

# Reactor Performance and Scale-Up

---

*Nothing in this world is to be feared. It is only to be understood.*

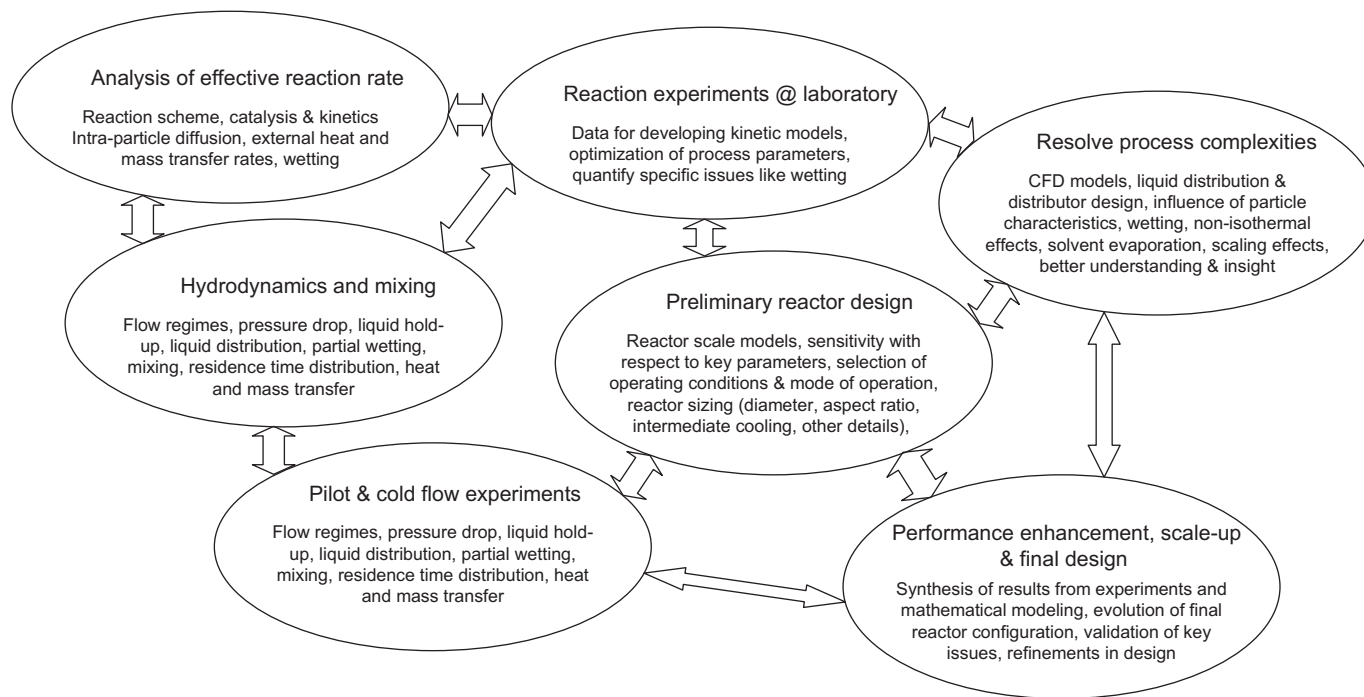
Marie Curie

## INTRODUCTION

Design, scale-up, and improving performance of a large-scale trickle bed reactor is essentially a multistep and multitask process. Issues, models, and methodologies discussed in Chapters 2–4 need to be used together to achieve this goal. A suggested approach is schematically shown in Fig. 1. Broadly the process involves the following steps:

- Estimate flow regimes, hydrodynamics, maldistribution, mixing (Chapter 2)
- Analyze reaction kinetics, effective rate, mass and heat transfer effects (Chapter 3)
- Establish relationship between hardware and performance (Chapter 4)

Information and correlations discussed in Chapter 2 can be used to identify prevailing flow regimes and estimate key design parameters. Using the basic reaction engineering models discussed in Chapter 3, reactor volume and operating conditions (gas and liquid flow rates, pressure, temperature) can be estimated for the desired conversion and efficiency. Often formulation of these models is based on many assumptions and the design parameters are calculated from the empirical correlations. These correlations are usually obtained from the cold flow experimental data collected with small-scale laboratory reactors using the air–water system. Therefore, extension of these models for realistic cases, scale-up, and designing of actual reactor hardware involves uncertainties. The computational fluid dynamics (CFD)-based models discussed in Chapter 4 can be used to understand important design aspects and reduce the uncertainties. Because of inherent complexities of multiphase flow through packed beds, the computational flow models will have their uncertainties as well. In this chapter, we discuss the overall approach and how models and information



**FIGURE 1** Schematic of the overall methodology for relating performance of the reactor with the hardware and the operating protocol.

discussed in Chapters 2–4 can be used to design and scale-up and to enhance performance of trickle bed reactors.

The following section discusses various issues affecting reactor performance. The overall reaction rate is affected by one or more steps (kinetics, mass transfer, heat transfer) and critical analysis of these steps is the key challenge in evaluating the performance of a reactor. The basic rate analysis discussed in Chapter 3 is extended here to include practical issues like influence of particle diameter, operating conditions (flow rate, temperature, and pressure), hysteresis, and so on. Aspects of liquid distribution, mixing, and residence time distribution (RTD) (including a brief summary of different distributors) are discussed in *Reactor Performance*. Key issues relevant to design and scale-up of trickle bed reactors are discussed in *Trickle Bed Reactor Design and Scale-Up*. A strategy for combining the models and methods discussed in Chapters 2–4 with the key aspects of practical trickle bed reactor engineering is discussed in the *Engineering of Trickle Bed Reactors* section. A summary is provided at the end.

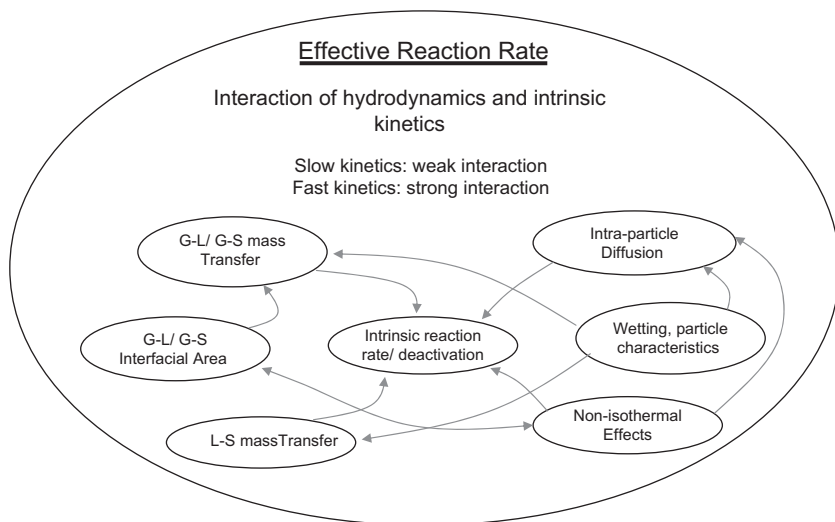
## REACTOR PERFORMANCE

### Effective Reaction Rate and Performance

Effective reaction rate is a function of various parameters such as interphase heat and mass transfer, intraparticle diffusion, and intrinsic reaction kinetics. In some situations, the effective rate is predominantly limited by one of these processes; allowing a simplified analysis of reactor performance. However, more often than not, effective rate is controlled by more than one processes. Interdependence among various factors is shown schematically in Fig. 2. Coupling between mass and heat transfer with wetting of catalyst particles can further complicate the determination of controlling steps and effective rates. It is not uncommon that reaction rates are kinetically controlled in some region of the reactor and mass transfer controlled in the other.

The first step in carrying out effective rate analysis is based on intrinsic kinetics assuming that the reactor is operated under ideal conditions such as absence of any transport limitations, complete wetting of catalyst particles, plug flow operation, and isothermal conditions. This provides a baseline with which influence of other transport-related parameters on effective rate is carried out:

- Gas–liquid mass transfer
- Gas–solid mass transfer over unwetted catalyst particles
- Liquid–solid mass transfer
- Diffusion of reactants inside the particle
- Reactions on the catalyst surface

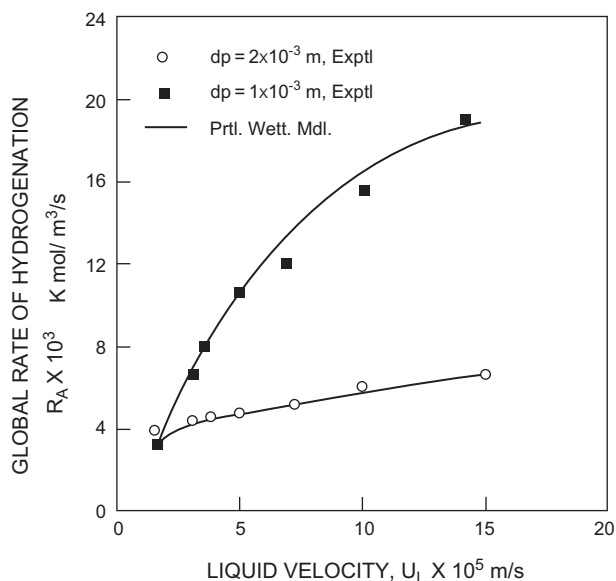


**FIGURE 2** Interdependence of hydrodynamic and reaction parameters in trickle bed reactors.

Such studies may provide insights into elementary processes useful for devising design guidelines and operating protocols. In the following sections, influence of various operating parameters on effective reaction rate is discussed.

If *intraparticle diffusion step* is limiting the overall reaction rates, one would get lower conversion in the actual reactor than kinetically controlled conditions. Such a situation occurs for many chemical reactions carried out in trickle bed reactors (Herskowitz & Mosseri, 1983) and the catalyst effectiveness factor was found to be in the range of 0.01–0.3. Decrease in the particle diameter improves the catalyst effectiveness factor considerably. Influence of particle diameter on effective (or global) reaction rate is illustrated in Fig. 3 and as expected, the global reaction rate is significantly higher for smaller particles. However, decrease in particle size may alter the performance of the reactor due to increase in wetting characteristics of the particles. Depending upon whether limiting reactant is in the gas or liquid phase, the performance of the reactor may increase or decrease with reduced wetting.

An increase in superficial *gas velocity* leads to decrease in the liquid holdup and therefore reduces overall conversion (reducing effective residence time for liquid phase). The gas velocity, however, has negligible influence on effective reaction rate (Goto & Smith, 1975; Julcour, Jaganathan, Chaudhari, Wilhelm, & Delmas, 2001; Rajashekharam, Jaganathan, & Chaudhari, 1998) provided that gas–liquid mass transfer is not controlling. In cases where gas–liquid mass transfer rate governs the effective rate, increase in gas

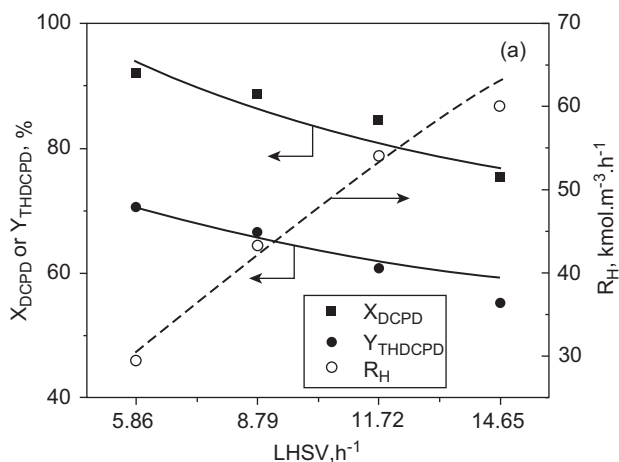


**FIGURE 3** Effect of particle diameter on global reaction rate (Rajashekharam et al., 1998). System: hydrogenation of 2,4-dinitrotoluene on 5% Pd/Al<sub>2</sub>O<sub>3</sub>;  $C_L = 0.2 \text{ kmol/m}^3$ ;  $H_2$  pressure = 1.4 MPa;  $U_G = 4.23 \times 10^{-3} \text{ m/s}$ ;  $T = 318 \text{ K}$ .

velocity enhances the reaction rates by improving gas–liquid mass transfer rate as observed by Metaxas and Papayannakos (2006) for hydrogenation of benzene.

The effect of *liquid velocity* on the effective reaction rate is more complex and not monotonic. Increase in liquid superficial velocity leads to shorter residence time and therefore reduces conversion (see, for example, Chaudhari, Jaganathan, Mathew, Julcour, & Delmas, 2002; Khadilkar, Wu, Al-Dahhan, Dudukovic, & Colakyan, 1996; Liu, Mi, Wang, Zhang, & Zhang, 2006; Rajashekharam et al., 1998). However, effective reaction rate may increase with liquid velocity because of enhanced wetting of catalyst particles. An example of this is shown in Fig. 4 for the reaction of hydrogenation of dicyclopentadiene. However, if the reaction is controlled by gas phase reactant, then the influence of liquid velocity on the rate is opposite, i.e., reaction rate decreases with liquid velocity. In such cases, enhanced wetting due to higher liquid velocity reduces a direct contact of gas phase reactant with the catalyst surface and hence reduces the overall reaction rate (see, for example, cases discussed by Chaudhari et al., 2002; Herskowitz & Mosseri, 1983; Ravindra, Rao, & Rao, 1997; and Fig. 11 in Chapter 3).

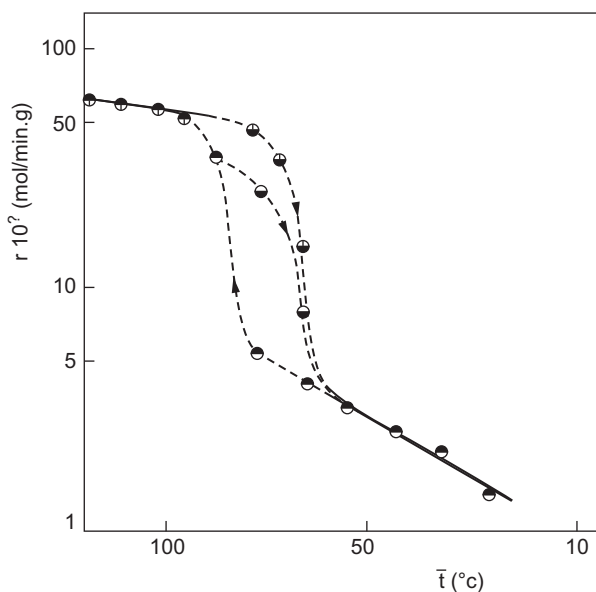
Increase in operating pressure or temperature generally enhances the conversion and effective reaction rates. Increase in pressure results in increased concentration of gas phase reactants and higher solubility. Solvent evaporation



**FIGURE 4** Effect of liquid velocity on conversion of dicyclopentadiene (DCPD) and tetrahydrodicyclopentadiene (THDCPD) and reaction rates (Liu et al., 2006). System: hydrogenation of dicyclopentadiene on 0.3%Pd/Al<sub>2</sub>O<sub>3</sub>;  $T_0 = 348.15$  K;  $P = 1.0$  MPa; LHSV = 8.79 h<sup>-1</sup>.

rate decreases with increase in the operating pressure which may result in higher temperatures within the bed. Increase in operating or prevailing temperature in the bed increases intrinsic reaction rates but with increase in temperature, mass transfer limitations can become significant. The influence of temperature on effective reaction rate can be mixed. If the solvent is very volatile, increase in temperature will lead to increased partial pressure of the solvent in gas phase which may reduce effective reaction rate as well as lowering of temperature rise due to evaporation. The vaporization may lead to partial drying of catalyst surface triggering the gas–solid reactions and multiplicity behavior due to simultaneous effect of exothermicity of the reactions. Such an effect is reported in many studies (Hanika, Lukjanov, Kirillov, & Stanek, 1986; Hanika, Sporka, Ruzicka, & Krausova, 1975; Hanika, Sporka, Ruzicka, & Pistek, 1977; Kheshgi, Reyes, Hu, & Ho, 1992; Kirillov & Koptug, 2005; Shigarov, Kuzin, & Kirillov, 2002) and is illustrated in Fig. 11 of Chapter 3 for the case of hydrogenation of cyclohexene at different temperatures. In this case, increase in operating temperature increases rate of liquid evaporation as well as dryness of the catalyst surface.

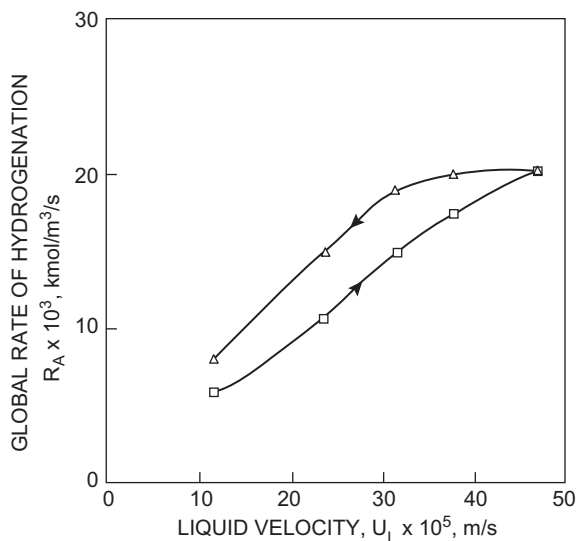
For non-volatile liquid reactant, reduction in wetting surface area results in deterioration of performance of the reactor due to decrease in liquid–solid contacting efficiency. For volatile liquid reactants, increase in dry surface enhances the reactor performance up to a limit because of direct gas phase reactions through dry surface with liquid reactants present in porous catalyst by capillary forces. Effect of increase in temperature on reactor performance for hydrogenation of cyclohexene is shown clearly by results (Fig. 5) of Hanika



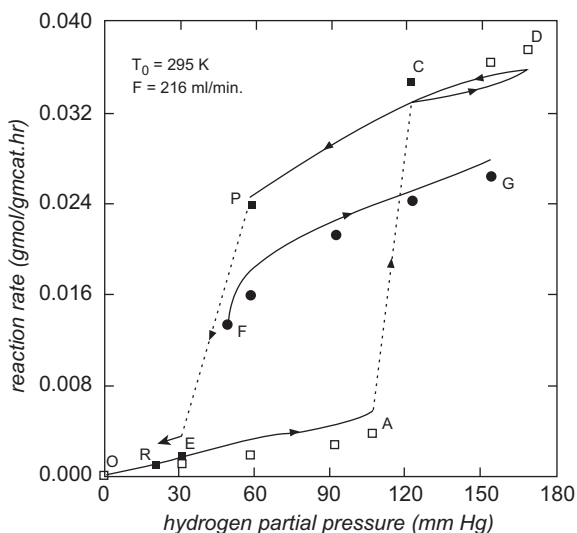
**FIGURE 5** Reaction rate variation due to phase transition (Hanika et al., 1975). System: hydrogenation of cyclohexene on 3% Pd/activated C, *Upper curve conditions:* CL = 5.9 wt%,  $F_L = 1 \text{ cm}^3/\text{s}$ ,  $F_{H_2} = 40 \text{ cm}^3/\text{s}$ ; *inner lower curve conditions:* CL = 25 wt%,  $F_L = 4.5 \text{ cm}^3/\text{s}$ ,  $F_{H_2} = 760 \text{ cm}^3/\text{s}$ .

et al. (1975). Increase in temperature results in phase change and discontinuity in the variation of rate with temperature since the reactions on gas-covered catalyst surface are significantly faster. In the range of 65–120 °C, phase transition occurs and both liquid phase and gas phase reactions contribute to the effective rate. The evaporation and condensation of liquid phase reactants in this case also result in a distinct hysteresis behavior along the paths of increasing and decreasing operating temperature.

The hysteresis is also observed for hydrogenation of 2,4-dinitrotoluene (see Fig. 6) even if there is no significant evaporation of the liquid phase. This physical phenomenon is attributed to the effect of exothermicity of the reaction and thermal inertia of particles. Along the path of decreasing liquid velocity, the particles are hotter than those along the path of increasing liquid velocity. This leads to higher reaction rates (Fig. 6) along the path of decreasing liquid velocity. Figure 7 illustrates the effect of change in hydrogen pressure on temperature and therefore on the reaction rates. For the liquid-filled catalyst, increase in hydrogen pressure follows lower branch of the temperature where liquid phase reactions are dominant. When hydrogen partial pressure is decreasing, it follows the upper branch of temperature where occurrence of condensation is not sufficient to mimic particle wetting conditions along the path of increasing hydrogen partial pressure. This pore-scale phenomenon is associated with an intricate interaction between heat, mass transfer, and capillary action inside the porous catalyst particle which is demonstrated in several theoretical and experimental studies (Hessari & Bhatia, 1997; Kim & Kim, 1981; Watson & Harold, 1993).



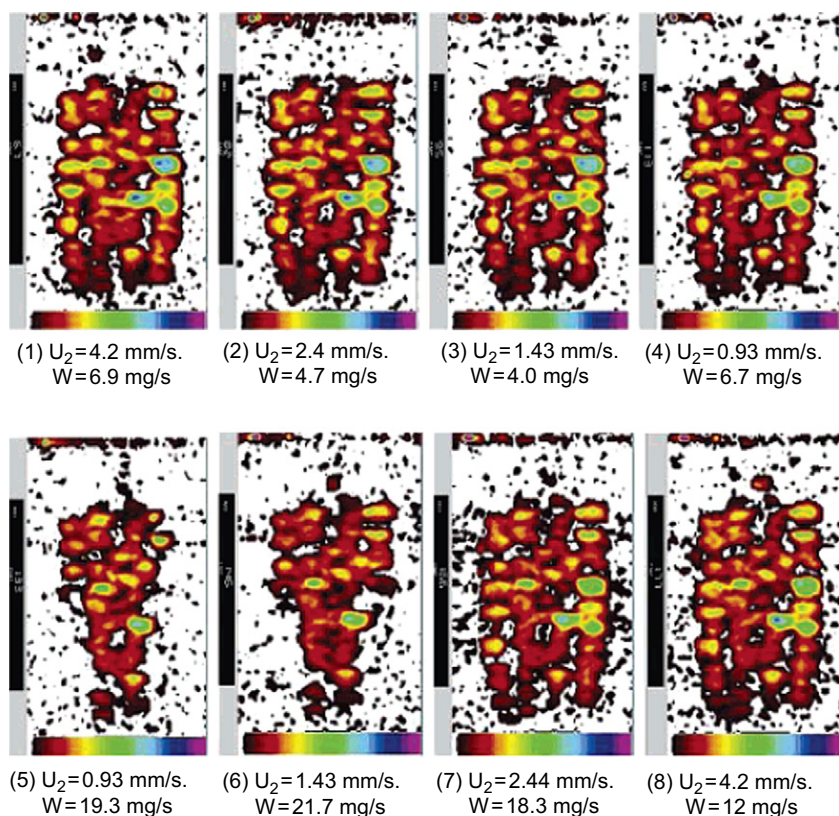
**FIGURE 6** Hysteresis of reaction rates associated with hydrodynamics of the bed (Rajashekharam et al., 1998). System: hydrogenation of 2,4-dinitrotoluene; Catalyst: 5% Pd/Al<sub>2</sub>O<sub>3</sub>;  $C_L = 0.5$  kmol/m<sup>3</sup>, H<sub>2</sub> pressure = 3 MPa;  $U_G = 4.23 \times 10^{-3}$  m/s;  $T = 328$  K.



**FIGURE 7** Hysteresis of reaction rate with hydrogen partial pressure (Hessari & Bhatia, 1997). System: hydrogenation of cyclohexene; Catalyst: 0.5%Pd/ $\gamma$ -alumina;  $T = 295$  K;  $F_L = 216$  ml/m<sup>3</sup>.

Flow maldistribution at bed scale, liquid spreading at particle scale, and internal catalyst wetting at pore scale interact with the heat and mass transfer with intrinsic reaction kinetics to influence the effective reaction rates in a complex way. It is difficult to quantify these interactions and their influence on effective rates without a proper mathematical model. Advanced imaging techniques like MRI enable direct visualization of these transport processes occurring at different scales which is illustrated in Fig. 8. Images shown in





**FIGURE 8** The particle-scale and bed-scale transport processes during the reaction using MRI techniques in the form of liquid distribution contours (Kirillov & Koptug, 2005,  $U_2$  = liquid superficial velocity,  $W$  is apparent output of trickle bed). System: hydrogenation of  $\alpha$ -methyl styrene to cumene and heptene on 1%Pd/ $\gamma$ - $Al_2O_3$ , +1%Mn with hydrogen velocity 10–50 cm/s.

Fig. 8 represent the fraction of liquid present inside the trickle bed reactor at various liquid flow rates. Images 1–4 indicate the variation of the liquid fraction with decreasing liquid flow rate. Fraction of the wetted particles decreases with the decreasing liquid flow rate. Further decrease in the flow rate below 0.93 mm/s leads to dry out phenomenon and runaway conditions. Images 5–8 indicate variation of the liquid fraction with increasing liquid flow rate. Increase in liquid flow rates at this point leaves the central bed in wetted condition while leaving rest of the bed in dry condition. Reactor performance was found to be the highest at this point due to the reactions on gas-covered surface of the catalyst (Kirillov & Koptug, 2005). Comparison of the images at the same liquid velocities suggests that hysteresis behavior is present at all different scales of the reactor and development of suitable modeling techniques to describe these phenomena is necessary to avoid unpleasant surprises.

## Particle Characteristics

Key characteristics of trickle bed reactors depend on packing of particles, which in turn depends on particle characteristics. Apart from selection of the catalyst, design of catalyst particle (shape and size) suitable for reactor operation is crucial for efficient and successful operation of the reactor. The key objective of designing catalyst particle size and shape is to accommodate maximum amount of catalyst per unit volume of the reactor without adversely affecting other factors such as pressure drop, liquid holdup, interfacial area, wetting, overall effectiveness factor of the catalyst, thermal, and mechanical aspects of the catalyst. Hydrodynamic parameters are function of underlying fluid dynamics in the bed void. How particle size, shape, and their arrangements influence the local fluid flow is discussed in Chapter 4 (Characterization of Packed Beds). Apart from fluid dynamics of the packed bed, particle size and shape significantly affect catalyst effectiveness factors and thereby effective reaction rates. This section discusses some of the key issues in selecting catalyst particle size and shape and their influence on performance of trickle bed reactors.

Particle characteristics are determined in terms of the following:

- Particle size (diameter, equivalent diameter, volume equivalent diameter, and size distribution)
- Shape of the particle (measured in terms of sphericity)
- External surface area (surface area per unit volume of the catalyst)
- Internal pore diameter (and pore size distribution)
- Internal surface area (internal surface area per unit volume of catalyst particle)
- Other parameters: density, surface roughness, wettability, and hardness/crushing strength

Bed characteristics affected by selection of the particles are as follows:

- Porosity (volume of catalyst particles per unit volume of bed) and tortuosity of the bed
- Specific surface area of reactor (external catalyst surface area of bed per unit volume of reactor)
- Bulk density of bed (total weight of catalyst per unit volume of reactor)

Conventionally spherical, cylindrical, and ring type of catalyst particles were obvious choices mainly due to easy manufacturability. In recent years, various other shapes such as trilobe, hollow cylinders, quadrilobes, and polylobes have been developed to enhance interface area, catalyst effectiveness, and mechanical strength (Sie, 1993). For the same outer diameter, trilobes or wagon wheels may provide more than twice surface area compared to the conventional spherical or cylindrical particles. For trickle bed operations, trilobes and quadrilobes are preferred (because of larger catalyst loading and less likelihood of stagnant regions) over hollow cylinder particles for avoiding stagnant region

and larger catalyst loading. Bruijn, Naka, and Sonnemans (1981) have demonstrated that activity (effectiveness) of polylobes is higher than cylindrical particle for equal volume of catalyst particle. From catalyst effectiveness point of view, smaller particles are preferred over larger particles. However, permissible pressure drop across the bed defines a lower limit on how smaller-sized catalyst particles can be used.

Influence of particle shape and size on overall bed characteristics (voidage and interfacial surface area) is reported in Table 1. Apart from the size and shape, the method of packing catalyst particles in a bed may have a significant impact on performance. Among various packing methods

**TABLE 1** Typical Characteristics of Particles Used in Trickle Bed Reactor

Shape	Size (mm)	Specific Area ( $\text{m}^2/\text{m}^3$ )	Bed Porosity	Source
Spherical	2		0.38	Larachi et al. (1991)
	3	1200	0.40	
	6	620	0.38	
	2.4		0.39	
	1.4		0.35	Larachi et al. (1991)
Cylindrical	$1.6d_p \times 4.7l_p$		0.437	Nemec and Levec (2005)
	$3.2d_p \times 3.4l_p$	1083	—	
Rasching rings	$10 \times (6.5 \times 5)$	924	0.67	
Extrudate	$1.5d_p \times 3.11l_p$		0.40	
	$3.17d_p \times 9.5l_p$		0.37	
	$1.2d_p \times 3l_p$		0.37	
Trilobes	$1.27d_p \times 5.5l_p$ ( $d_e = 1.41$ )		0.466–0.511	Nemec and Levec (2005)
	$1.27$ ( $d_{eqv} = 3.4$ mm)	$235 \text{ m}^2/\text{g}$	0.53	
Quadrilobes	$1.35 \times 5.2$		0.593	Nemec and Levec (2005)

reported by Al-Dahhan, Wu, and Dudukovic (1995), random loose packing (RLP) and random close packing (RCP) are the two commonly used methods for packing catalyst bed. Porosity variation due to these two packing methods can be as large as 16–20% (Klerk, 2003). RCP can be achieved by tapping bed continuously while filling the bed with catalyst particles. Trickle bed hydrodynamics and performance is quite sensitive to the bed porosity and therefore it is important to quantify bed porosity accurately while characterizing the catalyst bed. Particle density, surface roughness, wettability, and hardness/crushing strength are also important characteristics which influence hydrodynamic interactions. Surface properties of particles can be manipulated to achieve better catalyst surface wetting and better spreading of liquid. Effective wetting of catalyst bed also depends on liquid distribution. Some of the distributor designs used in practice are briefly discussed in the following.

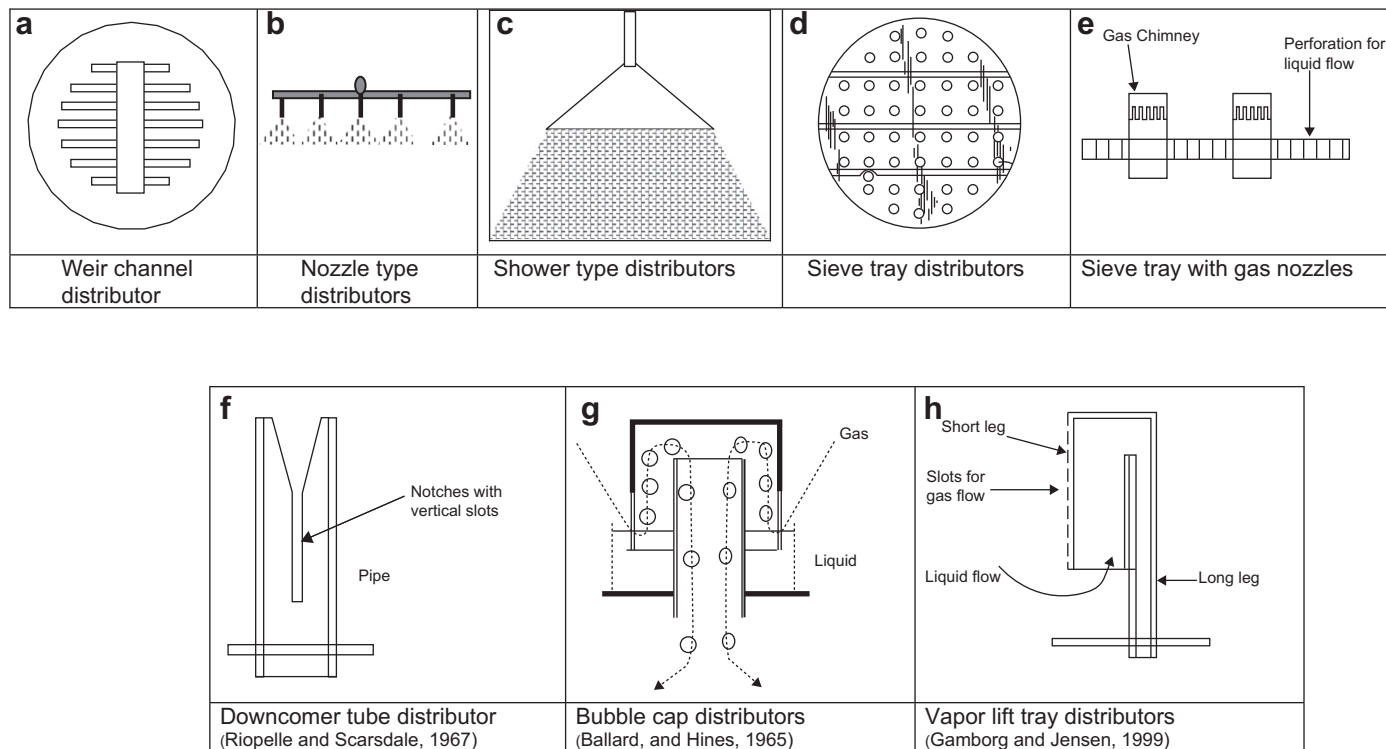
### Gas–Liquid Distributor

Liquid distribution in trickle bed reactors significantly influences its performance especially for liquid reactant-limiting reactions. Poor liquid distribution can lead to large gas or liquid pockets resulting in a poor overall external mass transfer of gas or liquid reactants to the catalyst surface and hence to lower reactor performance. If reaction is exothermic and comprises volatile liquid components, the gas phase reactions in non-wetted region cause formation of local hotspots leading to catalyst deactivation. Therefore, uniform distribution of the liquid at the inlet as well as in the bed is essential for achieving better performance of the reactor. Proper distribution at the inlet of the bed is one of the effective ways to minimize adverse effects of the liquid maldistribution. Despite uniform distribution at the inlet, liquid maldistribution may occur along the length of the column because of other factors such as packing characteristics and bed tilt. In such cases redistribution of liquid after certain height of the bed is necessary to control the liquid maldistribution. It is important to note that the porous bed of catalyst particles itself facilitates liquid distribution to a certain extent but if a proper distributor at the inlet is not used, a significant portion of the bed near the liquid inlet may remain unwetted.

Desired characteristics of liquid distributor are as follows:

- low pressure drop
- ability to operate over a broad range of gas–liquid flow rates
- less susceptibility to blockage and fouling
- ease of operation
- ease of installation and maintenance (cleaning)

Different types of liquid distributors used in trickle bed reactor are shown in Fig. 9. In many fine chemical applications, gas and liquid flow rates are



**FIGURE 9** Different types of liquid distributors used in trickle bed reactors.

moderate and the diameter of the column is rather small. For such reactors, simple distributor design such as sieve tray or layer of inert particles on the upper portion of the bed may serve the purpose. Resistance offered by the sieve tray or top layer of particles is adequate to spread the liquid radially across the bed cross-section. In petroleum and petrochemical applications (like hydro-processing or hydrocracking processes), reactor diameters are large ( $\sim 6$  m). Relatively, lower liquid flow rates further lead to difficulties in achieving uniform liquid distribution. Specially designed distributors are needed to achieve the uniform liquid distribution in such large column diameter reactors. In such cases, even a small tilt in the reactor orientation can lead to severe liquid maldistribution.

Weir channel-type distributors (as shown in Fig. 9a) are commonly used in many low to moderate diameter trickle bed reactors. In this type, liquid is centrally distributed in several radially arranged weirs which have triangular notches. These distributors offer very low pressure drop and the gas flows independently without much interaction with the liquid phase. Liquid distribution is affected by a number of weirs and number of notches provided in such distributors. The degree of distribution is sensitive to the correct orientation (deviation from horizontal level) of weir channels. Wide range of liquid flow rates can be handled with these distributors.

Nozzle-type and shower-type liquid distributors (see Fig. 9b and c) are generally used in small diameter columns due to large pressure drop associated with these columns. These distributors are not sensitive to the bed tilt. For smaller diameter columns, spray-type distributor is used and for medium diameter columns nozzle-type distributors are used. These distributors are not suitable for foaming liquids and low liquid flow rates.

Sieve (perforated) tray and sieve tray with gas nozzles (refer Fig. 9d and e) are the most commonly used distributors in trickle bed reactors. If gas flow rate is low to moderate, sieve tray distributor is used. For higher gas flow rates, sieve tray with gas nozzle is generally used to reduce pressure drop. These distributors are suitable for low as well as high gas–liquid flow rates. For high liquid flow rates, liquid flow can occur through weirs/notches of the gas nozzles. These distributors are also suitable for foaming liquids and are sensitive to the orientation of the tray.

The downcomer-type tube distributors (refer Fig. 9f) are suitable for large diameter columns and foaming liquids. In these distributors, liquid height is maintained on the perforated trays. Gas passes through the center of the vertical tube and liquid passes through the vertical notch on the wall of the tube. Liquid flow rate is proportional to the height of liquid pool. These distributors are moderately sensitive to the level of the tray.

In bubble cap distributors (shown in Fig. 9g), gas bubbles pass through the liquid pool maintained by a riser tube. These bubbles carry liquid along with it which flows from bottom of the tray to the vertical notches on riser tube. Through downcomer tube, vapor liquid mixture disengages in the bed. Bubble

cap distributor thus provides intimate gas–liquid contacting. This type of distributor can handle a wide range of gas and liquid flow rates and is suitable for large diameter columns. Pressure drop and sensitivity to the tilting of the tray are also moderate for this distributor.

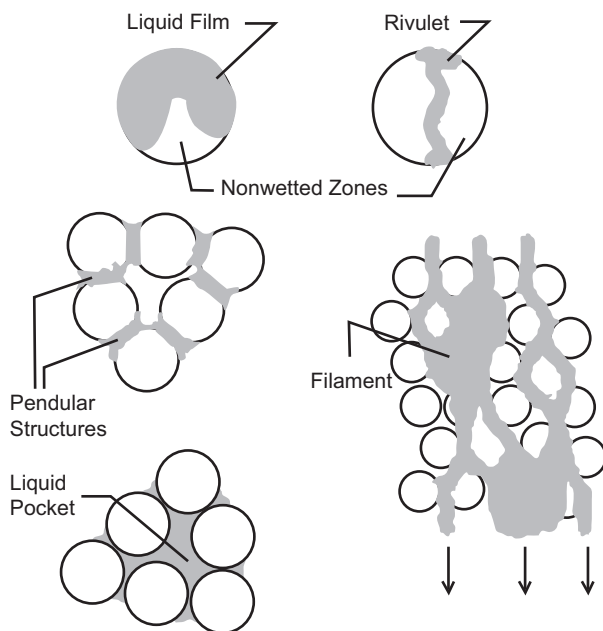
Construction of vapor lift tube distributor (as shown in Fig. 9h) is simpler than the bubble cap tray distributor and requires less space. This may allow use of more number of tubes to improve uniformity of the liquid distribution. Here, liquid height is maintained above the side cap so that vapor pressure outside the cap raises the liquid above riser tube with intimate contact with the gas. This type of distributor offers similar advantages to that of bubble cap distributor.

Various factors such as dimension of bed, gas–liquid flow rates, properties of the fluid (viscous, foaming, fouling, etc.), and pressure drop need to be considered while selecting the type of distributor. Influence of liquid distribution on the reactor performance is discussed in the next section.

## Liquid Maldistribution and Performance

Trickle bed reactors are generally operated at low liquid velocities; therefore inlet distributor and local bed properties play an important role in liquid distribution inside the bed. Liquid maldistribution directly affects the performance due to improper contacting of gas–liquid phases over catalyst surface and channeling of the flow. Gravity-driven nature of liquid flow offers relatively few degrees of freedom to tune/manipulate the liquid distribution. Liquid maldistribution in the trickle bed reactors can be classified into two categories: gross maldistribution and local maldistribution. Improper liquid distribution at the inlet causes gross maldistribution which can be minimized by proper design of the distributor (discussed in the previous sub-section). On the other hand, local maldistribution may occur due to various factors such as properties of particles (size, shape, surface roughness, etc.), arrangement of particles, packing density, and properties of the gas and liquid phases. In this section, details of local liquid maldistribution and its implications on reactor performance are discussed.

In many studies on trickle beds, influence of liquid distribution was accounted in terms of wetting efficiency (see, for example, Herskowitz & Smith, 1978; Sylvester & Pitayagulsarn, 1975; Weekman & Myers, 1964). However, subsequent experiments as well as mathematical modeling indicate that the liquid distribution effects are more significant than the wetting effects (modeling: Crine & L'Homme, 1984; Crine, M., Marchot, P., & L'Homme 1981; Fox, 1987; Funk, Harold, & Ng, 1990; experimental: Borda, Gabitto, & Lemcoff, 1987; Chou, 1984; Lutran, Ng, and Delikat, 1991). Quantification of maldistribution within the bed is rather difficult. Usually liquid distribution at the outlet is used to quantify liquid maldistribution (Borda et al., 1987; Herskowitz & Smith, 1978). However, usefulness of the above method is restricted to smaller-sized reactors. Fundamental understanding of liquid distribution and spreading within packed



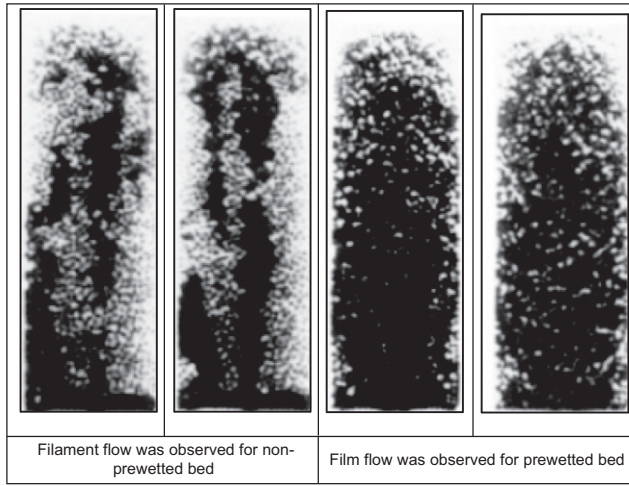
**FIGURE 10** Various liquid flow patterns proposed by Lutran et al. (1991).

beds gained importance in recent years. Using computer-assisted tomographic (CT) technique, Lutran, Ng, and Delikat (1991) have demonstrated various interesting flow features of the trickle flow regime (see Fig. 10).

Depending upon the flow rates and properties of the fluid and particles, liquid in the void may be present in the form of films, rivulets, pendular structure, filament, or stagnant pockets. Film flow and rivulets phenomena are associated with a single particle; while in multiparticle systems, various patterns can be observed such as pendular structure, filament, and stagnant liquid pockets. Pendular structure and stagnant liquid pockets are associated with the contact point between the particles and the capillary pressure. Filaments maintain the continuous liquid flow over the particle which can be in the form of liquid film or the rivulets. Formation of the filament-type flow is more likely when bed is not prewetted. The film flow is expected when bed is prewetted (see experimental results shown in Fig. 11).

Rivulet-type flow was also observed by Sederman and Gladden (2001) using MRI scanning method for non-prewetted bed. In non-prewetted bed, liquid preferentially flows near the wall. A small fraction of the flow occurs at the center in the form of filaments. Liquid filaments grow in size with increase in the liquid flow rates. This type of flow produces higher liquid velocity channels flowing in the confined region, where very small fraction of the column is wetted by the liquid. However, in the prewetted bed, spreading of the liquid enhances the wetting fraction of the bed considerably. Implications of





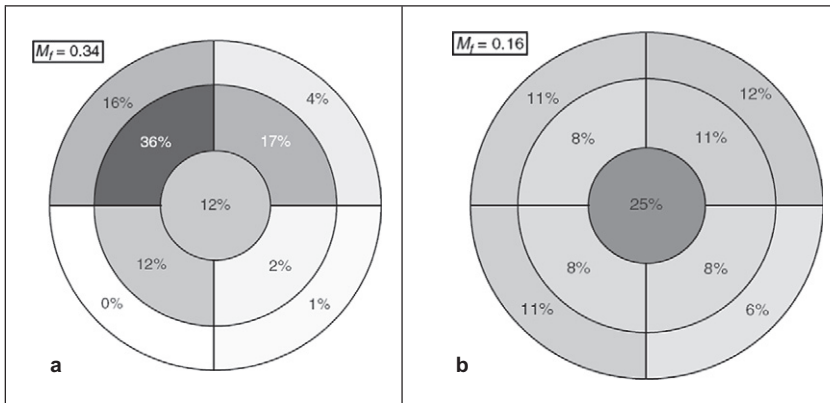
**FIGURE 11** Liquid distribution in trickle bed characterized using CT (Lutran et al., 1991). System: 3 mm of glass sphere as the particles and water as fluid with uniform distributor.

the local liquid flow structures are also reflected in the global hydrodynamic parameters. For example, filament flow has a little interaction with the gas as compared with the film flow which results in lower pressure drop. Scanning of the flow profile inside the bed provides valuable insight into the complex nature of the flow. In the industrial trickle bed reactors, combination of these flow patterns and their quantification is a major challenge.

Quantitative description of non-uniform liquid distribution can be performed by using the liquid collectors at the outlet of the bed. The use of concentric cylinders at the outlet to measure radial distribution of liquid was found to be a suitable method (Borda et al., 1987; Herskowitz & Smith, 1978; Marcandelli, Lamine, Bernard, & Wild, 2000). Their analysis suggests that radial liquid distribution changes along with the height of the column. For small diameter columns, radial spreading occurs earlier than the large diameter columns. Cylindrical particles produce excessive wall flow compared to the spherical particles. Further detailed information on liquid non-uniformities can be gained using azimuthally divided concentric cylinders (Marcandelli et al., 2000; Møller, Halken, Hansen, & Bartholdy, 1996). Using such approach, Marcandelli et al. (2000) have defined maldistribution factor as follows:

$$M_f = \sqrt{\frac{1}{N(N-1)} \sum \left( \frac{Q_{Li} - Q_{\text{mean}}}{Q_{\text{mean}}} \right)^2} \quad (1)$$

where,  $M_f$  is the maldistribution factor,  $N$  is the number of channels used for collecting liquid over the bed cross-section, and  $Q_{Li}$  and  $Q_{\text{mean}}$  are the flow rate of liquid in each channel and mean flow rate, respectively. A sample of

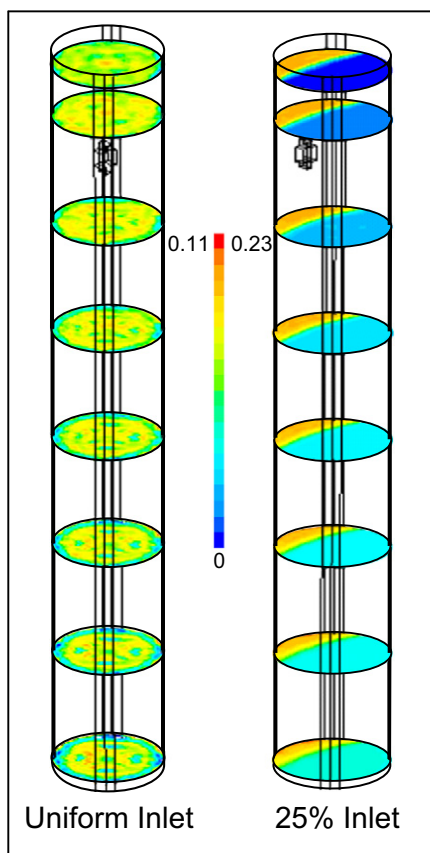


**FIGURE 12** Liquid distribution at the outlet without gas flow rate ( $U_L = 8$  mm/s) and with gas flow rate = 5 cm/s ( $U_L = 3$  mm/s), for column diameter = 0.1 m (Marcandelli et al., 2000).

their results for different gas–liquid velocities is shown in Fig. 12. The studies of Borda et al. (1984) and Sylvester and Pitayagulsarn (1975) suggest that gas flow has a significant effect on liquid distribution inside the bed and increase in gas velocity leads to increase in local liquid flow through the central region. The observations of Møller et al. (1996) also support this finding.

Modeling of liquid distribution in packed bed is rather difficult task due to complexity of packing structure and its interaction with the flowing fluid. Herskovitz and Smith (1978) have developed interconnecting cell model for prediction of liquid distribution. The proposed model predicts the key characteristics of liquid flow and demonstrates the effect of the particle and bed diameter and liquid phase properties. Funk et al. (1990) have modeled two-dimensional packed bed including the distributor and particles. Their model predicts the liquid flow distribution with single and multiple liquid inlets. However, a detailed representation of the fluid–fluid and fluid–solid interactions is lacking in these approaches.

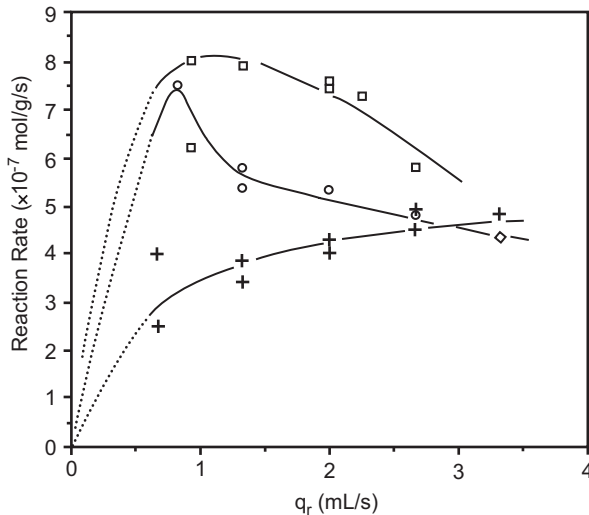
Recently, models based on CFD were proposed for understanding of the liquid distribution in trickle bed reactors (see, for example, Jiang, Khadilkar, Al-Dahhan, & Dudukovic, 1999, 2001; Gunjal, Ranade, & Chaudhari, 2003; Sun, Yin, Afacan, Nandakumar, & Chuang, 2000). Liquid distribution for single, two, and uniform inlets were predicted with fairly good accuracy using discrete cell modeling approach (Jiang et al., 1999, 2001). This model captures key features like formation of liquid channels at point sources and meandering and merging of channels within the bed. For a non-uniform inlet, complete three-dimensional modeling approaches are essential. Such approach was used by Gunjal et al. (2003) for simulating influence of uniform and non-uniform inlets on liquid distribution. A sample of their results is shown in Fig. 13. Their model predicts key features of liquid distribution



**FIGURE 13** Simulated liquid distribution using three-dimensional CFD model: contours of liquid volume fraction (Gunjal et al., 2003;  $D = 0.114$  m and  $d_p = 3$  mm;  $V_L = 2$  kg/m<sup>2</sup>s;  $V_G = 0.22$  m/s).

observed experimentally. Simulated results also indicate that there is little possibility of achieving better liquid distribution if inlet distribution is not adequate. Such an observation is also reported by the study of Funk et al. (1990) and Marcandelli et al. (2000).

Improper liquid distribution has a direct effect on the performance of the reactor. In maldistributed bed, extent of the bed wetting is poor due to the liquid segregation. Flow is dominated by filament type and merging of these filaments produces channeling effect. Poor wetting leads to under-utilization of catalyst bed. Influence of liquid maldistribution on reactor performance is different for gas-limited reactions and liquid-limited reactions. For liquid-limited reactions, extent of the wetting is directly related to the liquid distribution. Better liquid distribution leads to better liquid–solid contacting and therefore better reactor performance. Better wetting, however, does not necessarily increase effective reaction rate for the cases which are limited by gas phase reactants. This was clearly demonstrated by McManus, Funk, Harold, and Ng (1993) by carrying out the experiments of hydrogenation of



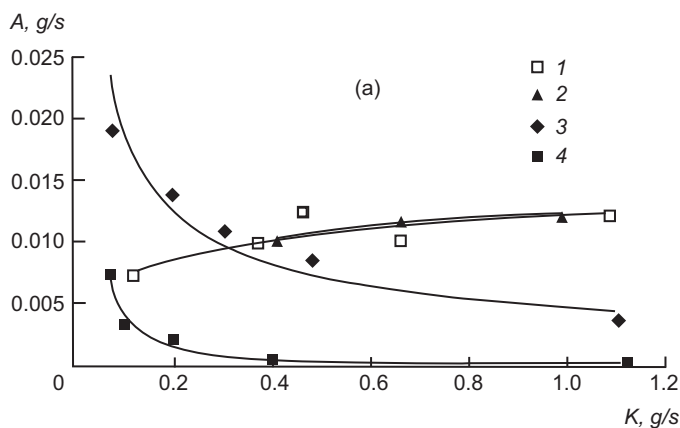
**FIGURE 14** Dependence of hydrogenation reaction rate of  $\alpha$ -methyl styrene on type of distributor (one tube (+), two tube (O) and four tubes ( $\square$ ); [McManus et al., 1993](#)).

$\alpha$ -methyl styrene with single inlet and multiple inlets. This reaction is hydrogen limited. It was observed that effective reaction rates are highest at intermediate wetting condition (see Fig. 14). This is also indirectly observed by [Kireenkov, Shigarov, Kuzin, Bocharov, and Kirillov \(2006\)](#). A sample of their results (for gas phase-limited reaction) which shows influence of column diameter on the reactor performance is shown in Fig. 15 (distribution in larger diameter column may be poorer than the smaller diameter column resulting in better performance of larger reactor).

Recent advances in computational modeling and non-intrusive experimental techniques enable better insights into the liquid distribution in trickle bed reactors. Gross-scale maldistribution is attributed to distributor design while small scale maldistribution is attributed to the local properties of the bed. Though, these sophisticated techniques provide detailed information about flow structures (rivulets, films filaments, stagnancy, etc.) inside the bed, its quantification and use for reaction engineering analysis is still at a preliminary stage.

## Residence Time Distribution

RTD has been used for many years to analyze and characterize mixing inside the reactor because of the unavailability of the detailed flow information inside the reactor. Most of the trickle bed reactors are operated at very low liquid flow rates and various studies have shown that dispersion effects are dominant in such cases. Dispersion coefficient lumps influence of complex



**FIGURE 15** Reactor output at different column diameters: (1) 4.2 cm, (2) 2.3 cm, (3) 1.2 cm, and (4) 0.6 cm (Kireenkov et al., 2006). System: hydrogenation of  $\alpha$ -methyl styrene on 15.2% Pt/ $\gamma$ -alumina;  $T_{in} = 75^\circ\text{C}$ ;  $L = 10$  mm;  $U_{H_2} = 31.8$  cm/s;  $d_p = 1$  mm.

flow non-idealities into a single parameter. Therefore, a careful analysis of RTD data is essential for extracting meaningful information. The work of Van Swaaij, Charpenter, and Villiermaux (1969) indicates that the dispersion effects are dominant at lower liquid velocities and follow a relation  $Pe \propto Re_L^\alpha$ , where  $\alpha$  is  $\sim 0.5$ . Several other studies (Cassanello, Martinez, & Cukierman, 1992; Hochman & Effron, 1969; Saroha, Nigam, Saxena, & Kapoor, 1998; Stegeman, van Rooijen, Kamperman, Weijer, & Westerterp, 1996) have also reported that the gas flow rate has negligible effect on dispersion while particle diameter has a strong influence on dispersion. Therefore, it is convenient to define the dispersion coefficient in terms of particle diameter  $Pe_d = Pe d_p / L$ . Mears (1971) has proposed a criterion, which relates the minimum length of the catalyst bed beyond which the axial dispersion effects are negligible, as:

$$\frac{L}{d_p} > \frac{20m}{Pe_d} \ln \frac{C_{in}}{C_{out}} \quad (2)$$

where  $m$  is the order of the reaction.

Analysis of experimental data by Montagna and Shah (1975) suggests that liquid dispersion effects in residue hydrodesulfurization are equally important as the wetting and liquid holdup; and the Mears criterion was found to be valid for this case.

Thus, RTD is found to be useful for understanding many aspects of trickle bed reactors such as kinetic processes (Ramachandran & Smith, 1978), wetting characteristics (Schwartz, Weger, & Dudukovic, 1976), channeling (Oliveros & Smith, 1982), flow maldistribution (Hanratty & Dudukovic, 1992), and liquid mixing (Gulijk, 1998; Higler, Krishna, Ellenberger, & Taylor, 1999).

Hydrodynamics and mixing in the trickle bed reactors are governed by several factors including non-uniform porosity distribution of the bed, capillary forces, wetting, and non-uniform distribution of flow at the inlet. In Chapter 2, we have seen that prewetted or non-prewetted bed conditions affect the hydrodynamic parameters such as, pressure drop, liquid holdup, and liquid distribution considerably. The implications of these changed hydrodynamic parameters on the mixing of the liquid phase reactants or products can be understood using RTD. RTD or exit age distribution  $E(t)$  for the trickle bed reactors under prewetted and non-prewetted bed conditions is shown in Fig. 22 of Chapter 2 for 0.1 m diameter column with 3 mm glass particles.

Dispersion is higher for a prewetted bed than non-prewetted bed at lower liquid flow rates. At low liquid flow rate, in the non-prewetted bed, liquid flows through the confined region within the bed due to the capillary effect and therefore, exit age distribution shows dominant plug flow-like characteristics. As liquid flow rate increases, the observed difference in the exit age distributions for the prewetted and non-prewetted conditions reduces. At high liquid flow rates ( $10 \text{ kg/m}^2\text{s}$ ), where capillary pressure effect is negligible, RTD is almost independent of extent of prewetting of the bed.

Extent of hysteresis in pressure drop and liquid holdup reduces with increase in particle diameter (Gunjal, Kashid, Ranade, & Chaudhari, 2005). These results indicate that capillary effects are smaller for larger particles. These effects are also reflected in exit age distribution (Gunjal et al., 2003). For a 6-mm particle bed, at low liquid flow rates, liquid dispersion was found to be lower than the 3-mm particle bed. The difference between the exit age distributions for the prewetted and non-prewetted was less for a 6-mm particle bed.

RTD can be simulated by CFD models which can account for details of reactor hardware, porosity distribution, and fluid–fluid interaction. These models can therefore be used to understand influence of various design and operating parameters on RTD. An example of CFD simulations of RTD is shown in Fig. 36 of Chapter 4 in which the model was shown to capture the influence of prewetting on RTD (Gunjal et al. 2003).

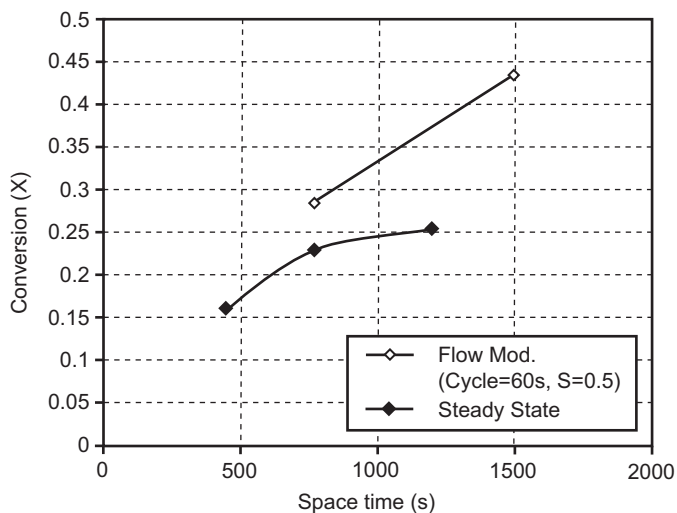
## Periodic Operation and Performance

The idea of periodic operation of trickle bed reactor was originally derived from the pulse flow operation where gas and liquid phases flow in the high interaction regime. However, realization of pulse flow regime is difficult in the large commercial-scale reactors. Therefore, the concept of forced pulsing or periodic operation (flow modulation) is gaining interest. Periodic operation enhances the gas phase mass transfer due to the direct access of the gaseous reactant to the solid surface in the liquid lean region. This was first demonstrated by Haure, Hudgins, and Silveston (1989) for  $\text{SO}_2$  oxidation reaction.

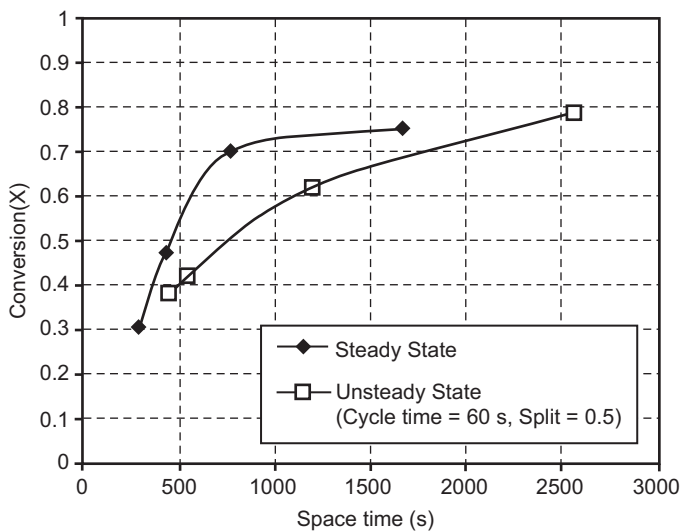
There are many advantages of gas and liquid phase-enriched flow regions which occur in periodic operations. Periodic operation results in higher gas–liquid or liquid mass transfer rates than steady-state operation of the trickle bed reactors. Presence of liquid-enriched zones enhances effective wetting and therefore more effective utilization of the bed. Periodic flow also enhances radial mixing and therefore reduces the extent of liquid maldistribution. Most of the reactions carried out in trickle bed reactors are exothermic. Hence efficient heat removal is essential for effective operation of the reactor. Possibility of liquid maldistribution with the steady-state operation of the trickle bed reactor may lead to existence of hotspots within the bed. Such hotspots influence the quality of the product and may some times cause runaway conditions. In a periodic operation, liquid-enriched zone replenishes the catalyst surface with fresh reactants and therefore significantly reduces problems associated with inadequate wetting, liquid distribution, stagnant zones, and the temperature non-uniformity. Some work on how and when periodic operation can be fruitful is briefly reviewed in the following (for more details see Boelhouwer, Piepers, & Drinkenburg, 2002; Silveston & Hanika, 2002).

Possible benefits of periodic flow operation depend on specific reaction system under consideration. If the reaction is kinetically controlled, periodic flow operation enhances the performance of the reactor compared to the steady-state operation because of better liquid distribution. However, extent of such improvement is rather small because most of the periodic flow operation requires considerably high gas and liquid flow rates. At such high gas and liquid flow rates, the contacting efficiencies are high even for steady operation. Periodic operation is beneficial for *gas-limiting reactions*. For such cases, in steady flow operation, partial wetting conditions are favorable due to direct access of gaseous reactant to the solid surface. However, ineffective heat removal from dry surfaces leads to overheating of catalyst. In contrast to this, periodic operation offers gas-rich zones which enhance the mass transfer effects and liquid-rich zones which effectively remove generated heat. Periodic operation also increases radial mixing and liquid-rich zone replenishes stagnant liquid pockets in the catalyst bed. There are many examples in published literature which demonstrate enhanced performance of trickle bed reactors with periodic operation (see, for example, Castellari & Haure, 1995; Gabarain, Castellari, Cechini, Tobolski, & Haure, 1997; Haure et al., 1989; Lange, Hanika, Stradiotto, Hudgins, & Silveston, 1994; Lee, Hudgins, & Silveston, 1995). A sample of results reported by Khadilkar, Al-Dahhan, and Dudukovic (1999) is shown in Fig. 16.

For *liquid-limiting reactions*, one may not expect significant benefits of the periodic operation over the steady operation. Some results reported by Khadilkar et al. (1999) are shown in Fig. 17 to illustrate this. In fact the periodic operation under-performs the steady-state operation at higher liquid velocities. However, these experiments were carried out using small diameter column



**FIGURE 16** Rate enhancement under periodic flow for gas-limiting reaction (from Khadilkar et al., 1999). System: hydrogenation of  $\alpha$ -methyl styrene on 0.5%Pd/alumina;  $d_p = 3.1$  mm spherical;  $T = 20\text{--}23^\circ\text{C}$ .



**FIGURE 17** Rate enhancement under periodic flow for liquid-limiting reaction (Khadilkar et al., 1999). System: hydrogenation of  $\alpha$ -methyl styrene on 0.5%Pd/alumina;  $d_p = 3.1$  mm spherical;  $T = 20\text{--}23^\circ\text{C}$ .



(2.2 cm), where liquid distribution and wetting do not affect reactor performance significantly.

## TRICKLE BED REACTOR DESIGN AND SCALE-UP

Reactor design involves evolution of reactor hardware and operating protocols which satisfy various process demands without compromising safety, environment, and economics. This therefore necessarily involves expertise from various fields ranging from thermodynamics, chemistry, and catalysis to reaction engineering, fluid dynamics, mixing, and heat and mass transfer. Reactor engineer needs to combine the basic understanding of the chemistry and catalysis with the methods described in this book to evolve suitable reactor design. More often than not, specific scale-up/scale-down methodologies need to be used to establish confidence in the developed design. In this section, some aspects of scale-up are discussed. The overall steps to evolve suitable trickle bed design are discussed in the next section (*Engineering of Trickle Bed Reactors*).

### Reactor Scale-Up/Scale-Down

Scale-up or scale-down is one of the important steps in reactor engineering of trickle bed reactors. Scaling of reactors involves transforming the information from one scale of reactor to another scale (either from a laboratory scale to pilot and commercial-scale reactor or from commercial-scale reactor to pilot and laboratory-scale reactor). Objectives of the scaling may vary from case to case. Scale-up is needed for transforming the newly developed technology at the laboratory-scale reactor to the commercial-scale reactor or simply to interpret and extrapolate laboratory results to the commercial-scale reactor. Reverse case, that is 'scale-down' is also equally important that mimics the large-scale operating process at a much smaller scale. This is used for diagnosis of existing operating reactor using appropriate experiments on the laboratory scale. It may be necessary to use intermediate scales between laboratory and commercial scales especially when transforming information from one scale to the other is not straightforward. Appropriate scaling methodology is required depending upon the specific objectives of the scaling exercise. These objectives could be (i) modification in the existing plant or operational reactor; (ii) increase in the capacity of the existing unit; (iii) modification in the feed or catalyst; and (iv) improvement in the product quality. Overall scaling methodology is schematically shown in Fig. 18.

Scale-up and scale-down methodology needs to estimate how key design parameters change with the reactor scales and then estimate influence of these changes on reactor performance. If the design parameters exhibit simple relationship with the scale of operation of the reactor, then scaling of reactor becomes relatively straightforward. However, for most of the practical

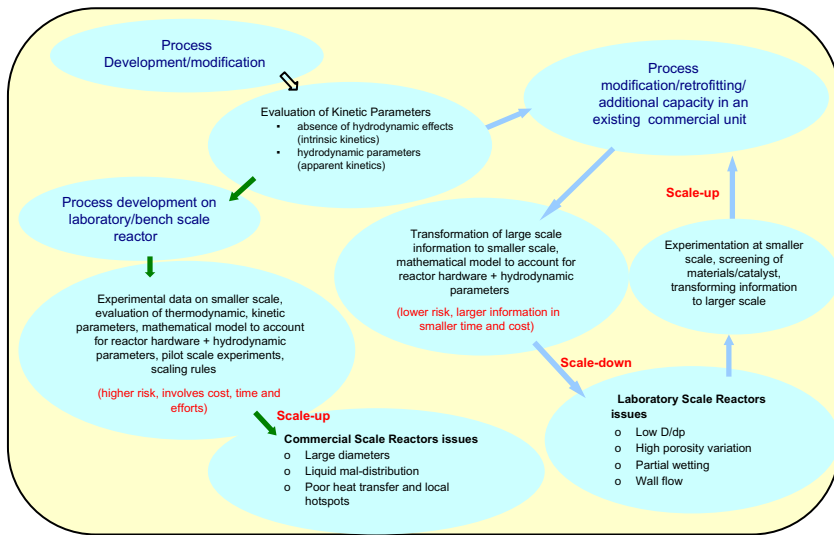


FIGURE 18 General methodology for trickle bed reactor scale-up.

problems this is not the case. Reaction rates, liquid phase mixing, wetting, and heat and mass transfer rates get affected by reactor scales with different degrees and therefore scale-up becomes rather complex. Reaction rate data collected on the laboratory scale forms the basis for scale-up of any process (Fig. 18). Usually the intrinsic reaction rates are studied in a stirred slurry or basket-type reactor. In these reactors, operating conditions such as pressure, temperature, stirring speed, and particle size are chosen such that obtained kinetic data are not influenced by any transport (heat and mass transfer) steps. The apparent reaction kinetics (in the presence of external transport limitations) can be obtained by conducting experiments in the laboratory-scale trickle bed reactor. Sensitivity of reactor performance with operating conditions (such as pressure, temperature, and feed composition) and apparent kinetics can be obtained from such test experiments. These data are useful for optimizing the process conditions to enhance reactor performance. Specific experiments are needed to identify the rate-limiting steps and to quantify influence of operating conditions on wetting, gas–liquid and liquid–solid mass transfer, back mixing, heat transfer, etc. Methods discussed in Chapters 2 and 3 can be used to interpret the laboratory-scale reactor experiments for optimizing operating process conditions. This is a pre-requisite for successful scale-up.

Laboratory-scale reactor can be operated at isothermal conditions which may not be possible for large industrial scale reactors. In small reactors, with lower reactor diameter to particle diameter ratio, liquid bypassing near the wall can affect reactor performance severely. On the other hand, large-scale reactor issues such as liquid segregations, poor heat transfer rates, formation of local

hotspots, and rivulet flow are considerably different. There are no general rules which can be applied for scaling-up. The laboratory data and associated mathematical models need to be used to reduce uncertainties associated with scale-up. The overall strategy of engineering of trickle bed reactors is discussed in *Engineering of Trickle Bed Reactors* while the scale-up methodologies are briefly discussed in the following.

## Reactor Scale-Up Methodologies

Conventionally scale-up is based on maintaining similarity (with the help of key dimensionless numbers) for different scales of reactors. Similarity could be geometric, kinematic, or thermal. Various stages involved in scale-up process are shown schematically in Fig. 19. For trickle bed reactors, maintaining geometric similarity is quite difficult after certain scale-up ratio ( $\sim 10$ – $20$ ). For high scale-up ratio, reactor becomes too tall which may not be practically feasible. For example, typical hydrotreating reactors may become 500 m tall if geometrical similarity is maintained with the laboratory-scale reactors.

Kinematic similarity involves maintaining the same dimensionless numbers based on velocities in the reactor. There are two ways to achieve kinematic similarity for scale-up (see Fig. 20): (i) maintain the same superficial velocities across the scales (and change the space velocity or the average residence time) and (ii) maintain the same average residence time or the space velocity (and change superficial velocities). Thermal similarity involves maintaining similar heat transfer characteristics. Small-scale reactors are generally operated under isothermal conditions. However, maintaining isothermal conditions in large-scaled reactors is often difficult and these are usually operated under

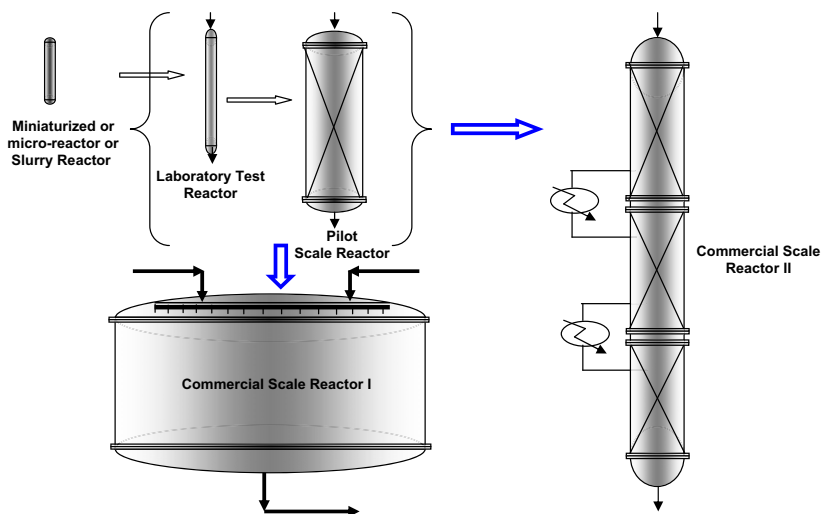
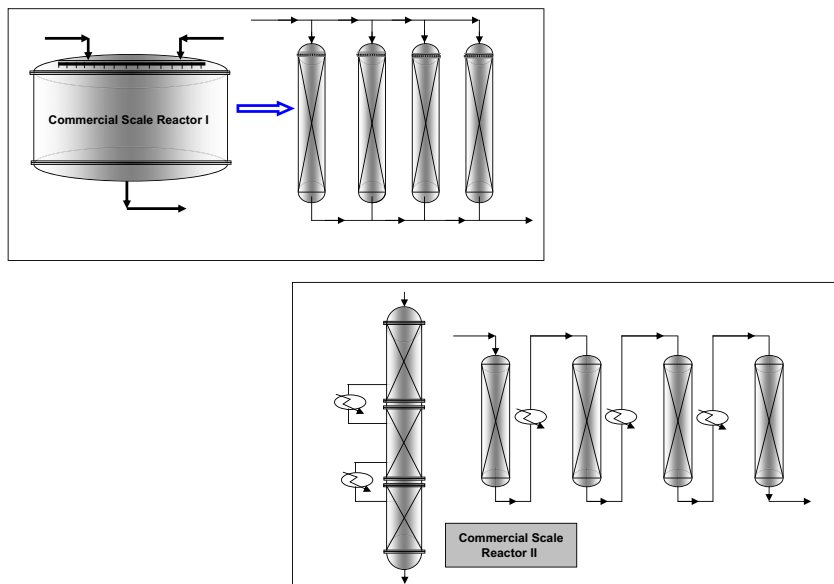


FIGURE 19 Various stages involved in the scale-up of trickle bed reactors.



**FIGURE 20** Methodologies to reduce the adverse effects of scale-up.

adiabatic conditions. When reactions are highly exothermic, consideration of thermal similarities is essential so that prevailing heat transfer and temperature field does not alter the hydrodynamics and therefore performance. In order to maintain the thermal similarity, additional inter-stage cooling or heating systems and addition of inerts are usually employed.

Influence of reactor scale on key design parameters and reactor performance is discussed in the following.

## Reactor Parameters, Scale-Up, and Performance

### *Pressure Drop*

The bed pressure drop is one of the important parameters while designing a commercial-scale reactor. In laboratory-scale reactors, pressure drop per unit length is negligible mainly due to smaller heights and higher porosity ( $\sim 0.5$ ). For lower  $D/d_p$  ratio ( $< 5$ ), porosity variation near wall is large. During the scale-up, change in particle diameter ( $\sim 1$ – $5$  times) is significantly lower than that in reactor diameter ( $\sim 20$ – $100$  times). Therefore, porosity variations near wall in large-scale reactors are usually negligible and average bed porosity is lower ( $\sim 0.4$ ).

Reactor pressure decreases along the length of the reactor. Possible reduction in density of fluids (due to pressure and temperature changes) and molar changes due to reaction may also influence pressure profile along the reactor length. Decrease in pressure along the length of the reactor can

affect reaction rate due to decrease in gas solubility especially when gaseous reactants are limiting. In many commercial reactors, pressure drop across the bed is high and therefore in addition to operating pressure, decrease in pressure along the bed must be taken into account during scale-up. Funk et al. (1990) have shown that reaction rates increase with liquid flow rates up to a certain extent and then decrease mainly because of large pressure drop. If reaction is not intraparticle diffusion limited, one may use larger-sized particles and reduce bed pressure drop ( $\Delta P/L \sim 1/d_p^2$ ).

### Reactor Aspect Ratio

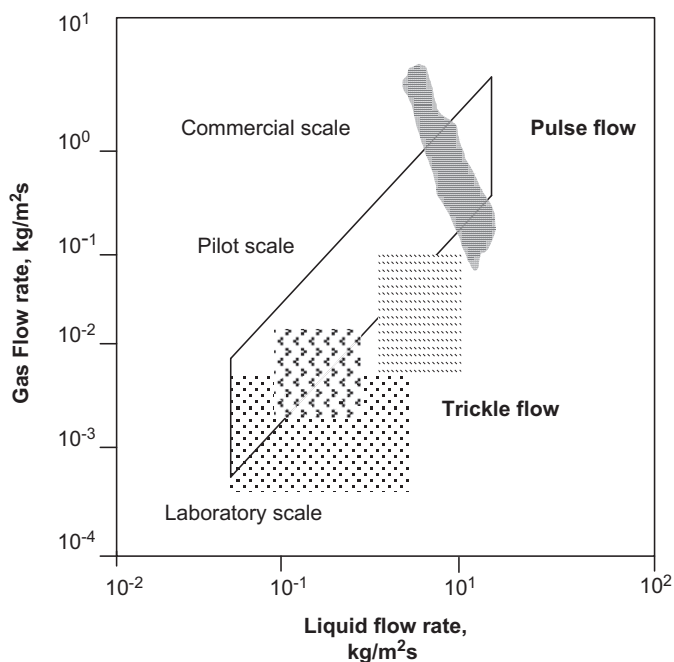
Aspect ratio of the scaled reactor needs to be designed based on geometric or kinematic similarities. Length to diameter ratio of commercial-scale reactors ( $\sim 0.5$ –10) is considerably different than pilot or bench-scale reactors ( $\sim 5$ –100). Salient features of tall and short reactors are listed in Table 2. These features can be useful for selection of appropriate aspect ratio for the case under consideration.

**TABLE 2** Effect of Reactor Aspect Ratio on Key Reactor Characteristics

Reactors with High Aspect Ratio	Reactors with Low Aspect Ratio
<ul style="list-style-type: none"> <li>• Higher gas–liquid superficial velocities</li> <li>• Approach plug flow behavior</li> <li>• Higher gas–liquid/liquid–solid mass transfer rates</li> <li>• Better radial liquid distribution</li> <li>• Liquid redistribution over the length may be required</li> <li>• Higher bed wetting can be achieved</li> <li>• Outer heating jackets/intermediate cooling is possible/suitable</li> <li>• Better control on temperature distribution within the bed</li> <li>• Physical strength of catalyst particle is important</li> <li>• Higher pressure drop/load on compressor</li> <li>• For diffusion-limited reactions, larger pressure drop across bed imposes limits on particle diameters which could be used</li> <li>• Enhances foaming</li> <li>• Suitable for pulse/periodic flow operation</li> </ul>	<ul style="list-style-type: none"> <li>• Lower superficial velocities</li> <li>• Higher deviation from plug flow</li> <li>• Lower gas–liquid/liquid–solid mass transfer rates</li> <li>• Difficult to achieve radially uniform distribution</li> <li>• Lower wetting efficiencies</li> <li>• Internal cooling/heating coils are suitable</li> <li>• Prone to non-uniform temperature in adiabatic operation</li> <li>• Prone to hotspots and runaway conditions in the case of strong exothermic reactions and adiabatic operation</li> <li>• Lower pressure drop/load on compressor</li> <li>• Use of smaller particle size is permissible due to low gas–liquid velocities and lower pressure drop</li> <li>• Reactors can be operated in series</li> <li>• Suitable for foaming liquids</li> <li>• Difficult to achieve/maintain pulse/periodic flow operation</li> </ul>

### Gas–Liquid Flow Rates

Maintaining similar gas and liquid superficial velocities in laboratory-scale and commercial-scale reactors is generally difficult. Typical gas–liquid flow rates in laboratory-scale, pilot-scale, and commercial-scale reactors are shown in Fig. 21. Most of the commercial-scale reactors are operated at higher throughputs. Due to high gas–liquid flow rate, performance of the commercial-scale reactor is considerably different from laboratory-scale reactor. Higher liquid flow rates in commercial-scale reactor increase liquid holdup, liquid–solid wetting, mass transfer rates, and to some extent heat transfer rates. Typical values of the gas–liquid flow rates for commercial-scale, pilot-scale, bench-scale reactors and micro-reactors are also listed in Table 3. Range of these parameters may vary depending upon the properties of the fluids and the reaction system. In typical hydrogenation and oxidation reactors, volume of material processed is considerably lower than the petroleum-refining processes. Superficial velocities used in petroleum processing reactors, however, can be considerably low due to large diameter of the reactors and requirement of complete conversion in the process. In typical hydrotreating trickle bed reactors, low liquid superficial velocity is desired for higher conversion. Therefore,



**FIGURE 21** Typical gas–liquid flow ranges for different scales of trickle bed reactors (Satterfield, 1975).

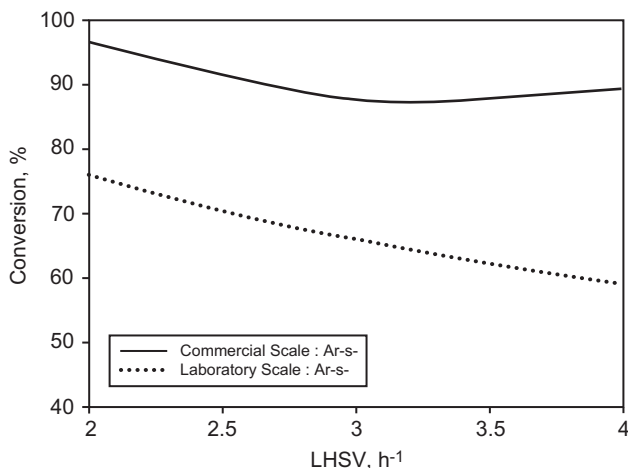
**TABLE 3** Typical Variation of Key Parameters with Different Scales of Trickle Bed Reactor

Parameters/Reactor scale	Commercial-Scale Reactor	Pilot-Scale Reactor	Bench-Scale Reactor	Micro-Reactor
Liquid flow rates (kg/m <sup>2</sup> /s)	2.5–25	0.8–6	0.08–0.25	0.03–0.09
Gas flow rates (kg/m <sup>2</sup> /s)	0.4–4	0.01–1	0.01–0.08	0.0001–0.05
Wetting efficiency	0.6–1	0.4–0.9	0.1–0.7	0.8–1
Liquid holdup	0.16–0.25	0.1–0.2	0.05–0.14	0.15–0.25
Gas–liquid mass transfer rates (s <sup>−1</sup> )	0.08–0.14		0.02–0.08	3–7
Liquid–solid mass transfer rates (s <sup>−1</sup> )	0.1–0.3		0.9–1.4	–
Length of bed (m)	16	1–4	0.3–1	0.008–0.5

wetting parameters in such reactors are considerably lower than the trickle bed reactors used for oxidation or hydrogenation reactions.

The simulated performance of typical laboratory-scale and commercial-scale hydrotreating reactors is shown in Fig. 22. In this case study, performance enhancement in commercial-scale reactor was found to be about 20–30% over the laboratory scale. This was mainly attributed to increased liquid holdup and mass transfer rates under commercial operating conditions. Uncertainty about the extent of wetting or maldistribution in large reactors is one of the key concerns in scale-up. The CFD models discussed in the previous chapter can provide useful insight and design guidelines for controlling and manipulating wetting and liquid distribution within the bed.

The ranges of parameters given in Table 3 are indicative. Trickle bed reactors are operated with a wide variety of conditions and these conditions differ considerably depending upon the type of application. For example, in typical oxidation reactions, higher gas–liquid mass transfer rates are desired for better performance of the reactor. Therefore, it is important to see how key parameters like interfacial area and mass transfer rates are changing with scale. For hydrocracking reactors, reactions are strongly exothermic, rather slow and often limited by liquid reactants. Therefore, for this case, heat transfer and adequate heat removal arrangement become far more crucial than the external mass transfer issues. Severe operating conditions ( $T = 300\text{--}450\text{ }^{\circ}\text{C}$ ,  $P = 100\text{--}250\text{ bar}$ ) alter the phase properties locally inside the reactor. Therefore, liquid



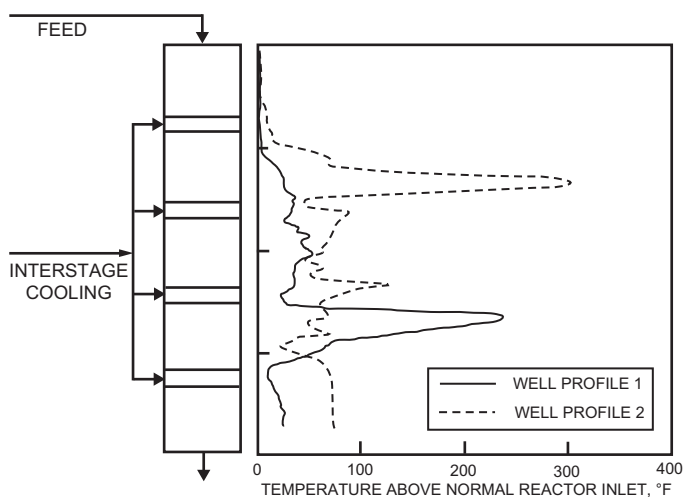
**FIGURE 22** Comparison of performance of the commercial-scale and laboratory-scale hydrotreating reactors (Gunjal & Ranade, 2007). System: hydrotreating reactors;  $P_{\text{lab-com}} = 4$  and 4.4 MPa;  $\text{LHSV}_{\text{lab-com}} = 2.0$  and  $3.0 \text{ h}^{-1}$ ;  $(Q_G/Q_L)_{\text{lab-com}} = 200$  and  $300 \text{ m}^3/\text{m}^3$ ;  $y_{\text{H}_2\text{S}} = 1.4\%$ .

holdup, wetting, extent of gas phase reactions, and mass transfer rates in commercial reactors can be considerably different from pilot-scale or bench-scale operation and not necessarily follow the trends shown in Table 3.

Most of the small-scale operations are carried out under isothermal conditions and uniform temperature in the bed. However, most of the commercial-scale reactors are operated under adiabatic conditions in which variation of local temperature affects the performance of reactor considerably. In fact, in some operations intermediate cooling or gas quenching is necessary to maintain the operating temperatures in the desired range, to avoid hotspots and runaway conditions. Many commercial-scale trickle bed reactors are multistage reactors typically 1–4 m in diameter and 4–6 m in length arranged in 3–4 stages. Intermediate cooling and liquid redistribution are possible using such arrangements. Despite these arrangements, formation of local hotspots is possible due to local liquid maldistribution effects. Because of liquid maldistribution, liquid flow rates are different in different regions of trickle bed reactors. The regions with low liquid flow rates may experience rise in temperature (Jaffe, 1976). An example of such local variation in reactor temperature for the hydrocracking reactor is shown in Fig. 23. Sharp peaks in temperature along the length of the bed indicate formation of hotspots, which may cause damage to the catalyst due to overheating. These results indicate that the formation of local hotspots is independent of position of interstage cooling and liquid maldistribution may be the most probable reason for formation of local hotspots.

Detection of low liquid flow regions or locations of hotspot is difficult under such high temperature and pressure conditions. Therefore, it is important to gain the information on extent of maximum adiabatic temperature rise, heat





**FIGURE 23** Axial temperature profile in commercial reactor is independent of interstage cooling (Jaffe, 1976). System: hydrocracking of oil.

dissipation rate, and extent of high temperature region. Such quantification is possible by using mathematical models based on mixing tank network where artificial flow obstacle produces low flow regions. Possibility of hotspots and sensitivity of these with key design and operating parameters can be estimated using the reaction kinetics and appropriate reactor models. Several assumptions associated with the flow simplification and bed characterization can be eliminated by making use of CFD-based model. The detailed three-dimensional CFD models can capture liquid maldistribution as well as axial and radial mixing of gas and liquid phases within the reactor. Such models are useful for providing the guidelines required for reducing the extent of hotspots, severity of the problem, and the risk associated with rising of temperature to the adiabatic flash point. The overall approach of engineering of trickle bed reactors is discussed in the following section. Some examples and case studies are discussed in Chapter 6.

## ENGINEERING OF TRICKLE BED REACTORS

Reactor engineering of trickle bed involves all the activities necessary to evolve best-possible hardware and operating protocols for carrying out the desired transformation of raw materials (or reactants) to value-added products. Naturally, it requires expertise from various fields ranging from thermodynamics, chemistry and catalysis to reaction engineering, fluid dynamics, mixing, and heat and mass transfer. Reactor engineer has to interact with chemists to understand the basic chemistry and peculiarities of the catalyst. Based on such understanding and proposed performance targets, reactor engineer has to

conceive a suitable reactor hardware and operating protocols. Typical “wish list” of a reactor engineer for the new process could be as follows:

- Stable operation within technologically feasible region
- Intrinsically safe operation
- Environmentally acceptable
- Maximum possible conversion of the feedstocks
- Maximum selectivity of reaction to the desired products
- Lowest capital and operating costs

Typical “wish list” for enhancing performance of the existing reactor technology could be as follows:

- More throughput per unit volume
- Improved selectivity and better quality product
- Safer operation
- Reduced energy consumption
- More environment friendly operation

The next step is to translate the wish list into a quantitative form and establish a relationship between items in the wish list and reactor hardware and operating protocols. The reactor engineer’s task is to design and tailor the reactor hardware and operating protocols to realize the wish list. Several activities are involved in this process. It may often turn out that some of the items in the wish list require contradictory options of hardware and operation. In such a case, a careful analysis of different items in wish list must be made to assign priorities. Operability, stability, and environmental constraints often get precedence over conversion and selectivity when such conflicting requirements arise.

The first step, in engineering of trickle beds, involves quantification of influence of reactant flow rate and operating temperature on performance of the reactor (conversion, selectivity, stability, and so on). The first step in such analysis is formulating a mathematical framework to describe the rate (and mechanism) by which one chemical species is converted into another in absence of any transport limitations (chemical kinetics). Kinetics of reactions need to be determined from experimental measurements. Measuring the rate of chemical reactions in the laboratory is itself a specialized branch of chemical engineering. More information about laboratory reactors used for obtaining intrinsic kinetics can be found in reviews/textbooks like Chaudhari, Shah, and Foster (1986), Doraiswamy and Sharma (1984), Levenspiel (1972), Ramachandran and Chaudhari (1983), and Smith (1970).

Once the intrinsic kinetics is available, the effective rate analysis can be carried out using the methods discussed in Chapter 3. The conventional reaction engineering models for trickle bed reactors can be developed based on this analysis which may help in establishing a relationship among operating conditions (flow rate, mode of operation, pressure, composition), reactor hardware (reactor volume and reactor configuration) and reactor performance.

As discussed in Chapter 3, in these models, some assumptions are made regarding the flow and mixing of various species in the reactor, instead of solving the detailed fluid dynamics equations. These models therefore cannot directly relate the reactor hardware with reactor performance. These models are however computationally much less demanding than the CFD-based models and can give a quick understanding of the overall behavior of the reactor. These models can be used to identify the important parameters/issues, which may require further study. Of course, the class of conventional chemical reaction engineering models itself contains a variety of models. It will be useful to distinguish between “learning” models and “design” models at this stage.

“Learning” models are developed to understand the basic concepts and to obtain specific information about some unknown processes. The results obtainable from such models may not directly lead to design information but are generally useful to take appropriate engineering decisions. “Design” models, on the other hand, yield information or results, which can be directly used for reactor design and engineering. It is first necessary to develop some design models to estimate reactor sizing and to evolve preliminary reactor configuration. Several “learning” models can then be developed to understand various reactor engineering issues like:

- Start-up and shut-down dynamics
- Multiplicity and stability of thermo-chemical processes occurring in the reactor
- Sensitivity of reactor performance with respect to mixing and RTD
- Selectivity and by-product formation

After establishing such understanding and analysis of the reaction system, the next most important question facing the reactor engineer is to evaluate consequences of the assumptions involved in such models for estimating the behavior of actual reactor. Questions like operability and stability of the flow regime need to be answered. Mixing, wetting as well as heat and mass transfer are intimately related to flow regimes and distributors of gas and liquid. The mixing in actual reactor may significantly deviate from that assumed for the reaction engineering models. This deviation can be caused by say channeling of fluid or by formation of stagnant regions within the reactor. RTD data and analysis is useful to get the bounds and limiting solutions of reactor performance. It must be remembered that more than one model may fit the observed RTD data. A general philosophy is to select the simplest possible model, which adequately represents the physical phenomena occurring in the actual reactor. The RTD data and models are useful to understand and quantify possible influence of static liquid holdup on reactor performance and product quality. The brief review of distributors given in *Reactor Performance* along with the references cited therein will be useful to finalize selection of distributors. It may be noted that even the small-scale hardware details like design of feed nozzles or weirs and reactor internals (cooling coils, baffles etc.) may have dramatic

influence on reactor performance. The issues of scale-up and scale-down may have to be resolved by following an iterative methodology. Engineering creativity, experience, and accumulated empirical information is generally used to evolve reactor configuration and designs. The discussion in Chapter 3 as well as in *Reactor Performance* and *Trickle Bed Reactor Design and Scale-Up* will be useful to implement these steps.

The understanding gained by development and implementation of these steps will be helpful to identify the needs for developing more sophisticated simulation models/data for establishing the desired trickle bed reactor design. It is important at this stage to identify gaps between available knowledge and that required for fulfilling the “wish list.” The identified gaps can then be bridged by carrying out experiments in the laboratory and/or pilot plant(s) and by developing more comprehensive fluid dynamic models. Despite the advantages, conventional chemical reaction engineering models are not directly useful for understanding the influence of reactor hardware on reactor performance. For example, how the design of distributor affects the radial distribution of liquid in trickle bed and thereby the reactor performance will be difficult to predict without developing the detailed fluid dynamic model of the reactor or without carrying out experiments on a scale model. The CFD-based approach will make valuable contributions at this stage by providing the required insight, by helping to devise right kind of experiments, and by allowing screening of alternative configurations and tools for extrapolation and scale-up. The methodology and models discussed in Chapter 4 will be useful for this purpose.

The whole process of reactor engineering is not sequential! All the steps interact with and influence each other. The results obtained in the laboratory experiments on hydrodynamics and RTD or from the computational flow model may demand changes and revisions in the earlier analysis and the whole process is iterated until the satisfactory solution emerges. In this book, we have tried to provide adequate details of models and methodologies useful to carry out different components of reactor engineering of trickle beds. Some applications of this engineering methodology are discussed in the next chapter (Chapter 6).

## SUMMARY

In engineering practice, reactor engineering solution is composed of three main steps: (i) analysis of transport and reaction rate parameters; (ii) identifying uncertainties associated with design parameters; and (iii) resolving process complexities and conflicting demands. In trickle bed reactors, interaction between reaction kinetics and hydrodynamics is often complex. This chapter complements discussion covered in Chapters 2–4 and provides a methodology for engineering of trickle bed reactors.

Key practical aspects involving rate analysis including hysteresis and multiplicity, particle and bed properties (particle size/shape/orientation), distributor effects, liquid phase maldistribution, and mixing of phases along the

length of the column are discussed. Issues related to selection of reactor aspect ratio and issues pertaining to scale-up and scale-down are discussed. An overall methodology combining experiments and computational modeling is presented at the end. Some examples of engineering of trickle beds as well as a brief review of recent developments and path forward in trickle bed reactors are discussed in the following chapter. It is evident from current state of the art that in spite of considerable advances in our understanding of different phenomena occurring in trickle beds, it is futile to attempt a single comprehensive model for a trickle bed reactor incorporating all the processes. It is therefore recommended to use a suite of models comprising many ‘learning’ and ‘design’ models. This modeling efforts need to be complemented by appropriately designed experiments of three categories: learning, calibration and validation. Such a composite approach based on the methodology discussed here will be useful for engineering of trickle bed reactors.

## REFERENCES

- Al-Dahhan, M. H., Wu, Y. X., & Dudukovic, M. P. (1995). Reproducible technique for packing laboratory-scale trickle-bed reactors with a mixture of catalyst and fines. *Industrial and Engineering Chemistry Research*, 34, 741.
- Ballard, J. H., & Hines, J. E. (1965). Vapor Liquid Distribution Method and Apparatus for the Conversion of Hydrocarbons. *U.S. Patent No 3,218,249*.
- Boelhouwer, J. G., Piepers, H. W., & Drinkenburg, A. A. H. (2002). Liquid-induced pulsing flow in trickle-bed reactors. *Chemical Engineering Science*, 57, 3387–3399.
- Borda, M., Gabitto, J. F., & Lemcoff, N. O. (1987). Radial liquid distribution in a trickle bed reactor. *Chemical Engineering Communications*, 60, 243–252.
- Bruijn, A.de, Naka, I., & Sonnemans, J. W. M. (1981). Effect of the noncylindrical shape of extrudates on the hydrodesulfurization of oil fractions. *Industrial and Engineering Chemistry Process Design and Development*, 20, 40–45.
- Cassanello, M. C., Martinez, O. M., & Cukierman, A. L. (1992). Effect of the liquid axial dispersion on the behavior of fixed bed three phase reactors. *Chemical Engineering Science*, 47(13–14), 3331–3338.
- Castellari, A. T., & Haure, P. M. (1995). Experimental study of the periodic operation of a trickle-bed reactor. *AIChE Journal*, 41, 1593–1597.
- Chaudhari, R. V., Jaganathan, R., Mathew, S. P., Julcour, C., & Delmas, H. (2002). Hydrogenation of 1,5,9-cyclododecatriene in fixed-bed reactors: down- vs. upflow modes. *AIChE Journal*, 48 (1), 110–125.
- Chaudhari, R. V., Shah, Y. T., & Foster, N. R. (1986). Novel gas–liquid–solid catalytic reactors. *Catalysis Reviews – Science and Engineering*, 28, 431.
- Chou, T. S. (1984). Liquid distribution in a trickle bed with redistribution screens placed in the column. *Industrial and Engineering Chemistry Process Design and Development*, 23, 501.
- Crine, M., & L’Homme, G. A. (1984). In L. K. Doraiswamy (Ed.), *Recent advances in the engineering analysis of chemically reacting systems* (pp. 430). New York: Wiley.
- Crine, M., Marchot, P., & L’Homme, G. (1981). Liquid flow maldistributions in trickle-bed reactors. *Chemical Engineering Communications*, 7, 377–388.
- Doraiswamy, L. K., & Sharma, M. M. (1984). *Heterogeneous Reactions: Analysis, Examples and Reactor Design*, Vol 2. New York: John Wiley.

- Fox, R. (1987). On the liquid flow distribution in trickle-bed reactor. *Industrial and Engineering Chemistry Research*, 26, 2413–2419.
- Funk, G. A., Harold, M. P., & Ng, K. M. (1990). A novel model for reaction in trickle beds with flow maldistribution. *Industrial and Engineering Chemistry Research*, 29, 738–748.
- Gabarain, L., Castellari, A. T., Cechini, J., Tobolski, A., & Haure, P. M. (1997). Analysis of rate enhancement in a periodically operated trickle-bed reactor. *AIChE Journal*, 43, 166–177.
- Gamborg, M. M., & Jensen, B. N. (1999). Two-Phase Downflow Liquid Distribution Device. *U.S. Patent No. 5,942,162*.
- Goto, S., & Smith, J. M. (1975). Trickle-bed reactor performance. Part-I: holdup and mass transfer effects. *AIChE Journal*, 21, 706.
- Gulijk, C. V. (1998). Using computational fluid dynamics to calculate transversal dispersion in a structured packed bed. *Computers and Chemical Engineering*, 22, 5767–5770.
- Gunjal, P. R., Kashid, M. N., Ranade, V. V., & Chaudhari, R. V. (2005). Hydrodynamics of trickle-bed reactors: experiments and CFD modeling. *Industrial and Engineering Chemistry Research*, 44, 6278–6294.
- Gunjal, P. R., & Ranade, V. V. (2007). Modeling of laboratory and commercial scale hydro-processing reactors using CFD. *Chemical Engineering Science*, 62, 5512–5526.
- Gunjal, P. R., Ranade, V. V., & Chaudhari, R. V. (2003). Liquid-phase residence time distribution in trickle bed reactors: experiments and CFD simulations. *The Canadian Journal of Chemical Engineering*, 81, 821.
- Hanika, J., Lukjanov, B. N., Kirillov, V. A., & Stanek, V. (1986). Hydrogenation of 1,5-cyclo-octadiene in a trickle bed reactor accompanied by phase transition. *Chemical Engineering Communications*, 40, 183.
- Hanika, J., Sporka, K., Ruzicka, V., & Krausova, J. (1975). Qualitative observations of heat and mass transfer effects on the behaviour of a trickle bed reactor. *Chemical Engineering Communications*, 2, 19.
- Hanika, J., Sporka, K., Ruzicka, V., & Pistek, R. (1977). Dynamic behavior of an adiabatic trickle bed reactor. *Chemical Engineering Science*, 32, 525.
- Hanratty, P. J., & Dudukovic, M. P. (1992). Detection of flow maldistribution in trickle-bed reactors via tracers. *Chemical Engineering Science*, 47, 3003–3014.
- Haure, P., Hudgins, R. R., & Silveston, P. L. (1989). Periodic operation of a trickle-bed reactor. *AIChE Journal*, 35, 1437–1444.
- Herskowitz, M., & Mosseri, S. (1983). Global rates of reaction in trickle-bed reactors: effects of gas and liquid flow rates. *Industrial and Engineering Chemistry Fundamentals*, 22, 4–6.
- Herskowitz, M., & Smith, J. M. (1978). Liquid distribution in trickle bed reactors. *AIChE Journal*, 24, 439.
- Hessari, F. A., & Bhatia, S. K. (1997). Hysteresis and phase transitions in a single partially internally wetted catalyst pellet: thermo-gravimetric studies. *Chemical Engineering Communications*, 157, 109–133.
- Higler, A. P., Krishna, R., Ellenberger, J., & Taylor, R. (1999). Counter-current operation of a structured catalytically packed-bed reactor: liquid phase mixing and mass transfer. *Chemical Engineering Science*, 54(21), 5145–5152.
- Hochman, J., & Effron, E. (1969). Two-phase cocurrent downflow in packed beds. *Industrial and Engineering Chemistry Fundamentals*, 8(1), 63–69.
- Jaffe, S. B. (1976). Hot spot simulation in commercial hydrogenation processes. *Industrial and Engineering Chemistry Process Design and Development*, 15(3), 410–416.
- Jiang, Y., Khadilkar, M. R., Al-Dahhan, M. H., & Dudukovic, M. P. (1999). Two-phase flow distribution in 2D trickle-bed reactors. *Chemical Engineering Science*, 54, 2409–2419.

- Jiang, Y., Khadilkar, M. R., Al-Dahhan, M. H., & Dudukovic, M. P. (2001). CFD modeling of multiphase flow distribution in catalytic packed bed reactors: scale down issues. *Catalysis Today*, 66, 209–218.
- Julcours, C., Jaganathan, R., Chaudhari, R. V., Wilhelm, A. M., & Delmas, H. (2001). Selective hydrogenation of 1,5,9-cyclododecatriene in up- and down-flow fixed-bed reactors: experimental observations and modeling. *Chemical Engineering Science*, 56, 557–564.
- Khadilkar, M. R., Al-Dahhan, M. H., & Dudukovic, M. P. (1999). Parametric study of unsteady-state flow modulation in trickle-bed reactors. *Chemical Engineering Science*, 54, 2585–2595.
- Khadilkar, M. R., Wu, X., Al-Dahhan, M. H., Dudukovic, M. P., & Colakyan, M. (1996). Comparison of trickle-bed and upflow reactor performance at high pressure: model predictions and experimental observations. *Chemical Engineering Science*, 51(10), 2139–2148.
- Kheshgi, H. S., Reyes, S. C., Hu, R., & Ho, T. C. (1992). Phase transition and steady-state multiplicity in a trickle-bed reactor. *Chemical Engineering Science*, 47, 1771.
- Kim, D. H., & Kim, Y. G. (1981). An experimental study of multiple steady states in a porous catalyst due to phase transition. *Journal of Chemical Engineering of Japan*, 14, 311–317.
- Kireenkov, V. V., Shigarov, A. B., Kuzin, N. A., Bocharov, A. A., & Kirillov, V. A. (2006). Effect of the nonuniformity of the inlet liquid distribution on the trickle-bed reactor output in an exothermic reaction accompanied by evaporation. *Theoretical Foundations of Chemical Engineering*, 40(5), 472–482.
- Kirillov, V. A., & Koptuyg, I. V. (2005). Critical phenomena in trickle-bed reactors. *Industrial and Engineering Chemistry Research*, 44, 9727–9738.
- Klerk, A. de (2003). Voidage variation in packed beds at small column to particle diameter ratio. *AIChE Journal*, 49(8), 2022–2029.
- Lange, R., Hanika, J., Stradiotto, D., Hudgins, R. R., & Silveston, P. L. (1994). Investigations of periodically operated trickle-bed reactors. *Chemical Engineering Science*, 49(24B), 5615–5621.
- Larachi, F., Laurent, A., Midoux N., & Wild, G. (1991). Experimental study of a trickle-bed reactor Operating at high pressure: two-phase pressure drop and liquid saturation, *Chemical Engineering Science*, vol. 46, no. 5,6, pp. L233–L246.
- Lee, J. K., Hudgins, R. R., & Silveston, P. L. (1995). Cycled trickle-bed reactor for SO<sub>2</sub> oxidation. *Chemical Engineering Science*, 50, 2523–2530.
- Liu, G., Mi, Z., Wang, L., Zhang, X., & Zhang, S. (2006). Hydrogenation of dicyclopentadiene into *endo*-tetrahydrodicyclopentadiene in trickle-bed reactor: experiments and modeling. *Industrial and Engineering Chemistry Research*, 45, 8807–8814.
- Lutran, P. G., Ng, K. M., & Delikat, E. P. (1991). Liquid distribution in trickle beds: an experimental study using computer-assisted tomography. *Industrial and Engineering Chemistry Research*, 30, 1270–1280.
- Marcandelli, C., Lamine, A. S., Bernard, J. R., & Wild, G. (2000). Liquid distribution in trickle-bed reactor. *Oil & Gas Science and Technology — ‘Revue d’IFP Energies nouvelles’*. IFP, 55 (4), 407–415.
- McManus, R. L., Funk, G. A., Harold, M. P., & Ng, K. M. (1993). Experimental study of reaction in trickle-bed reactors with liquid maldistribution. *Industrial and Engineering Chemistry Research*, 32, 510–514.
- Mears, D. E. (1971). The role of axial dispersion in trickle flow laboratory reactors,. *Chemical Engineering Science*, 26, 1361.
- Metaxas, K. C., & Papayannakos, N. G. (2006). Kinetics and mass transfer of benzene hydrogenation in a trickle-bed reactor. *Industrial and Engineering Chemistry Research*, 45, 7110–7119.

- Møller, L. B., Halken, C., Hansen, J. A., & Bartholdy, J. (1996). Liquid and gas distribution in trickle-bed reactors. *Ind. Eng. Chem. Res.*, 35, 926–930.
- Montagna, A. A., & Shah, Y. T. (1975). The role of liquid holdup, effective catalyst wetting, and back-mixing on the performance of a trickle bed reactor for residue hydrosulfurization. *Industrial and Engineering Chemistry Process Design and Development*, 14(4), 479–483.
- Nemec, D., & Levec, J. (2005). Flow through packed bed reactors: 1. Single phase flow. *Chemical Engineering Science*, 60, 6947–6957.
- Oliveros, G., & Smith, J. M. (1982). Dynamic studies of dispersion and channeling in fixed beds. *AIChE Journal*, 28, 751–759.
- Rajashekharan, M. V., Jaganathan, R., & Chaudhari, R. V. (1998). A trickle-bed reactor model for hydrogenation of 2,4 dinitrotoluene: experimental verification, *Chemical Engineering Science*, 53(4), 787–805.
- Ramachandran, P. A., & Chaudhari, R. V. (1983). *Three Phase Catalytic Reactors*. New York, USA: Gordon and Breach.
- Ramachandran, P. A., & Smith, J. M. (1978). Dynamic behavior of trickle bed reactor. *Chemical Engineering Science*, 34, 75–91.
- Ravindra, P. V., Rao, D. P., & Rao, M. S. (1997). A model for the oxidation of sulfur dioxide in a trickle-bed reactor, *Industrial and Engineering Chemistry Research*, 36, 5125–5132.
- Riopelle, J. E., & Scarsdale, N. Y. (1967). Bed Reactor with Quench Deck. *U.S. Patent No 3,353,924*.
- Saroja, A. K., Nigam, K. D. P., Saxena, A. K., & Kapoor, V. K. (1998). Liquid distribution in trickle-bed reactors. *AIChE Journal*, 44, 2044–2052.
- Satterfield, C. N. (1975). Trickle bed reactors. *AIChE Journal*, 21(2), 209–228.
- Schwartz, J. G., Weger, E., & Dudukovic, M. P. (1976). A new tracer method for the determination of liquid–solid contacting efficiency in trickle bed reactors. *AIChE Journal*, 22, 953.
- Sederman, A. J., & Gladden, L. F. (2001). Magnetic resonance imaging as a quantitative probe of gas–liquid distribution and wetting efficiency in trickle-bed reactors. *Chemical Engineering Science*, 56, 2615–2628.
- Shigarov, A. B., Kuzin, N. A., & Kirillov, V. A. (2002). Phase disequilibrium in the course of an exothermic reaction accompanied by liquid evaporation in a catalytic trickle-bed reactor. *Theoretical Foundations of Chemical Engineering*, 36, 159–165.
- Silveston, P. L., & Hanika, J. (2002). Challenges for the periodic operation of trickle-bed catalytic reactors. *Chemical Engineering Science*, 57, 3373–3385.
- Smith, J.M., 1970, *Chemical Engineering Kinetics*, 2 Edition, McGraw-Hill Book.
- Stegeman, D., van Rooijen, F. E., Kamperman, A. A., Weijer, S., & Westerterp, K. R. (1996). Residence time distribution in the liquid phase in a cocurrent gas–liquid trickle bed reactor. *Industrial and Engineering Chemistry Research*, 35, 378–385.
- Sun, C. G., Yin, F. H., Afacan, A., Nandakumar, K., & Chuang, K. T. (2000). Modelling and simulation of flow maldistribution in random packed columns with gas–liquid countercurrent flow. *Chemical Engineering Research and Design*, 78(3), 378–388.
- Sylvester, W. D., & Pitayagulsarn, P. (1975). Radial liquid distribution in cocurrent two phase downflow in packed beds. *The Canadian Journal of Chemical Engineering*, 53, 599.
- Van Swaaij, W. P. M., Charpentier, J. C., & Villermaux, J. (1969). Residence time distribution in the liquid phase of trickle flow in packed columns. *Chemical Engineering Science*, 24, 1083–1095.
- Watson, P. C., & Harold, M. P. (1993). Dynamic effects of vaporization with exothermic reaction in a porous catalytic pellet. *AIChE Journal*, 39, 989–1006.
- Weekman, V. W., Jr., & Myers, J. (1964). Fluid flow characteristics of cocurrent gas–liquid flow in packed beds. *AIChE Journal*, 10, 951.