

CHAPTER 1

Catalytic reactor types and their industrial significance

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Abstract

The present chapter is aimed to provide a simplified overview of the catalytic reactors used in chemical industry. Each reactor type is described in terms of its key geometric properties, operating characteristics, advantages, and drawbacks among its alternatives and typical areas of use. The significance of the reactors is explained in the context of selected industrial examples. Industrial reactors that do not involve the use of solid catalysts are also discussed.

1.1 Introduction

Today's chemical markets involve many different products with diverse physical and chemical properties. These products are produced in chemical plants with different architectures and characteristics. Despite these differences, general structure of a chemical plant can be described by three main groups of unit operations, namely, upstream operations, downstream operations, and the reaction section, as shown in Figure 1.1. Among these groups, the reactor is the most critical section that determines the plant profitability via metrics such as reactant conversion, product selectivity, and yield: high per-pass conversions will reduce the operating expenses involved in product separation and purification steps as well as the recycling costs (Figure 1.1). At this stage selection of the appropriate reactor type and ensuring their efficient operation become critical issues to be addressed.

In almost all reactors running in the chemical industry, the desired product throughput and quality are provided by catalysts, the functional materials that allow chemical synthesis to be carried out at economic scales by increasing the reaction rates. Owing to this critical feature, more than 98% of the today's industrial chemistry is involved with catalysis. Since catalysts have direct impact on reactor performance, they have to be operated at their highest possible effectiveness, which is determined by the degree of internal and external heat and mass transport resistances defined and explained in detail in Chapter 2. At this stage, the function of the reactor is to provide

conditions such that the catalyst particles can deliver the best possible performance (e.g., activity, selectivity, yield) at sufficient stability. For example, for a highly exothermic reaction system such as Fischer–Tropsch (FT) synthesis, heat transport/removal rates within the reactor should be very high to prevent undesired temperature elevations that can negatively affect product distribution and, more importantly, cause thermally induced deactivation of the catalysts. Considering the fact that transport rates are favored by good mixing of the reactive fluid at turbulent conditions, the selected reactor type should allow a wide operating window in terms of pressure drop, which is a limit against the occurrence of well-mixed conditions. The possibility of integration and operation of effective external heat exchange systems should also be taken into account in the selected reactor type. The final selection is carried out in the context of fixed capital investment, operating expenses, and profitability of the technically feasible solutions.

Synthesis of commercial chemical products having different physical and chemical functional properties involves the existence of different combinations of catalytic chemistry, thermodynamic properties, and heat and mass transport conditions (e.g., nature of the catalyst and fluids) within the reactor volume. As a result, several reactor types are being proposed. Classification of the reactors can be carried out based on various criteria such as compatibility with the operating mode (batch vs. continuous reactors) and the number of phases (homogeneous vs. heterogeneous reactors). In this chapter, reactors are classified according to the position of the catalyst bed, that is, whether it is fixed or mobile. In packed-bed, trickle-bed, and structured (i.e., monolith and micro-channel) reactors, catalyst bed is fixed, while it is mobile in fluidized-bed, moving-bed, and slurry reactors. The descriptions of these reactor types are summarized in the following sections.

1.2 Reactors with fixed bed of catalysts

1.2.1 Packed-bed reactors

In packed-bed reactors (PBRs), the solid particulate catalyst particles forming the bed are fixed in an enclosed volume. The

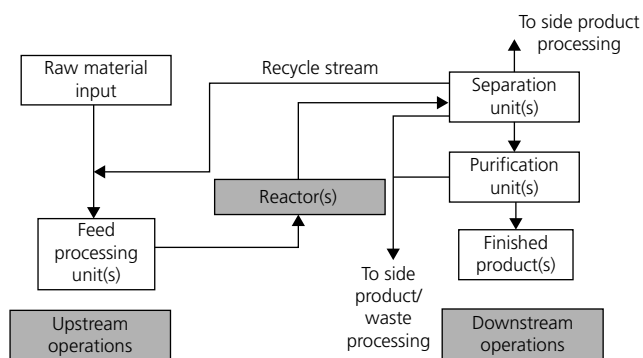


Figure 1.1 Outline of a chemical process.

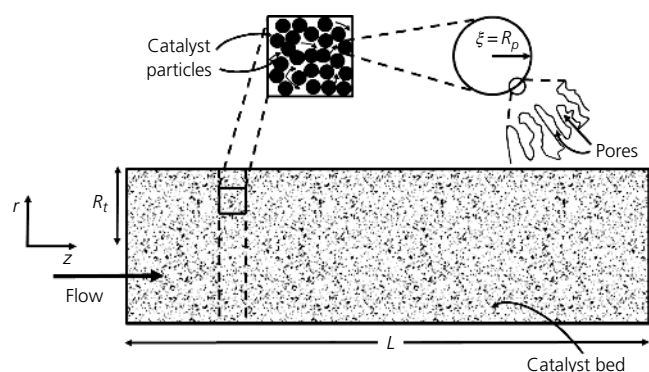


Figure 1.2 Schematic presentation of a packed-bed reactor. (Source: Onsan and Avci [1]. Reproduced with permission of Elsevier.)

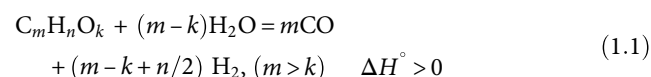
particles are randomly packed, so there is not a regular structure, and, as a result, fluid flow takes place through irregular, random paths. Reactions take place over the active sites that are buried within the pores of the catalyst particles. A simple description of the PBR operation is shown in Figure 1.2 [1]. Owing to their relatively simple configuration and operation, PBRs are widely used in the chemical industry. They are used in high-throughput, continuous operations. Since the catalyst is considered as a separate solid phase and the fluid types are either gas only or gas-liquid mixtures, PBRs are classified as heterogeneous reactors. In the case of coexistence of three phases with concurrent down-flow of liquid and gas over the solid packing, the reactor is called as a trickle-bed reactor (see Section 1.2.4). The geometry of the catalyst-containing volume, which can be either a tube or a vessel, dictates the type of the PBR. Descriptions of the so-called tubular and vessel-type PBRs are given later.

1.2.1.1 Tubular PBRs

PBRs are known to have inherently weak heat transfer properties due to the presence of voids within the catalyst bed (Figure 1.2 [1]) that act as resistances against the transport of heat along the reactor. The tubular PBR geometry, which involves the location of catalyst-containing tubes in a particular pattern within a shell, is preferred over a regular vessel when high rates of heat input or removal are essential for highly

endothermic or exothermic reactions, respectively. This advantage of the tubular configuration, however, comes at the expense of higher pressure drop. It is also worth noting that the process of catalyst packing and unloading in tubular geometry is more difficult than that involved in vessels. Therefore, catalyst lifetime in tubular PBRs should be long enough to minimize the downtimes for and costs associated with catalyst changeover.

The shell/tube configuration of tubular PBRs depends on the nature of the catalytic reaction. For highly endothermic reactions such as catalytic steam reforming, the reactor geometry is similar to that of a fired furnace in which the catalyst-packed tubes are heated by the energy released by the combustion of a fuel on the shell side. Catalytic steam reforming involves the conversion of a hydrocarbon to a hydrogen-rich mixture in the presence of steam:



The process is known as the conventional method of producing hydrogen for meeting the hydrogen demands of the refining and petrochemical industry. The most widely used fuel in steam reforming is natural gas, which is mostly composed of methane:



Methane steam reforming is conventionally carried out over Ni-based catalysts. Owing to the high endothermicity and slow kinetics, the process depends strongly on the input of external energy at high rates for ensuring commercially viable throughput of hydrogen. The critical energy demand of the reaction is met in a reactor (also called as the reformer) where multiple Ni-based catalyst-packed tubes are heated mainly via radiative heat generated by homogeneous combustion of a fuel, typically natural gas, in a process furnace. This configuration sets the basis for the development and use of various types of commercial steam reforming reactors described in Figure 1.3 [2], which differ in the positions of heat source and the degree of delivery of the combustion energy to the so-called reformer tubes. A further detailed representation of a tubular reformer is provided in Figure 1.4 [2]. Depending on the capacity of the reactor, the number of tubes can be increased up to 1000, each having outer diameter, wall thickness, and heated length ranges of 10–18 cm, 0.8–2.0 cm and 10–14 m, respectively. The degree of furnace-to-tube heat transfer affecting the rate of Reaction 1.2 and hydrogen production capacity of the reactor is limited by thermal stability of the tube material which is found to decrease significantly with temperature above ca. 850°C [3]. Therefore special alloys, particularly microalloys, composed of 25Cr 35Ni Nb Ti are used to improve the operating window of the reactor [3].

The multitubular PBR configuration is preferred when convection is not sufficient for delivering the necessary heat flux to sustain the operation. However, in most of the exothermic and endothermic reactions, the temperature of the catalyst bed can be regulated by convective external heat transfer. In

Figure 1.3 Furnace configurations for multitubular packed-bed reformers. (Source: Dybkjaer [2]. Reproduced with permission of Elsevier.)

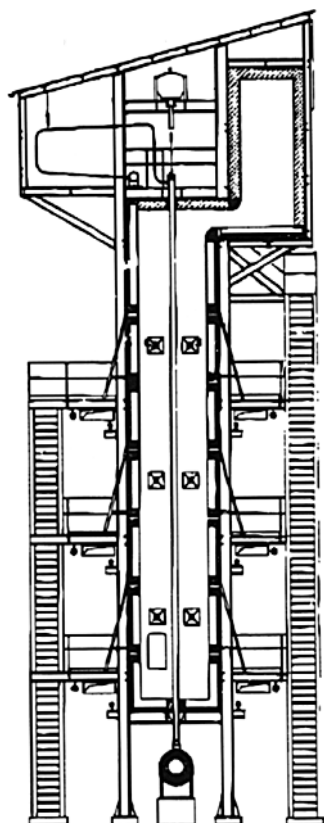
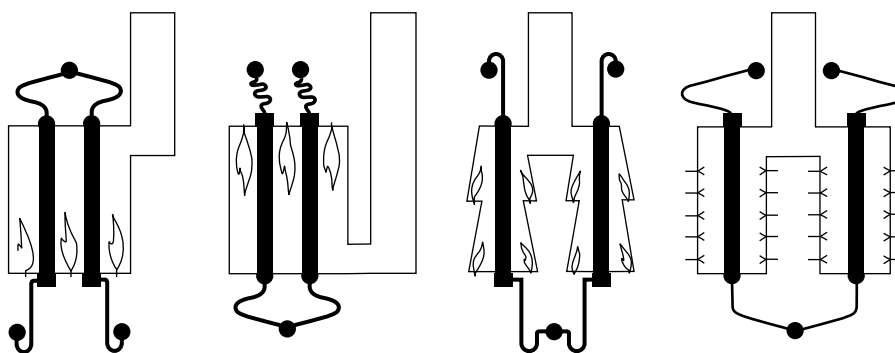


Figure 1.4 Side-fired tubular reformer design by Haldor-Topsøe. (Source: Dybkjaer [2]. Reproduced with permission of Elsevier.)

such cases, the catalyst-containing tubes are bundled in a shell-and-tube heat exchanger like configuration involving circulation of the heat transfer fluid on the shell side. This PBR concept is described in Figure 1.5 [4] in which alternative methods of circulation of the heat transfer fluid around the packed tubes are introduced. In mildly endothermic or exothermic reactions, heat transfer can be realized to provide nearly isothermal conditions in cross-flow and parallel flow configurations shown in Figure 1.5a and b [4], respectively. In such reactors, inside diameters and lengths of the tubes are reported to vary between 2–8 cm and 0.5–15 m, respectively [4]. For endothermic cases, the heating medium can be a gas or a liquid, with the latter

offering better heat transfer rates due to higher convective heat transfer coefficients of liquids. Cooling in exothermic reactions is carried out either by circulation of a heat transfer fluid or by boiling heat transfer. In the former case, fluids such as molten salts are force-circulated around the tube bundle. The heated liquid leaving the reactor is then passed through an external steam generator and cooled for the next cycle. In the case of boiling heat transfer (Figure 1.5c [4]), however, the cooling fluid that is fed from the bottom of the reactor rises up due to natural circulation induced by the decreasing density profile that is caused by continuous heat absorption from the tubes. Partial evaporation of the cooling water is also observed. Vapor bubbles agitate the liquid and increase the convective heat transfer coefficient. The resulting vapor–liquid mixture is then let to settle in a steam drum where steam is separated, and the remaining liquid sent back to the cooling cycle together with some makeup water. Even though this configuration eliminates the need for cooling fluid transportation equipment, the tubes may be overheated if heat generation in the tubes becomes excessive to evaporate cooling water on the shell side. In such a case, the rate of convective heat removal will be less than the rate of catalytic heat generation, and the tubes are subjected to the risk of burning out.

In multitubular PBRs heat management can be improved by increasing the heat transfer area per catalyst volume, which is possible by using tubes with smaller diameters. In this case, definite amounts of catalyst will be packed into a higher number of tubes, which will offer increased external tube surface area for heat transfer. Due to the reduced tube cross-sectional area, smaller tube diameters will also increase the linear flow rate of the reactive mixture and favor well-mixed conditions that increase the heat transport rates. However, these advantages are naturally limited by pressure drop, as higher flow rates will cause increased frictional loss of mechanical energy of the reactive fluid and will require increased pumping/compression costs. Nevertheless, the trade-off between heat transfer rates and pressure drop can be relaxed by the possibility of using different combinations of size, shape, and material of the catalyst pellets [4, 5]. For example, pellet shapes offering higher void fractions and larger hydraulic diameters allow lower pressure drop operations. It is worth noting that the rate of catalytic reactions increases with the surface area of the catalyst bed that necessitates the use of smaller pellets. Therefore pellet size also requires careful optimization.

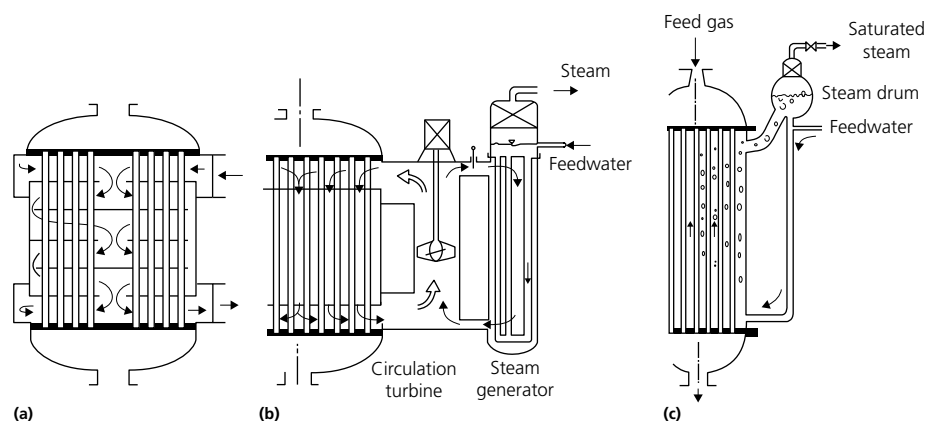


Figure 1.5 Heat transfer strategies in multitubular packed-bed reactors. (a) Cross-flow, (b) parallel flow, and (c) boiling-water cooling. (Source: Eigenberger [4]. Reproduced with permission of John Wiley & Sons, Inc.)

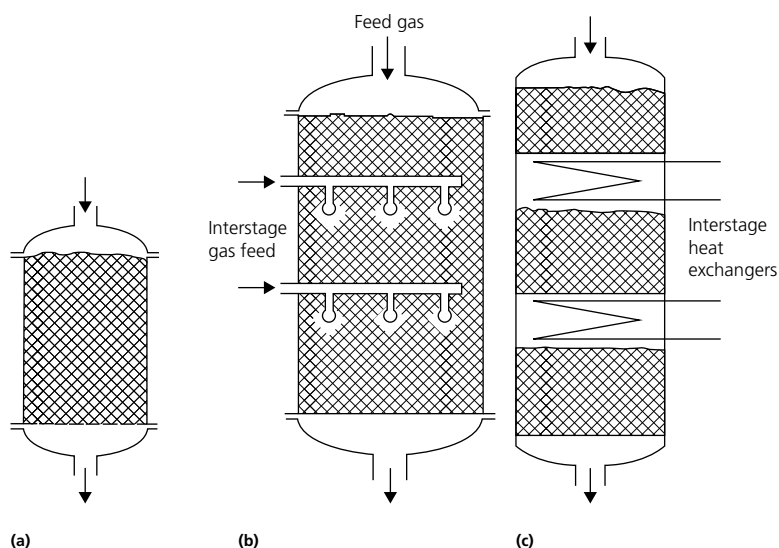


Figure 1.6 Various configurations of vessel-type packed-bed reactors. (a) Single-bed adiabatic packed-bed reactor, (b) adiabatic reactor with interstage gas injection, and (c) multiple adiabatic beds with interstage heat exchange. (Source: Eigenberger [4]. Reproduced with permission of John Wiley & Sons, Inc.)

The length and diameter of the tube and the particle size (hydraulic diameter) also affect flow distribution within the packed tube. If the ratio of the tube diameter to that of the particle diameter is above 30, radial variations in velocity can be neglected, and plug (piston) flow behavior can be assumed. The ratio of the tube length to particle diameter is also important; if this ratio exceeds 50, axial dispersion and axial heat conduction effects can be ignored. These effects bring notable simplifications into the modeling of PBRs, which are discussed in Chapter 3.

1.2.1.2 Vessel-type PBRs

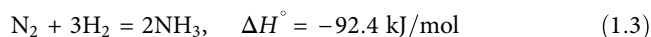
The design and operational requirements explained for tubular PBRs are also valid for PBRs in which the catalyst bed is packed in one vessel as described schematically in Figure 1.6a [4]. This reactor configuration is preferred when the reaction is carried out at adiabatic conditions. However, as demonstrated in Figure 1.6b and c [4], bed temperature can be changed by heat addition to/removal from the bed for obtaining a temperature

profile as close as possible to that of the optimum. Figure 1.6b [4] is a representation of addition or removal of heat to/from the catalyst bed by direct injection of hot or cold feed to the bed. This heat management strategy can be used where the heats of reactions are low. Successful implementation of this strategy depends on careful consideration of mixing and redistribution of the injected fluid with that of the reactive mixture and of the adiabatic temperature change upon injection, which should be within acceptable limits. A better regulation of the bed temperature is possible by the use of interstage heat exchangers between multiple adiabatic beds (Figure 1.6c [4]). This configuration is more suitable for improving conversions or product selectivities in reactions limited by chemical equilibrium. The possibility of using different heat exchange equipment between the stages helps in handling high reaction enthalpies. For endothermic reactions, interstage heating is usually carried out by means of fired heating, in which the heat transfer fluid is heated in a fired furnace and then circulated between the beds to provide heat to the reactive fluid. Adiabatic heat generated during

exothermic reactions is removed by contacting the hot bed effluent with interstage heat exchange tubes in which a coolant, for example, water, is circulated for steam generation purposes.

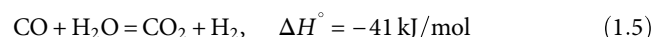
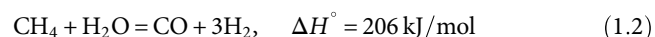
Multiple adiabatic beds with interstage heat exchange configuration compete with tubular PBR geometry, as both configurations provide regulation of the bed temperature to improve reactant conversion and product selectivity. In this respect, the tubular PBR alternative is better, because it offers continuous control over the bed temperature. However, although temperature regulation is only possible through a stepwise pattern in the multiple adiabatic beds, they do offer several practical advantages such as the possibility of (i) changing the catalyst bed in individual stages at different times, (ii) distributed stagewise feeding of a reactant instead of its total feeding at the inlet, and (iii) drawing a limiting product from an intermediate stage in case of reactions limited by equilibrium [4, 5].

Vessel-type PBRs are widely used in chemical industry. A descriptive example is ammonia synthesis, which is an exothermic equilibrium reaction:



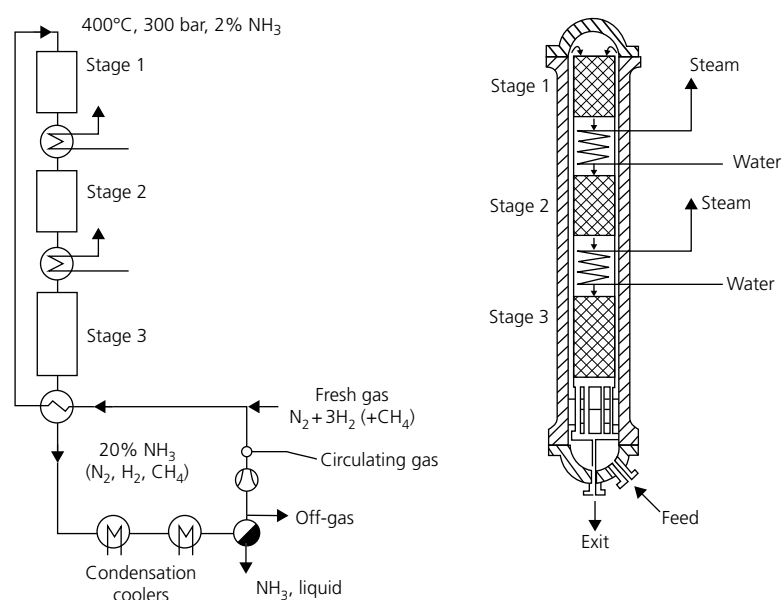
The reaction is carried out in a multistage PBR with interstage cooling (Figure 1.7 [4]) in the 400–500°C range and involves the use of iron-based catalysts. In order to favor ammonia production by shifting the chemical equilibrium to the product side, pressures up to 300 bar are required. As adiabatic temperature rise hinders conversion due to the equilibrium limit, the reactive mixture is cooled down between the beds, and the recovered heat is used for steam generation. The resulting conditions deliver a product mixture including ca. 20% NH_3 which is separated by a series of condensers. Upon separation, unreacted mixture of N_2 and H_2 is combined with fresh makeup feed and recycled to the first stage of the reactor.

Another commercial example involving the use of a vessel-type PBR is autothermal reforming (ATR) of natural gas. It is a key step in gas-to-liquid (GTL) processes and is used to produce synthesis gas ($\text{CO} + \text{H}_2$) for FT synthesis in which a mixture of hydrocarbons in the $\text{C}_1\text{--C}_{30+}$ range is synthesized [6]. In ATR, noncatalytic oxidation (Reaction 1.4) and Ni-catalyzed steam reforming of natural gas (Reaction 1.2) are combined, and product distribution is affected by water-gas shift (Reaction 1.5), an important side reaction of steam reforming [3, 7]:



ATR is carried out in an adiabatic PBR as described in Figure 1.8 [7]. Natural gas, steam, and oxygen (or enriched air) are cofed to a mixer-burner unit for ensuring combustion of the homogeneous mixture of reactants taking place in the combustion chamber. Heat produced in the combustion zone, where temperature can be well above ca. 1500°C, is then transferred to the Ni-based catalyst bed on which Reactions 1.2 and 1.5 take place to produce a mixture of H_2 and CO at molar ratios close to 2 at temperatures above ca. 1000°C and at pressures up to ca. 30 bar [3, 7]. Success of the reactor depends on keeping the exothermic heat within the vessel, that is, operating the reactor adiabatically. For this purpose, the inner wall of the steel pressure vessel is lined with multiple layers of refractory insulation. A special catalyst pellet shape including numerous holes is used to minimize pressure drop along the bed and to avoid bypass of gas through the refractory layer.

Figure 1.7 Packed-bed reactor with multiple adiabatic beds for ammonia synthesis.
(Source: Eigenberger [4]. Reproduced with permission of John Wiley & Sons, Inc.)



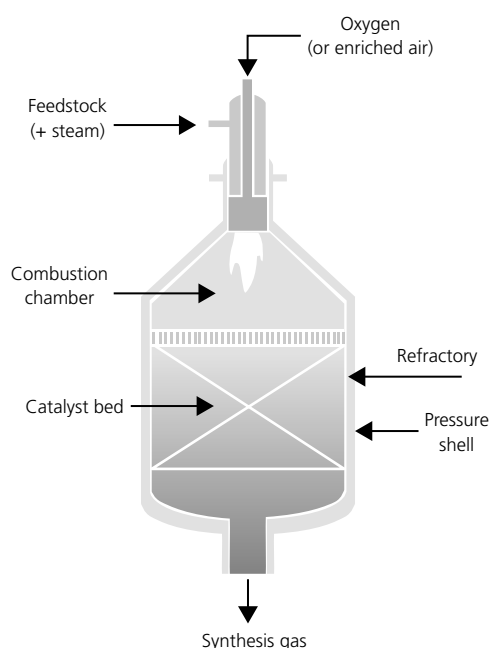


Figure 1.8 Packed-bed reactor configuration for autothermal reforming of methane to synthesis gas.
(Source: Aasberg-Petersen et al. [7]. Reproduced with permission of Elsevier.)

1.2.2 Monolith reactors

Monolith reactors are composed of a large number of parallel channels, all of which contain catalyst coated on their inner walls (Figure 1.9 [1]). Depending on the porosity of the monolith structure, active metals can be dispersed directly onto the inner channel walls, or the catalyst can be washcoated as a separate layer with a definite thickness. In this respect, monolith reactors can be classified among PBR types. However, their characteristic properties are notably different from those of the PBRs presented in Section 1.2.1. Monolith reactors offer structured, well-defined flow paths for the reactive flow, which occurs through random paths in PBRs. In other words, the residence time of the reactive flow is predictable, and the residence time distribution is narrow in monoliths, whereas in a PBR, different elements of the reactive mixture can pass through the bed at different rates, resulting in a wider distribution of residence times. This is a situation that is crucial for reactions where an intermediate species is the desired product and has to be removed from the reactor before it is converted into an undesired species.

Hydraulic diameters of monolithic channels range between ca. 3×10^{-4} m and 6×10^{-3} m [8]. Combination of such small diameter channels leads to surface areas per reactor volume in the order of $\sim 10^4$ m²/m³ (which is $\sim 10^3$ m²/m³ for PBRs) and void fractions up to $\sim 75\%$ (which is $\sim 40\%$ for PBRs). As shown in Figure 1.10 [9], these design properties allow monolith reactors to operate with pressure drops that are up to three orders of magnitude less than those observed in PBRs.

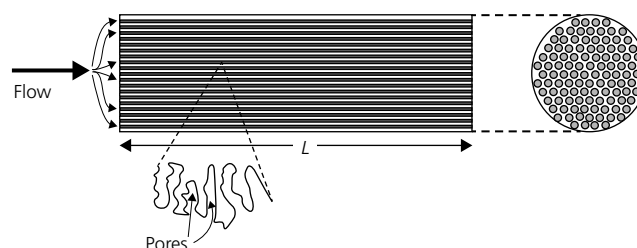


Figure 1.9 Schematic presentation of a monolith reactor.
(Source: Onsan and Avci [1]. Reproduced with permission of Elsevier.)

Monolith reactors differ from PBRs in terms of transport properties. Owing to the small channel diameters, the flow regime is laminar. In this case, channel shape and diameter dictate the values of heat and mass transfer coefficients according to the definitions of the Nusselt ($Nu = h_f d_h / \lambda_f$) and Sherwood ($Sh = k_g d_h / D_{AB}$) numbers, respectively. Assuming that the flow is fully developed, values of Nu and Sh are constant for a given channel shape [10]. However, in the case of PBRs, where turbulent flow conditions are valid, transport coefficients improve with the degree of turbulence and mixing within the reactor. It is worth noting that transport coefficients in monolith channels can be slightly affected by the flow rate if the surface of the channel is tortuous. The reader is directed to Chapter 8 for a detailed analysis and discussion of monolith reactors.

Heat management in monolith reactors via external heating or cooling is not as effective as in PBRs due to lack of convective heat transport in the radial direction. At this point, the material of construction of the monolithic structure affects the overall performance. Monolith reactors can be made of metals or ceramics. In case of nonadiabatic reactions, metallic monoliths are preferred due to their higher thermal conductivity which partially eliminates the lacking convective contribution. Ceramic monoliths, on the other hand, have very low thermal conductivities (e.g., 3 W/m.K for cordierite [11]) and are suitable for use in adiabatic operations.

Despite their notable advantages in terms of residence time distribution and pressure drop, the operating windows of monolith reactors are narrower than those of PBRs. As the catalyst is integrated to the monolithic structure, replacement of the catalyst bed in case of its irreversible deactivation becomes a serious issue. Moreover, small channels are subject to the risk of plugging either by the dirt and scale that can come together with the feed stream or by phenomena such as coking that may occur during reactions involving hydrocarbons conducted at high temperatures. In such as case, flow distribution and residence time in the channels will be disturbed, and product distribution will be adversely affected. Prevention of these risks is possible by careful selection and control of the operating conditions, which in turn put some limitations on the versatility of using monolith reactors.

The capability of offering high surface area-to-volume ratios together with low pressure drop makes monolith reactors the

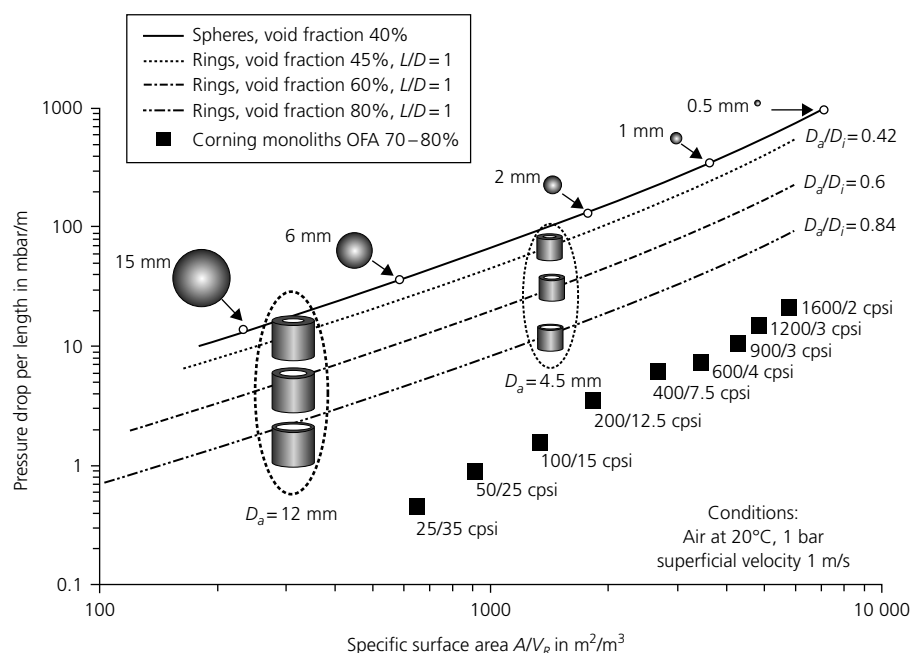


Figure 1.10 Comparison of pressure drop in various configurations of monoliths and packing structures. (Source: Boger et al. [9]. Reproduced with permission of American Chemical Society.)

unique choice for use as three-way catalytic converters in vehicles to regulate the emission levels. The compact nature of the monolithic catalytic converters allows their integration into the exhaust gas aftertreatment zone of the vehicles. These converters involve washcoated layers of precious metal catalysts that are capable of reducing the NO_x , CO, and unburned hydrocarbon content of the exhaust gas below the legislative limits. Apart from vehicular use, monolith reactors are also used in NO_x removal from flue gases in power stations because of their capability of providing adiabatic conditions with low pressure drop. It is worth noting that monolith reactors are not limited for use only in gas-phase reactions and can also be used for handling gas-liquid-type reactive mixtures [10].

1.2.3 Radial flow reactors

In addition to monolith reactors, pressure drop in fixed-bed operation can be reduced by employing radial flow reactors. These units are essentially packed-bed type, with gaseous reactive flow being in the radial direction, that is, perpendicular to the catalyst bed, instead of being in the axial direction (Figure 1.11 [4]). The radial flow pattern is achieved by directing the flow to the catalyst pellets that are packed between two perforated cylinders or concentric screens. The flow orientation is flexible, that is, can be either from outside cylinder to inside cylinder or vice versa. In this design, radial flow distance along the catalyst bed is constant and is independent of the amount of catalyst packed. This unique feature makes radial flow reactors suitable for use in cases where large catalyst volumes are needed in high-pressure operations with strict pressure drop limitations. During operation, however, the catalyst bed settles down and causes a gap for bypassing of the fresh feed through the upper

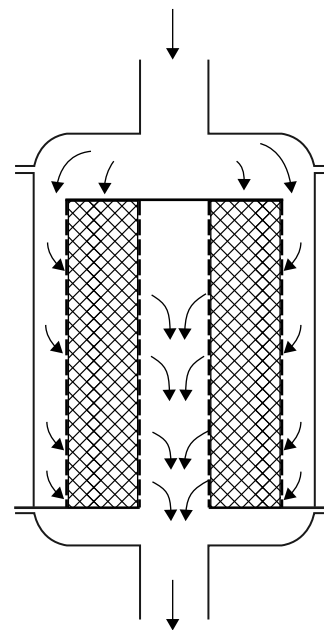


Figure 1.11 Radial flow reactor concept. (Source: Eigenberger [4]. Reproduced with permission of John Wiley & Sons, Inc.)

part of the perforated cylinder. This issue can be addressed by refining the design of the upper closure [4]. Radial flow reactors are used in such applications as the synthesis of ammonia (Figure 1.12 [12]) and methanol.

1.2.4 Trickle-bed reactors

Trickle-bed reactors are similar to the PBR geometry described in Section 1.2.1.2, with the main difference being the coexistence

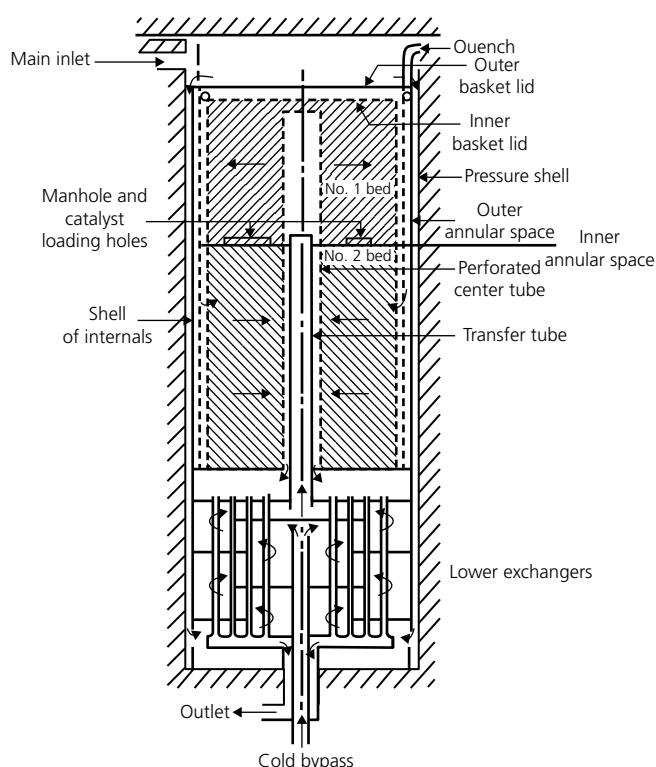


Figure 1.12 Radial flow ammonia synthesis converter by Haldor-Topsoe. (Source: Couper et al. [12]. Reproduced with permission of Elsevier.)

of gas and liquid phases in the reactive mixture and putting trickle-bed reactors among those classified as three-phase (gas–liquid–solid) reactors. In gas–solid PBRs described in Section 1.2.1.2, headspace above the catalyst bed is usually filled with inert ceramic balls to ensure uniform distribution of the gaseous feed over the entire bed. Cocurrent feeding of gas and liquid phases, however, calls for using a more sophisticated distributor design that is expected to mix the two phases and then distribute them uniformly across the catalyst bed to ensure sufficient wetting of the catalyst pellets and to prevent channeling of the gas and liquid components in the feed. The requirement of sophisticated distributors such as bubble cap trays is another factor that differentiates trickle-bed reactors from gas–solid PBRs. Status of feed mixture distribution to the catalyst bed dictates the diameter of the reactor, which is usually under 5 m. Height-to-diameter ratio is usually in the range of 5 and 25 [13]. Typical sizes of the catalyst pellets, which can be cylinder, sphere, extrudate, needle, or bead in shape, range between 1 and 5×10^{-3} m and give bed void fractions between ~ 0.35 and 0.40 [13]. Details on the design, analysis, and operation of trickle-bed reactors are provided in Chapters 5 and 13.

Trickle-bed reactors are mainly used in key petroleum refining applications such as hydrocracking, hydrodesulfurization, and hydroisomerization. The process involves the combination of hydrogenation/hydrotreating and cracking of

vacuum gas oil and residues (liquid phase) to produce lighter hydrocarbons such as gasoline in the presence of hydrogen (gas phase) over a catalyst (solid phase) in the 300–600°C range and at pressures up to ~ 150 atm to ensure high solubility of the gaseous phase in the liquid. Conventional hydrocracking catalysts, such as Pt on aluminosilicates or zeolites, involve two components, namely, an acidic component for cracking and isomerization reactions and a noble metal component for the hydrogenation reactions [14]. The trickle-bed reactor involves the presence of up to six successive catalyst beds. Since hydrocracking reactions are exothermic, adiabatic temperature rise in each bed is regulated by interstage cooling enabled by the injection of cold hydrogen quenches; the gas–liquid mixture is remixed and redistributed prior to its entrance to the succeeding bed. In hydrodesulfurization, which is an important operation in crude oil refining, the organic sulfur components, that is, sulfides, disulfides, thiols, and thiophenes existing in crude oil (liquid phase), are converted to hydrogen sulfide in the presence of hydrogen (gas phase) over alumina-supported Co–Mo or Ni–Mo catalysts (solid phase) in the 350–400°C range. The resulting H_2S is then removed by processing over beds of ZnO. In hydroisomerization, on the other hand, the light alkanes in the C_4 – C_6 range are converted to branched-chain isomers in the presence of hydrogen for producing high-octane component additives for being blended into gasoline. The process, carried out in trickle-bed reactors, involves the use of catalysts such as Pt supported on chlorinated alumina or on acidic zeolites. In contrast with hydrocrackers, interstage heat exchange is not used in hydroisomerization reactors which involve milder conditions, with temperatures and pressures ranging between ca. 110–180°C and 20–70 atm, respectively. As exothermic equilibrium reactions are involved in hydroisomerization, the catalyst should be able to operate at low temperatures to favor the desired conversions.

1.2.5 Short contact time reactors

Pressure drop in fixed beds can be reduced by minimizing the amount of catalyst used, which leads to the existence of short contact times. In addition to reduction of pressure drop, these reactors are ideal for carrying out reactions whose extent and product distribution depend strongly on the contact time (e.g., direct partial oxidation of hydrocarbons to synthesis gas). A typical concept of such a reactor, called the disk reactor, is shown in Figure 1.13 [4]. The reactor involves a thin layer of catalyst in the form of wire gauzes or pellets, whose height and diameter are in the orders of centimeters and meters, respectively. Quenching at the downstream of the catalyst bed helps in halting further conversion of the products into other unwanted species.

In addition to the disk reactor, short contact times can also be achieved in monolith reactors (Section 1.2.2) and in microchannel reactors (Section 1.2.5), the latter involving fluid mechanical

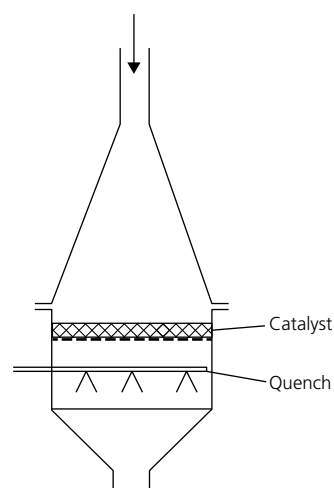


Figure 1.13 Disk reactor concept.
(Source: Eigenberger [4]. Reproduced with permission of John Wiley & Sons, Inc.)

properties and architectures similar to those of monoliths, where the existence of thin layers of washcoated porous catalysts together with high fraction of void space allows fast fluid flow almost without compromise from pressure drop (Figure 1.14 [1]). These factors lead to the occurrence of contact times in the order of milliseconds, whereas it is in the order of seconds in PBRs. Like in the case of monoliths, the existence of a structured flow pattern in microchannel units leads to precise control of residence times that promotes selective productions. Even though such similarities exist between monolith and microchannel reactors, they differ in certain aspects. Microchannel units have channel diameters in the submillimeter range, whereas larger diameter channels up to 6×10^{-3} m are used in monoliths. Owing to the constant Nu and Sh numbers per cross-sectional channel shape, higher heat and mass transport coefficients can be obtained in microchannels as a result of the smaller hydraulic diameters which also lead to higher surface area-to-volume ratios (i.e., up to $\sim 5 \times 10^4$ m²/m³) than those of monoliths. These factors favor precise regulation of reaction temperature, an important benefit for strongly exothermic reactions. Due to their special manufacturing techniques involving micromachining and bonding of the plates (Figure 1.14 [1]), various nonlinear patterns (e.g., wavy shapes) along the channel length, which induce static mixing and improve heat transport, can be implemented in microchannels [15]. On the other hand, in monoliths, channels are limited to have straight axial patterns. Finally, the range of materials of construction is versatile (e.g., various metals and ceramics, polymers, silicon) in microchannels, whereas monoliths can be made of ceramics and metals only.

In addition to their advantages stated earlier, compact dimensions of the microchannel reactors allow inherently safe productions, as the risks associated with reactions (e.g., thermal runaway) are not significant due to the small quantities in the

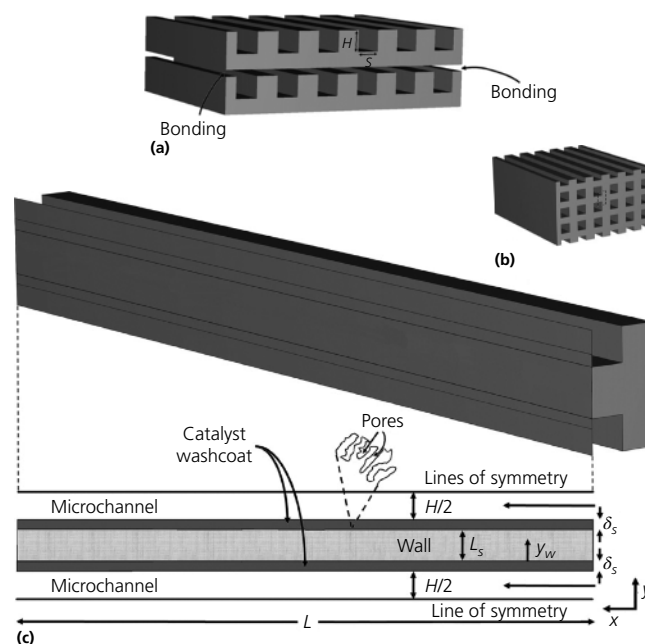


Figure 1.14 Schematic presentation of a microchannel reactor. (a) Machined plates with microchannels, (b) microchannel reactor block obtained after bonding the plates, and (c) characteristic section of the multichannel reactor. (Source: Onsan and Avci [1]. Reproduced with permission of Elsevier.)

order of microliters processed in each channel. Even though small throughput is a disadvantage of short contact time reactors, the capacity of the microchannel reactors can be rapidly increased through the so-called numbering-up approach, which is much simpler than the traditional scaling-up approach. The resulting capacities are expected to be suitable for small-scale throughput industries such as pharmaceuticals and fine chemical productions. Applications of microchannel reactors in these industries are provided by Hessel et al. [16]. Nevertheless, production capacities of the microchannel units and other short contact time reactors are far from being able to compete with those of the continuously operating commercial reactors involved in the petroleum and petrochemical industries. The reader is directed to Chapters 9 and 14 for more detailed information about the microchannel reactors.

1.3 Reactors with moving bed of catalysts

1.3.1 Fluidized-bed reactors

Fluidized-bed reactors (FBRs) are continuously operating units of the gas–solid type, involving a catalyst bed which is fluidized when the volumetric flow rate of the gaseous feed stream exceeds a limiting value called the *minimum fluidization* flow rate. The resulting degree of mixing between the gas and solid phases in the FBR brings several operational advantages over a gas–solid PBR (Section 1.2.1). FBRs offer uniform temperature distribution due to intensive mixing, which minimizes the chance of hot spot formation in exothermic reactions. Heat management

in FBRs is conventionally carried out by the heat transfer surfaces that are immersed into the reactor vessel. In this respect, fluidization favors heat transfer coefficients and subsequent fast heat exchange between the bed and immersed heat transfer surfaces. Mobility of the catalyst phase widens the operating window for allowable pressure drop. Therefore, pellet sizes smaller than those involved in PBRs can be used in FBRs, and higher reaction rates can be obtained due to increased catalytic surface area per unit bed volume. Even though higher heats of reactions evolve with increased rates, the possibility of fast heat exchange helps in effective regulation of the bed temperature. FBRs also allow constant catalytic activity either by online addition of fresh catalyst or by its continuous regeneration in a separate zone, like in the case of the fluidized catalytic cracking (FCC) operation described later. Modeling and design aspects of FBRs are explained in detail in Chapter 4.

The advantages listed previously for FBRs, however, have to be considered together with several operational limitations. Fluidization of the catalyst pellets at high velocities can cause unavoidable acceleration of the erosion of both reactor vessel and heat exchange surfaces, and their undesirable breakdown into smaller particle sizes eventually calls for the need of cost-intensive catalyst separation/gas purification equipment. In contrast with breakdown, the pellets can also merge into each other, and the resulting increase in particle weights can cause defluidization, which can seriously disturb the reactor operation. Moreover, residence time distribution is not narrow in FBRs due to the chaotic movement of reactive fluid inside the vessel. Another operational drawback of FBRs is linked with their high sensitivity against the presence of sulfur in the gaseous feed mixture. Once they enter the reactor, sulfur-containing molecules can immediately poison the entire bed due to intense mixing of the phases and the highly exposed surface area of small catalyst particles and can eventually cause a sudden drop in pressure. This serious drawback, however, is less serious in gas–solid PBRs as sulfur poisoning moves like a wave front. In other words, at the beginning of the operation, only the section of the packed bed near the inlet will be poisoned, while pellets at the downstream will remain active until the ones at the upstream are saturated with sulfur.

Apart from the operational drawbacks stated earlier, capital and operating expenses involved in an FBR exceed those of a PBR of equivalent capacity due to requirements of larger vessel volume for handling fluidization and of installing gas purification and solid circulation components. Chaotic nature of the operation also calls for a tedious preliminary study of the process of interest at the pilot scale that should be followed by a labor and cost-intensive scaling-up stage, all of which eventually increase the capital cost of the commercial FBR unit.

Although not as widely used as a gas–solid PBR, FBR remains as the only choice for processes such as FCC and high-temperature Fischer–Tropsch (HTFT) synthesis, both of which have key roles in the petroleum processing and petrochemical industries. FCC is a critical step in petroleum refining and involves catalytic breakdown of heavy gas oil molecules into

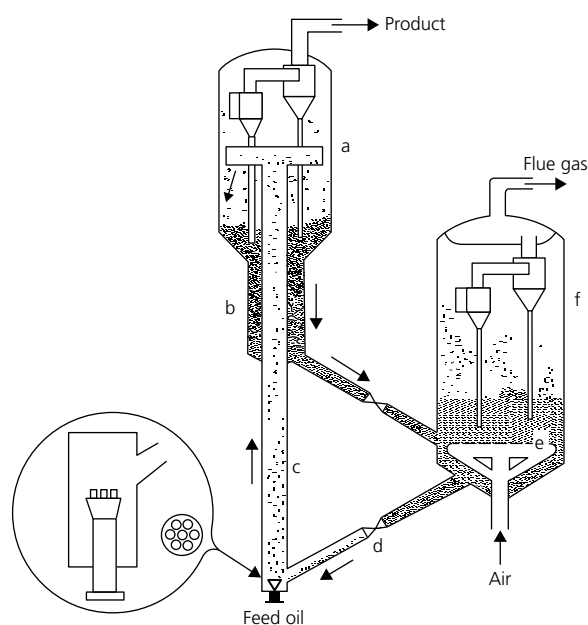


Figure 1.15 Riser cracking process by UOP. (a) Reactor, (b) stripper, (c) riser, (d) slide valve, (e) air grid, and (f) regenerator. (Source: Werther [17]. Reproduced with permission of John Wiley & Sons, Inc.)

commercially valuable products such as gasoline, diesel, and olefins. The FBR reactor, shown in Figure 1.15 [17], is composed of a riser and a regenerator between which the catalyst is circulated continuously at rates that can exceed 100 tons/min. Endothermic cracking reactions that take place in the riser at temperatures of 500–550°C unavoidably deposit coke on the surface of the zeolite-based catalyst pellets [17]. Spent catalysts are continuously transported to the regenerator in which coke is burned off with hot air at ca. 730°C for the restoration of the catalytic activity. The cycle is completed when the regenerated catalysts are conveyed back to the riser unit. Heat needed to drive the endothermic cracking reactions is supplied by the hot catalysts that come from the regenerator. HTFT synthesis, on the other hand, involves catalytic conversion of synthesis gas into a hydrocarbon mixture rich in olefins and gasoline. The process is carried out at 340°C and 20 atm over iron-based catalysts. As FT synthesis is strongly exothermic and the product distribution is a strong function of temperature, the catalyst bed should be maintained at isothermal conditions. This requirement is met by the circulating fluidized-bed (CFB) reactor, known as the Sasol Synthol reactor, shown in Figure 1.16a [12], in which heat released during reactions is absorbed by the cooling coils immersed into the reactor vessel to produce steam [18, 19]. These reactors can operate with capacities up to 8×10^3 barrels/day (3.3×10^5 tons/year). CFB reactors are then replaced by turbulent FBRs, known as Sasol Advanced Synthol reactors (Figure 1.16b [19]), due to their smaller size, lower capital expense requirements and maintenance costs, and their ability to operate at higher conversions and capacities up to 2×10^4

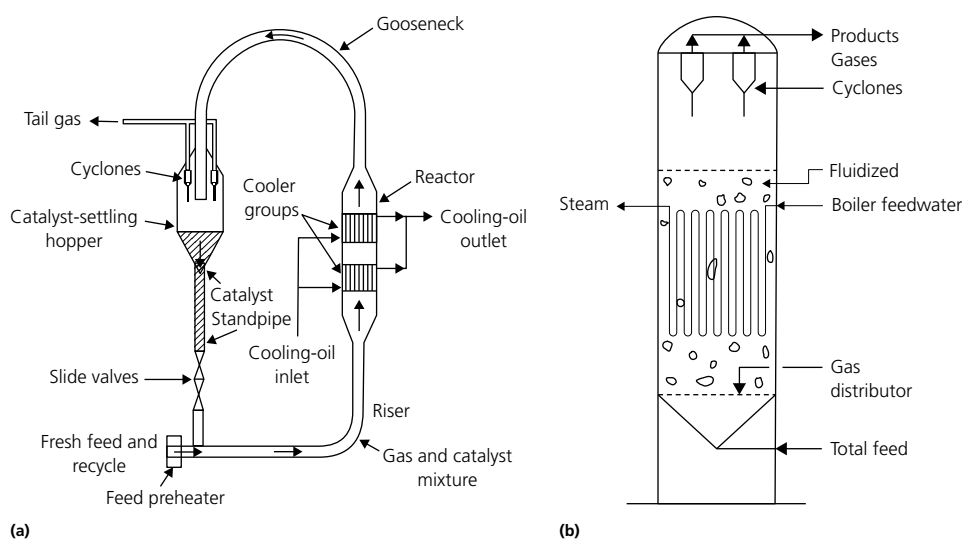


Figure 1.16 High-temperature Fischer-Tropsch synthesis reactors. (a) Sasol Synthol circulating fluidized-bed reactor. (Source: Couper et al. [12]. Reproduced with permission of Elsevier.) (b) Sasol Advanced Synthol turbulent fluidized-bed reactor. (Source: Steynberg et al. [19]. Reproduced with permission of Elsevier.)

barrels/day (8.5×10^5 tons/year) with lower pressure drop [18, 19]. The use of FBRs in HTFT is extensively discussed in Chapter 12.

1.3.2 Slurry reactors

Slurry reactors involve the coexistence and intense mixing of gas, liquid, and solid phases in the same volume. The possibility to run slurry reactors in the batch, semibatch, or continuous modes differentiates these reactors from others in terms of operational flexibility. In slurry reactors, the roles of the three phases can be different, that is, liquid can be a reactant, a product, or an inert that serves as a contacting medium for gas and solids. Similarly, dissolved gas can either be a reactant or an inert for inducing mixing of liquid and solids via bubbling. The solid phase usually corresponds to the finely dispersed catalyst particles with diameters lower than 5×10^{-3} m [20].

Slurry reactors are typically used for highly exothermic reactions. Heat removal from the reaction mixture is provided by cooling coils immersed into the reactor vessel. Intense mixing, which is enabled either by gas bubbling or by a mechanical agitator, increases the heat transfer coefficient between the reaction mixture and coils and improves the rate of heat removal. High heat capacity and heat transfer coefficients of the slurries are other factors that further promote heat transport and temperature control. Excellent heat management capabilities of slurry reactors make them promising candidates for several processes, with the most popular one being the low-temperature Fischer-Tropsch (LTFT) synthesis that involves conversion of syngas into a hydrocarbon mixture heavier than that synthesized in HTFT. LTFT is carried out in the ~ 190 – 250°C range and at

pressures between 20 and 40 atm over Co-based catalysts [6, 18]. As Co is more active than the Fe catalyst of HTFT [21], exothermic heat generation is higher, and the demand for fast heat removal becomes more critical. The reaction starts in the gas–solid mode, where the synthesis gas with a molar H_2/CO ratio of ~ 2 contacts the Co-based catalyst pellets. In the course of reaction, the liquid phase, called wax, is produced first in the pores of the pellets and then in the entire reactor. These conditions can be handled in a slurry bubble column reactor (SBCR), a special version of the slurry reactor, described in Figure 1.17 [21]. The same process can also be carried out in a multitubular PBR involving trickle flow. However, the slurry bubble column offers several advantages such as lower pressure drop (ca. 1 atm in SBCR vs. 4 atm in PBR), higher intrinsic catalytic activity due to the possibility of using small particle sizes that minimize intraparticle diffusion limitations, higher mass transfer coefficients due to well mixing, longer runs due to possibility of online addition/removal of the catalyst, better temperature control improving reactant conversion and product selectivity, and lower capital expenditure requirements [21]. Nevertheless, the drawbacks brought by the mobility of the catalyst phase, that is, the need for catalyst–wax separation and the risk of immediate catalyst poisoning, should not be underestimated in SBCR operation. Apart from LTFT synthesis, slurry reactors are used in other applications such as oxidation and hydroformylation of olefins, methanation and polymerization reactions, and ethynylation of aldehydes [20]. Further information regarding the modeling and design of the slurry reactors is presented in Chapter 6. The reader is also directed to Chapter 12 for a detailed discussion about the use of slurry reactors in LTFT.

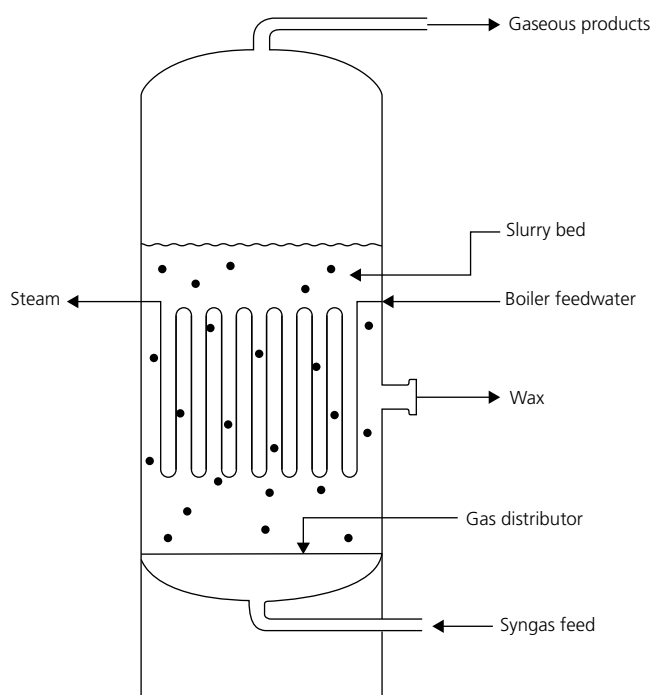


Figure 1.17 Slurry bubble column reactor for low-temperature Fischer-Tropsch synthesis. (Source: Espinoza et al. [21]. Reproduced with permission of Elsevier.)

1.3.3 Moving-bed reactors

Moving-bed reactors are preferred when there is a need for continuous catalyst regeneration. In this operation, fresh catalyst is fed from the top of the reactor, and it moves in the downflow direction by gravitational forces. Spent catalyst leaving the reactor at the bottom is usually replaced in the continuous mode. While the catalyst movement is downward, reactive mixture flow can be cocurrent or countercurrent to that of the catalyst flow.

Moving-bed reactors do not involve intense mixing of the catalyst bed with the reaction mixture. In this respect, heat management within the bed is not as efficient as that involved in FBRs or in slurry reactors. High heat capacity of the circulating catalyst pellets dictates the heat transport in the moving-bed reactors. As described in Chapter 13, these reactors are used in catalytic hydrotreating of heavy oils, in which the moving bed ensures steady conditions for the catalyst and therefore minimizes the need for periodic shutdowns.

1.4 Reactors without a catalyst bed

The reactor types introduced in Sections 1.2 and 1.3 depend on the existence of a catalyst bed, either fixed or moving, for the operation. However, there are multiphase reactions, such as the gas-liquid type, which do not involve the use of a solid catalyst. Gas cleaning/purification applications, such as removal of

CO₂ or H₂S from gas streams via mono-/diethanolamine or di-/triethylene glycol solutions and removal of nitrogen oxides by water; liquid-phase processes of oxidation, nitration, alkylation, hydrogenation, or manufacturing of products such as sulfuric acid, nitric acid, and adipic acid; and biochemical processes such as fermentation and oxidation of wastewater are examples of industrial applications of gas-liquid reactions [22]. Depending on factors such as residence time distribution of the phases, throughput demand of the process, and heat transfer requirements, gas and liquid phases can be contacted in various configurations; that is, gas can be distributed into the bulk liquid in the form of bubbles (bubble columns, plate columns), liquid can be sprayed to the bulk gas in the form of droplets (spray columns), or both phases can be contacted as thin films over an inert packing or on the reactor wall (packed columns, wetted wall columns). The common direction for liquid flow is from the top to the bottom of the reactor, and gas flow is usually in the opposite direction. Column-type reactors presented here involve a vessel and the particular components required to introduce or contact the phases (e.g., spargers for gas bubbling, spraying equipments for showering down the liquid, packing materials for contacting gas and liquid films, liquid distributors for ensuring uniform wetting of the packings, sieve plates for directing the liquid flow and for providing cross-contact with the rising gas). In general, reactor performance is affected by the gas solubility, which is expected to be high for improved rates. Operating temperature should be low, while pressure should be high for increasing gas solubility in the reactor. Depending on the heat of reaction, heat transfer equipment can be integrated to the reactor structure for regulating the temperature in the desired limits.

In some gas-liquid reactions, a mechanical agitator can be integrated into the reactor for improving mixing and mass transfer between the phases. In this case, the reactor is called as a stirred-tank reactor (Figure 1.18 [12]). The agitator is composed of an impeller that is mounted on a mechanically rotated shaft. Rotation and desired level of fluid mixing are provided by a variable speed electric motor that is placed on the reactor vessel. Gas-liquid stirred-tank reactors are also equipped by spargers for dispersing the gas bubbles into the liquid and by baffles to minimize swirl and vortex formations. In general, four baffles, each of which is one-tenth of the vessel diameter, are placed into the inner perimeter of the vessel. Aspect ratio, which is defined as the ratio of the liquid height in the tank to the tank diameter, is usually set up to be ~3 for increasing the residence time of the gas and improving the extent of reaction between phases. In such configurations, mixing is provided by multiple impellers mounted on the same shaft with distances up to one tank diameter [23].

In stirred-tank reactors, the possibility of regulating the agitation speed and the selection of various impeller types and diameters allow control over the degree of mixing of different fluids, which is quantified by the impeller Reynolds number ($Re = D^2 S \rho / \mu$; D , impeller diameter; S , speed of agitation; ρ , fluid

density; μ , fluid viscosity). The impeller types not only affect the mixing characteristics but also the power consumption determined by the dimensionless power number ($Po = P/\rho S^3 D^5$; P : power consumption). Plots of Po versus Re define the power

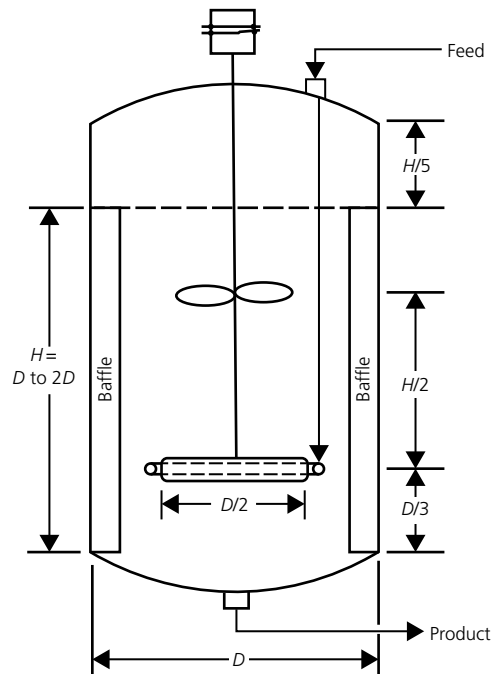


Figure 1.18 Stirred-tank reactor with typical dimensions. (Source: Couper et al. [12]. Reproduced with permission of Elsevier.)

characteristics of the impeller which is affected by factors such as its position in the tank and its diameter. In the laminar regime, characterized by $Re < 10$, Po decreases linearly with Re , whereas in the turbulent regime ($Re > 10^4$), Po remains constant and reaches an asymptotic value which is a function of the impeller type [23].

Heat transfer into/from the stirred-tank reactors is made possible by various configurations (Figure 1.19 [12]). Low heat duties can be realized by the heat transfer fluid flowing in a jacket surrounding the vessel (Figure 1.19a). For higher heat duties coils (Figure 1.19b) or internal tubes (Figure 1.19c) are immersed into the vessel for heat transfer fluid circulation. Heating/cooling of the reactive mixture in an external heat exchanger via a circulating loop (Figure 1.19d) is also possible. Other possible heat transfer configurations are shown in Figure 1.19e and f. In all cases, heat transfer coefficient on the reactor side is known to increase with the degree of mixing.

In addition to processes involving gas-liquid reactions, stirred-tank reactors can also be used for single (liquid)-phase reactions. Moreover, their operation is not limited to the continuous mode, and they can be easily adapted for use in semibatch and batch modes. The absence of a gas phase does not pose important structural and operational differences from those stated earlier for multiphase systems. However, in the case of single-phase operation, the aspect ratio is usually kept lower (~ 1) to ensure well mixing of the reactive liquid. Regardless of the number of phases involved, stirred-tank reactors can approach their ideal states if perfect mixing is established. Under such conditions, it is assumed that reaction takes place immediately just

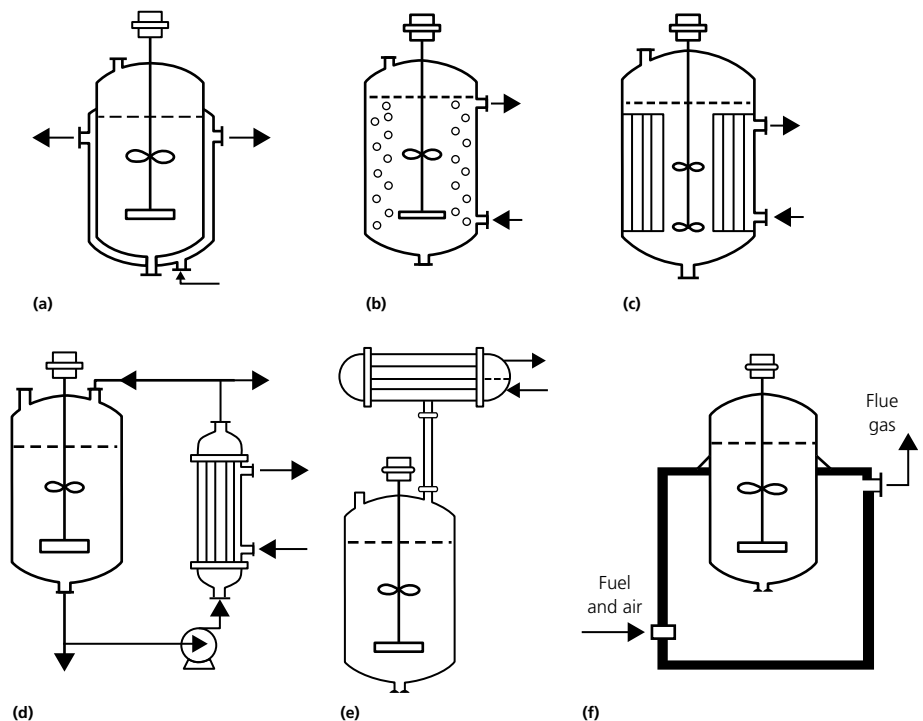


Figure 1.19 Heat transfer strategies in stirred-tank reactors. (a) Jacket, (b) internal coils, (c) internal tubes, (d) external heat exchanger, (e) external reflux condenser, and (f) fired heater. (Source: Couper et al. [12]. Reproduced with permission of Elsevier.)

after the entrance of the reactants, and the properties of the exit stream are the same with those of the reactive mixture. Nevertheless, depending on the fluid properties and the specific internal geometry of the vessel, poorly mixed zones causing selectivity issues may develop in real operations.

1.5 Summary

Catalytic reactors are critical processing units of industrial chemistry. The complex combination of several factors such as conditions of the key reactions, requirements, and limitations of the catalytic chemistry and the demand for meeting the commercial targets for conversion and yield have led to the evolution of numerous catalytic reactor types. Besides technical requirements, fixed and operating capital expenses of the reactors determine the final decision for the selection of the appropriate reactor type. This chapter aims to provide an overview of all the factors involved that may help readers in understanding the key features of these complex reactors and their significance in chemical industry. The contents of this chapter are prepared to set the basis for the following chapters, each of which provides detailed information about the analysis, design, and modeling of the multiphase reactors covered in this book.

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