should be considered.

The extent of a chemical reaction is calculated by

$$X_i = \frac{\text{moles of species } j \text{ formed by the reaction}}{\text{stoichiometric coefficient of species } j \text{ in the reaction}} = \frac{(n_j - n_{j_0})}{s_j} \tag{2}$$

The extent is called sometimes the *reaction coordinate*. When the extents of the independent reactions are known, all the species compositions can be readily determined. For batch reactors, the content of species j at time t is related to the extents of the independent reactions by

$$N_j(t) = N_j(0) + \sum_{m}^{n_{ind}} (s_j)_m \cdot X_m(t) \tag{3}$$

where $X_m(t)$ is the extent of the m-th *independent* reaction in operating time t and $(s_j)_m$ is the stoichiometric coefficient of species j in the m-th independent reaction. For continuous reactors (flow reactors) operating at steady state, the molar flow rate of species j at the reactor outlet is

$$F_{j_{out}} = F_{j_{in}} + \sum_{m}^{n_{ind}} (s_j)_m \cdot \dot{X}_m \tag{4}$$

where $\dot{X}_m$ is the extent per time of the m-th independent reaction converted in the reactor.

Three stoichiometric parameters are commonly used to characterize the performance of a chemical reactor: (*1*) reactant conversion, (*2*) product yield, and (*3*) product selectivity. The conversion is defined as the fraction of the reactant that has been consumed. For batch reactors, the conversion of Reactant A at operating time t is defined by

$$f_A(t) \equiv \frac{\text{moles of Reactant A consumed in time, } t}{\text{moles of Reactant A charged to the reactor}} = \frac{N_A(0) - N_A(t)}{N_A(0)} \tag{5}$$

For flow reactors operating at steady state, the conversion of Reactant A in the reactor is defined by

$$f_{A_{out}} \equiv \frac{\text{rate Reactant A is consumed in the reactor}}{\text{rate Reactant A is fed to the reactor}} = \frac{F_{A_{in}} - F_{A_{out}}}{F_{A_{in}}} \tag{6}$$

The conversion is related to the composition (or flow rate) of a reactant and not to a specific chemical reaction. In general, a reactant may be consumed in several chemical reactions. However, if species A is produced by any independent chemical reaction, the conversion of A is not defined.

The yield of the desirable product (Product V) is defined as the amount V produced relative to the amount that could have been formed if only the desirable reaction took place and has proceeded to completion. For steady batch reactors, the yield of Product V at operating time t is defined by

$$\eta_V(t) \equiv \left(\frac{s_A}{s_V}\right)_{des} \frac{N_V(t) - N_V(0)}{N_A(0)} \tag{7}$$

where s_A and s_V are the stoichiometric coefficients of the limiting Reactant A and Product V, respectively, in the desirable reaction – the stoichiometric relation tying the reactant and the products. For steady flow reactors, the yield of Product

V is defined by

$$\eta_{V_{out}} \equiv \left(\frac{s_A}{s_V}\right)_{des} \frac{F_{V_{out}} - F_{V_{in}}}{F_{A_{in}}} \tag{8}$$

The selectivity of desirable product V is defined as the amount of Product V produced relative to the amount of V that could have been formed from the *consumed* Reactant A if only the desirable reaction took place. It is obtained by dividing the yield by the reactant conversion.

$$\sigma_V \equiv \frac{\text{yield of Product V}}{\text{conversion of Reactant A}} = \frac{\eta_V}{f_A} \tag{9}$$

Both the yield and the selectivity are defined such that their numerical values are between zero and 1.

3.2. Chemical Kinetics. Chemical kinetics is the branch of chemistry that concerns with the rates of chemical reactions (3–5). Many chemical reactions involve the formation of unstable intermediates (eg, free radicals). Chemical kinetics is the study of the mechanisms involved in pursue of obtaining a rate expression for the chemical reaction (the reaction pathway). In most instances, the reaction rate expression is not available, and should be determined experimentally (see later Section 5.1).

The formation rates of chemical species are defined in several ways, depending on the type of chemical reaction that takes place. For homogeneous reactions, a volume-based formation rate, (r_j), is defined,

$$(r_j) \equiv \frac{\text{moles of species } j \text{ formed}}{(\text{volume}) \cdot (\text{time})} = \frac{1}{V}\frac{dN_j}{dt} \tag{10}$$

For heterogeneous chemical reactions, the surface-based formation rate of species j, $(r_j)_S$, is defined

$$(r_j)_S \equiv \frac{\text{moles of species } j \text{ formed}}{(\text{surface}) \cdot (\text{time})} = \frac{1}{S}\frac{dN_j}{dt} \tag{11}$$

In some cases, it is convenient to define the mass-based formation rate of species j (on the basis of the mass of solid catalyst),

$$(r_j)_W \equiv \frac{\text{moles of species } j \text{ formed}}{(\text{mass}) \cdot (\text{time})} = \frac{1}{W}\frac{dN_j}{dt} \tag{12}$$

These definitions are related to each other by

$$(r_j) = \left(\frac{S}{V}\right) \cdot (r_j)_s = \left(\frac{W}{V}\right) \cdot (r_j)_W \tag{13}$$

Hence, when any one of these rates is known, the other two can be determined if the properties of the reactor (mass of solid catalyst per unit volume or catalyst surface per unit volume) are provided.

The rate of a chemical reaction is defined in a similar way, depending on the type of reaction. For a homogeneous chemical reaction, the volume-based rate of a reaction is defined by

$$r \equiv \frac{\text{extent of reaction}}{(\text{volume}) \cdot (\text{time})} = \frac{1}{V}\frac{dX}{dt} \tag{14}$$

When multiple chemical reactions take place simultaneously, a chemical species may participate in several reactions, formed by some and consumed by others. The formation rate of species j relates to the rates of the individual chemical reactions by

$$(r_j) = \sum_{i}^{n_{all}} (s_j)_i \cdot r_i \tag{15}$$

where $(s_j)_i$ is the stoichiometric coefficient of species j in the i-th chemical reaction, and r_i is the rate of the i-th reaction. The summation in eq. 15 is over *all* the chemical reactions that take place in the reactor for both dependent and independent reactions.

The rate of a chemical reaction depends on the temperature, the concentrations of the reactants, and, if present, the catalyst. The relationship between the reaction rate and these parameters is commonly called the "rate expression" or, sometimes, the "rate law." For most chemical reactions, the rate expression is a product of two functions, one of temperature, $k(T)$, and the second of species concentrations, $h(C_j{'}s)$,

$$r = k(T) \cdot h(C_j{'}s) \tag{16}$$

The function $k(T)$, commonly called the "reaction rate constant," (since it is constant at a given temperature). For most chemical reactions, the reaction rate constant relates to the temperature according to the Arrhenius equation,

$$k(T) = k_0 \cdot e^{-\frac{E_a}{R \cdot T}} \tag{17}$$

where E_a is a parameter called the activation energy, k_0 is a parameter called the frequency factor or the pre-exponential coefficient, and R is the universal gas constant. Both parameters are characteristic of the chemical reaction and the presence of a catalyst. The dimensions and units of k_0 depend on the form of function $h(C_j{'}s)$.

The concentration function, $h(C_j{'}s)$, appears in many forms, depending on the reaction type and mechanism. For many *homogeneous* chemical reactions, $h(C_j{'}s)$ is expressed as a power relation of the reactant concentrations,

$$h(C_j{'}s) = C_A^{\alpha} \cdot C_B^{\beta} \cdots \tag{18}$$

where C_A, C_B, ... are the concentrations of the different reactants. The powers in eq. 16 are called the orders of the reaction: α is the order of Reactant A, β is the order of the Reactant B, etc, and the sum of the orders is called the overall order of the reaction. The orders can be either integers or fractions and should be determined experimentally. Other forms of function $h(C_j's)$ are used for certain types of homogenous chemical reactions. For example, the rate expression of many biological and enzymatic reactions (Michaelis-Menten mechanism) has the form (5)

$$r = k(T) \cdot \frac{C_A}{K_m + C_A} \tag{19}$$

where $k(T)$ is the reaction rate constant, and K_m is a parameter that depends on the enzyme concentration and should be determined experimentally.

Heterogeneous gas-solid catalytic reactions occur between gaseous reactants at a catalytic site on the solid surface. These reactions involve three consecutive steps: (*1*) adsorption of reactant(s) on the surface, (*2*) surface reaction at the catalytic site, and (*3*) desorption of the reactants from the surface. The rate of the reaction depends on the rates of the individual steps and the interactions between the catalytic site and the species. A procedure, known as the Langmuir-Hishelwood-Hougen-Watson (LHHW) formulation, is used to determine and verify the reaction rate expressions of heterogeneous catalytic reactions (5–8). In many instances, one step is much slower than the other two, and is referred to as "the rate limiting step." The form of the rate expression depends on the relative rates of the three steps and on the interactions between the reactants and the catalytic sites. For many gas-solid catalytic reactions of the form

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{S} + \mathrm{R},$$

the rate expression has the form,

$$r = k(T) \cdot \frac{C_A \cdot C_B - \frac{1}{K} C_S \cdot C_R}{(1 + K_A \cdot C_A + K_B \cdot C_B + K_S \cdot C_S + K_R \cdot C_R)^n} \tag{20}$$

where the parameters K_A, K_B, K_S, K_R, K, and n have to be determined experimentally. Often, the species concentrations are expressed in terms of their partial pressure.

In gas–liquid reactions, the gaseous reactant is absorbed (dissolves) in the liquid-phase where it reacts with the liquid reactant. Hence, the solubility affects the rate of the chemical reaction (9,10).

3.3. Transport Effects. The rate expressions derived above describe the dependence of the rate expressions on kinetic parameters related to the chemical reactions. These rate expressions are commonly referred to as the "intrinsic" rate expressions of the chemical reactions. In many instances, the local species concentrations depend also on the rate that the species are transported in the reacting medium. Consequently, the actual reaction rates (also known as the "global reaction rates") are affected by the transport rates of the reactants and products.

Effects of species transport rates on reaction rates are prevalent in three general cases: (*1*) fluid-solid catalytic reactions, (*2*) noncatalytic fluid–solid reactions, and (*3*) fluid–fluid (liquid–liquid, gas–liquid) reactions, where the species transport to the interface, solubility, and diffusion play an important role. Incorporating the effects of transport rates to obtain the global rates of the chemical reactions is a difficult task since it requires knowledge of the local flow patterns (hydrodynamics) and numerous physical and chemical properties (eg, porosity, pore size and size distribution, equilibrium).

The transport flux of a species to an interface is often described by a product of a mass-transfer coefficient, k_M, and a concentration difference between the bulk and the interface. The mass-transfer coefficient is correlated to the local flow conditions (6,10–13). For example, for mass transfer from the bulk of the fluid to the surface of a particle in a packed bed, the correlation has the form

$$Sh = \frac{k_M \cdot d_p}{D} = C \cdot Re^{0.5} \cdot Sc^{0.33} \tag{21}$$

where Sh is the Sherwood number, Re is the Reynolds number based on the particle diameter and the superficial fluid velocity, ie, the velocity the fluid would have if there were no particle packing, Sc is the Schmidt number, D is the diffusivity of the fluid, and C is a dimensionless constant. Similar correlations are available for mass transfer between two immiscible fluids (6,11–14).

In *catalytic gas-solid reactions*, the reaction takes place at catalytic sites on the surface of the solid. To obtain appreciable reaction rates, porous solids are used and the reactions take place on the surface of the pores in the interior of the particle. Hence, catalytic gas–solid reactions involve seven steps (1,2,15–18): (*1*) transport of a reactant from the bulk of the fluid to the mouth of the pore; (*2*) diffusion of the reactant to the interior of the pore; (*3*) adsorption of the reactant to the surface of the solid; (*4*) surface reaction at the catalytic site; (*5*) desorption of the product from the surface; (*6*) diffusion of the products to the mouth of the pore; and (*7*) transport of the products to the bulk of the fluid. Steps (*3*), (*4*), and (*5*) represent the kinetics of heterogeneous catalytic reactions discussed above (LHHW formulation).

Often the global reaction rate of gas–solid catalytic reactions is affected by the pore diffusion, and the external mass transfer rate of the reactants and the products. When the diffusion rate in the pores is slow, a reactant concentration profile develops in the interior of the particle, resulting in a different reaction rate at different radial locations inside the catalytic particle. To relate the global reaction rate to various concentration profiles that may develop, a kinetic effectiveness factor is defined (1,2,7,8,19) by

$$\begin{pmatrix} \text{Kinetic} \\ \text{Effectiveness} \\ \text{Factor} \end{pmatrix} = \frac{(\text{actual reaction rate})}{(\text{reaction rate at the bulk condition})} \tag{22}$$

Hence, to express the actual reaction rate, the reaction rate at the bulk condition is multiplied by a correction factor which accounts for the diffusion effects. The effectiveness factor depends on the ratio between the reaction rate and the diffusion rate which is expressed in terms of a modulus (Thiele modulus), ϕ, defined by

$$\phi^2 = \frac{(\text{characteristic reaction rate})}{(\text{characteristic diffusion rate})} \tag{23}$$

The expression of the modulus depends on the intrinsic reaction rate of the catalytic reaction and the size of the catalytic pellets. For first-order reactions, the modulus is

$$\phi = L\sqrt{\frac{k}{D_{eff}}} \tag{24}$$

where k is the volume-based reaction rate constant, D_{eff} is the effective diffusion coefficient in the particle (depending on the reactants and products, the size and size distribution of the pore, and the porosity of the pellet), and L is a characteristic length of the pellet obtained by the volume of the pellet divided by its exterior surface area. The relationship between the effectiveness factor and the Thiele modulus for first-order reactions is shown in Figure 5. Note that for exothermic catalytic chemical reactions the effectiveness factor may be larger than one because the temperature of the catalytic pellet is higher than the bulk temperature (2,5,6). The derivation of the Thiele modulus for LHHW rate expressions is not an easy task, nor is the derivation of the relationship between the effectiveness factor and the Thiele modulus.

Noncatalytic solid-fluid reaction is a class of heterogeneous chemical reactions where one reactant is a solid and the other reactant is a fluid. Some examples of such reactions are: combustion of coal; coal gasification; reactions in the mineral-processing, such as roasting of pyrites; and production of steel in a blast furnace. The products of solid-fluid reactions may be either fluid products, solid products, or both.

The rates of solid–fluid reactions depend on the phenomena affecting the transport of the fluid reactant to the surface of the solid reactant. The reaction takes place in a narrow zone that moves progressively from the outer surface of the solid particle toward the center. For convenience, noncatalytic fluid–solid reactions are divided into four categories, according to the changes that the particle undergoes during the reaction (1,2,6,20):

1. Shrinking particle occurs when the particle consists entirely of the solid reactant, and the reaction products are either volatile or dissolve in the fluid. The reaction takes place on the surface of the particle, and as it proceeds, the particle shrinks, until it is consumed completely.
2. Shrinking core with an ash layer occurs when one of reaction products forms a porous layer (ash, oxide, etc). As the reaction proceeds, a layer of ash is formed in the section of the particle that has reacted, externally to a

shrinking core of the solid reactant. The fluid reactant diffuses through the ash layer, and the reaction occurs at the surface of a shrinking core until the core is consumed completely.

3. Shrinking core occurs when the solid reactant is spread in the particle among grains of inert solid material. As the reaction proceeds, the particle remains intact, but a core containing the solid reactant is formed inside by a layer of the inert grains. The fluid reactant diffuses through the layer, and the reaction occurs at the surface of a shrinking core until the core is consumed completely.
4. Progressive conversion occurs when the gaseous reactant penetrates through pores in the particles and reacts with the solid reactant (distributed throughout the particle) at all time. The concentration of the solid reactant progressively reduced until it is consumed completely. The size of the particle does not vary during the reaction.

In each of these cases, the global reaction rate depends on three factors: (*1*) the rate the fluid reactant is transported from the bulk to the outer surface of the particle, (*2*) the rate the fluid reactant diffuses through the porous solid (ash or particle) to the surface of the unreacted core, and (*3*) the reaction rate. The global reaction rate depends on the ratios of the rates of these phenomena, as well as the dimensions of the ash layer and the unreacted core. Various mathematical models are available in the literature, providing the time needed for complete conversion of the solid reactants (1,2,6,20).

Fluid–fluid reactions are reactions that occur between two reactants where each of them is in a different phase. The two phases can be either gas and liquid or two immiscible liquids. In either case, one reactant is transferred to the interface between the phases and absorbed in the other phase, where the chemical reaction takes place. The reaction and the transport of the reactant is usually described by the two film model, shown schematically in Figure 6. Consider Reactant A is in Phase I and Reactant B is in Phase II. The reaction occurs in Phase II. The overall rate of the reaction depends on the following factors: the rate Reactant A transfers to the interface; the solubility of Reactant A in the phase II; the diffusion rate of the Reactant A in Phase II; the reaction rate; and the diffusion rate of Reactant B in Phase II. Different situations may develop, depending on the relative magnitude of these four factors, and on the form of the rate expression of the chemical reaction (first order, etc). To discern the effect of reactant transport and the reaction rate, a reaction modulus is usually used. Commonly, the transport flux of Reactant A in Phase II is described in two ways: by a diffusion equation (Fick's law); and/or a mass transfer coefficient (transport through a film resistance) (1,2). The modulus is called Hatta number (sometimes it is also referred to as Damkohler number), and it is defined by

$$Ha^2 = \frac{(\text{maximum reaction rate in the film})}{(\text{maximum transport rate through the film})} \tag{25}$$

For second-order reactions (first order with respect to each reactant), the Hatta number is

$$Ha = L\sqrt{\frac{k \cdot C_B}{D}} = \frac{\sqrt{k \cdot C_B \cdot D}}{k_{A_{II}}} \tag{26}$$

where k is the reaction rate constant, and D is the diffusion coefficient of Reactant A in Phase II, L is a characteristic length (usually the film thickness), and $k_{A_{II}}$ is the mass transfer coefficient of Reactant A across the film. The kind of the fluid-fluid reaction is characterized by the value of the Hatta number. When $Ha > 2$, the reaction is fast and takes place only in the film near the interface. When $0.2 < Ha < 2$, the reaction is slow enough such that Reactant A diffuses to the bulk of Phase II. When $Ha < 0.02$, the reaction is slow and takes place throughout Phase II.

3.4. Global Rate Expression. The global rate expression is a mathematical function that expresses the rate of a chemical reaction per unit volume of the reactor, accounting for all the phenomena and mechanisms. For heterogeneous chemical reactions, the global reaction rate depends on three factors: (*1*) the interfacial surface per unit volume; (*2*) chemical kinetics (the intrinsic reaction rate); and (*3*) the rates that chemical species are transported (transport limitations). Hence, even when a kinetic-transport model is carefully constructed, using the approaches described in the previous section, it is necessary to determine the interfacial surface per unit volume which depends on the forms of the two phases, droplet or particle size, and their holdup in the reactor which in turn depends on the hydrodynamics in the reactor. Usually, the hydrodynamics is not known *a priori*; therefore, estimating reliable global rate expressions in one of the most challenging tasks in designing chemical reactors.

3.5. Species Balance Equation. The genesis of the reactor design equations is the conservation of mass. Since reactor operations involve changes in species compositions, the mass balance is written for individual species and it is expressed in terms of moles rather than mass. In general, the species balances are carried out in one of two ways—as microscopic balances or macroscopic balances.

Microscopic species balances, often referred to as the "species continuity equations," are carried out over a differential element and describe what takes place at a given "point" in a reactor. When integrated over the entire volume of the reactor, they provide the species-based design equations.

Macroscopic species balances are carried out over the entire reactor and provide the design equations. The material balance equation of species j over a chemical reactor is

$$\begin{pmatrix}\text{Rate}\\ \text{species } j\\ \text{flows out of}\\ \text{the reactor}\end{pmatrix} = \begin{pmatrix}\text{Rate}\\ \text{species } j\\ \text{flows into}\\ \text{the reactor}\end{pmatrix} + \begin{pmatrix}\text{Rate}\\ \text{species } j\\ \text{formed in}\\ \text{the reactor}\end{pmatrix} - \begin{pmatrix}\text{Rate}\\ \text{species } j\\ \text{accumulates}\\ \text{in the reactor}\end{pmatrix} \tag{27}$$

In mathematical symbols, the species balance equation is expressed by

$$F_{j_{out}} = F_{j_{in}} + \int_{V_R} (r_j) \cdot dV - \frac{dN_j}{dt} \tag{28}$$

where (r_j) is the local volume-based formation rate of species j (defined in eq. 10), and the integral represents the summation of the local generation rate of species j over all elements dV in the reactor. Relating the formation rate of species j to the rates of chemical reactions (eq. 15), the species balance equation is

$$F_{j_{out}} = F_{j_{in}} + \int_{V_R} \sum_{i}^{n_{all}} (s_j)_i \cdot r_i \cdot dV - \frac{dN_j}{dt} \tag{29}$$

where r_i is the local *global* rate of the i-th reaction. Equation 29 is the general species-based design equation written for species j, relating the production of species j (F_{jout}) to the reactor volume (V_R) and the rates of the chemical reactions ($r_i's$).

In batch reactor operations no species are fed or withdrawn from the reactor, and the species balance equation reduces to

$$\frac{dN_j}{dt} = \int_{V_R} \sum_{i}^{n_{all}} (s_j)_i \cdot r_i \cdot dV \tag{30}$$

For steady flow reactors, there is no species accumulation and the species balance equation reduces to

$$F_{j_{out}} = F_{j_{in}} + \int_{V_R} \sum_{i}^{n_{all}} (s_j)_i \cdot r_i \cdot dV \tag{31}$$

Eqs. 30 and 31 are the general species-based design equations (written for species j) for batch and continuous reactors, respectively. Both of these species balance equations are expressed in general terms and solving them is discussed in Section 4.

3.6. Energy Balance Equation.

The variation of the reactor temperature is obtained from the energy balance equation (first law of thermodynamics). Most chemical reactor operations take place at constant (or near constant) pressure and the energy of the reacting fluid is expressed in terms of enthalpy. Also, in most reactor operations, the kinetic and potential energy terms are negligible.

For batch reactors, the energy balance equation reduces to

$$\frac{dT}{dt} = \frac{1}{\sum N_j \cdot \bar{c}_{p_j}} \left[\dot{Q} - \sum_{m}^{n_{ind}} \Delta H_{R_m}(T_0) \cdot \frac{dX_m}{dt} \right] \tag{32}$$

where $\dot{Q}$ is the rate heat is transferred to the reactor and it is expressed by

$$\dot{Q} = U \cdot (T_F - T) \cdot \left(\frac{S}{V}\right) \cdot V_R \tag{33}$$

where T_F is the temperature of the heating (or cooling) fluid, U is the overall heat transfer coefficient and ΔH_{R_m} is the heat of reaction of the m-th independent reaction.

For continuous reactors the general energy balance reduces to

$$\frac{dT}{dV_R} = \frac{1}{\sum F_j \cdot \bar{c}_{p_j}} \left[\frac{d\dot{Q}}{dV_R} - \sum_{m}^{n_{ind}} \Delta H_{R_m}(T_0) \cdot \frac{d\dot{X}_m}{dt}\right] \tag{34}$$

The heat capacity of the reacting fluid ($\sum N_j \cdot \bar{c}_{p_j}$ in batch reactor and $\sum F_j \cdot \bar{c}_{p_j}$ for flow reactors) depends on both composition and the temperature. In practice, the energy balance equation is expressed at three levels of complexity: (*1*) The heat capacity of the reacting fluid is independent on both the temperature and the composition. This situation occurs in most liquid-phase reactions, and in gas-phase reactions where the heat capacities of the products are close to those of the reactants and they do not vary with the temperature. (*2*) The heat capacity of the reacting fluid depends on the composition but is independent of the temperature. This situation occurs in gas-phase reactions when the heat capacities of the individual species are independent of the temperature. (*3*) The heat capacity of the reacting fluid depends on both the composition and the temperature. This situation occurs in gas-phase reactions that take place over a large temperature range.

3.7. Momentum Balance Equation. When the pressure of the reacting fluid varies substantially and affects the reaction rates, the momentum balance equation is written to express the pressure variation. This occurs in rare applications, eg, gas-phase reactions in a long tubular reactor, with high velocity (28).

4. Reactor Design Equations

Reactor design equations provide relationships between quantities related to the reactor operation, eg, species compositions, species flow rates, reactant conversion, etc and a relevant independent operating variable. For batch and semi-batch operations the independent variable is the operating time; for flow reactors the independent variable is the reactor volume.

To describe the reactor operation, it is necessary to know *global* rates of all the chemical reactions, $r_i's$, at every point in the reactor. Since the reaction rates depend on the species concentrations and the temperature, their local values throughout the reactor should be provided. Hence, solving the design equation is a formidable task that requires solving simultaneously the three local transport equations: the momentum balance equation; the individual species continuity equations; and the energy balance equation. To circumvent these difficulties, simplified "idealized" mathematical models are used. The design of a reactor for "idealized" operating conditions provides an approximate description of the reactor operations.

4.1. Idealized Reactor Models. The following simplified reactor models are commonly used:

Ideal batch reactor: A well-mixed batch reactor with same operating conditions (concentrations and temperature) throughout the reactor. Under these conditions, the species-based design equation reduces to:

$$\frac{dN_j}{dt} = \sum_{i}^{n_{all}} (s_j)_i \cdot r_i \cdot V_R \tag{35}$$

The ideal batch reactor model is applicable when there is a good agitation in the tank. Good mixing is readily achieved in lab-scale and small industrial vessels, but it requires careful attention in very large vessels (21–27).

Continuous stirred tank reactor (CSTR): A well-mixed continuous reactor, operated at steady state, having the same conditions (concentrations and temperature) throughout the reactor. The species-based design equation is:

$$F_{j_{out}} - F_{j_{in}} = \sum_{i}^{n_{all}} (s_j)_i \cdot r_{i_{out}} \cdot V_R \tag{36}$$

The CSTR model is applicable in well-agitated vessels. Note that, in the design equation, the reactions rates are at the conditions of the outlet (which is the same condition anywhere in the reactor).

Plug flow reactor (PFR): A continuous reactor, operated at steady state with a flat velocity profile. While the species composition and the temperature vary along the reactor, at each cross-section of the reactor, the species concentrations and the temperature are uniform (no lateral profiles). The species-based design equation, written for a differential volume dV_R, is:

$$dF_j = \sum_{i}^{n_{all}} (s_j)_i \cdot r_i \cdot dV_R \tag{37}$$

The plug-flow model is applicable in the following cases: Tubular reactor with a sufficiently large length-to diameter ratio (>20 for turbulent flow, and >200 for laminar flow); and packed-bed reactors (the packing dispersed the fluid laterally across the bed).

Other variations of the ideal models such as cascade of CSTRs, semi-batch operation with well-mixed tank, distillation reactor, etc are also commonly used.

In order to solve the design equations it is necessary to express individual reaction rates (r_i's) in terms of the species contents (N_j's) in batch reactors, and the species flow rates, F_j's, in flow reactors. Hence, a design equation should be written for every species that appears in the reaction rate expressions, and these equations should be solved simultaneously. Also, since the reaction rates depend on the temperature, the design equations should be solved simultaneously with the energy balance equation. For ideal batch reactors and for plug-flow reactors, a series of non-linear first-order differential equations (initial value problem) should be solved. For the CSTR, a series of algebraic equations should be solved.

Two design formulations are described in the literature; one for reactors with single reactions, and one for reactors with multiple reactions. For chemical reactors with single reactions, only one design is needed, and it is usually written for the limiting reactant. The design equation is expressed in terms of the conversion of the limiting reactant, f_A, (defined in eqs. 5 and 6), and the operation of the reactor is described in terms of how the conversion varies with time for batch reactors or with volume for flow reactors. For reactors with multiple chemical reactions, eqs. 35, 36, or 37 (written for each species) are solved. The operation of the reactor is described in terms of the species contents, $Nj(t)$, as a function of time for batch reactors, or in terms of the species flow rates at the reactor outlet, F_{jout}, as a function of the reactor volume for flow reactors.

Two additional comments on the reactor design equations:

1. The plug flow and the CSTR models represent two limiting cases of flow reactors. The former represents continuous reactor without any mixing, where the reactant concentrations decreases along the reactor (Fig. 7**a**). The latter represents a reactor with complete mixing where the outlet reactant concentration exists throughout the reactor (Fig. 7**b**). Since in practice reactors are neither plug flow nor CSTR, it is common to obtain the performance of these two ideal reactors to identify the performance boundaries of the actual reactors.
2. The reactor design equations are expressed in terms of extensive quantities (V_R, molar flow rates, etc), unlike design equations of most operations in the process industries where they are expressed in terms of dimensionless or extensive quantities. Since most reactor design equations are solved numerically, it is necessary to tailor the solution for each case.
3. For flow reactors, the reactor volume is often expressed in terms of space time. The space time is defined by

$$\begin{pmatrix}\text{Space}\\ \text{time}\end{pmatrix} = \frac{\text{Reactor volume}}{\text{Reference volumetric flow rate}} \tag{38}$$

   The space time is merely the reactor volume expressed in terms of time. It is a superficial quantity since its numerical value depends on the selection of the reference stream. In some instances, the reciprocal of the space time, referred to as the "space velocity," is used.

Recently, a unified dimensionless design formulation for reactors with both single and multiple chemical reactions has been derived (28). The formulation is based on transforming the species balance equations to reaction-based design equations. These equations describe the progress of the chemical reactions in terms of their extents and provide additional insight on the reactor operation. The solutions of the design equations provide the extent of the reactions as a function of operating time for batch reactor or of the reactor volume for flow reactors. The species compositions (or flow rates) are readily determined (using stoichiomtric relations) from the reaction extents. Both the design equations and the energy balance equation are reduced to dimensionless form by selecting a reference state for batch reactors or a reference stream for flow reactors and by defining a characteristic reaction time. The characteristic reaction time is determined in a consistently from the rate expression of a selected reaction (the desired reaction) at a selected reference temperature. All the factors that affect the heat-transfer eg, surface per volume, heat transfer coefficient, are combined into a dimensionless number.

To illustrate the formulation, consider the cracking of a light hydrocarbon represented by the following reversible chemical reactions:

$$\text{Reaction 1:}\quad \mathrm{A} \rightleftarrows 2\mathrm{B}$$

$$\text{Reaction 2:}\quad \mathrm{A} + \mathrm{B} \rightleftarrows \mathrm{C}$$

$$\text{Reaction 3:}\quad \mathrm{A} + \mathrm{C} \rightleftarrows \mathrm{D}.$$

Reaction 1 is endothermic, and Reactions 2 and 3 are exothermic. The reactions take place in a tubular reactor placed in a furnace (to supply the heat for the cracking). Figure 8**a** shows the reaction curves of the three independent reactions (the three forward reactions), Figure 8**b** shows the species composition curves, and Figure 8**c** shows the temperature curve.

4.2. Refinements. When the behavior of an existing reactor is not adequately described by one of the idealized models, a more complex model is constructed. In such models the reactor is divided into sections, each is assumed to have its own species concentrations and temperature, with material and heat interchanged between them (2,29). The volume of each zone and the interchange rates are parameters that are determined from the reactor operating data. When avaiable, residence time distribution data (see Section 5.6) is also used to determine the model parameters (1,2,6). The advantage of such refined models is that they provide a more realistic representation of the reactor, based on actual operating data. However, their applications is limited to an existing specific reactors.

Recent advances in computerized fluid dynamics (CFD) and developments of advanced mathematical methods to solve coupled nonlinear differential equations may provide tools for phenomenological representations of reactor hydrodynamics (21,30). High speed and reduced cost of computation and increased cost of laboratory and pilot-plant experimentation make such tools increasingly attractive. The utility of CFD software packages in chemical reactor simulation depends on the following factors: reliability of predicting the flow patterns; easy incorporation of the chemical kinetics, adequacy of the physical and chemical representations; scale of resolution for the application and numerical accuracy of the solution algorithms; and skills of the user. CFD has been successfully applied to simulate combustion (30,31).

5. Common Practices

Inherently, the selection and design of a chemical reactor are done iteratively because, in many instances, the global reaction rates are not known *a priori*. In fact, the flow patterns of the reacting fluid (which affect the global rates) can be estimated only after the reactor vessel has been specified and the operating conditions have been selected. This section provides a review of the common practices used in chemical reactor technology.

5.1. Experimental Reactors. Often the chemical kinetics of the chemical reaction and whether or not the reaction rate is affected by transport limitation are not known *a priori*. The intrinsic rate expression and its parameters are determined from data obtained on experimental reactors. Laboratory-scale experimental reactors are structured such that they are operated isothermally and can be described by one of three ideal reactor models: ideal batch, CSTR, and plug-flow. Isothermicity is achieved by providing a large heat transfer surface and maintaing the reactor in a constant-temperature bath. Common experimental reactors are suitable for homogeneous reactions and for heterogeneous catalytic reactions. The selection of the experimental reactor should be done after careful analysis of the anticipated reaction characteristics, specific chemical and physical properties of the reactants and products, and the objectives of the investigation. Experiments are conducted at different initial or inlet reactant proportions to determine the form of the rate expression and at different temperatures to determine the activation energy.

A batch experimental reactor is used for slow reactions, since species compositions can be readily measured with time. The reaction rate is determined from the design equation (eq. 35). A tubular plug-flow experimental reactor is suitable for fast reactions and high temperature experiments. The species composition at the reactor outlet is measured for different feed rates, and the reaction rate is determined from the design equation (eq. 37). In both cases it is necessary to differentiate the collected data to obtain the reaction rate. Also, short packed-beds are used as differential reactors to obtain instantaneous reaction rates. An experimental CSTR is a convenient tool in determining reaction rate, since the reaction rate is directly obtained from the design equation (eq. 36).

The rate expressions of catalytic heterogenous reactions are generally carried out in flow reactors. When a packed-bed reactor is used (Fig. 9**a**), it is necessary to acertain that a plug-flow behavior is maintained. This is achieved by a sufficiently high velocity, and having a tube-to-particle diameter ratio of at least 10 to avoid bypassing near the wall, where the void fraction is higher than in the bed. However, the tube diameter should not be too large to avoid radial gradient of temperature and concentrations. A spinning basket reactor (Fig. 9**b**) is a tool for determining the reaction rate of heterogeneous catalytic reactions and the effectiveness factor (eq. 23). At a sufficiently high rotation speed, the external transport rate (between the bulk to the surface of the catalytic pellet) does not affect the overall reaction rate. The effectiveness factor is determined by conducting a series of experiments with different pellet diameters.

The rates of fluid-fluid reactions are determined from experiments carried out in special reactors where the interfacial area is known (ie, falling film, laminar liquid jets).

When the heat of reaction is not known, experiments are conducted on a well-stirred batch or continuous calorimeter. The adiabatic temperature change is measured and the heat of reaction is determined from the energy balance equation. Special calorimeters are available for stability testing and assessing potential runaway reactions (see Section 5.4) (32).

5.2. Selection of Reactor Configuration. The first step in the design of a chemical reactor is the selection of the operating mode – batch or continuous. The selection is made on the basis of both economic and operational considerations. Batch operations are suitable for small quantity production of high-value products, and for producing multiple products in the same equipment. Batch reactors are also used when the reacting fluid is very viscous eg, in the manufacture of polymer resins. Batch operations require down time between batches for charging, discharging and cleaning, and a drawback of this mode is variations among batches. Batch reactors have relative low capital investment, but their operating cost is relatively high. Continuous reactor operations are suitable for large volume production, and provide good product uniformity. Continuous reactors require relatively high capital investment, but their operating expense is relatively low.

Next, it is necessary to identify the dominating factors that affect the chemical reactions, and select the most suitable reactor configuration. For homogeneous chemical reactions, one of three factors often dominates (*1*) equilibrium limitation of the desirable reaction, (*2*) the formation of undesirable products (by side reactions), and (*3*) the amount of heat that should be transferred. For example, if a low concentration of the reactants suppresses the formation of the undesirable product, a CSTR is preferred over a tubular reactor even though a larger reactor volume is needed. When high heat transfer rate is required, a tubular reactor with relatively small diameter (providing high surface-to-volume ratio) is used.

For heterogeneous catalytic reactions, the size of the catalyst pellets is usually the dominating factor. Packed-beds with large diameter pellets have low pressure drop (and low operating cost), but the large pellets exhibits high pore diffusion limitation and require a larger reactor. Often, the pellet size is selected on the basis of economic considerations balancing between the capital cost and the operating cost. When fine catalytic particles are requires, a fluidized bed is used. Unlike packed-bed reactors that are described by the plug-flow model, in fluidized bed reactors the reacting fluid mixed extensively and a portion of it passes through the reactor in large bubbles with little contact with the catalytic particles. Consequently, a larger reactor volume is needed.

In many noncatalytic gas-sold reactions, the feeding and movement of the solid reactant is dominating. For fluid-fluid reactions, contacting between the reactants (the interfacial area per unit volume) dominates.

5.3. Selection of Operating Conditions. Once the reactor type and configuration have been selected, the reactor operating conditions should be selected. For example, should the reactor be operated such that high conversion of the reactant is achieved, or should it be operated at lower conversion (with higher recycle of the unconverted reactant). The selection of the reactor operating conditions is done on the basis of an optimization of an objective function, eg, maximizing profit, maximizing product yield or selectivity, minimizing generation of pollutants. When an economic criterion is used, the performance of the entire process, ie, the reactor, separation system, utilities, is considered rather than the performance of reactor alone.

5.4. Operational Considerations. The design equations describe the reactor operation at steady-state conditions. Additional considerations should be given that the reactor is operational (ie, startup and shut-down), controllable and it does not create any safety hazards. Further, reactors can operate at multiple conditions. The design and energy balance equations may have multiple solutions and some of them unstable. Such situation is illustrated in Figure 10 which shows the heat generation and heat removal curves of CSTR with an exothermic reaction (5,14). The intersections of the two curves represent plausible operating conditions. Operating point "*b*" is unstable since any upset in the operating conditions will result in the reactor operating at point "*a*" or "*c*".

Safe operation is a paramount concern in chemical reactor technology. Runaway reactions occur when the heat generated by the chemical reactions exceed the heat that can be removed from the reactor. The surplus heat increases the temperature of the reacting fluid, causing the reaction rates to increase further (heat generation increases exponentially with temperature while the rate of heat transfer increases linearly). Runaway reactions lead to rapid rise in the temperature and pressure, which if not relieved, may cause an explosion. Experience has shown that the following factors are prevalent in accidents involved chemical reactors: inadequate temperature control; inadequate agitation; little knowledge of the reaction chemistry and thermo-chemistry; raw material quality (32,34).

5.5. Scale-up. The objective of scale-up is to design to industrial-sized reactors on the basis of experimental data obtained of laboratory-scale reactors. A reliable scale-up requires insight of the phenomena and mechanisms that affect the performance of the lab-scale reactor. Once these factors are identified and quantified, the task is to establish similar conditions in the industrial-size reactor. The difficulty arises from the fact that not all the factors can be maintained similar simultaneously upon scale-up (35). For example, it is often impossible to maintain similar flow conditions (eg, Reynolds number) and the same surface heat transfer area per unit volume. Good understanding of the phenomena and mechanisms can enable the designer to account for the different conditions. Unfortunately, in many instances, considerable uncertainties exist with regards to the mechanisms and the values of the parameters. As a result, an experimental investigation on a pilot-size reactor is conducted to improve the reliability of the design of an industrial-size reactor.

In many processes that apply an agitated tank (either batch or continuous operations) the main task in is to maintain sufficient mixing during scale-up. Considerable information is available in the literature on scaling up of agitated tanks (21–27).

5.6. Diagnostic Methods. In practice, especially in large-scale reactors, plug-flow and complete mixing are rarely achieved and it is desirable to quantify the deviation from these idealized flow conditions. Also, when a chemical reactor does not perform at the expected level, it is necessary to identify the reason. A diagnostic method that is applied in such situations is based on measuring the resident time distribution (RTD) in the reactor. An inert tracer material is injected at the reactor inlet and its concentration at the reactor outlet is measured with time. By comparing the outlet concentration curve to the inlet concentration curve, the RTD curve of the fluid passing through the reactor can be constructed (2,6,29).

The measured mean residence time and shape of the RTD curve provide valuable information on the flow of the reacting fluid through the reactor. Based on fundamental physical concepts, the mean residence time is the quotient of the volume of the reacting fluid in the reactor and its volumetric flow rate,

$$\bar{t} = \frac{V}{v} \tag{39}$$

Since mean residence time and the volumetric flow rate are known, value of V, the "active volume" of the fluid in the reactor, is readily calculated. If the calculated value of V is smaller than the reactor volume, it is an indication that a stagnant zone (not available to the flowing fluid) exists in the reactor and the actual reactor volume available for the reaction is smaller than designed. In heterogeneous fluid-fluid reactors, measuring the mean residence time of each fluid provides the hold-up of each in the reactor. Comparing the RTD curve to that of CSTR and PFR provides an indication on the deviations of the actual flow patterns from those of idealized flows.

It is important to recognize the limitations of the RTD method. Residence time distribution does not discern between a reacting fluid that is mixed on the molecular level (micro-mixing) and one that flows in segregated blobs. Also, the same RTD is obtained when mixing occurs near the entrance or near the exit. Both of these phenomena affect the chemical reactions and the performance of the reactor. Hence, flow models that are derived from RTD measurements should be verified by other means.

6. Industrial Reactors

Figure 11 shows the structures of two industrial reactors used to produce two of the largest volume chemicals in the word. Figure 11**a** shows the internals of an ammonia converter, and Figure 11**b** shows schematically the fluidized bed catalytic cracking (FCC) reactor that converts heavy petroleum crude to lighter hydrocarbon cuts.

The ammonia synthesis reaction is an exothermic reversible reaction that is carried out in a packed-bed of catalytic pellets. The removal of the heat generated by the reaction is the dominating factor in the design of the reactor. Since the reaction is reversible, an increase in the temperature limits the conversion (equilibrium-limited). The intricate reactor was designed to provide an efficient heat-transfer and to use some of the heat of reaction to preheat the feed.

The FCC unit consists of two fluidized-bed reactors, one used as the cracking reactor and the second as a catalyst regenerator. During the cracking reaction, carbon builds up on the catalytic particles, causing deactivation. To regenerate the catalytic particles, they are transported to a regeneration unit where the carbon is burned with air. The heat generated by the combustion of the carbon is carried by the hot particles to the cracking reactor; hence, the circulating particles provide the heat for the endothermic cracking reaction.

7. Summary

The underlying theme of this article is the diversity and complexity of chemical reactor operations. The article attempts to convey three main messages:

1. The difficulty in obtaining a global reaction rate expression: an expression that accounts for both intrinsic kinetics and transport limitations. Insight into the detailed kinetic and transport mechanism is necessary as well as a methodology to determine relevant model parameters.
2. The inherent difficulty in designing chemical reactors which is due to two factors: (*1*) Global reaction rates depend on the local flow conditions which are not known *a priori*. (*2*) Even when the global reaction rate expressions are available, solving the design equations is a formidable task that rarely can be performed in the design exercise.
3. Approximate engineering approaches can be successfully employed to estimate reactor operations and guesstimate the limits of its performance.

Numerous chemical reactors are operated safely and profitably to produce a wide variety of products in diverse industries. Most of them have been developed and refined within a technological context focused on a specific product or a process. Nevertheless these reactors serve as a testimony to the successful application of fundamental concepts and methodologies of chemical reaction engineering.

8. Nomenclature

C	concentration (mol/m^3)
c_p	specific molar-base heat capacity (J/mol °K)
D	diffusion coefficient (m^2/s)
Da	Damkohler number
d	diameter (m)
d_p	particle diameter (m)
E_a	activation energy (J/mol)
F	molar flow rate (mol/sec)
f	conversion of a reactant (dimensionless)
ΔH_R	heat of reaction (J/mol)
$k(T)$	reaction rate constant (units depend on the rate expression)
k_M	mass-transfer coefficient (m/s)
N	molar content (mol)
Q	heat transferred (J)
Re	Reynolds number
RTD	residence time distribution

Sc	Schmidt number
Sh	Sherwood number
s_j	stoichiometric coefficient of species j
T	temperature (K)
t	time (s)
U	heat transfer coefficient (J/m^2 K)
V	volume (m^3)
V_R	reactor volume (m^3)
v	volumetric flow rate (m^3/s)
X	reaction extent (mol extent)

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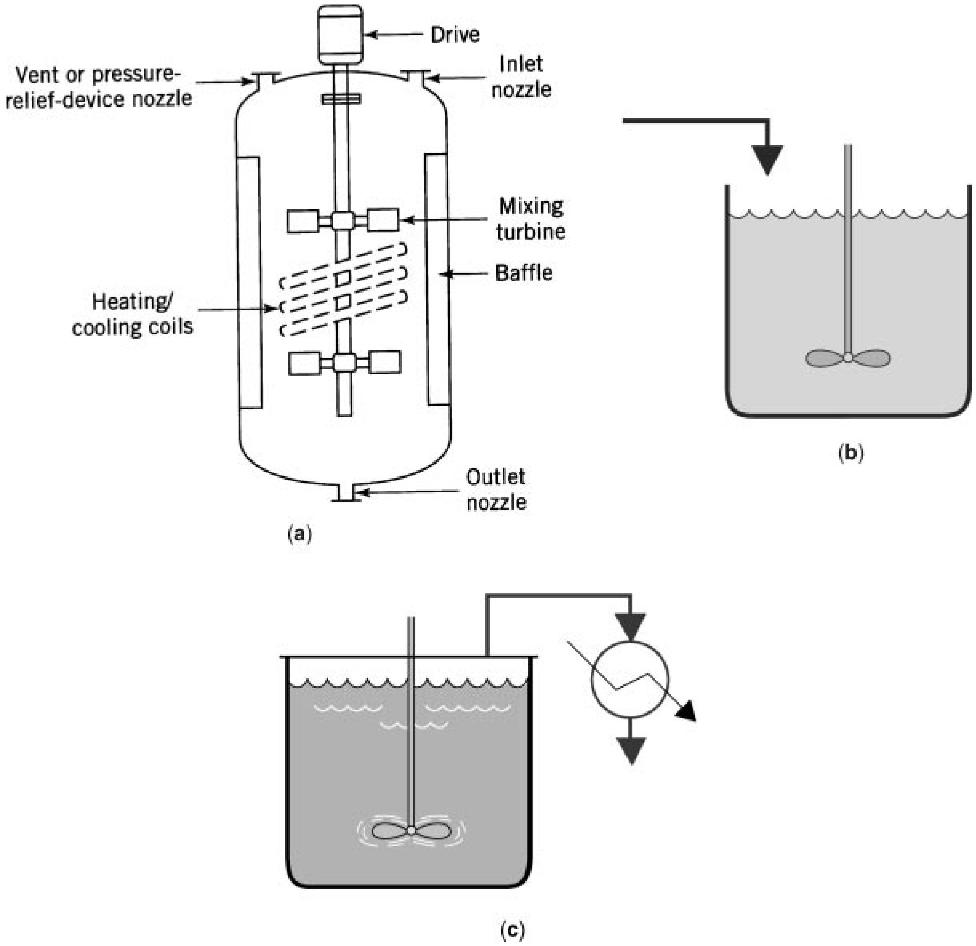


Fig. 1. Reactor modes of operation. (**a**) Batch reactor (from Ref. 1, with permission). (**b**) Semibatch reactor. (**c**) Distillation reactor.

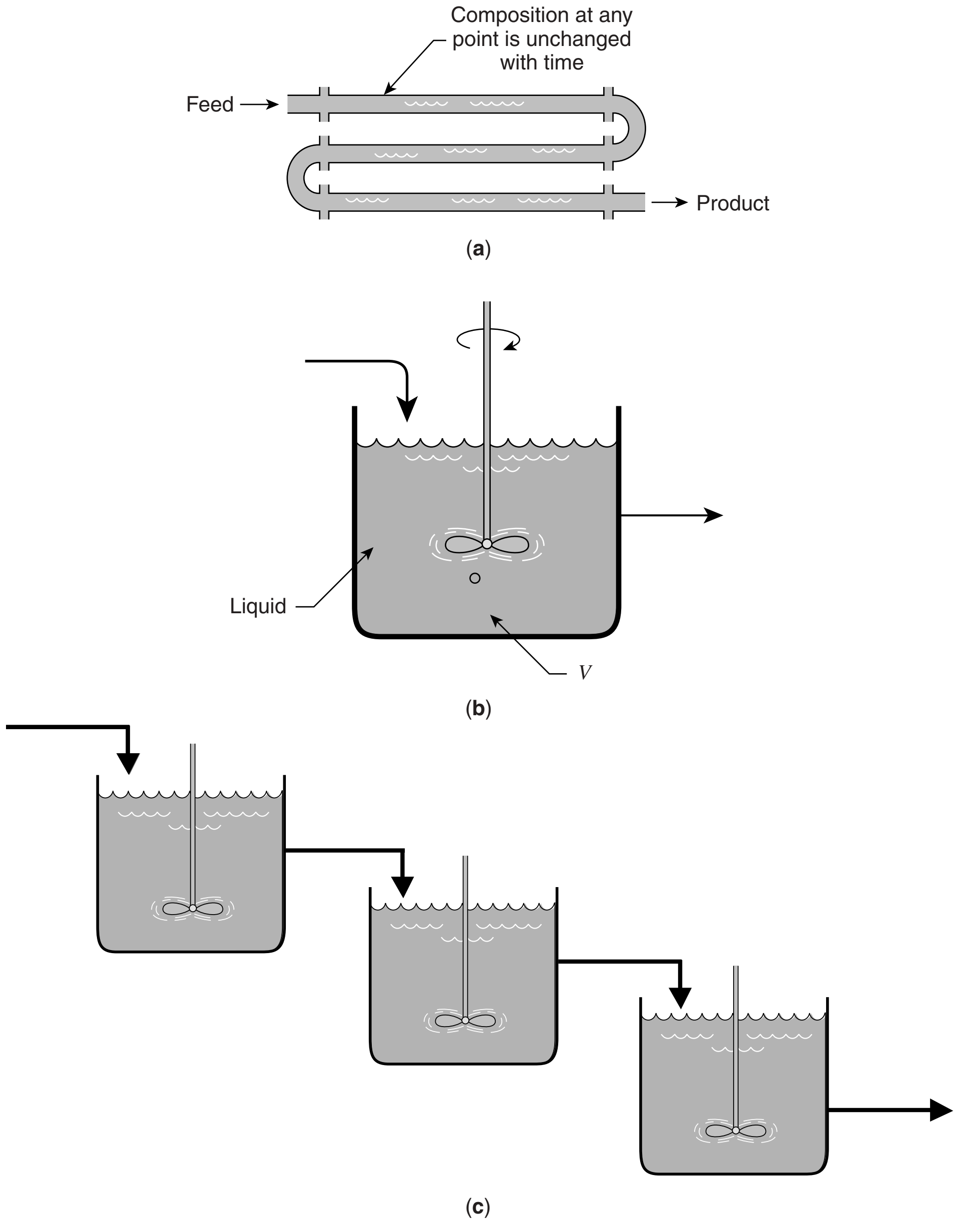


Fig. 2. Continuous reactor configurations. (**a**) Tubular reactor (from Ref. 2, with permission). (**b**) Continuous stirred tank reactor (CSTR). (**c**) Cascade of CSTRs.

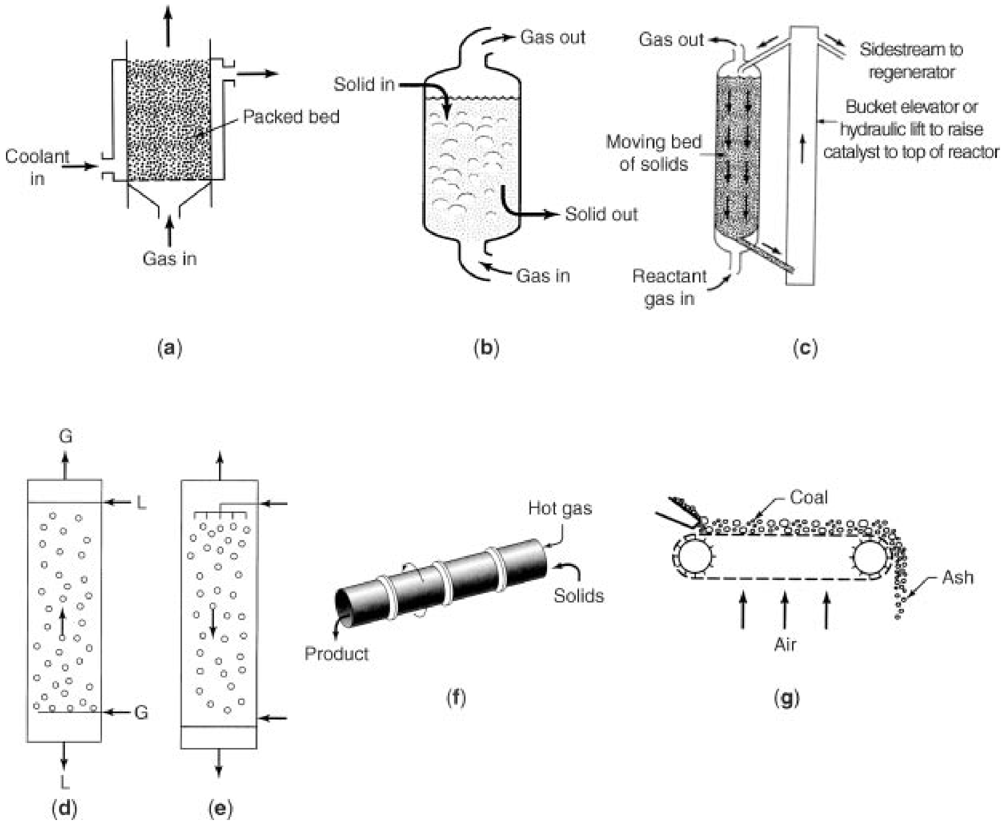


Fig. 3. Multiphase reactor contacting patterns. (**a**) Packed-bed reactor (from Ref. 2, with permission). (**b**) Fluidized-bed reactor (from Ref. 2, with permission). (**c**) Moving bed reactor (from Ref. 2, with permission). (**d**) Bubble column reactor (from Ref. 1, with permission). (**e**) Spray reactor (from Ref. 1, with permission). (**f**) Kiln reactor (from Ref. 2, with permission). (**g**) Moving grate reactor (from Ref. 2, with permission).

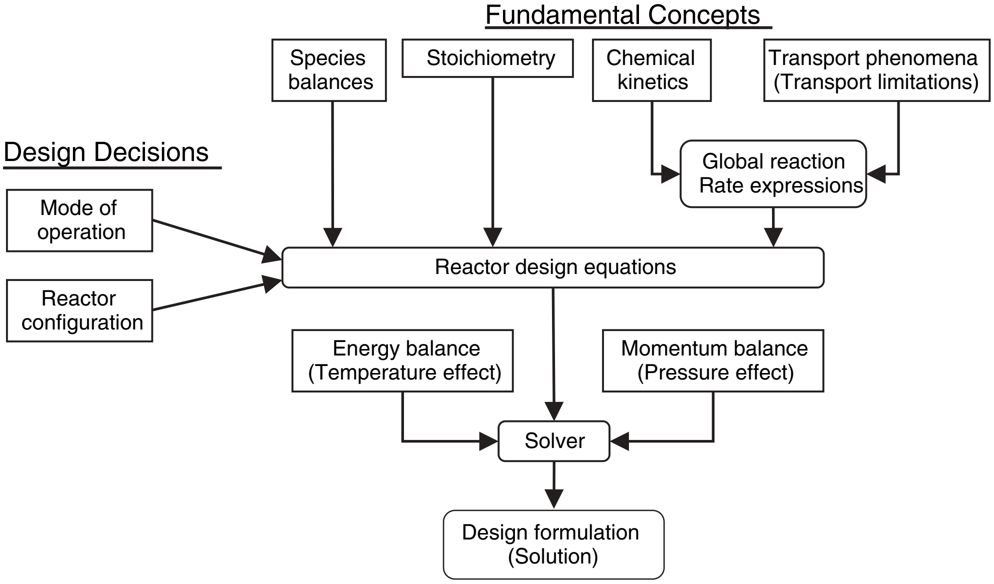


Fig. 4. Framework of formulating and solving reactor design equations.

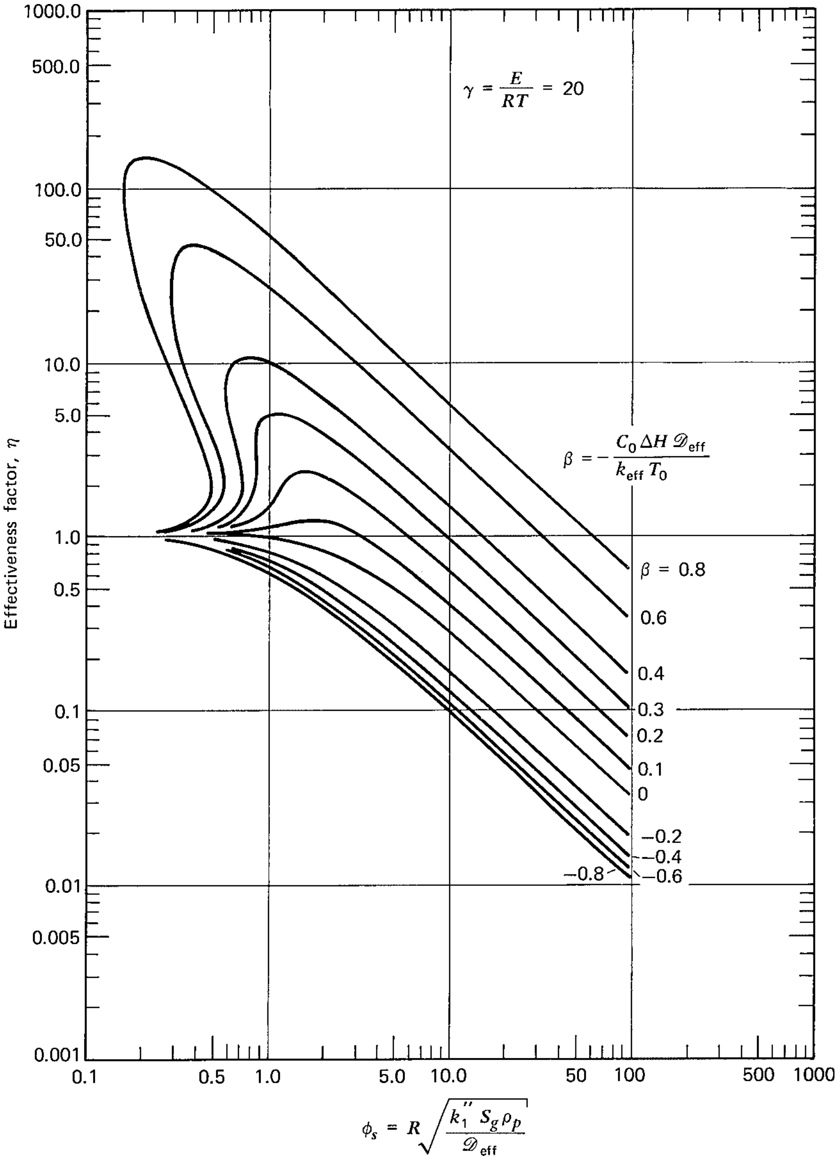


Fig. 5. Effectiveness factor for exothermic first-order catalytic reactions (from Ref. 5, with permission).

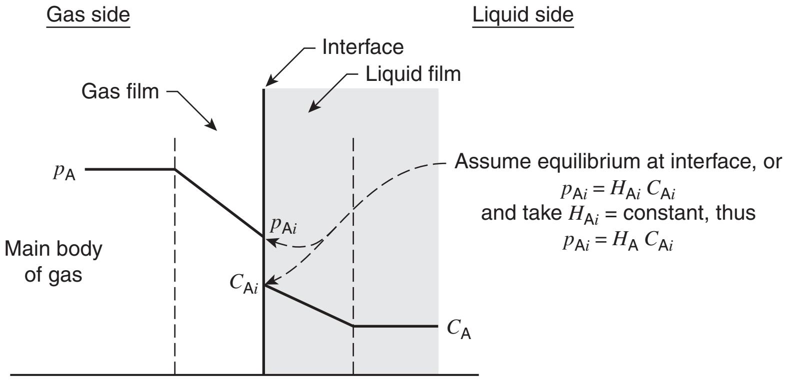


Fig. 6. The two-film model for fluid–fluid reactions (from Ref. 2, with permission).

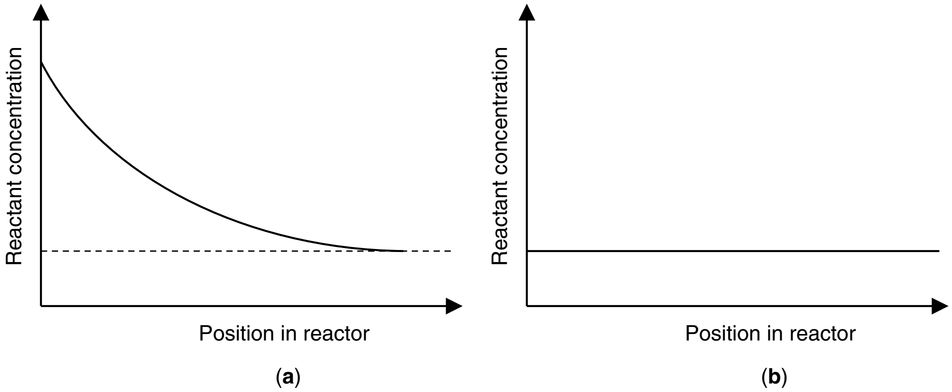


Fig. 7. Reactant concentration profile. (**a**) PFR. (**b**) CSTR.

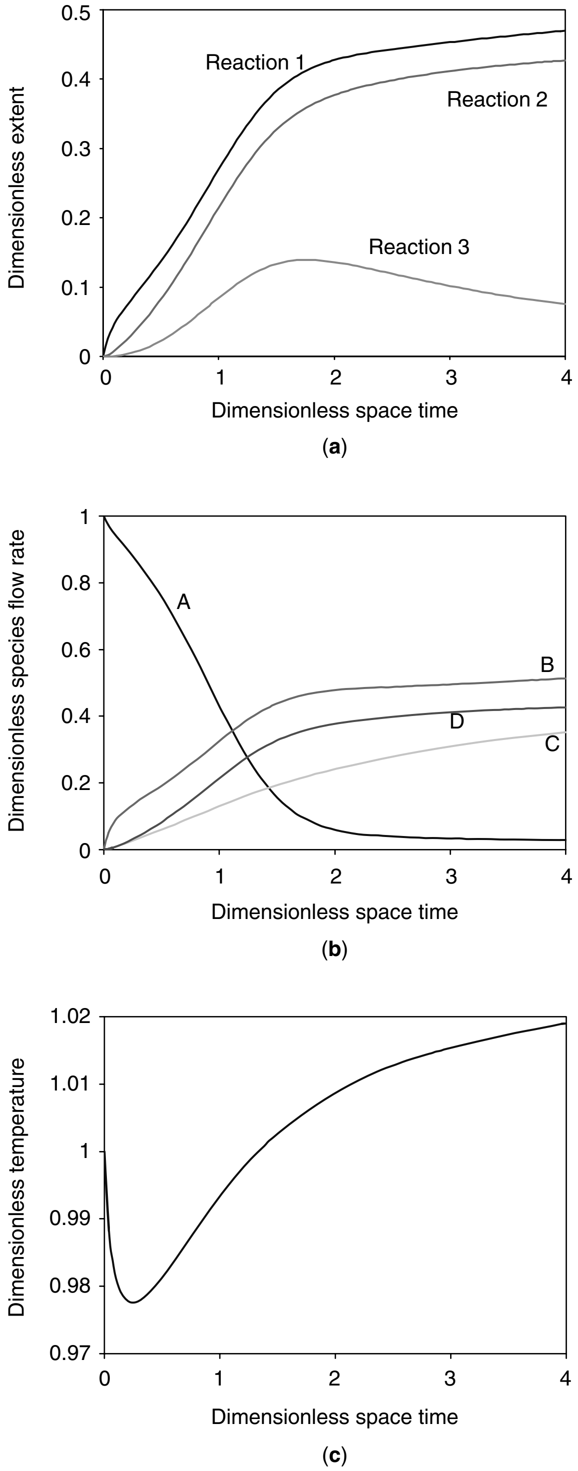


Fig. 8. Example results. (**a**) Reaction curve. (**b**) Species curves. (**c**) Temperature curve.

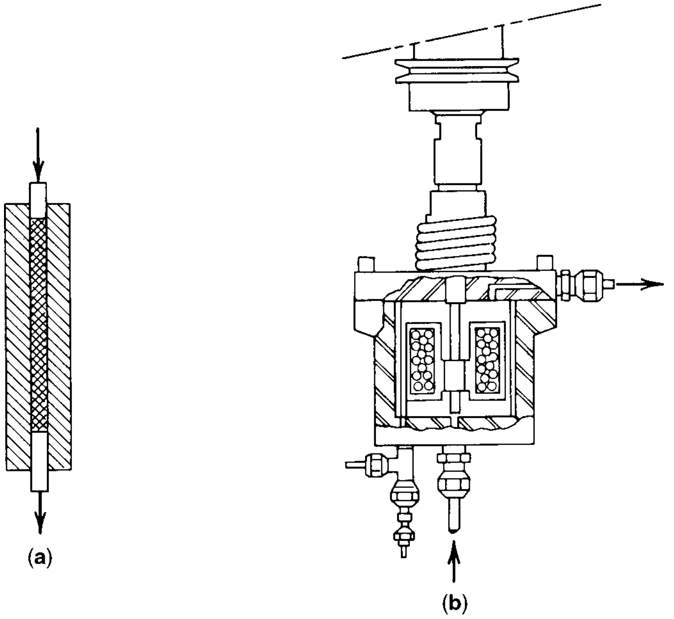


Fig. 9. Experimental reactors for heterogeneous catalytic reactors (from Ref. 6, with permission). (**a**) Tubular reactor. (**b**) Spinning basket reactor.

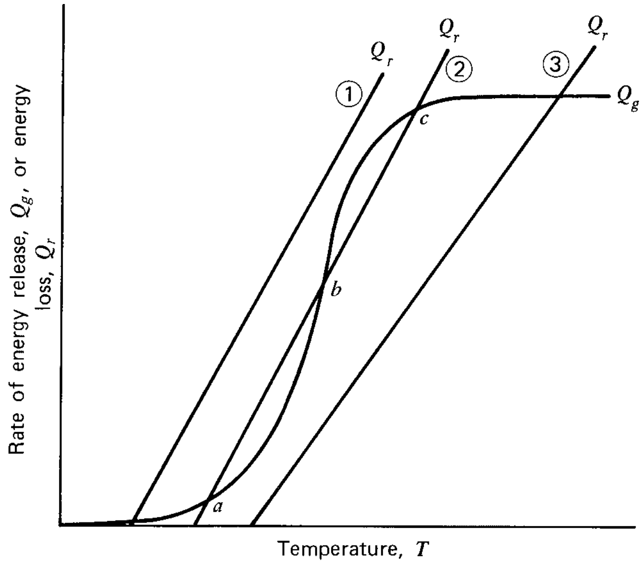
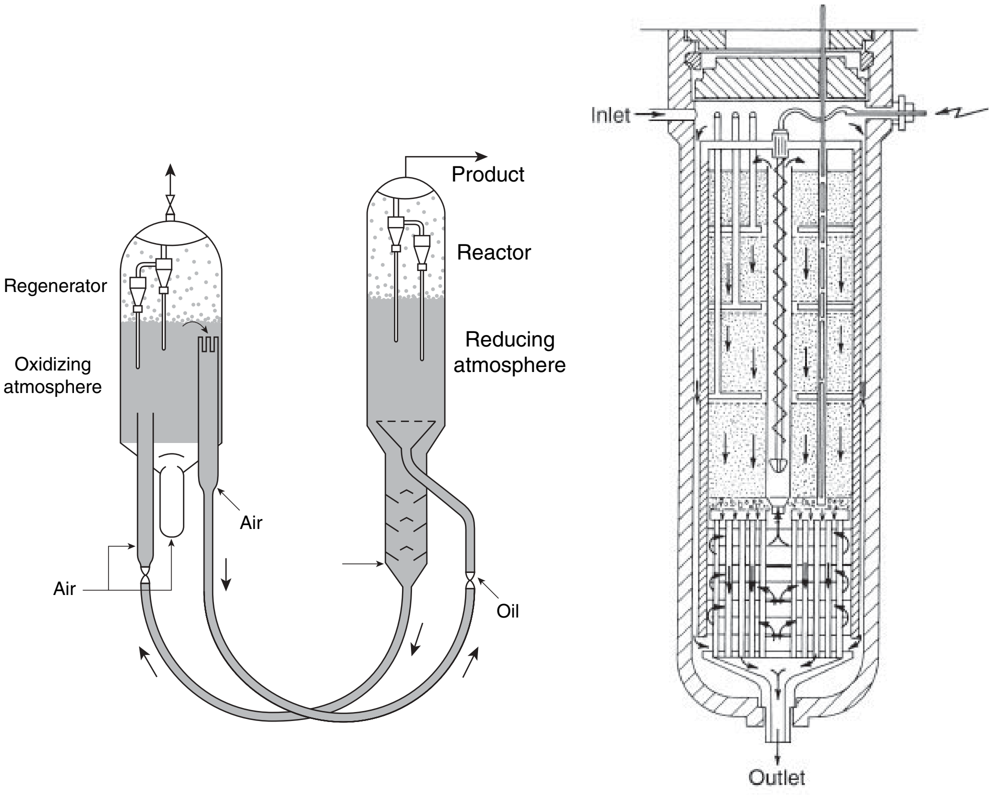


Fig. 10. Heat generation and removal curves in CSTR (from Ref. 5, with permission).



(a) (b)

Fig. 11. Industrial reactors. (**a**) Ammonia converter (from Ref. 6, with permission). (**b**) Fluidized-bed catalytic cracking (FCC) reactor (from Ref. 2, with permission).