
1

OVERVIEW OF CHEMICAL REACTION ENGINEERING*

Chemical reaction engineering (CRE) is the branch of engineering that encompasses the selection, design, and operation of chemical reactors. Because of the diversity of chemical reactor applications, the wide spectrum of operating conditions, and the multitude of factors that affect reactor operations, CRE encompasses many diverse concepts, principles, and methods that cannot be covered adequately in a single volume. This chapter provides a brief overview of the phenomena encountered in the operation of chemical reactors and of the concepts and methods used to describe them.

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 configuration and its operating conditions are selected to achieve certain objectives such as maximizing the profit of the process, and minimizing the generation of pollutants, while satisfying several design and operating constraints (safety, controllability, availability of raw materials, etc.). Usually, the performance of the chemical reactor plays a pivotal role in the operation and economics of the entire process since its operation affects most other units in the process (separation units, utilities, etc.).

*This chapter is adopted from *Kirk-Othmer's Encyclopedia of Chemical Technology*, 7th ed, Wiley Interscience, NY (2007).

Chemical reactors should fulfill three main requirements:

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

In many instances these three requirements are not complimentary, and achieving one of them comes at the expense of another. Chemical reaction engineering 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).

1.1 CLASSIFICATION OF CHEMICAL REACTIONS

For convenience, chemical reactions are classified in two groups:

- Homogeneous reactions—Reactions that occur in a single phase
- Heterogeneous reactions—Reactions that involve species (reactants or products) that exist in more than one phase. Heterogeneous reactions are categorized further as:
 - Fluid–fluid reactions—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 contains the products). In many instances, the overall reaction rate depends on the interface area available, the miscibility of the reactant, and the transfer rates (e.g., diffusion) of the reactants to the interface and in the reacting phase.
 - Noncatalytic gas–solid reactions (e.g., combustion and gasification of coal, roasting of pyrites). These reactions occur on the surface of the solid. The gaseous reactant is transported to the interface, where it reacts with the solid reactant. Gaseous products are transported to the gas phase, and solid products (e.g., ash) remain in 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.
 - 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 commonly used. The reaction takes place on the surface of the pores in the interior of the particle.

In many instances, the overall reaction rate is determined by the diffusion rate of reactants into the interior of the pore, and the diffusion of the product out of the pore.

- Catalytic gas–liquid–solid reactions—Reactants are gases and liquids, and the reaction takes place at a solid surface where a catalytic reagent is deposited (e.g., hydrogenation reactions). 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 that should be described quantitatively.

1.2 CLASSIFICATION OF CHEMICAL REACTORS

Chemical reactors are commonly classified by the three main characteristics:

1. Mode of operation (e.g., batch, continuous, semibatch)
2. Geometric configuration (e.g., tubular, agitated tank, radial flow)
3. Contacting patterns between phases (e.g., packed bed, fluidized bed, bubble column)

In addition, reactor operations are also classified by the way their temperature (or heat transfer) is controlled. Three operational conditions are commonly used: (i) isothermal operation—the same temperatures exist throughout the reactor, (ii) adiabatic operation—no heat is transferred into or out of the reactor, and (iii) non-isothermal operation—the operation is neither isothermal nor adiabatic.

The following terms are commonly used:

- Batch reactors (Fig. 1.1*a*)—Reactants are charged into a vessel at the beginning of the operation, and products are discharged at the end of the operation. The chemical 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.
- Semibatch reactor (Fig. 1.1*b*)—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 one reactant (the injected reactant) at low concentration to improve the selectivity of the desirable product and to supply (or remove) heat.
- Distillation reactor (Fig. 1.1*c*)—A batch reactor where volatile products are removed continuously from the reactor during the operation.
- Continuous reactor (flow reactors)—A vessel into which reactants are fed continuously and products are withdrawn continuously from it. The chemical

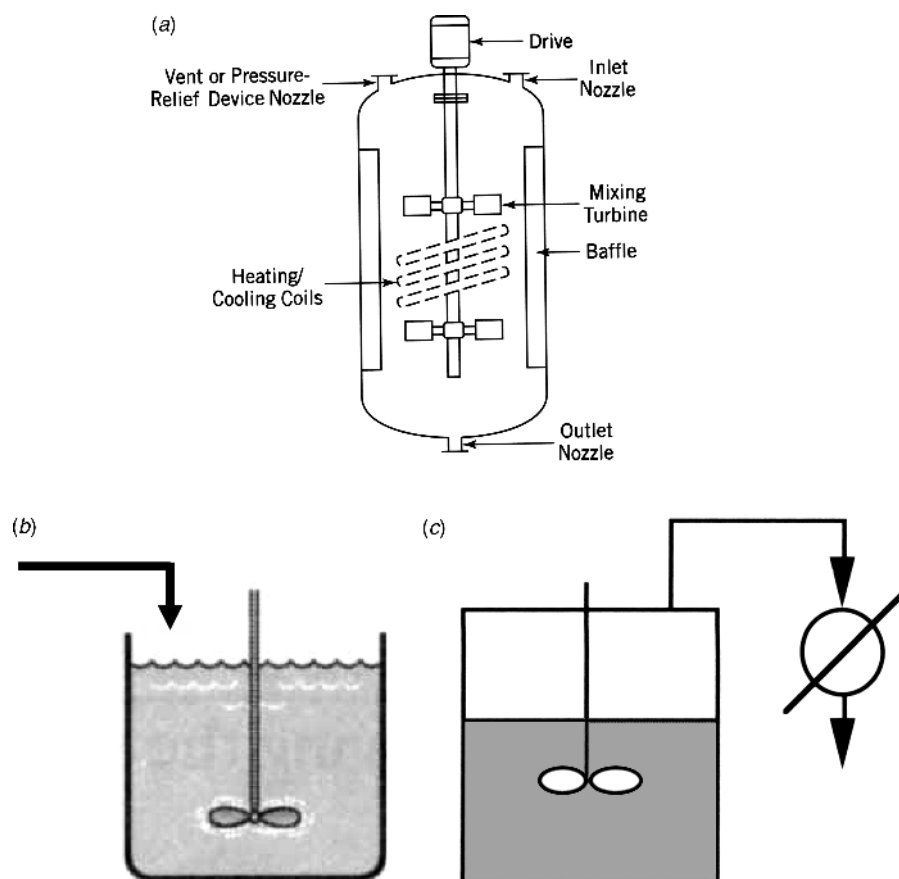


Figure 1.1 Batch operations: (a) batch reactor, (b) semibatch reactor, and (c) distillation reactor.

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. 1.2a)
- Continuous stirred-tank reactor (CSTR) (Fig. 1.2b)
- Cascade of CSTRs (Fig. 1.2c)
- For multiphase reactions, the contacting patterns are used as a basis for classifying the reactors. Common configurations include:
 - Packed-bed reactor (Fig. 1.3a)—A vessel filled with catalytic pellets and the reacting fluid passing through the void space between them. Relatively large pellets (e.g., 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.

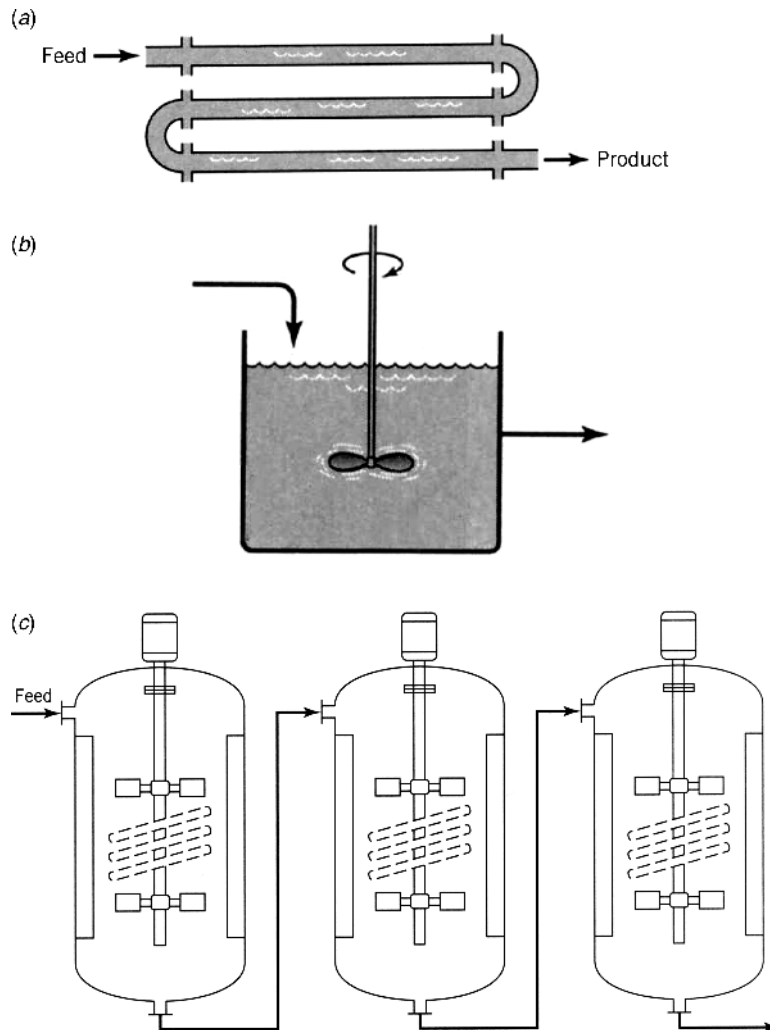


Figure 1.2 Continuous reactors: (a) tubular reactor, (b) continuous stirred-tank reactor (CSTR), and (c) cascade of CSTRs.

- Moving-bed reactor (Fig. 1.3b)—A vessel where solid particles (either reactant or catalyst) are continuously fed and withdrawn. The gas flow is maintained to allow the downward movement of the particles.
- Fluidized-bed reactor (Fig. 1.3c)—A vessel filled with fine particles (e.g., smaller than 500 μm) that are suspended by the upward flowing fluid. The fluidized bed provides good mixing of the particles and, consequently, a uniform temperature.
- Trickle-bed reactor—A packed bed where a liquid reactant is fed from the top, wetting catalytic pellets and a gas reactant, fed either from the top or

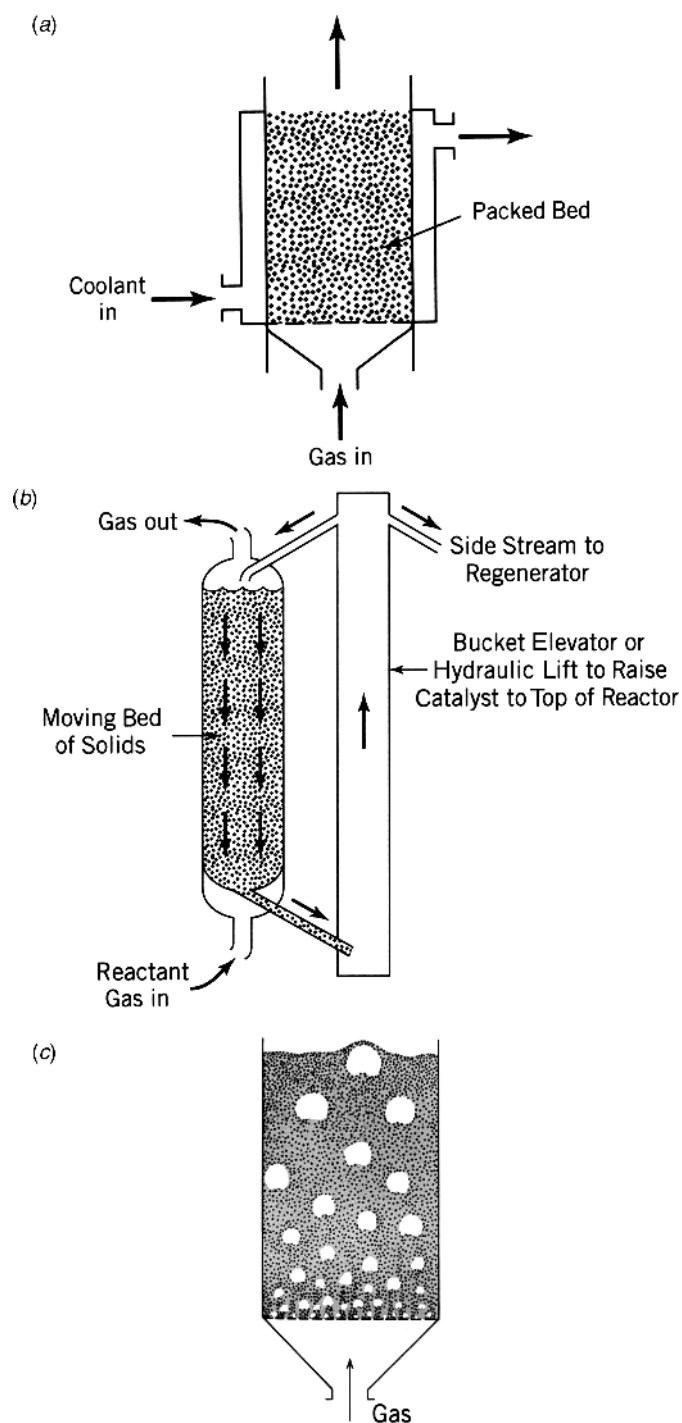


Figure 1.3 Multiphase reactors: (a) packed-bed reactor, (b) moving-bed reactor, (c) fluidized-bed reactor, (d) bubbling column reactor, (e) spray reactor, and (f) kiln reactor.

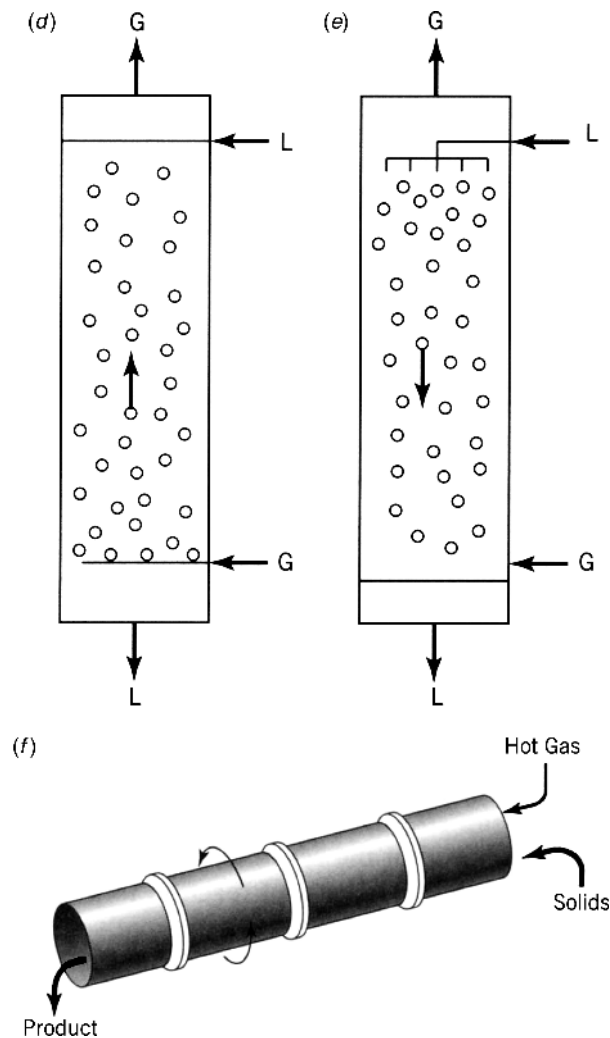


Figure 1.3 (Continued).

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 at the surface of the pellets.

- **Bubbling column reactor (Fig. 1.3d)**—A vessel filled with a liquid reactant and a gas reactant, fed from the bottom, moves upward in the form of bubbles. The liquid reactant is fed from the top and withdrawn from the bottom. The gaseous reactant is absorbed in the liquid reactant, and the reaction takes place in the liquid phase.
- **Others [e.g., spray reactor (Fig. 1.3e), slurry reactor, kiln reactor (Fig. 1.3f), membrane reactor, etc.]**.

Due to the diverse applications and numerous configurations of chemical reactors, no generic design procedure exists to describe reactor operations. Rather, in each case it is necessary to identify the characteristics of the chemical reaction and the main features that the reactor should provide. Once these are identified, the appropriate physical and chemical concepts are applied to describe the selected reactor operation.

1.3 PHENOMENA AND CONCEPTS

The operation of a chemical reactor is affected by a multitude of diverse factors. 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 1.4 shows schematically how various fundamental and engineering concepts are combined in formulating the reactor design equations.

1.3.1 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. Chapter 2 covers in detail the stoichiometric concepts and definitions used in reactor analysis.

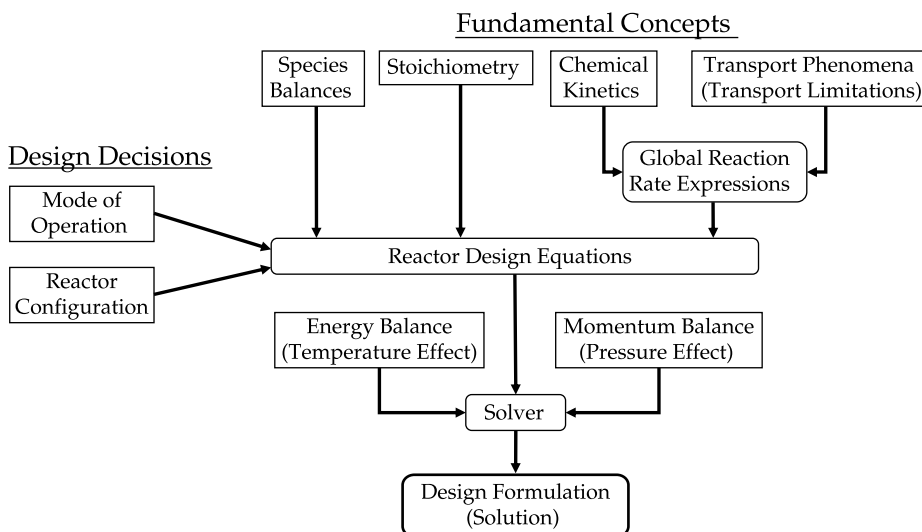


Figure 1.4 Schematic diagram of reactor design formulation.

1.3.2 Chemical Kinetics

Chemical kinetics is the branch of chemistry concerned with the rates of chemical reactions [3, 14, 19, 36–41]. Many chemical reactions involve the formation of unstable intermediate species (e.g., free radicals). Chemical kinetics is the study of the mechanisms involved in 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. Chapter 3 covers the definitions and relations used in reactor analysis and design.

1.3.3 Transport Effects

The rate expressions obtained by chemical kinetics describe the dependency of the reaction rate on kinetic parameters related to the chemical reactions. These rate expressions are commonly referred to as the “intrinsic” rate expressions of the chemical reactions (or intrinsic kinetics). However, 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 rate (also referred to as the *global reaction rate*) is affected by the transport rates of the reactants and products.

The effects of transport phenomena on the global reaction rate are prevalent in three general cases:

1. Fluid–solid catalytic reactions
2. Noncatalytic fluid–solid reactions
3. Fluid–fluid (liquid–liquid, gas–liquid) reactions

Incorporating the effects of species transport rates to obtain the global rates of the chemical reactions is a difficult task since it requires knowledge of the local temperature and flow patterns (hydrodynamics) and numerous physical and chemical properties (porosity, pore size and size distribution, viscosity, diffusion coefficients, thermal conductivity, etc.).

The species transfer flux to/from 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 [13, 21, 26–29]. For example, in a packed bed the mass-transfer coefficient from the bulk of the fluid to the surface of a particle is obtained from a correlation of the form

$$\text{Sh} = \frac{k_M d_p}{D} = C \text{Re}^{0.5} \text{Sc}^{0.33}, \quad (1.3.1)$$

where Sh is the Sherwood number, Re is the Reynolds number (based on the particle diameter and the superficial fluid velocity—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.

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) transport of the reactant from the fluid bulk 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 from the mouth of the pore to the bulk of the fluid. Steps 3–5 represent the kinetic mechanism of heterogeneous catalytic reactions. The rate of the reaction depends on the rates of these individual steps and the interactions between the catalytic site and the species, and the adsorption equilibrium constants of the various species present. A procedure, known as the Langmuir–Hishelwood–Hougen–Watson (LHHW) formulation, is used to derive and verify the reaction rate expressions for catalytic reactions [1, 3, 5, 7, 8, 14–18]. In many instances, one step is much slower than the other two steps and it determines the overall rate. This step is referred to as *the rate-limiting step*.

Often the global reaction rate of heterogeneous catalytic reactions is affected by the diffusion in the pore and the external mass-transfer rate of the reactants and the products. When the diffusion in the pores is not fast, a reactant concentration profile develops in the interior of the particle, resulting in a different reaction rate at different radial locations inside the catalytic pelet. To relate the global reaction rate to various concentration profiles that may develop, a kinetic effectiveness factor is defined [1, 3, 4, 7, 8] by

$$\left(\text{Effectiveness factor} \right) \equiv \frac{\text{Actual reaction rate}}{\text{Reaction rate at the bulk condition}} \quad (1.3.2)$$

Hence, to express the actual reaction rate, we have to multiply the reaction rate based on the bulk condition 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 and is expressed in terms of a modulus (Thiele modulus), ϕ , defined by

$$\phi^2 = \frac{\text{Characteristic reaction rate}}{\text{Characteristic diffusion rate}} \quad (1.3.3)$$

The function expressing the Thiele modulus in terms of kinetic parameters and the catalyst properties depends on the intrinsic reaction rate. For first-order reactions, the modulus is

$$\phi = L \sqrt{\frac{k}{D_{\text{eff}}}} \quad (1.3.4)$$

where k is the volume-based reaction rate constant, and 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. Figure 1.5 shows the relationship between the effectiveness factor and the Thiele modulus for first-order reactions. Note that for exothermic reactions the effectiveness factor may be larger than one because of the heating of the catalytic pellet. The

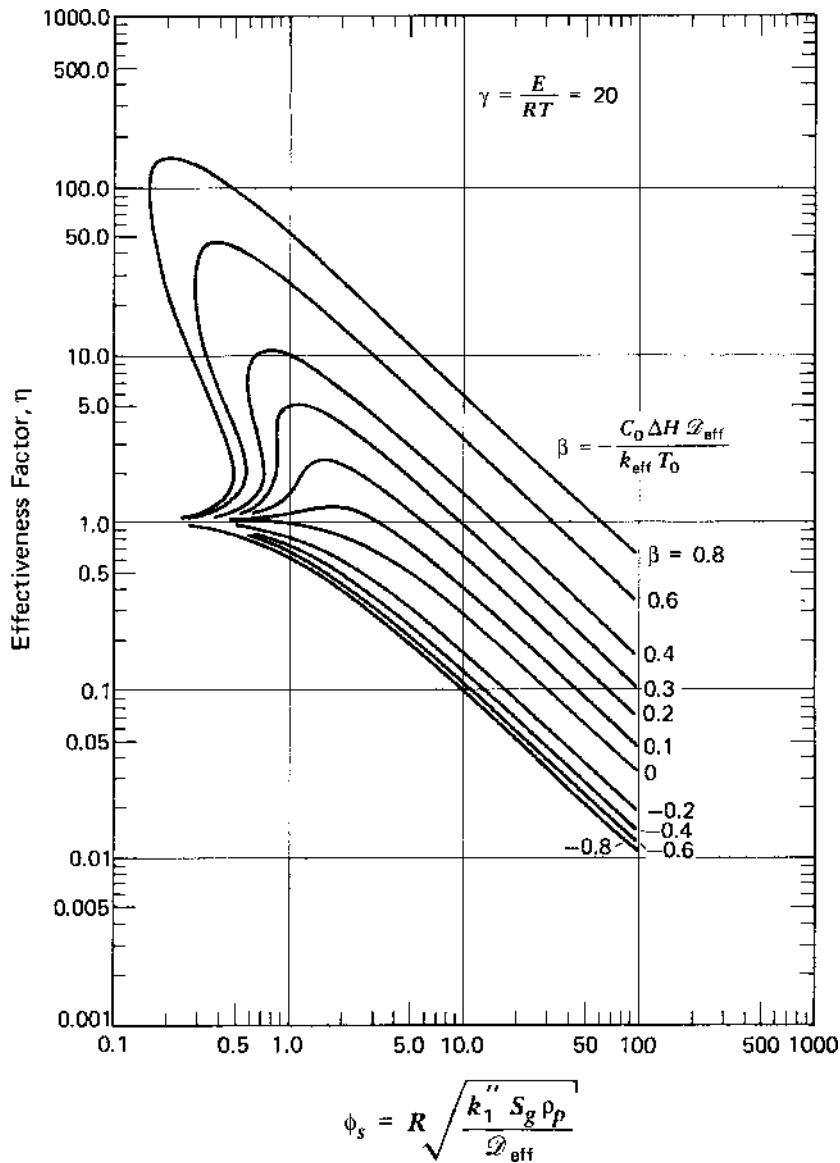


Figure 1.5 Effectiveness factor of gas-phase heterogeneous catalytic reactions.

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. 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 several categories, according to the changes that the solid particle undergoes during the reaction [1, 7, 9, 23]:

1. *Shrinking Particle* This occurs when the particle consists entirely of the solid reactant, and the reaction does not generate any solid products. 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* This occurs when one of the 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* This 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 covered 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* This occurs when the solid reactant is in a porous particle. The gaseous reactant penetrates through pores 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 the cases described above, the global reaction rate depends on three factors: (i) the rate the fluid reactant is transported from the bulk to the outer surface of the particle, (ii) the rate the fluid reactant diffuses through the porous solid (ash or particle) to the surface of the unreacted core, and (iii) the reaction rate. The global reaction rate is usually expressed in terms of 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, 7, 9, 23].

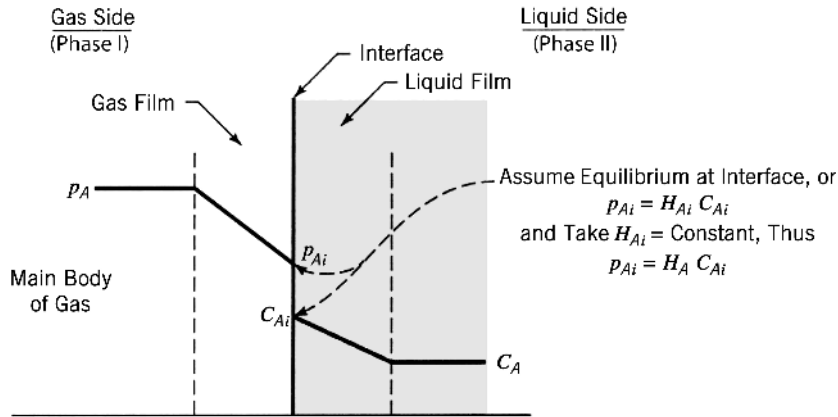


Figure 1.6 Two films presentation of fluid–fluid reactions.

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 are usually described by the two-film model, shown schematically in Figure 1.6. Consider reactant A is in phase I, reactant B is in phase II, and the reaction occurs in phase II. The overall rate of the reaction depends on the following factors: (i) the rate at which reactant A is transferred to the interface, (ii) the solubility of reactant A in phase II, (iii) the diffusion rate of the reactant A in phase II, (iv) the reaction rate, and (v) the diffusion rate of reactant B in phase II. Different situations may develop, depending on the relative magnitude of these factors, and on the form of the rate expression of the chemical reaction. 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: (i) by a diffusion equation (Fick's law) and/or (ii) a mass-transfer coefficient (transport through a film resistance) [7, 9]. The dimensionless modulus is called the Hatta number (sometimes it is also referred to as the Damkohler number), and it is defined by

$$\text{Ha}^2 = \frac{\text{Maximum reaction rate in the film}}{\text{Maximum transport rate through the film}} \quad (1.3.5)$$

For second-order reactions (first order with respect to each reactant), the Hatta number is calculated in one of two ways, depending on the available parameters [7, 9]:

$$\text{Ha} = L \sqrt{\frac{k C_B}{D}} = \sqrt{\frac{k C_B D}{k_{AII}}} \quad (1.3.6)$$

where k is the reaction rate constant, D is the diffusion coefficient of reactant A in phase II, L is a characteristic length (usually the film thickness), and k_{AII} is the mass-transfer coefficient of reactant A across the film. Fluid–fluid reaction are 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 $Ha < 0.2$, the reaction is slow and takes place throughout phase II [7, 9, 22, 24, 25].

1.3.4 Global Rate Expression

The global rate expression is a mathematical function that expresses the *actual* rate of a chemical reaction per unit volume of the reactor, accounting for *all* the phenomena and mechanisms that take place. Knowledge of the global reaction rate is essential for designing and operating chemical reactors. For most homogeneous chemical reactions, the global rate is the same as the intrinsic kinetic rate. However, for many heterogeneous chemical reactions, a priori determination of the global reaction rate is extremely difficult.

The global reaction rate depends on three factors; (i) chemical kinetics (the intrinsic reaction rate), (ii) the rates that chemical species are transported (transport limitations), and (iii) the interfacial surface per unit volume. Therefore, even when a kinetic-transport model is carefully constructed (using the concepts described above), it is necessary to determine the interfacial surface per unit volume. The interfacial surface depends on the way the two phases are contacted (droplet, bubble, or particle size) and the holdup of each phase in the reactor. All those factors depend on the flow patterns (hydrodynamics) in the reactor, and those are not known a priori. Estimating the global rate expression is one of the most challenging tasks in chemical reaction engineering.

1.3.5 Species Balance Equation and Reactor Design 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. Species balances and the reactor design equations are discussed in detail in Chapter 4. To obtain a complete description of the reactor operation, it is necessary to know the local reaction rates at all points inside the reactor. This is a formidable task that rarely can be carried out. Instead, the reactor operation is described by idealized models that approximate the actual operation. Chapters 5–9 cover the applications of reactor design equations to several ideal reactor configurations that are commonly used.

For flow reactors, the plug-flow and the CSTR models represent two limiting cases. The former represents continuous reactor without any mixing, where the reactant concentrations decrease along the reactor. The latter represents a reactor with complete mixing where the outlet reactant concentration exists throughout

the reactor. 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.

When the behavior of a reactor is not adequately described by one of the idealized models, a more refined 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 [6, 7, 10, 11, 43]. The volume of each zone and the interchanges are parameters determined from the reactor operating data. The advantage of such refined models is that they provide a more detailed representation of the reactor, based on actual operating data. However, their application is limited to existing 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 [40–43]. 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: (i) reliability of predicting the flow patterns, (ii) ease of incorporating of the chemical kinetics and adequacy of the physical and chemical representations, (iii) scale of resolution for the application and numerical accuracy of the solution algorithms, and (iv) skills of the user.

1.3.6 Energy Balance Equation

To express variations of the reactor temperature, we apply the energy balance equation (first law of thermodynamics). Chapter 5 covers in detail the derivation and application of the energy balance equation in reactor design. The applications of the energy balance equation to ideal reactor configurations are covered in Chapters 5–9.

1.3.7 Momentum Balance Equation

In most reaction operations, it is not necessary to use the momentum balance equation. For gas-phase reaction, when the pressure of the reacting fluid varies substantially and it affects the reaction rates, we apply the momentum balance equation to express the pressure variation. This occurs in rare applications (e.g., long tubular reactor with high velocity). The last section of Chapter 7 covers the application of the momentum balance equation for plug-flow reactors.

1.4 COMMON PRACTICES

Inherently, the selection and design of a chemical reactor are made iteratively because, in many instances, the global reaction rates are not known a priori. In

fact, the flow patterns of 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 commonly used practices.

1.4.1 Experimental Reactors

Often the kinetics of the chemical reaction and whether or not the reaction rate is affected by transport limitation are not known a priori. Lab-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). Isothermal operation is achieved by providing a large heat-transfer surface and maintaining the reactor in a constant-temperature bath. 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 determination of reaction rate expression is described in Chapter 6. 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. Short packed beds are used as differential reactors to obtain instantaneous reaction rates. The reaction rate is determined from the design equation, as described in Chapter 7. An experimental CSTR is a convenient tool in determining reaction rate since the reaction rate is directly obtained from the design equation, as discussed in Chapter 8.

The rate expressions of catalytic heterogeneous reactions are generally carried out in flow reactors. When a packed-bed reactor is used (Fig. 1.7*a*), it is necessary to ascertain that a plug-flow behavior is maintained. This is achieved by 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). The tube diameter should not be too large to avoid radial gradient of temperature and concentrations. A spinning basket reactor (Fig. 1.7*b*) is a useful tool for determining the reaction rate of heterogeneous catalytic reactions and the effectiveness factor. At sufficiently high rotation speeds, 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.

When the heat of reaction is not known, experiments are conducted on a well-stirred calorimeter (either batch or continuous). The adiabatic temperature change is measured and the heat of reaction is determined from the energy balance equation.

1.4.2 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

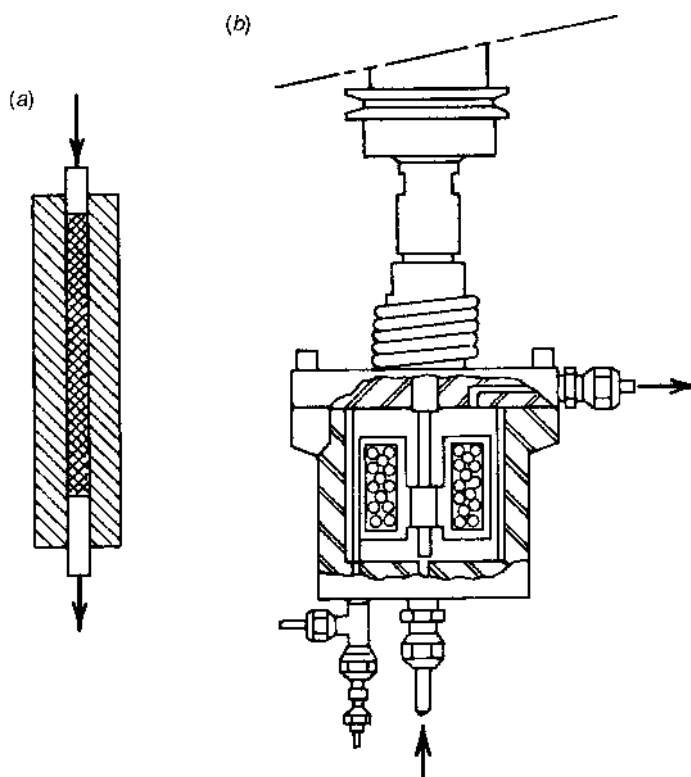


Figure 1.7 Experimental reactors for gas-phase catalytic reactions: (a) packed-bed and (b) spinning basket.

and operational considerations. Batch operations are suitable for small quantity production of high-value products, and for producing multiple products with the same equipment. Batch reactors are also used when the reacting fluid is very viscous (e.g., in the manufacture of polymer resins). Batch operations require downtime between batches for charging, discharging, and cleaning. Another drawback of this operation 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: (i) equilibrium limitation of the desirable reaction, (ii) the formation of undesirable products (by side reactions), and (iii) 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 exhibit 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 required, a fluidized bed is used. 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–solid 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.

1.4.3 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 objective function (e.g., maximizing profit, maximizing product yield or selectivity, minimizing generation of pollutants), as discussed in Chapter 10. When an economic criterion is used, the performance of the entire process (i.e., the reactor, separation system, utilities) is considered rather than the performance of the reactor alone.

1.4.4 Operational Considerations

Considerations should be given to assure that the reactor is operational (i.e., startup and shutdown), controllable, and does not create any safety hazards. Also, chemical reactors can operate at multiple conditions (the design and energy balance equations have multiple solutions), some of them may be unstable. Such situation is illustrated in Figure 1.8, which shows the heat generation and heat removal curves of CSTR with an exothermic reaction [2, 3]. 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 operations. 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,

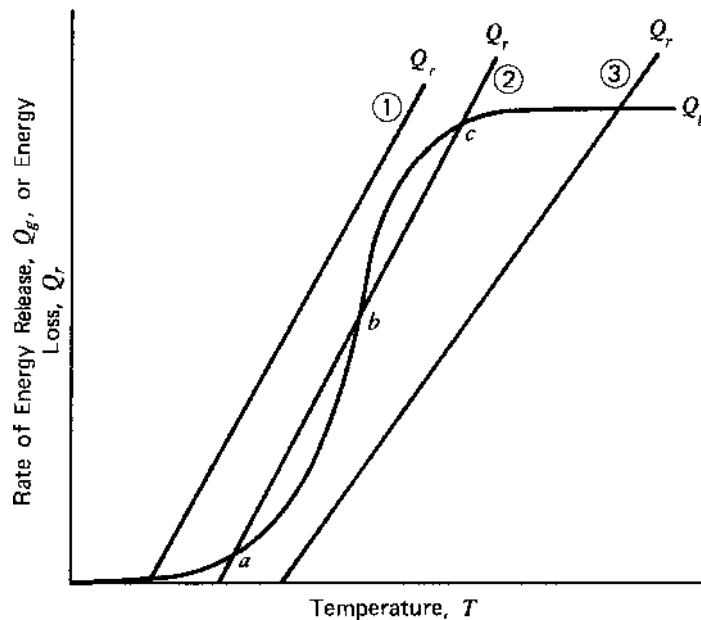


Figure 1.8 Heat generation and removal in CSTR.

which if not relieved may cause an explosion. Experience has shown that the following factors are prevalent in accidents involving chemical reactors: (i) inadequate temperature control, (ii) inadequate agitation, (iii) little knowledge of the reaction chemistry and thermochemistry, and (iv) raw material quality [12, 20].

1.4.5 Scaleup

The objective of scaleup is to design industrial-sized reactors on the basis of experimental data obtained from lab-scale reactors. A reliable scaleup requires insight of the phenomena and mechanisms that affect the performance of the reactor operation. 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 scaleup [37]. For example, it is often impossible to maintain similar flow conditions (e.g., 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 regard to the mechanisms and the magnitude of the parameters. As a result, an experimental investigation on a pilot-scale reactor is conducted to improve the reliability of the design of an industrial-scale reactor.

In many processes that apply to an agitated tank, the main task is to maintain sufficient mixing during scaleup. Considerable information is available in the literature on scaling up of agitated tanks [30–36].

1.4.6 Diagnostic Methods

In practice, especially in large-scale reactors, plug-flow or complete mixing are rarely achieved, and it is desirable to quantify the deviation from those 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 residence time distribution (RTD) in the reactor. An inert tracer 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 reacting fluid in the reactor can be constructed [1, 7, 10, 43].

The measured mean residence time and shape of the RTD curve provide valuable information on the flow of the reacting fluid in 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:

$$\bar{t} = \frac{V}{v} \quad (1.4.1)$$

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 indicates that a stagnant zone (not available to the flowing fluid) exists in the reactor. In heterogeneous fluid–fluid reactors, measuring the mean residence time of each fluid provides the holdup of each in the reactor. Comparing the RTD curve to that of CSTR and plug-flow reactor 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 (micromixing) and one that flows in segregated blobs. Also, the same RTD is obtained when the reacting fluid is mixed near the entrance or near the exit. Both of these factors affect the chemical reactions and the performance of the reactor.

1.5 INDUSTRIAL REACTORS

Figure 1.9 shows the structures of two industrial reactors used to produce two of the largest volume chemicals. Figure 1.9*a* shows the internals of an ammonia converter, and Figure 1.9*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

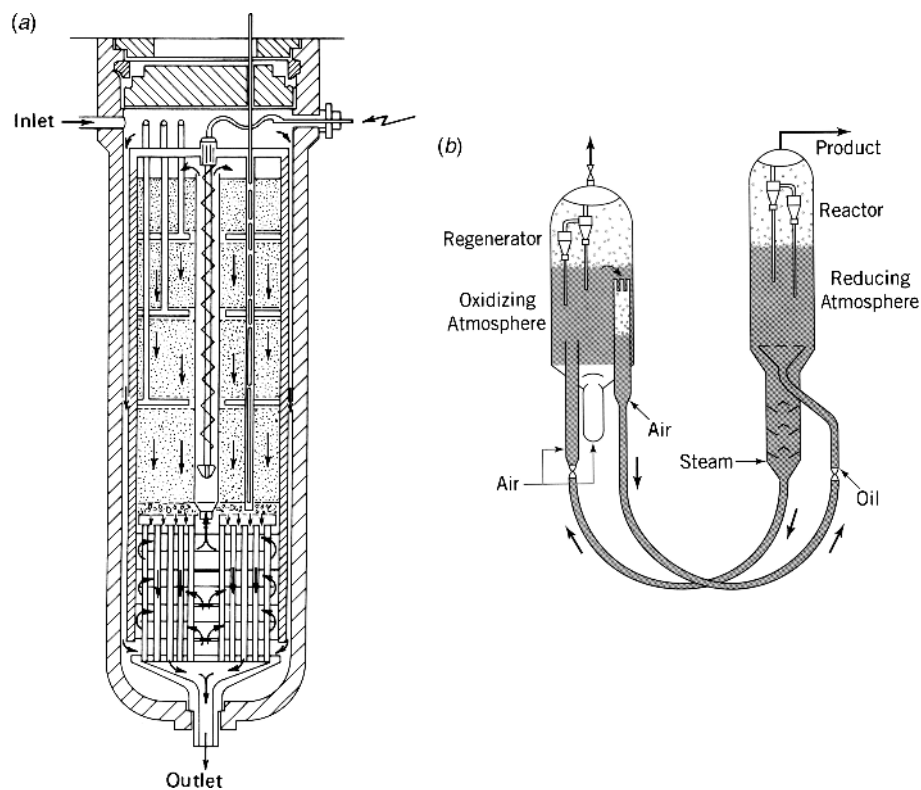


Figure 1.9 Industrial reactors: (a) ammonia reactor and (b) fluidized-bed catalytic cracking reactor.

reaction is reversible, an increase in the temperature limits the conversion (equilibrium limited). The intricate reactor was designed to provide efficient heat transfer and to use some of the heat of reaction to heat 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 during the combustion of the carbon is carried with the hot particles to the cracking reactor; hence, the circulating particles provide the heat for the endothermic cracking reaction.

1.6 SUMMARY

The objective of this chapter was to describe the diversity and complexity of chemical reactor operations and to provide an overview of the phenomena encountered,

and the concepts used to describe them. The chapter attempts to convey three points:

1. The difficulty in obtaining a global reaction rate expression—an expression that accounts for both intrinsic kinetics and transport effects.
2. The inherent difficulty in designing chemical reactors, which is due to two factors: (i) Global reaction rates depend on the local flow conditions, which are not known a priori, and (ii) even when the global reaction rate expressions are known, solving the reactor design equations is a formidable task that rarely can be performed in the design exercise.
3. Approximate engineering approaches are successfully employed (using ideal reactor models) to estimate the reactor operations and guesstimate the limits of its performance.

This volume describes a methodology to describe the operations ideal chemical reactor.

REFERENCES

Additional discussions of chemical reactor design can be found in:

1. G. F. Froment and K. B. Bischoff, *Chemical Reactor Analysis and Design*, 2nd ed., Wiley, New York, 1990.
2. K. G. Denbigh and J. C. R. Turner, *Chemical Reactor Theory*, Cambridge University Press, New York, 1971.
3. C. G. Hill, *An Introduction to Chemical Engineering Kinetics and Reactor Design*, Wiley, New York, 1977.
4. L. D. Schmidt, *The Engineering of Chemical Reactions*, 2nd ed., Oxford University Press, New York, 2005.
5. M. E. Davis and R. J. Davis, *Fundamentals of Chemical Reaction Engineering*, McGraw-Hill, New York, 2003.
6. K. R. Westerterp, W. P. M. van Swaaij, and A. A. C. M. Beenackers, *Chemical Reactor Design and Operation*, 2nd ed., Wiley, New York, 1988.
7. O. Levenspiel, *Chemical Reaction Engineering*, 3rd ed., Wiley, New York, 1999.
8. H. S. Fogler, *Elements of Chemical Reaction Engineering*, 4th ed., Prentice-Hall, Englewood Cliffs, NJ, 2005.
9. R. W. Missen, C. A. Mims, and B. A. Saville, *Introduction to Chemical Reaction Engineering and Kinetics*, Wiley, New York, 1999.
10. E. B. Numan, *Chemical Reactor Design, Optimization, and Scale-up*, McGraw-Hill, New York, 2002.
11. M. Baerns, H. Hofmann, and A. Renken, *Chemische Reaktionstechnik*, Thieme, Stuttgart, 1999.
12. A. K. Coker, *Modeling of Chemical Kinetics and Reactor Design*, Butterworth-Heinemann, Boston, 2001.

13. L. K. Doraiswamy and M. M. Sharma, *Heterogeneous Reactions, Analyses, Examples and Reactor Design, Vol. 2, Fluid–Fluid Solid Reactions*, Wiley, New York, 1984.

More detailed treatments of chemical kinetics, reaction mechanisms, catalysis, and the theoretical basis for the rate expression can be found in:

14. R. M. Masel, *Chemical Kinetics and Catalysis*, Wiley Interscience, Hoboken, NJ, 2001.
15. R. M. Masel, *Principles of Adsorption and Reaction on Solid Surfaces*, Wiley, New York, 1996.
16. C. H. Bartholomew and R. J. Farrauto, *Fundamentals of Industrial Catalytic Processes*, Wiley Interscience, Hoboken, NJ, 2006.
17. B. C. Gates, *Catalytic Chemistry*, Wiley, New York, 1992.
18. B. C. Gates, J. R. Katzer, and G. C. A. Schuit, *Chemistry of Catalytic Processes*, McGraw-Hill, New York, 1979.
19. K. J. Laidler, *Chemical Kinetics*, 3rd ed., Harper & Row, New York, 1987.
20. J. Barton and R. Rodgers, eds., *Chemical Reaction Hazards*, Institution of Chemical Engineers, Rugby, Warwickshire, UK, 1993.

More detailed treatments of multi-phase reactions can be found in:

21. H. H. Lee, *Heterogeneous Reactor Design*, Butterworth, Boston, 1985.
22. P. V. Danckwerts, *Gas-Liquid Reactions*, McGraw-Hill, New York, 1970.
23. J. Szekeley, J. W. Evans, and H. Y. Sohn, *Gas-Solid Reactions*, Academic, New York, 1976.
24. Y. T. Shah, *Gas–Liquid–Solid Reactor Design*, McGraw-Hill, New York, 1979.
25. L. S. Fan and K. Tsuchiya, *Bubble Wake Dynamics in Liquids and Liquid–Solid Suspensions*, Butterworth-Heinemann, Boston, 1990.

More detailed treatments of transport phenomena and their effects on chemical reactions can be found in:

26. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, 2nd ed., Wiley, Hoboken, NJ, 2002.
27. J. R. Welty, C. E. Wicks, and R. E. Wilson, *Fundamentals of Momentum Heat and Mass Transfer*, 2nd ed., Wiley, New York, 1984.
28. G. Astarita, *Mass Transfer with Chemical Reaction*, Elsevier, Amsterdam, 1967.
29. L. A. Belfiore, *Transport Phenomena for Chemical Reactor Design*, Wiley Interscience, Hoboken, NJ, 2003.

More detailed treatments of mixing technology and scale-up can be found in:

30. J. Y. Oldshue, *Fluid Mixing Technology*, McGraw-Hill, New York, 1983.
31. M. Zloknic, *Stirring: Theory and Practice*, Wiley-VCH, Hoboken, NJ, 2001.
32. E. L. Paul, V. Atiemo-Oberg, and S. M. Kresta, eds., *Handbook of Industrial Mixing: Science and Practice*, Wiley Interscience, Hoboken, NJ, 2003.
33. N. Harnby, M. F. Edward, and A. W. Nienow, *Mixing in the Process Industry*, Butterworth-Heinemann, Boston, 1997.

34. G. B. Tatterson, *Fluid Mixing and Gas Dispersion in Agitated Tanks*, McGraw-Hill, New York, 1991.
35. J. J. Ulbrecht, *Mixing of Liquids by Mechanical Agitation*, Taylor & Francis, Boston, 1985.
36. A. Bisio and R. L. Kabel, *Scaleup of Chemical Processes*, Wiley, New York, 1985.

More detailed treatments of fluidization technology can be found in:

37. D. Kunii and O. Levenspiel, *Fluidization Engineering*, 2nd ed., Butterworth-Heinemann, Boston, 1991.
38. J. G. Yates, *Fundamentals of Fluidized-Bed Chemical Processes*, Butterworth, London, New York, 1983.
39. J. F. Davidson and D. Harrison, *Fluidised Particles*, Cambridge University Press, New York, 1963.

More detailed treatments of computational fluid dynamics and modeling of low systems can be found in:

40. V. V. Ranade, *Computational Flow Modeling for Chemical Reactor Engineering (Process Systems Engineering)*, Academic, New York, 2001.
41. R. V. A. Oliemans, ed., *Computational Fluid Dynamics for the Petrochemical Process Industry*, Kluwer Academic, The Netherlands, 1991.
42. R. J. Kee, *Chemically Reacting Flow*, Wiley Interscience, Hoboken, NJ, 2003.
43. C. Y. Wen and L. T. Fan, *Models for Flow Systems and Chemical Reactors*, Marcel Dekker, New York, 1975.