

Fixed-Bed Reactors

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In addition to the standard symbols defined in the front matter and on pp. 6–9 and 121–123 of this volume, the following symbols are used:

a_p	specific outer surface area of catalyst, m^2/m^3 packing	\dot{N}	energy required for coolant circulation, kW
A	flow cross-sectional area, m^2	Nu	Nusselt number
c	molar concentration, mol/m^3	\dot{Q}	heat flow to be transferred, kW
c_0	feed concentration, mol/m^3	Re	Reynolds number
c_{pG}	specific heat of reaction gas, $kJ kg^{-1} K^{-1}$	Sc	Schmidt number
c_s	specific heat of catalyst, $kJ kg^{-1} K^{-1}$	Sh	Sherwood number (Eq. 2.10)
D	diffusion coefficient, m^2/s	T	temperature, K
d_p	catalyst particle diameter, m	T_0	feed gas temperature, K
d_h	hydraulic diameter ($d_h = 4 A/U$), m	U	circumference, m
$f_{1,2}$	Ergun coefficients (Eqs. 2.4, 2.5)	U_w	gas-catalyst heat-transfer coefficient, $Wm^{-2} K^{-1}$
G_z	mass-flow velocity, $kg m^{-2} s^{-1}$	v_G	interparticle velocity, m/s
k_G	gas-catalyst mass-transfer coefficient, m/s	\dot{V}	volume flow rate, m^3/s
L	length of catalyst bed, m	V_R	reactor volume, m^3
		w	migration velocity of reaction zone, m/s
		z	space coordinate, m
		Z_L	reactor length, m
		α_w	wall heat-transfer coefficient, $Wm^{-2} K^{-1}$

ε	void fraction, m^3 free space/ m^3 packing
η	dynamic viscosity, N s m^{-2}
Δh_r	reaction enthalpy, kJ/mol
Δp	pressure drop, N/m^2
ΔT_{ad}	adiabatic temperature change, K
ΔT_c	cooling temperature change between inlet and outlet, K
Δx	molar conversion, mol/mol
λ_{eff}	effective axial thermal conductivity, $\text{W m}^{-1} \text{K}^{-1}$
λ_G	molecular gas thermal conductivity, $\text{W m}^{-1} \text{K}^{-1}$
λ_r	effective radial thermal conductivity, $\text{W m}^{-1} \text{K}^{-1}$
ρ	density, kg/m^3
ρ_G	gas density, kg/m^3
ρ_s	density of catalyst particle, kg/m^3
ξ	pressure drop coefficient

1. Introduction

Catalytic fixed-bed reactors are the most important type of reactor for the synthesis of large-scale basic chemicals and intermediates. In these reactors, the reaction takes place in the form of a heterogeneously catalyzed gas reaction on the surface of catalysts that are arranged as a so-called fixed bed in the reactor. In addition to the synthesis of valuable chemicals, fixed-bed reactors have been increasingly used in recent years to treat harmful and toxic substances. For example, the reaction chambers used to remove nitrogen oxides from power station flue gases constitute the largest type of fixed-bed reactors as regards reactor volume and throughput, while automobile exhaust purification represents by far the most widely employed application of fixed-bed reactors.

With regard to application and construction, it is convenient to differentiate between fixed-bed reactors for adiabatic operation and those for nonadiabatic operation. Since temperature control is one of the most important methods of influencing a chemical reaction, adiabatic reactors are used only where the heat of reaction is small, or where there is only one major reaction pathway; in these cases no adverse effects on selectivity or yield due to the adiabatic temperature development are expected. The characteristic feature of adiabatic reaction control is that the catalyst is present in the form of a uniform

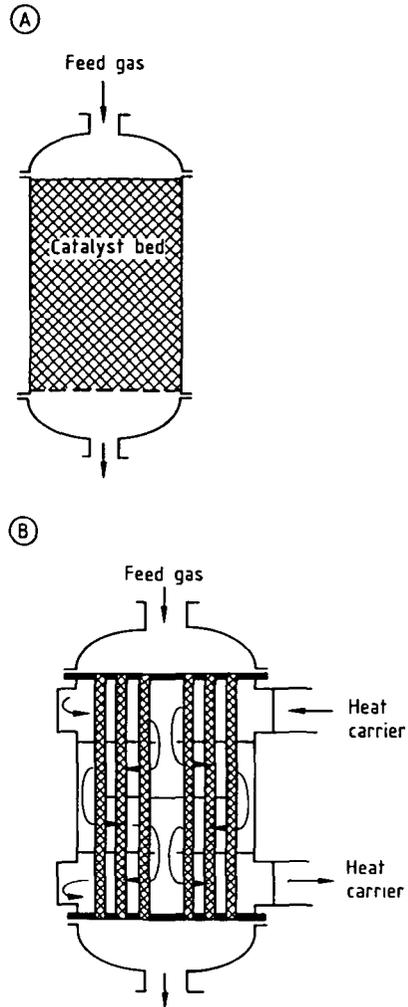


Figure 1.1. Basic types of catalytic fixed-bed reactors
A) Adiabatic fixed-bed reactor; B) Multitubular fixed-bed reactor

fixed bed that is surrounded by an outer insulating jacket (Fig. 1.1 A). Adiabatic reactor designs are discussed in Chapter 3.

Since the incoming reaction gases in most cases must be heated to the ignition temperature of the catalytic reaction, adiabatic reaction control is often coupled with heat exchange between the incoming and exiting reaction gas resulting in so-called autothermal reaction control. This type of reaction control offers certain specific features and development perspectives, which are discussed in Chapter 5.

Reactions with a large heat of reaction as well as reactions that are extremely temperature-sensitive are carried out in reactors in which indirect heat exchange occurs via a circulating heat transfer medium integrated in the fixed bed.

Since in most cases the task of the heat-transfer cycle is to maintain the temperature in the fixed bed within a specific range, this concept is frequently described as an "isothermal fixed-bed reactor". However, isothermal reaction control does not provide optimum selectivity or yield in all cases, and for this reason the concept of heat exchangers integrated in the fixed bed is also being increasingly used to achieve nonisothermal temperature profiles.

The most common arrangement is the multi-tubular fixed-bed reactor, in which the catalyst is arranged in the tubes, and the heat carrier circulates externally around the tubes (Fig. 1.1 B). Fixed-bed reactors with an integrated heat supply or removal are discussed in Chapter 4.

Fixed-bed reactors for industrial syntheses are generally operated in a stationary mode (i.e., under constant operating conditions) over prolonged production runs, and design therefore concentrates on achieving an optimum stationary operation. However, the nonstationary dynamic operating mode is also of great importance for industrial operation control. In

particular, fixed-bed reactors with a strongly exothermic reaction exhibit an, at times, surprising operational behavior which is discussed in more detail in Chapter 6.

Within a production plant the reactor may justifiably be regarded as the central item of apparatus. However, compared to the remaining parts of the plant for preparing the feed and for separating and working-up the products, often it is by no means the largest and most cost-intensive component. In many cases the achievable conversion in the reactor is limited for thermodynamic (equilibrium) and kinetic reasons (selectivity). It is then usual to separate the material discharged from the reactor into products and unreacted feed components (see Fig. 1.2), which are recycled to the feedstock. This recycling procedure involves costs

- 1) For product separation
- 2) For recycle compression
- 3) For repeated heating and cooling of the circulating material to the reaction temperature and the temperature of the separating device
- 4) Due to loss of product resulting from the need to remove part of the circulating material to limit the amount of inert substances or byproducts in the recycle stream (bleed stream).

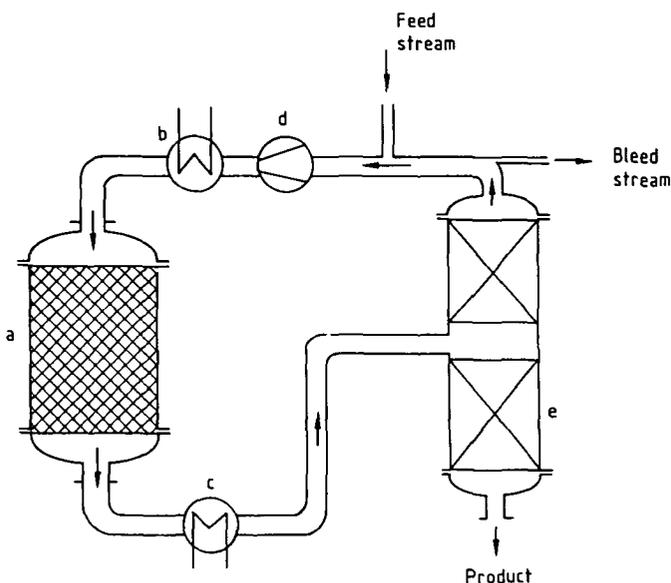


Figure 1.2. Reaction cycle for synthesis reactions with incomplete conversion

a) Fixed-bed reactor, b) Feed preheater; c) Exit cooler; d) Recirculation compressor, e) Separation column

To minimize these costs it is therefore necessary to maximize the conversion in the reactor and avoid as far as possible inert accompanying substances in the reaction mixture. With irreversible reactions (e.g., partial oxidations) the trend is therefore towards a highly concentrated, approximately stoichiometric feed composition, which may occasionally be in the explosive range. The resulting problems are discussed in Chapters 4 and 6.

2. Catalyst Forms for Fixed-Bed Reactors

The heart of a fixed-bed reactor and the site of the chemical reaction is the catalyst. The processes taking place on the catalyst may formally be subdivided into the following separate steps:

- 1) Diffusion of the reactants from the gas space through the outer gas-particle boundary layer, macropores, and micropores
- 2) Chemisorption on active centers
- 3) Surface reactions
- 4) Desorption of the products
- 5) Back-diffusion of the products into the gas space

Since most reactions take place with a considerable heat of reaction, a corresponding heat transport is superimposed on the mass transport.

The control of the microkinetics, consisting of micropore diffusion, chemisorption, surface reaction, and desorption, is the task of the catalyst developer and is not discussed further here. If the catalyst is specified together with its microkinetic properties, then reaction conditions (feedstock concentrations, pressure, temperature profile, and residence time) can be found that lead to optimum yields. The reaction engineer must determine these conditions and ensure that they are maintained in an industrial reactor.

In the case of selectivity-sensitive multistep reactions, any deviation from the optimum values inevitably leads to a decrease in yield. This applies to deviations from the uniform residence time distribution due to flow dispersion and flow bypass phenomena in the fixed bed, as well as to deviations from uniform reaction conditions in the catalyst as a result of mass-transport resistance in the particles and the outer boundary layer [2.1].

The influence of mass-transport resistance in the particles can only be excluded if the critical reaction rate is substantially lower than the mass transport velocity. This leads on the one hand to the need for good external mass transfer (i.e. to reasonable flow conditions in the packed bed), as well as to short diffusion paths in catalyst particles and sufficiently large pores. On the other hand (in the case of exothermic reactions) the local reaction rate must be controlled and limited by the packed-bed temperature.

Temperature control thus plays a predominant role in selective reaction control in general, and in particular in the case of exothermic multistep reactions. Under nonadiabatic conditions, catalysts must therefore be assembled and arranged in the fixed bed in such a way as to ensure good heat transport to the heat-transfer medium.

A further requirement placed on the catalyst is a low flow pressure loss. This applies particularly if the reaction conversion in a single throughput is low, so that the reaction has to be carried out with a large circulating gas ratio (Fig. 1.2), as well as to off-gas purification, in which large off-gas streams must be handled with minimal additional cost.

Finally, the catalyst should be available in a sufficiently high concentration in order to keep the construction volume of the reactor low. The decisive parameters here are the specific external catalyst surface a_p (= square meters of cata-

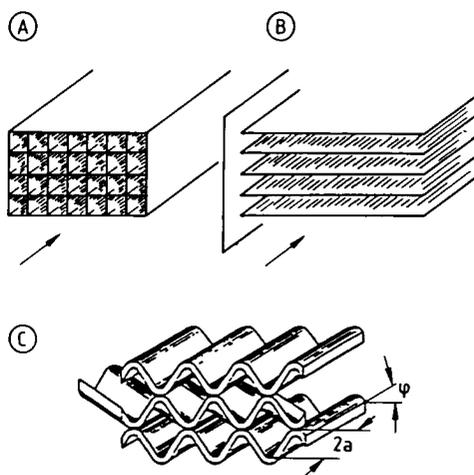


Figure 2.1. Usual shapes of monolith catalysts
A) Square-channel monolith. B) Parallel-plate monolith.
C) Corrugated-plate monolith

lyst surface per cubic meter reactor volume) for reactions controlled by external mass transfer, the catalyst fraction $1 - \epsilon$, where ϵ = cubic meters of free gas space per cubic meter of reactor volume, describing the void fraction of the fixed bed.

The above requirements are to some extent contradictory, which has led to the proposition of a large number of different catalyst forms and arrangements. However, only a few of these have proved really effective in practical operation. Suitable catalyst forms and arrangements include random packings of spheres, solid cylinders, and hollow cylinders, as well as uniformly structured catalyst packings in the form of monoliths with parallel channels, parallel stacked plates, and crossed, corrugated-plate packets (Fig. 2.1).

2.1. Gas-Catalyst Mass and Heat Transfer

2.1.1. Random Packings

Industrial fixed-bed reactors are generally operated with a cross-sectional loading $G_z \geq 1$ kg gas per square meter of reactor cross section per second. This loading produces a suffi-

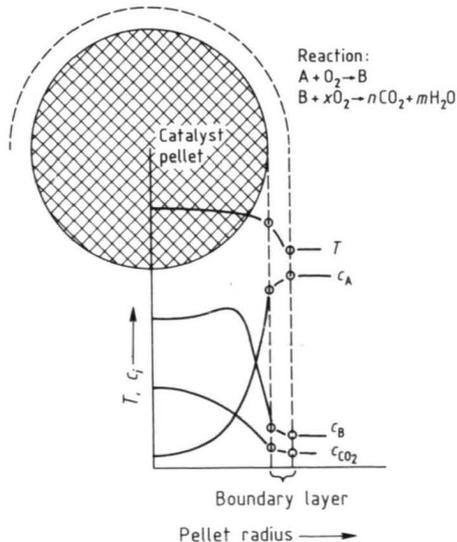


Figure 2.2. Temperature and concentration profiles for a partial oxidation reaction in a spherical catalyst pellet

ciently strong turbulence in random packing. As a result the external gas-catalyst mass-transfer resistance is small compared to the transport resistance in the catalyst pores.

However, generally the thermal conductivity of the catalyst matrix is larger than of the gas. This means that the external gas-catalyst heat transport resistance exceeds the thermal conduction resistance in the catalyst particles. The temperature and concentration conditions established in a spherical catalyst are illustrated for a partial oxidation reaction in Figure 2.2. The conditions can be calculated from the model equations given in \rightarrow Model Reactors and Their Design Equations, pp. 141–142, under the assumptions made there. An essential precondition is that the catalyst particle is uniformly exposed over its entire surface to a flow with uniform temperature and concentration. This is, of course, never the case in random packings. Figure 2.3 shows the local mass-transfer distribu-

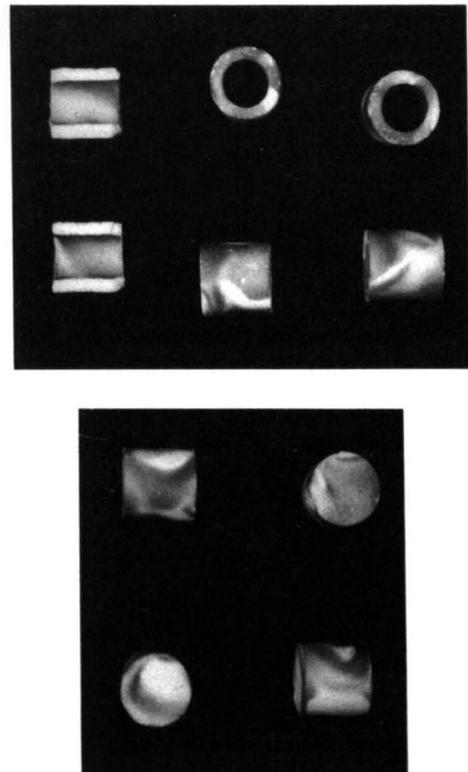


Figure 2.3. Local mass-transfer distribution at the surface of individual cylindrical or ring-shaped catalyst pellets in a fixed-bed packing

tion, providing an insight into the overall highly inhomogeneous conditions. The visualization technique is based on the reaction of traces of ammonia in the gas stream with a catalyst surface impregnated with manganese chloride solution. The conversion to manganese dioxide is already so fast under ambient conditions that it practically depends only on the external mass-transfer resistance of the gas boundary layer. The intensity of the dark coloration is thus directly proportional to the local reaction rate of the surface reaction. At a constant ammonia concentration in the gas flow it is thus also proportional to the local mass transfer, and if the mass transfer and heat transfer are equivalent, also to the local heat transfer [2.2].

Figure 2.3 shows that the local conditions in random packings are much more complex than assumed in current conventional models. Nevertheless, the models for fixed beds containing a larger number of catalyst particles over the cross section can provide reliable information if it is borne in mind that they only describe the mean value of a process that varies greatly as regards detail. For the same reason, it is inappropriate to compare model predictions with a few local temperature or concentration measurements. Indeed, a certain degree of averaging is also necessary in the measurement procedure (see Section 2.2).

The literature contains a number of correlation equations for the mean gas-catalyst mass transfer and heat transfer as a function of gas properties, catalyst geometry, and flow conditions [2.3], [2.4]. However, in practice they play only a minor role for catalyst packings since design and simulation calculations are frequently performed with a model that is quasi-homogeneous, at least with regard to temperature (\rightarrow Model Reactors and Their Design Equations, pp. 140–144). The reason for this are the above-mentioned strong local fluctuations, which make differentiation between the gas temperature and catalyst temperature difficult.

2.1.2. Monolith Structures

In contrast to random packings, the external heat transfer and mass transfer in monolith catalysts is much more uniform, but they can also become limiting factors at high reaction rates. This applies in particular to channel-type monoliths with narrow parallel channels, where the

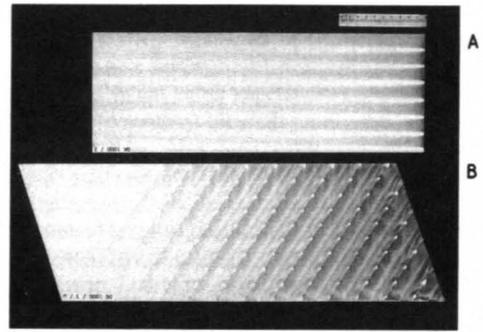


Figure 2.4. Visualization of mass transfer in monolith structures (flow from left to right)
A) Square duct; B) Corrugated monolith [2.5]

flow is generally laminar under industrial operating conditions. Examples include monolith catalysts with a square-channel cross section for automobile exhaust purification and for the removal of nitrogen oxides from flue gases.

Figure 2.4 shows results of the visualization of the local mass transfer by using the ammonia-manganese chloride reaction (Section 2.1.1). The marked decrease in coloration in the flow direction is mainly the result of the increasing consumption of ammonia in the wall boundary layer, so that the reactants diffusing to the wall have to travel an ever increasing distance from the flow core (build up of the laminar boundary layer). The depletion is particularly pronounced in the corners, since two reaction surfaces meet here. The more acute their enclosed angle, the greater is the depletion in the corner region and the smaller is the contribution of the wall surface

Table 1. Asymptotic dimensionless laminar flow heat or mass-transfer coefficients $Nu = \alpha_w \cdot d_h / \lambda_G$ (constant wall conditions) and fanning friction factor f for pressure drop $\Delta p = 2 f (\eta Z_L / d_h^2) \cdot v_G$ for ducts of different cross section [2.6]

Geometry	Nu	f	d_h
	2.47	13.33	$2a/\sqrt{3}$
	2.98	14.23	a
	3.34	15.05	$2\sqrt{3}a$
	3.66	16.00	a
	7.54	24.00	$2a$

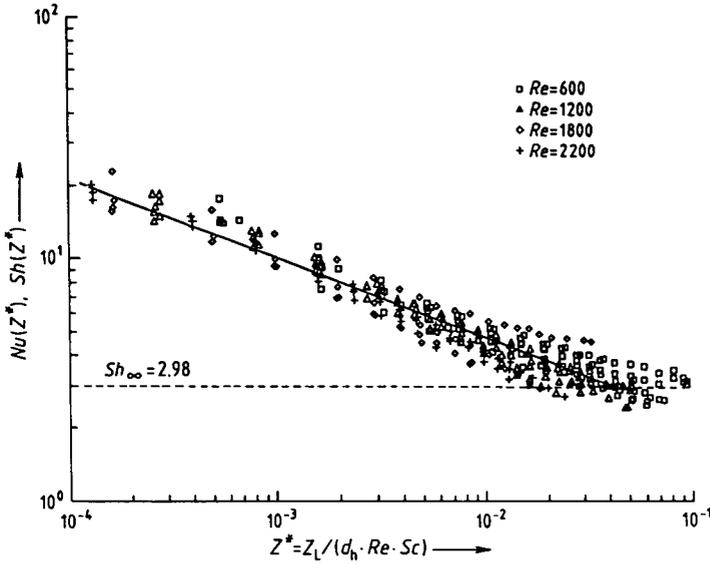


Figure 2.5. Behavior of the dimensionless heat-transfer and mass-transfer coefficients over the dimensionless tube length $Nu = z_w d_h / \lambda_G$, $Sh = k_G d_h / D$

to further heat transfer and mass transfer. The efficiency of channel monoliths of equal cross-sectional area but different shape therefore decreases in the sequence: circle, hexagon, rectangle, triangle. This is illustrated in Table 1, which gives the asymptotic dimensionless mass-transfer and heat-transfer coefficients for tubes of the above cross sections. As Figure 2.5 shows, the asymptotic limiting value is established after a flow length roughly corresponding to 10 times the hydraulic channel diameter. The asymptotic limiting value from Table 1 can therefore be used to perform estimation calculations in conventional industrial monolith catalysts with a large length-to-diameter ratio. For more accurate calculations the radially and axially variable velocity, concentration, and temperature profiles must also be taken into account [2.7].

In contrast to the monolith types discussed so far, the flow conditions in corrugated-plate monoliths (Fig. 2.1 C) are turbulent under normal industrial velocities. The uniformity of the mass-transfer distribution [2.8] depends on geometrical parameters (wave form, amplitude, wavelength, angle of incidence). The transfer coefficients are considerably higher than those of laminae traversed channel monoliths (Fig. 2.4 B), but the pressure loss is also high. These structures offer considerable advantages

for convective heat transport transverse to the flow direction and for transverse mixing, which are discussed in more detail in the following sections.

2.2. Flow and Pressure Loss in Fixed Beds

Conventional industrial catalyst forms differ considerably as regards pressure loss. For example, for equal mean dimensions and the same proportion of empty space, random packings generally have a considerably higher pressure loss than monolith structures, and among these, corrugated structures have a higher pressure loss than monoliths with straight parallel channels. Mass transfer and heat transfer are strongly correlated with the pressure loss. For reasons of energy demand, the catalyst form for a given process is chosen to combine the required mass transport and heat transport with the lowest pressure loss. However, it should be borne in mind that the flow into the fixed-bed reactor (Fig. 1.1) is generally achieved by means of a feed pipe and a distribution hood. These must therefore be constructed so that the fixed bed or tube bundle is uniformly traversed, and the gas residence time in each tube or each flow filament

of the fixed bed is the same. This requirement can always be met simply if the pressure loss in the fixed bed or tube bundle is substantially greater than in the entrance hood. In this case it need only be ensured that the fixed bed is packed so uniformly that no flow bypass is formed or, in the case of a multitube reactor, the pressure loss is equalized in all the individual tubes of the bundle. Because the pressure loss increases with the square of the flow velocity, a uniform distribution of the flow then occurs automatically.

Obtaining a uniform flow distribution is substantially more difficult if the pressure loss of the fixed bed is small. This holds in particular for monolith reactors with straight, laminarly traversed channels (see Section 2.3).

The Hagen-Poiseuille equation is used to calculate the pressure loss in laminarly traversed monolith channels

$$\Delta p = \frac{32\eta Z_L v_G}{d_b^2} \quad (2.1)$$

The pressure loss of packed tubes can be described either by means of a pressure loss coefficient and the pressure drop equation

$$\Delta p = \zeta \cdot \frac{\rho}{2} \cdot v_G^2 \quad (2.2)$$

or by the Ergun equation:

$$\Delta p = f_1 v_G + f_2 v_G^2 \quad (2.3)$$

where for spherical packings:

$$f_1 = 150 \cdot \eta \cdot \frac{(1 - \varepsilon)^2}{\varepsilon^3 \cdot d_p^2} \quad (2.4)$$

$$f_2 = 1.75 \cdot \rho \cdot \frac{(1 - \varepsilon)}{\varepsilon^3 \cdot d_p} \quad (2.5)$$

Thus the pressure drop depends very strongly on the void fraction ε of the packing. Of the standard forms for packed catalysts, hollow cylinders of thin wall thickness ($\varepsilon \approx 0.6-0.8$) are therefore preferred to spheres ($\varepsilon \approx 0.37-0.4$) and solid cylinders ($\varepsilon \approx 0.35$).

The strong dependence of the pressure loss on the void fraction underlines the importance of packing catalyst beds carefully to avoid bypass flow due to local variations in the packing density. For the same reason the tubes of multitubular reactors for highly exothermic, selectivity-sensitive reactions are often filled uniformly by

means of special devices and if necessary individually compensated for pressure loss.

The pressure loss coefficient ζ (Eq. 2.2) can be determined for typical packing forms, for example, according to [2.9].

2.3. Heat Transport Transverse to the Flow Direction

With nonadiabatic reaction control, heat must be transported perpendicular to the flow direction through the fixed bed to the heat exchange surfaces. At the usual mass flow rates of $G_z = 1 \text{ kg m}^{-2} \text{ s}^{-1}$, this heat transport takes place mainly by convection, i.e., the fixed bed must be constructed so that flow components transverse to the main flow direction occur locally. Monolith structures with straight parallel channels are thus unsuitable for nonadiabatic reaction control.

In catalyst packings transverse flow components are automatically established as a result of the nonuniform arrangement and the twisted flow around the pellets. Hollow and full cylinders with a length-to-diameter ratio of 1 to 3 are particularly effective in this respect.

Despite the fact that radial heat transport in the form of twisted flow takes place mainly by convection, it is formally described by means of a so-called effective thermal conductivity λ_r transverse to the flow direction.

In addition to heat transport through the fixed bed perpendicular to the main flow direction, the heat transport at the boundary between the fixed bed and heat exchange surface is also decisive for the heat exchange. The latter heat transport is generally described by a wall heat-transfer coefficient α_w , in which the complex interplay between convective flow at the tube wall and conduction transport by contact between the fixed bed and the heat exchange surface is described in overall terms. Heat transport in packed tubes has been investigated and discussed in detail [2.4], [2.10]. However, the correlations for α_w and λ_r given in the literature do not adequately take account of the actual velocity distribution in packed tubes. Plug flow was generally assumed, although the actual velocity profile is nonuniform with a pronounced slip at the wall. This is due to the fact that the pellets make only point contact with the wall, whereas they overlap and cross over one another inside the packing.

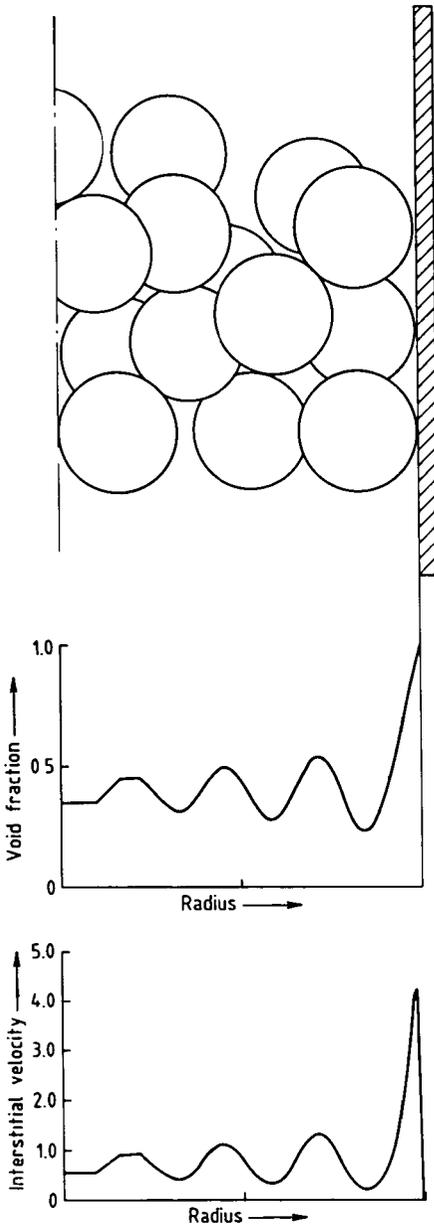


Figure 2.6. Radial distribution of the void fraction and axial flow velocity in a tube packed with spheres

thereby reducing the free volume and hence the velocity. The conditions for a spherical packing are illustrated schematically in Figure 2.6. The radially varying empty space distribution and velocity distribution must be taken into account in detailed reactor calculations, as well as in

the determination of accurate heat-transport parameters [2.12], [2.13].

Existing correlation equations for calculating the heat-transport parameters were obtained from heating or cooling experiments without reactions and assuming plug flow; they therefore permit only a semiquantitative evaluation. However, this is adequate for qualitative comparison of catalyst structures.

2.4. Comparison and Evaluation of Different Catalyst Forms

The choice of a suitable catalyst form is always an optimization problem that can be completely specified only for a specific process. Even then, however, weighting the performance function is not easy since, for example, small pressure losses, uniform flow through the reactor, and good mass- and heat-transfer properties generally represent opposing requirements. The following assessment is therefore only a rough guide.

2.4.1. Catalyst Forms for Adiabatic Operation

Decisive parameters for adiabatic operation include:

- 1) The active catalyst surface available per unit reactor volume
- 2) The quality of the mass and heat transfer between the flowing gas and the active catalyst surface
- 3) The flow pressure loss
- 4) The uniformity of the flow through the reactor and thus the degree of utilization of the fixed bed

The major proportion of the active catalyst surface is located in the interior of the porous catalyst structure. However, if it is assumed that, in the case of sufficiently fast reactions, the reaction site is restricted to a thin layer underneath the external surface, then the active catalyst surface area can be taken as proportional to the specific external catalyst surface area a_p . If the uniform distribution of the flow entering the fixed bed is regarded as a separate problem, then for given kinetic conditions the evaluation may be restricted to three parameters: specific external surface area a_p , gas-solid mass-transfer coefficient k_c , and the flow pressure loss. The evaluation becomes particularly simple if, with a

single dominant reaction, the external gas–solid mass transfer limits the reaction, since in this case the specific reaction kinetics have no influence. The relationships for a concentration c of a key component A and a simple reaction $A + \dots \rightarrow \text{products}$ are outlined in [2.11]. Assuming mass-transfer limitation, the material balance for the key component along the flow path is

$$\varepsilon \cdot v_G \cdot \frac{\partial c}{\partial z} = -k_G \cdot a_p \cdot c \tag{2.6}$$

If the reaction has a conversion of 99%, i.e., an outflow concentration of 1% of the inflow concentration, the length of the fixed bed Z_L is, by integration,

$$Z_L = - \frac{\ln 0.01 \cdot \varepsilon \cdot v_G}{k_G \cdot a_p} = \frac{4.6 \cdot \varepsilon \cdot v_G}{k_G \cdot a_p} \tag{2.7}$$

For the required reactor volume V_R with the cross-sectional area A :

$$V_R = Z_L \cdot A = 4.6 \cdot \frac{\dot{V}}{k_G \cdot a_p} \tag{2.8}$$

Correlations for k_G can be found in [2.3], [2.4]. The computation is particularly simple for straight, laminarily traversed channels. The asymptotic limiting value given in Table 1 (Section 2.1) for the square channel

$$Sh = \frac{k_G \cdot d_h}{D} \approx 3 \tag{2.9}$$

gives, with $a_p = \frac{4}{d_h \cdot \varepsilon}$,

$$k_G \cdot a_p \approx \frac{12 D}{d_h^2 \cdot \varepsilon} \tag{2.10}$$

and

$$V_R = 0.38 \frac{\dot{V} \cdot d_h^2 \cdot \varepsilon}{D} \tag{2.11}$$

If Equation (2.1) is used for the pressure loss, then for the laminarily traversed monolith channel, from Equations (2.7) and (2.10)

$$\Delta p = \frac{12.28 \cdot \eta}{D} \cdot v_G^2 \cdot \varepsilon^2 \tag{2.12}$$

Using the above equations, reactor variants for catalytic off-gas purification with a given volume flow \dot{V} were calculated in [2.11]. The result is shown in Figure 2.7. The pressure drop of the fixed bed over the required reactor length is plotted; the curve parameter is the hydraulic diameter d_h of the monolith channel or packing body for different empty-tube gas velocities $v_e = \varepsilon \cdot v_G$. According to Equation (2.11) the required fixed bed volume V_R with square monolith catalysts and a given throughput \dot{V} depends only on d_h , whereas the geometric arrangement (small bed cross section A and long bed length Z_L , or large bed cross section and short bed) has no influence on V_R . However, the bed cross-sectional area A for a given gas throughput \dot{V} determines via

$$\dot{V} = A \cdot v_G \cdot \varepsilon \tag{2.13}$$

the interparticle velocity v_G , and according to Equation (2.12) this then appears as a quadratic term in the pressure loss.

In conclusion, a minimum catalyst volume with minimum pressure loss is obtained by using a very flat bed with a large flow cross-sectional area A and small hydraulic channel diameter or particle diameter d_h . This result applies in general to all catalyst forms. The main difficulty with this arrangement is the uniform distribution of the flow velocity. Figure 2.7 shows the improvement in pressure loss that can be achieved by channel monoliths as compared to spherical packings. Other catalyst forms such as Raschig rings or corrugated-plate packets lie between these boundary curves.

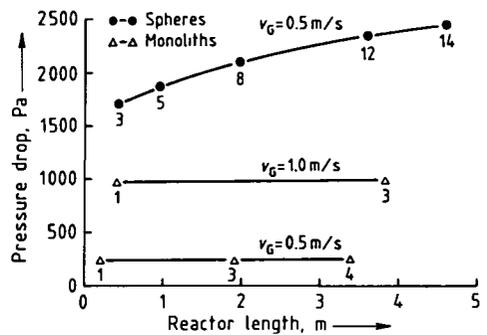


Figure 2.7. Pressure drop over the fixed-bed length for a catalytic combustion reactor with given throughput and 99% conversion as a function of the hydraulic catalyst diameter d_h for different gas empty-tube velocities v_G [2.11]

2.4.2. Catalyst Forms for Isothermal Operation

In addition to the previously discussed quantities, the lateral heat-transport parameters of the fixed bed are further decisive parameters in isothermal reaction control. As shown in Section 2.3, heat transport can be characterized by the effective thermal conductivity perpendicular to the main flow direction λ_r , and the wall heat transfer coefficient α_w . Both quantities are strongly dependent on the filling or packing form. Since transport in the industrially interesting region mainly occurs by convection, they are approximately proportional to the mass throughput.

For the purposes of overall comparison, the corresponding characteristic parameters are

given in Figure 2.8 for some industrially important filling and packing forms in a tube of 50 mm internal diameter with a mass-flow velocity of $G_z = 1 \text{ kg m}^{-2} \text{ s}^{-1}$.

The dimensions of the packing bodies were chosen so that their specific external surface area a_p is ca. $500 \text{ m}^2/\text{m}^3$. Under these conditions hollow, thin-walled cylinders have clear advantages over other packing forms, exhibiting the lowest pressure loss and the highest thermal conductivity. Only as regards wall heat transfer are they inferior to spheres or cylinders. However, good wall heat transfer is apparently less decisive from a reaction engineering viewpoint than good radial thermal conductivity, since the former can be compensated by an appropriate temperature profile of the heat-transfer medium, whereas the radial thermal conductivity directly influences

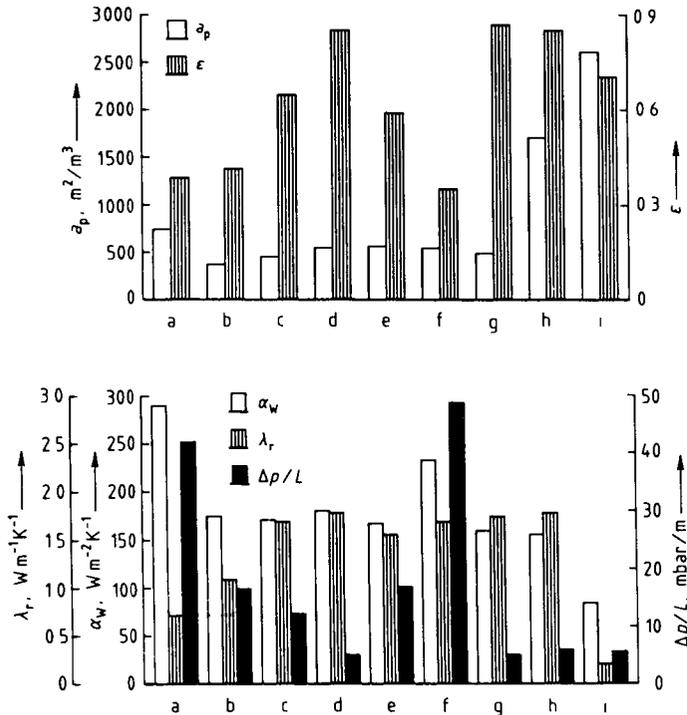


Figure 2.8. Specific outer surface area a_p , void fraction ϵ , effective radial heat conductivity λ_r , wall heat-transfer coefficient α_w , and pressure drop Δp for different packings in a tube of 50 mm internal diameter and an air mass-flow velocity $G_z = 1 \text{ kg m}^{-2} \text{ s}^{-1}$ at ambient conditions

- a) Glass spheres, $d_p = 5 \text{ mm}$, b) Glass spheres, $d_p = 10 \text{ mm}$, c) Raschig rings, ceramic, $d_s = 10 \text{ mm}$, $d_i = 6 \text{ mm}$, $l = 11 \text{ mm}$.
- d) Raschig rings, stainless steel, $d_s = 10 \text{ mm}$, $d_i = 9 \text{ mm}$, $l = 11 \text{ mm}$, e) Hollow ceramic cylinders of irregular length, $d_s = 9 \text{ mm}$, $d_i = 4.5 \text{ mm}$, $l \approx 15 \text{ mm}$.
- f) Full ceramic cylinders of irregular length, $d_s = 5 \text{ mm}$, $l = 11 \text{ mm}$, g) Crossed corrugated metal-plate packing (Sulzer Katapak) wide channels, h) Crossed corrugated metal-plate packing, narrow channels, i) Automotive exhaust monolith, Cordirith, square channels, $d = 0.9 \text{ mm}$

the uniformity of the reaction conditions over the tube cross section. On the other hand, solid cylinders with a large length-to-diameter ratio have good heat transport values, but at the cost of a very high pressure loss.

Despite its poor heat transport properties, a monolith with straight, parallel channels, such as used for automobile exhaust control, is included in the comparison.

Monolith forms have very high specific surfaces combined with a very low pressure loss. Crossed corrugated structures are considerably more favorable for isothermal reaction control. They have a very high radial thermal conductivity that is almost independent of the specific surface area; the latter can be varied over a wide range by means of the channel dimensions. The catalyst of a reaction tube can thus be structured so that wide packings of small specific surface area can be used in the region of the main reaction zone, while packings of increasingly narrower structure, i.e., large specific surface area, are used downstream. In this way a more uniform reaction rate and temperature profile can be achieved over the tube length (see Section 4.3.3).

However, it must be remembered that with crossed corrugated structures, convective radial heat transport occurs only in one plane perpendicular to the main flow direction. In addition, the flow behavior in tubes of circular cross section is rather nonuniform over the circumference, which is why it is advantageous to arrange short packing sections in series, each section being displaced by 90° . The heat transport parameters in Figure 2 8 were determined for structures arranged in this way.

A general problem in the use of monolith structures in reaction tubes is incomplete wall contact. Since individual tubes of multitubular reactors always have a diameter tolerance of ca. 1 mm and interlocking of the structure with the tube wall must be avoided, the bypass of flow at the wall is even greater than with random packings. Up to now there have been no specific investigations of the magnitude and effects of this phenomenon.

3. Adiabatic Reaction Control

Adiabatic fixed-bed reactors are the oldest fixed-bed reactor configuration. In the simplest case they consist of a cylindrical jacket in which

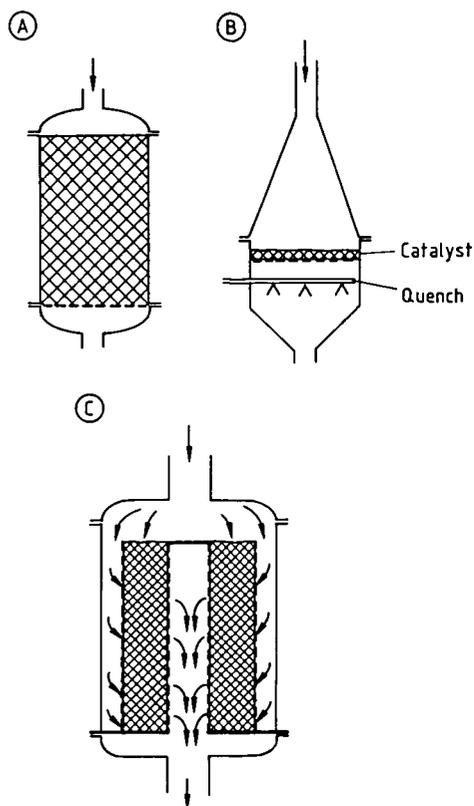


Figure 3.1. Main design concepts for adiabatic reactors. A) Adiabatic packed-bed reactor, B) Disk reactor, C) Radial-flow reactor

the catalyst is loosely packed on a screen and is traversed in the axial direction (Fig. 3.1 A). To avoid catalyst abrasion by partial fluidization, catalyst packings are always traversed from top to bottom. If fixed beds composed of monolith catalyst sections are used, the flow direction is arbitrary.

As discussed in Section 2 4.1, the requirement for a low pressure loss leads to a fixed bed of large diameter and low height (Fig. 3.1 B). Such an arrangement (disk concept) is used particularly when very short residence times, followed by direct quenching of the reaction, are required. Examples include ammonia oxidation in nitric acid production (\rightarrow Nitric Acid, Nitrous Acid, and Nitrogen Oxides, A17, pp 295–325) and oxidative dehydrogenation on silver catalysts (e.g., synthesis of formaldehyde by dehydrogenation of methanol. \rightarrow Formaldehyde, A11,

pp. 624–628). In the first case the “fixed bed” consists of several layers of platinum wire gauzes, and in the second case, of a porous silver layer several centimeters in height. The bed diameters can be up to several meters.

On account of the difficulties involved with obtaining uniform flow as well as for structural reasons, the disk concept is limited to small catalyst volumes. The radial flow concept (Fig. 3.1 C) is used where large amounts of catalyst are involved. The catalyst packing is accommodated in the space between two concentric screen rings or perforated plate rings, and is traversed radially, either from the inside to the outside or from the outside to the inside. This design is particularly suitable for large catalyst volumes as well as for operation at elevated pressure, since at moderate reactor diameters the catalyst volume can be varied over a wide range by altering the reactor length, without affecting the flow-through length of the packing.

A critical feature of packed radial-flow reactors is the shape of the upper bed closure. A simple horizontal covering is not practicable since a gap through which unreacted gas can pass is then formed due to the unavoidable settling of the packing. The arrangement shown in Figure 3.2 has proved effective since it produces mixed axial and radial flow through the bed in the upper bed closure. The required geometrical shape must be determined by simulation of the local two-dimensional flow through the packing [3.1].

The advantages of monolith catalysts with straight, parallel channels for adiabatic reactors have already been referred to in Section 2.4.1. Since monolith catalysts are usually produced with a rectangular cross section, the fixed bed is constructed by arranging these individual monoliths in rows in the form of a large “box”. Conventional DENOX reactors for removing NO_x from power station flue gases are therefore designed as rectangular chambers (Fig. 3.3). The catalyst is often arranged in the form of several layers in series, the spaces between the individual layers permitting cross-mixing, so that the influence of nonuniform flow as well as any possible local blockage of the next layer can be compensated to some extent.

Reference is made in Section 2.2 to the importance of uniform flow into and through adiabatic fixed-bed reactors. This is not easy to achieve, particularly with low-pressure-loss monolith reactors, and requires a careful design

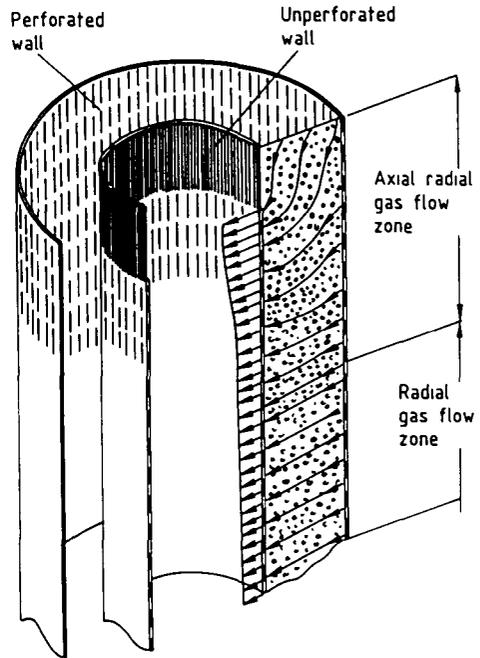


Figure 3.2. Upper bed closure in a radial-flow reactor [3 1]

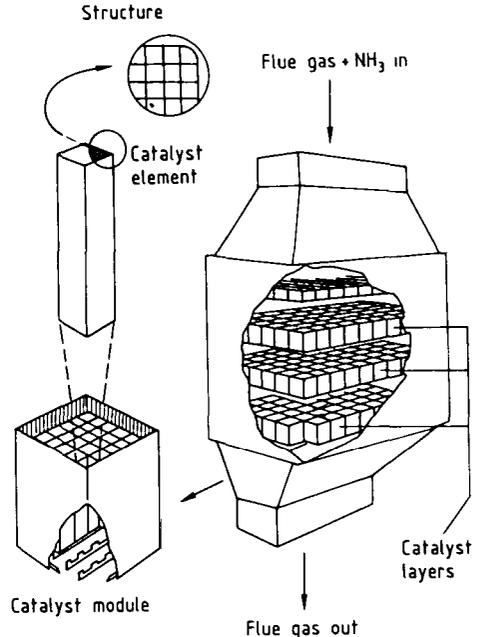


Figure 3.3. Reaction chamber for removal of nitrogen oxides from power station flue gas [3 2]

of the inflow hood. On account of the low pressure loss, unfavorable flow conditions in the outflow hood may also affect the flow behavior through the catalyst bed.

Figure 3.4 shows the velocity distribution in front of the monolith inlet for an industrially housed automobile catalyst [2.11]. Since the flow cannot follow the sudden widening of the inlet funnel, one third of the total cross section is traversed at a velocity that is roughly three times the mean velocity. It can be estimated that, with uniform flow through the catalyst, half the catalyst volume would be sufficient for the same mean conversion. Also, bends in the feedpipe can lead to swirl-type components and thus contribute to nonuniform flow.

Purely adiabatic fixed-bed reactors are used mainly for reactions with a small heat of reaction. Such reactions are primarily involved in gas purification, in which small amounts of interfering components are converted to noninterfering compounds. The chambers used to remove NO_x from power station flue gases, with a catalyst

volume of more than 1000 m^3 , are the largest adiabatic reactors, and the exhaust catalysts for internal combustion engines, with a catalyst volume of ca. 1 L, the smallest. Typical chemical applications include the methanation of CO and CO_2 residues in NH_3 synthesis gas, as well as the hydrogenation of small amounts of unsaturated compounds in hydrocarbon streams. The latter case requires accurate monitoring and regulation when hydrogen is in excess, in order to prevent complete methanation due to an uncontrolled rise in temperature, a so-called runaway (see Chap. 6).

4. Reaction Control with Supply or Removal of Heat in the Reactor

4.1. Introduction

In the majority of fixed-bed reactors for industrial synthesis reactions, direct or indirect supply or removal of heat in the catalyst bed is utilized to adapt the temperature profile over the flow path as far as possible to the requirements of an optimal reaction pathway. Here a clear developmental trend can be observed, which is illustrated schematically in Figure 4.1.

Development started with the adiabatic reactor (Fig. 4.1 A), which on account of the adiabatic temperature change could only be operated to give a limited conversion. Higher conversions were achieved at the same mean temperature level when several adiabatic stages were introduced, with intermediate heating or cooling after each stage. The simplest form involves injecting hot or cold gas between the stages (Fig. 4.1 B). For a constant tube diameter, the main disadvantages of this temperature control strategy are cross-sectional loading, which increases from stage to stage, and the mixing of hot and cold streams, which is energetically unfavorable. The composition is changed by injection, which can have a positive or negative effect on the desired reaction.

The next development was the replacement of injection cooling by interstage heat exchangers, through which the required or released heat of reaction is supplied or removed (Fig. 4.1 C).

The development of reactors in which the heat-exchange surfaces are integrated in the fixed bed to supply or remove the heat of reaction as close as possible to the reaction site occurred in parallel with the development of multistage adiabatic reactors with intermediate

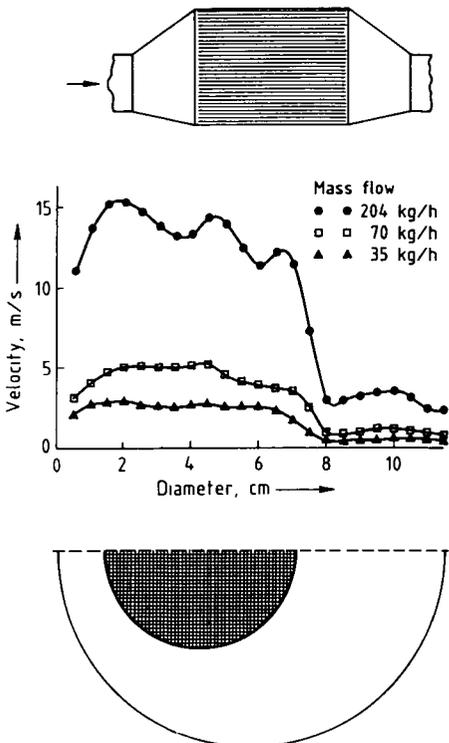


Figure 3.4. Velocity distribution in an industrially housed automobile catalyst [2.11]

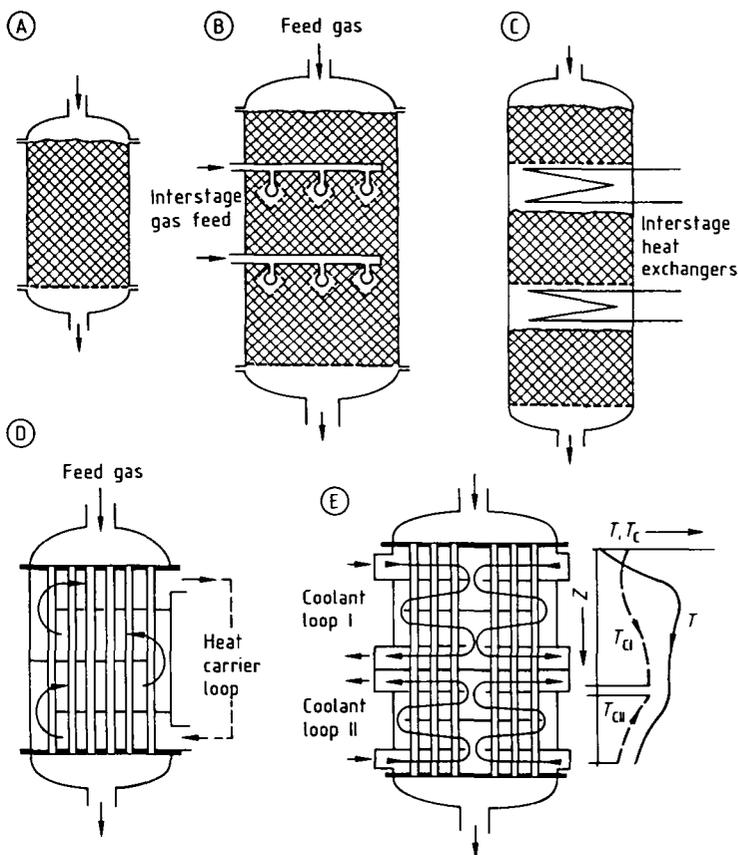


Figure 4.1. Development of fixed-bed reactors

A) Single-bed adiabatic packed-bed reactor; B) Adiabatic reactor with interstage gas feed (ICI concept); C) Multibed adiabatic fixed-bed reactor with interstage heat exchange; D) Multitubular fixed-bed reactor; E) Multitubular fixed-bed reactor with two cooling circuits and nonisothermal cooling temperature (the temperature profile shown is for a strongly exothermic reaction)

heating or cooling. The multitubular fixed-bed reactor (Fig. 4.1 D) constitutes the oldest and still predominant representative of this class of fixed-bed reactors. Here the catalyst packing is located in the individual tubes of the tube bundle. The heat-transfer medium is circulated around the tube bundle and through an external heat exchanger, in which the heat of reaction is supplied or removed. Whereas with endothermic reactions, circulating gas can be used as heat-transfer medium, for strongly exothermic reactions exclusively liquid or boiling heat-transfer media are used. Only in this way can the catalyst temperature (e.g. in the case of partial oxidations) be held in the narrow temperature range necessary for selective reaction control.

Initially, the integration of heat exchange in the fixed bed was utilized to ensure as isothermal a reaction control as possible, which is why reactors of the type shown in Figure 4.1 D are also commonly termed "isothermal reactors". They are characterized by reaction tubes of 20–80 mm internal diameter and a carefully designed flow control of the liquid heat-transfer medium, with largely constant heat-transfer conditions throughout the tube bundle and maximum temperature changes of the heat-transfer medium in the tube bundle of a few degrees.

The latest concepts are aimed at establishing a freely selectable (within limits) optimum temperature profile over the tube length. This requires complex heat-transfer medium control

with several sections and temperature levels (Fig. 4.1 E).

The stimulus for the developments outlined in Figure 4.1 was the need for total raw material utilization as regards both mass and energy. This involves as main criteria the yield of primary end products (maximum), the yield of byproducts that must be removed and eliminated (minimum), the thermal energy consumption or recovery, and the mechanical energy requirements (gas compression, circulation of heat-transfer medium). In addition to the running costs, which are determined by the above criteria, the investment costs are decisive in an investment decision, and naturally rise sharply with increasing complexity of the reaction cycle.

On account of cost degression the projected plant size and the subsequent degree of utilization as well as the technological sophistication are decisive in calculating the product price. Several of the fixed-bed reactor variants illustrated in Figure 4.1 can, depending on the location of the production site and the estimated output, be used for the same process. For example, multistage adiabatic reaction systems with intermediate superheated steam feed, multitubular reactors with circulating gas heating, and strictly isothermal designs with multitubular reactors heated with molten salt are currently used for the endothermic synthesis of styrene from ethylbenzene. Also, exothermic, equilibrium-limited reactions such as methanol synthesis are carried out in multistage adiabatic reactors with interstage cooling as well as in multitubular reactors. Overall, however, there is a trend towards the more highly integrated designs, which will accelerate with rising energy and raw material prices. Adiabatic multistage designs and reactors with heat exchange integrated in the fixed bed are discussed in the following sections. Autothermal reaction control, in which the heat of reaction of moderately exothermic reactions is utilized to heat the incoming feedstock, is discussed separately in Chapter 5.

4.2. Adiabatic Multistage Reactors with Interstage Heat Transfer

Adiabatic multistage fixed-bed reactors with intermediate cooling or heating are nowadays used particularly where the reaction proceeds selectively to give a single product but is limited by

the equilibrium conditions. Intermediate cooling or heating is used to displace the gas temperature in the direction of higher equilibrium conversion. Typical examples include the synthesis of ammonia, sulfur trioxide, and methanol. In these exothermic reactions the equilibrium conversion to the target product decreases with increasing temperature, as shown in Figure 4.2 A. For a given conversion x a temperature can therefore be found at which the reaction rate, with respect to the target product, becomes a maximum. This temperature must be below the equilibrium temperature but not so low that the reaction becomes too slow for kinetic reasons. The points obtained in this way can be joined to form a maximum reaction rate curve (Fig. 4.2 B).

Since, in the case of adiabatic reaction control the temperature increases linearly with the achieved conversion Δx according to the equation,

$$\Delta T = - \frac{\Delta h_R \cdot c_0}{\varrho_G \cdot c_{pG}} \cdot \Delta x \quad (4.1)$$

each adiabatic reaction pathway of an exothermic reaction lies on a straight line of gradient $\Delta T/\Delta x$ (see Fig. 4.2 A).

A practicable reaction pathway for a multistage adiabatic reaction can thus be derived from Figure 4.2 by joining straight-line sections for the adiabatic reaction to vertical lines for the temperature reduction due to indirect intermediate cooling (Fig. 4.2 C).

The kinetically optimum reaction pathway with the smallest required catalyst volume results when the trajectory follows, in a large number of small steps, the line of maximum reaction rate. In practice, the apparatus and equipment expenditure involved in a large number of stages must be weighed up against the savings in catalyst. Conventional multistage reactors for this class of reaction therefore have three to five stages. Figure 4.3 shows the layout of an ammonia synthesis reactor designed on this basis. For structural reasons the heat exchanger is incorporated between the inflow and outflow in the lowest part of the pressure casing. The reaction gas then flows upward in the annular gap between the pressure casing and the fixed beds, whereby it is further heated and at the same time protects the pressure-bearing structural components against excessively high fixed-bed temperatures. The three adiabatic fixed-beds are traversed from top to

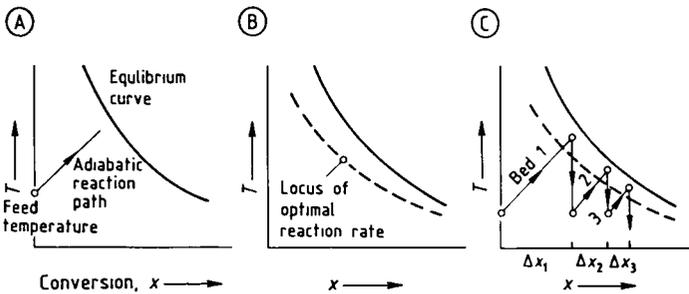


Figure 4.2. Equilibrium limitation of exothermic reactions

A) Equilibrium conversion as a function of temperature, B) Optimum reaction rate curve, C) Improvement of conversion by interstage cooling

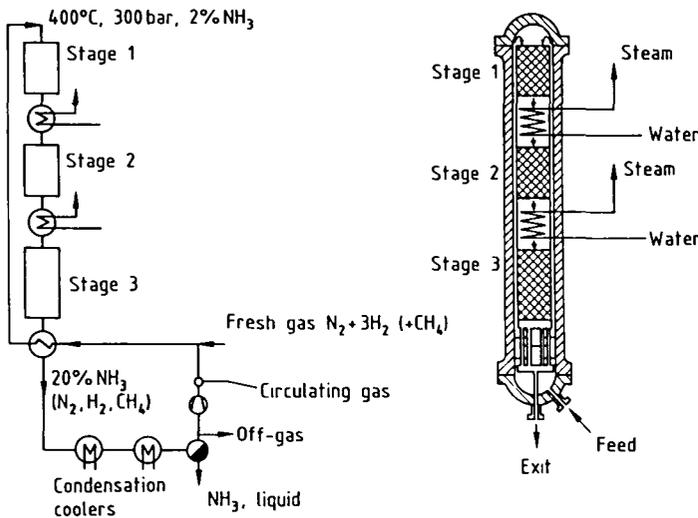


Figure 4.3. Schematic of a multistage reactor for ammonia synthesis

bottom, part of the heat of reaction being utilized to generate steam in the two intermediate heat exchangers. To start up the cold reactor, hot gas must be added to the uppermost bed, for example through an external start-up preheater.

Industrial adiabatic multistage reactors often differ in many details from Figure 4.3, although they are of a comparable basic design. For example, radially instead of axially traversed beds can achieve a smaller pressure loss with a more favorable structural arrangement; heat exchange with the cold feedstock can be effected by heat exchange surfaces integrated in the first catalyst bed; or a cold gas quench can be used to achieve additional temperature regulation.

Modern, adiabatic multistage reactors may thus become so complex that the question arises whether a multitubular design according to Figure 4.1 D or E does not represent the more favorable alternative. The required heat-exchange surface area in the case where heat exchange is integrated in the fixed bed is smaller than in the case of free gas flow on account of the positive effect of the catalyst packing. Furthermore, it does not involve any additional pressure loss, and the optimum reaction rate curve (Fig. 4.2 B) can be better approximated by controlling the cooling temperature profile (see Section 4.3.2.) than by a stepwise temperature reduction

On the other hand, a multistage arrangement may be considered for structural, operating technology, or kinetic reasons in the following cases:

- 1) If, in the case of large single-train plants, subdivision into several individual items of apparatus is necessary for reasons of transport or construction
- 2) If a catalyst must be replaced in individual stages at different times on account of different catalyst compositions and/or aging
- 3) If a gradual addition of a reactant has kinetic advantages compared to the total addition to the feed (here a suitably designed intermediate heat exchanger ensures a uniform distribution and mixing with the reaction gas stream)
- 4) If the intermediate stages are used to extract a limiting product in the case of equilibrium-limited reactions; an example is the intermediate absorption of SO_3 before the last stage of the SO_3 synthesis
- 5) With reaction temperatures above 300°C intermediate cooling can be performed directly with boiling water, whereas in a fixed bed a high-temperature heat-transfer medium must be used as coolant (see Section 4.3.1)

4.3. Reactors with Heat Exchange integrated in the Fixed Bed

The aim of reaction control with heat exchange integrated in the fixed bed using a circulating heat-transfer medium is to maintain the catalyst temperature in a narrow optimum range under all operating conditions. With strongly exothermic successive reactions, such as partial oxidations and partial hydrogenations, on account of the danger of a runaway reaction (see Section 6.2) this requirement can be met only if

- 1) The temperature of the heat-transfer medium is close to the desired catalyst temperature
- 2) Large heat-exchange surfaces are available per unit catalyst volume
- 3) A sufficiently large mass flow velocity of the reaction gases ensures good heat transport from the packing to the heat-exchange surface

With exothermic equilibrium reactions and endothermic reactions these requirements are less stringent since these reactions cannot run-

away, although here too it is beginning to be recognized that a tight and uniform temperature control over the reactor cross section is advantageous.

4.3.1. Heat Transfer Media for Fixed-Bed Reactors

The first of the above requirements presupposes an assortment of heat-transfer media that covers the whole temperature range of interest for gas-phase reactions in fixed-bed reactors. It is convenient to distinguish between gaseous, liquid, and vaporizing heat-transfer media. Gaseous heat-transfer media in the form of hot flue gases are used in the temperature range above 500°C exclusively to supply heat for endothermic reactions.

Conversely, vaporizing heat-transfer media are used exclusively to remove heat from exothermic reactions. Whereas formerly petroleum fractions such as kerosene (e.g., in ethylene oxide synthesis) were more widely used, they have now been largely replaced by boiling water on account of their flammability, lower heat of vaporization, and the need to produce steam in a downstream condenser/heat exchanger. Depending on the saturated vapor pressure, the temperature range from 100 to 310°C (100 bar) can be covered with boiling water. In this range it is the preferred heat-transfer medium for evaporative cooling if an isothermal cooling temperature is required.

Locally variable cooling temperature profiles can be established most easily with liquid heat-transfer media that do not vaporize in the intended operating range. In order to avoid cavitation, pressurized water should be used only up to ca. 220°C ; heat-transfer oils cover the temperature range up to 300°C , while above this temperature salt melts are now used exclusively in reaction technology [4.1]. Compared to heat-transfer oils they have the advantage that they are incombustible and stable, although they have the disadvantage that they solidify at about 200°C (nitrate melts) or 400°C (carbonate melts). The temperature ranges of possible heat-transfer media are compared in Figure 4.4. In addition to the thermal stability, the energy \dot{N} per unit amount of transported heat \dot{Q} required to circulate a heat-transfer medium is an important criterion of choice

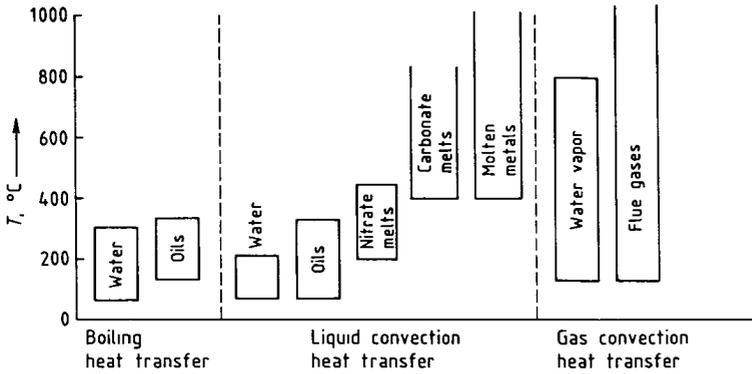


Figure 4.4. Application ranges for common heat-transfer media

The following equation has been derived for the evaluation of heat-transfer media without phase change [4.11]:

$$\frac{\dot{Q}}{\Delta T_c} \sim \frac{\rho^{0.73} \cdot c_p}{\eta^{0.09} \cdot \dot{N}^{0.36}} \quad (4.2)$$

where \dot{Q} is the heat flow transferred by the heat-transfer medium while its temperature increases by exactly ΔT_c , \dot{N} is the required pump power, and ρ , c_p , and η are the density, specific heat capacity, and viscosity of the heat-transfer medium. For liquid heat-transfer media, the equation is derived from the pressure drop in a turbulently traversed, hydraulically smooth pipe. It is practical to solve Equation (4.2) for the pump power:

$$\dot{N} \sim \left[\frac{\dot{Q}}{\Delta T_c} \right]^{2.75} \cdot \frac{\eta^{0.25}}{c_p^{2.75} \cdot \rho^2} \quad (4.3)$$

Thus the required power varies as almost the third power of $\dot{Q}/\Delta T_c$. The component $\eta^{0.25}/c_p^{2.75} \cdot \rho^2$, which depends only on the physical properties of the heat-transfer medium, is plotted as a function of temperature in Figure 4.5. This shows the exceptional heat-transfer properties of water that result from its density and, in particular, its high specific heat, as well as the properties of gases (air) and vapors (water vapor), which are about seven orders of magnitude worse. Common heat-transfer oils and salt melts (sodium nitrate) lie close together, but about an order of magnitude above water. The poor performance of molten sodium compared to heat-transfer oils and salt melts is noteworthy

To test Equation 4.3 on a more realistic example of the cooling of a multitubular reactor, a quadratic tube bundle (cross section 1.5×1.5 m) with fourfold passage of the coolant was designed by using detailed equations for pressure drop and heat transfer [4.12] for various heat-transfer media. The heat release of 1650 kW in 1591 (37×43) tubes of 30 mm external diameter and 4 m length corresponds to the conditions in a partial oxidation reaction. A temperature rise between feed and outlet of $\Delta T_c = 5$ K was assumed for the heat-transfer medium (additionally 150 K for air and water vapor). Table 2 lists as results the required pump power \dot{N} , the pressure drop in the cooling circuit Δp (whereby $p = 1$ bar exit pressure was assumed for water vapor and air), and the excess temperature of the reactor wall above the heat-transfer medium temperature ΔT_w , assuming constant wall temperature along the length of the tube. It was shown that the results of these more precise design equations for the liquid heat-transfer media can be correlated with the equation

$$\dot{N} = 7800 \left[\frac{\dot{Q}}{\Delta T_c} \right]^{2.73} \cdot \frac{\eta^{0.27}}{c_p^{2.73} \cdot \rho^2} \quad (4.4)$$

This represents a good confirmation of Equation (4.3).

Water is thus the ideal heat-transfer medium within its temperature range. For higher temperatures molten salts have increasingly replaced the previously more commonly used heat-transfer oils. Salt melts cover a larger temperature range and have the particular advantage over oils that they are incombustible. The potential

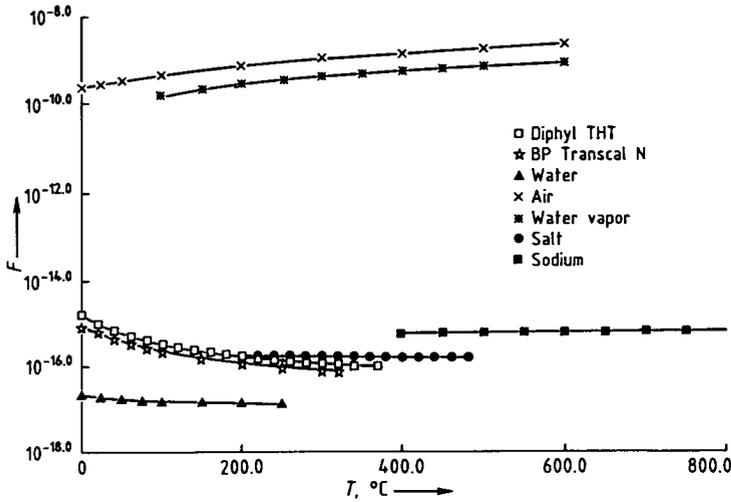


Figure 4.5. The material-specific factor $F = \eta^{0.25} / c_p^{2.75} \cdot \rho^2$ for various heat-transfer media as a function of temperature

Table 2. Results of the example calculation

Heat-transfer medium	Producer	Pump power \dot{N} , kW	Pressure drop Δp , bar	Mean temperature difference ΔT_w , K	Permitted cooling temperature increase ΔT_c , K
Water		0.060	0.008	0.75	5
Transcal N	BP	0.629	0.042	2.32	5
Diphyl THT	Bayer	0.862	0.054	2.35	5
Sodium		4.54	0.150	0.04	5
HT salt		1.31	0.105	1.45	5
Water vapor		0.119×10^6	8.759	1.30	5
Water vapor		0.254×10^3	0.175	14.22	150
Air		0.229×10^6	18.001	1.08	5
Air		0.456×10^3	0.341	12.29	150

danger of a relatively large amount of hot salt melt obviously exists, but is reliably dealt with by experienced reactor construction companies. Special nitrate melts (HITEC) can be used in the temperature range 200–500 °C. Gradual decomposition begins above this temperature, which can accelerate violently above 600 °C. Access of organic components to the melt (nitrate decomposition) and of water (steam explosion) must be excluded [4.1]. New salt melts, for example, based on carbonates, are being developed for the temperature range 400–800 °C. In this case it is not so much the thermal stability of the molten salt but rather the corrosion of the reactor materials that presents problems.

Gases are the only heat transfer media usable over the entire temperature range, but because of their low density they have an unfavorable heat

transport behavior (Fig. 4.5). They are therefore used exclusively as flue gases to supply heat at high temperatures. However, large temperature differences between the heat-transfer medium and the reactor wall, with possible adverse effects on the uniformity of the heat supply, must then be accepted.

4.3.2. Reactor Designs

As with adiabatic reactors, a principal task of reactor development is to produce uniform reaction conditions over the whole reactor and maintain such conditions during the entire operating time. This involves the conditions in the catalyst packing (residence time, catalyst concentration and activity, heat transport) and in the heat-

transfer medium circuit (throughput, temperature, heat transfer). When liquid or vaporizing heat-transfer media are used, the heat-transfer coefficients are usually one order of magnitude greater than those on the catalyst side, which facilitates the task as regards the heat-transfer medium. On the other hand, with strongly exothermic, selectivity-sensitive reactions (especially partial oxidations), a temperature constancy of the heat-transfer medium of ca. 1°C is often required. This leads to a high energy requirement for circulation (according to Eq. 4.4) and necessitates extremely careful design and control of the heat-transfer medium circuit.

Tubular reactors of the type shown in Figure 4.1 D have been in use longest and have been furthest developed. In the case of a vaporizing heat-transfer medium an arrangement as shown in Figure 4.6 is generally chosen, in which the liquid heat-transfer medium surrounds the stationary tube bundle. The rising vapor bubbles escape through the ascending pipe into a vapor drum, where they are separated from the liquid. A circulation flow is established due to the difference in density in the downpipe (pure liquid) and in the reactor jacket, which means that circulating pumps are generally not required. The heat-transfer medium temperature is regulated via the saturated vapor valve. Specific details of this regulation are discussed in Section 6.6.

If uniform supply and removal of heat-transfer medium via annular channels is ensured, this arrangement provides reliable isothermal reaction control. Since a steam cushion can form under the upper tube floor, the active catalyst layer should begin only at a deeper level.

Apart from the type of multitubular reactor shown in Figure 4.6, other multitubular reactors are sometimes used in which the catalyst bed is arranged around the tubes and the heat-transfer medium flows through the tubes (Fig. 4.7 B). An interesting new development has been introduced by Linde (Fig. 4.7 A): the tube bundle is composed of counterwound spirals in which upwardly flowing water is evaporated. The tubes run into a vertical vapor drum located at the reactor head. The tube bundle is connected to a central downpipe at the bottom so that, as in the arrangement in Figure 4.6, a natural circulation of the evaporating water is established. Advantages in construction and in the heat transfer from the reaction gas to the tubes of the bundle are claimed for this design [4.13].

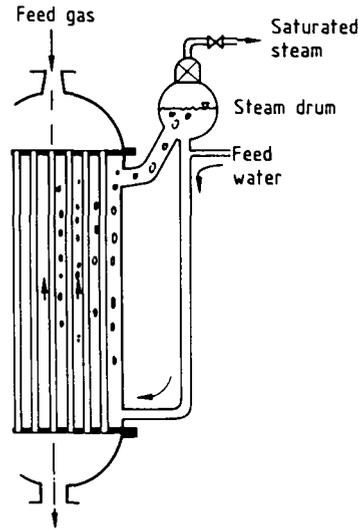


Figure 4.6. Multitubular reactor with boiling water cooling

Circulation systems with parallel and crossed cocurrent or countercurrent flow of the heat-transfer medium (Fig. 4.8) are commonly employed for liquid heat-transfer media. The main part of the heat-transfer medium is generally circulated with a high-capacity pump in order to achieve uniform heat-exchange conditions, while a partial stream is passed through a heat exchanger for supplying or removing the heat of reaction. The desired heat-transfer medium temperature is attained by regulating this partial stream. With exothermic reactions the heat exchanger is normally a steam generator which produces saturated steam at a pressure corresponding to a boiling point of $30\text{--}80^{\circ}\text{C}$ below the maximum cooling temperature.

A superheater fed with a further partial stream of the heat-transfer medium can if necessary be connected downstream of the steam generator. The arrangement with separate external units, shown schematically in Figure 4.8 has structural and maintenance advantages over a common arrangement in the tube-free interior of the reactor [4.14].

Apparatus construction companies specializing in these reactors have developed a detailed and comprehensive know-how as regards flow control of the heat-transfer medium [4.15]. This concerns the uniform supply and removal of the heat-transfer medium, which generally takes place via external annular channels, as well as the

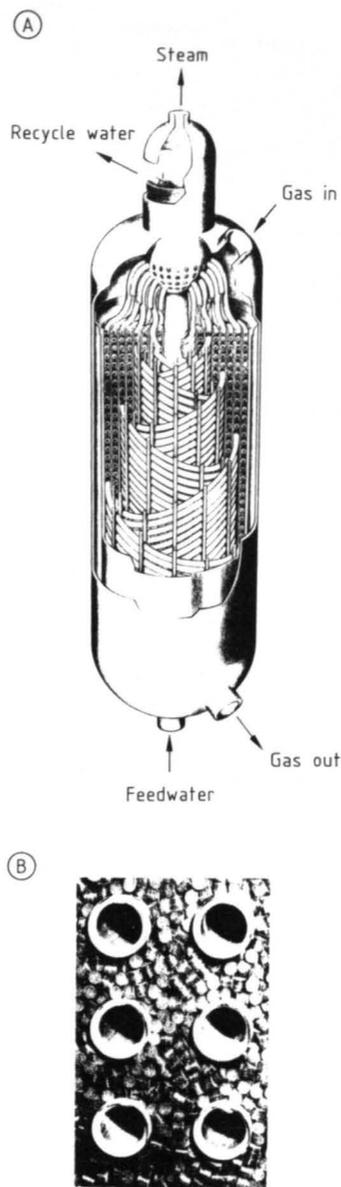


Figure 4.7. A) Design concept of the Linde isothermal reactor for methanol synthesis; B) Cut through the tube bundle surrounded by catalyst pellets (from [4.16])

flow control within the reactor. Here a distinction is made between parallel flow control and crossed flow control. Parallel flow control (Fig. 4.8B) is achieved by two rectifier plates with narrow bores. On account of the pressure loss through the bores suitably arranged over the

reactor radius, a uniform flow profile is produced over the cross section with uniform heat removal conditions between the distributor plates. The advantage of this arrangement is that the whole reactor can be equipped with tubes.

However, due to the nonuniform flow conditions in the inflow and outflow region of the heat-transfer medium, only the region between the distributor plates should be filled with active catalyst. Heat transfer is low because of the parallel flow of the heat transfer medium, and the pressure loss in the distributor plates does not contribute to improving the heat transport. For this reason this arrangement is preferably used for reactions with a moderate heat of reaction.

In reactions with a large heat of reaction, especially partial oxidations, transverse flow control is more widely used, generally in a radially symmetrical arrangement with baffle plates, as illustrated in Figure 4.8A. Since the heat removal conditions are poorly defined in the region of the flow deflection, with the change from a transverse stream to a parallel stream and back to a transverse stream, this region should be free of tubes. A difficulty arises from the constant change of the flow cross section in the radial direction. However, this can be alleviated, for example, by providing pressure-relief bores in the baffle plates, increasing in number towards the reactor axis. In this way constant heat-transfer conditions should be achieved over the reactor radius. In summary, ensuring uniform heat transfer conditions as regards the heat-transfer medium thus requires a considerable flow technology know-how. Some recent publications illustrate the major differences in the behavior of different tube sections that can arise due to an inadequate design and layout of the heat-transfer medium circuit [4.2]–[4.4].

4.3.3. Influencing the Course of the Reaction

The course of the reaction (i.e., the conversion and selectivity or yield) can be decisively influenced by the arrangements made for controlling the heat-transfer medium. The most obvious, although technically most complex solution, is to arrange different heat-transfer medium circuits so as to achieve a stepwise approximation of an optimum temperature profile. The purposeful utilization of the temperature change of the heat-transfer medium flowing through the reactor is, however, technically simpler, and is

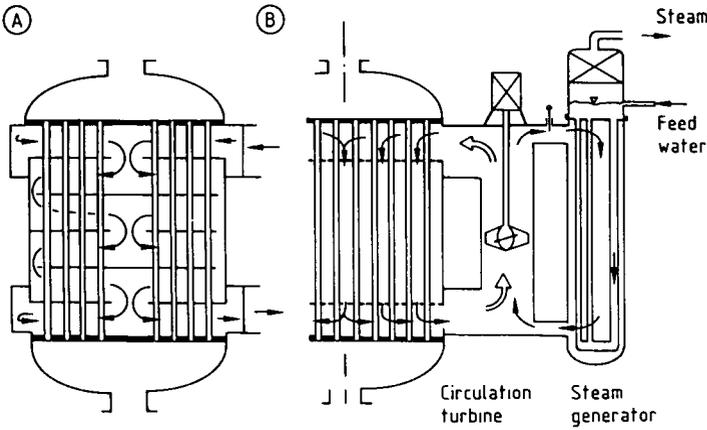


Figure 4.8. Heat-transfer medium control in tube-bundle fixed-bed reactors
 A) Cross flow. B) Parallel flow

discussed here in connection with cocurrent or countercurrent cooling of a fixed-bed reactor involving an exothermic reaction.

Figure 4.9 shows temperature profiles for three different ways of controlling the cooling stream in a partial oxidation reaction. If the coolant is circulated so fast that its temperature in the reactor scarcely alters, then its flow direction is irrelevant and a temperature profile with a pronounced temperature maximum becomes established; this is typical of strongly exothermic reactions (Fig. 4.9 A). If the coolant is circulated in cocurrent and its velocity is chosen so that it becomes noticeably hotter over its path, an almost isothermal temperature behavior can be achieved (Fig. 4.9 B). This is because the reactive gas at the inlet is in contact with the coldest coolant and the cooling temperature rises in step with the consumption of the reactants, so that the reaction rate remains virtually constant over a fairly long section [4.5]–[4.7]. This stabilizing effect of cocurrent cooling has hardly been exploited up to now in industrial reactors. This may be due to the fear that, at the required low flow velocity (in the example of Fig. 4.9 B, $v_s = 0.01$ m/s), heat transfer will be inadequate and natural convection will occur in the cooling jacket. However, v_s describes the mean coolant velocity parallel to the tube axis. With a cross-cocurrent flow of the coolant, the actual flow velocity may in fact be substantially larger, depending on the number of deflections, with the result that the aforementioned problems do not arise.

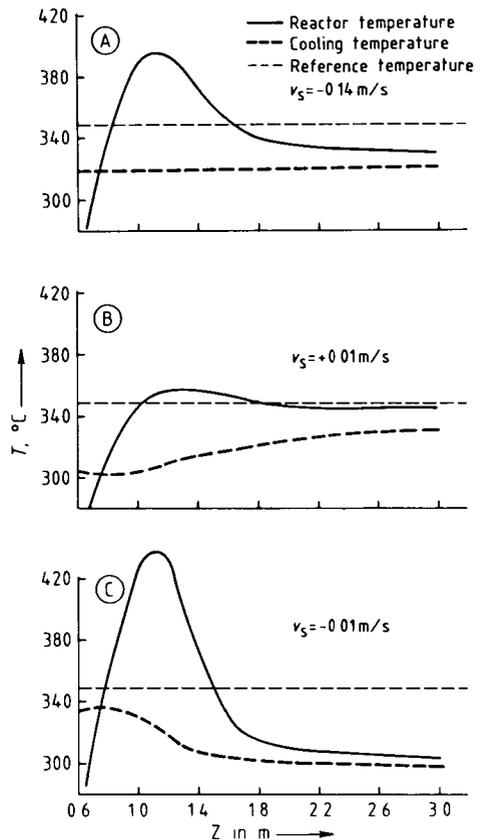


Figure 4.9. Influence of the coolant flow direction and flow velocity v_s on the reaction temperature profile
 A) Isothermal. B) Cocurrent flow. C) Countercurrent flow

Compared to cocurrent flow, countercurrent flow has a markedly destabilizing effect at low flow velocities (Fig. 4.9C). Since the incoming reaction mixture in this case is in contact with the warm coolant outflow, the maximum temperature rises to much higher values. Countercurrent cooling can even lead to the occurrence of several stationary states, and in general favors the runaway of a strongly exothermic, irreversible reaction (see Section 6.3). In contrast to heat exchange without a reaction, countercurrent control of the heat-transfer medium in reactors involving exothermic reactions should therefore be chosen only in particular cases.

The temperature control of an exothermic equilibrium reaction can constitute such a case. As illustrated in Figure 4.2 B, the optimum temperature profile should in this case decrease with increasing conversion, i.e., along the tube length. On account of the equilibrium inhibition of the reaction, it is not possible for the reaction to runaway in the front region. Countercurrent flow of the heat-transfer medium is also advantageous for endothermic equilibrium reactions. Figure 4.10 shows the calculated temperature and concentration profiles with different heating conditions in the synthesis of styrene (dehydrogenation of ethylbenzene). With adiabatic and isothermal reaction control, styrene formation decreases with increasing tube length, whereas it remains roughly constant with countercurrent control.

A significant advantage of nonisothermal control of the heat-transfer medium in cocurrent or countercurrent flow is the saving in circulation energy, since much smaller heat transfer-medium streams must be circulated. Overall, the combination of several heat-transfer medium circuits (Fig. 4.1 E) and the purposeful utilization of the temperature change of the heat-transfer medium in the reactor offer a wide range of possibilities of establishing optimum temperature profiles for a given reaction, and of counteracting any changes in activity that occur during the operating life of the catalyst by altering the temperature profiles.

A further possibility of influencing the course of the reaction is to use catalysts of different activities over the reactor length. Particularly with strongly exothermic reactions that are liable to runaway, such as partial oxidations, a less active catalyst is occasionally used in the front part of the reactor in order to avoid too high a maximum temperature. Figure 4.11 A illustrates

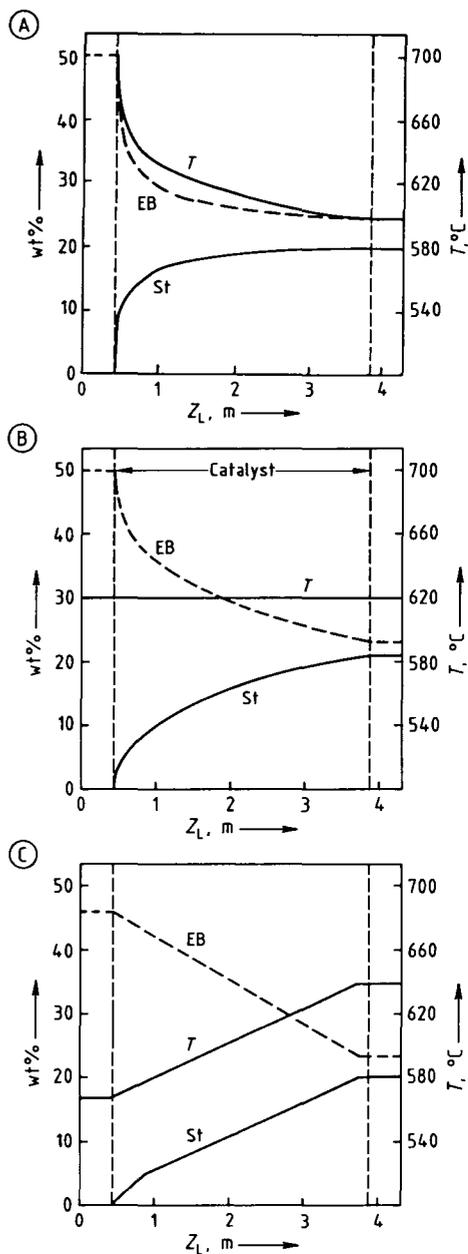


Figure 4.10. Influence of the heating agent flow direction on the temperature profile in styrene synthesis
 A) Adiabatic. B) Isothermal. C) Countercurrent
 EB = ethylbenzene. St = styrene

the use of two catalysts of differing activity in series. The resulting temperature profiles have a typical double-hump shape [4.8], [4.9]. This can

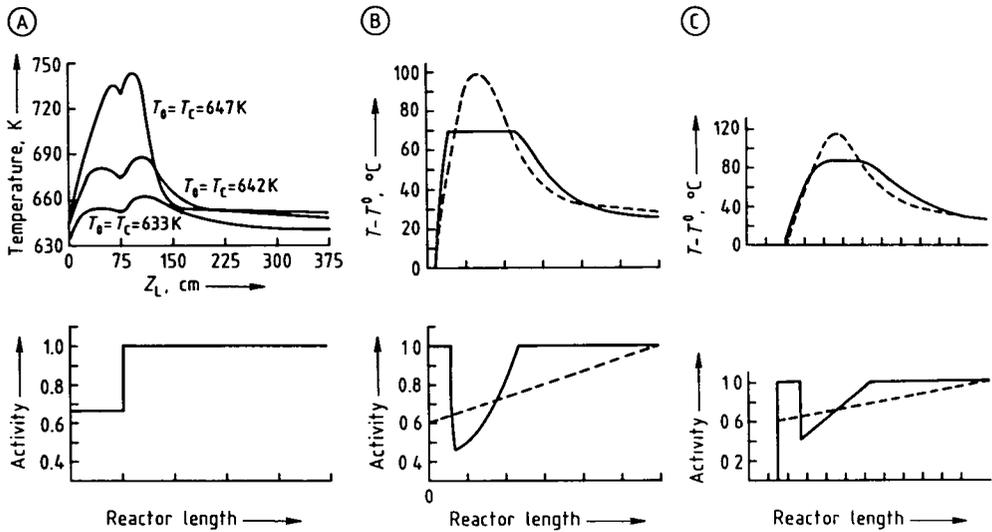


Figure 4.11. Influence of activity profiles on the temperature profile of a strongly exothermic reaction
 A) Catalyst with 66% activity in the front section of the tube and 100% activity in the rear section of the tube [4, 8]; B) Linear (broken line) and optimal catalyst activity distribution (full line) for limiting the maximum temperature to 370 °C (simulation result); C) Experimental verification of B [4, 10]

be avoided if an activity profile is established by using a continuously varying mixture of catalysts with different activities (Fig. 4.11 B, C) [4,10]. In these cases the fully active entry region (relative activity 1) is designed so that the temperature rises to a preselected maximum value. In order to maintain the temperature at this value, the activity in the following region is sharply decreased and is then raised to a relative activity of 1 as the reaction rate drops due to the depletion of the reactants. A smooth temperature profile can be achieved even if the optimized activity profile in Figure 4.11 B is only approximately realized (Fig. 4.11 C).

The control of the maximum temperature by using locally differing catalyst activities presents problems if the main reaction zone moves into the region of high catalyst activity due to changes in the operating conditions. For example, in the case of Figures 4.11 B and C, a decrease in the throughput may already result in reaction runaway in the short, fully active front region. This can be counteracted by reducing the activity of this zone. Catalyst deactivation occurring during operation may have more serious effects. If, for example, the catalyst is poisoned in a front migrating from the entrance to the rear, the main reaction zone finally migrates to the highly active

rear catalyst region, which may lead to excessively high temperatures that can no longer be controlled.

In general, influencing the reaction course via control of the cooling stream (see p. 222) is more flexible than incorporating catalysts of different activities. Particularly with nonisothermal control of the heat-transfer media, the reaction course can be influenced over a wide range by means of the inflow temperature of the heat-transfer medium as well as by its volumetric flow rate.

5. Autothermal Reaction Control

5.1. Introduction

The expression autothermal reaction control is used with fixed-bed reactors if the heat of reaction is utilized to heat the reactor feed to the ignition temperature of the catalyst. Then, neither addition nor removal of heat occurs during stationary operation of the reactor. It thus follows that autothermal reaction control is restricted to exothermic reactions in which a moderately large amount of heat is produced. As a measure of the heat release, the adiabatic tem-

perature increase ΔT_{ad} is usually used. This characterizes the temperature increase that the reaction mixture would experience at the maximum possible conversion Δx if no heat were released. As already given in Equation (4.1):

$$\Delta T = - \frac{\Delta h_R \cdot c_0}{\varrho_G \cdot c_{pG}} \cdot \Delta x$$

If the conversion is not limited by the reaction equilibrium, then $\Delta x = 1$ and ΔT_{ad} depends only on the inflow concentration c_0 of a key component. Autothermal reaction control is used in practice if the adiabatic temperature increase is in the range $20 \text{ K} \leq \Delta T_{ad} \leq 300 \text{ K}$. Autothermal reaction control can be realized in several ways, the simplest being to couple an adiabatic reactor with a countercurrent heat exchanger in which the hot outflow heats the cold inflow (Fig. 5.1 A). If the heat exchanger is not to become impractically large, this arrangement is suitable only for an adiabatic temperature increase $> \text{ca. } 200 \text{ K}$. If the heat exchange is integrated in the reactor (Fig. 5.1 B), then a better heat transfer can be achieved inside the catalyst-filled tubes as well as around the tubes as a result of the transverse flow, so that also gases with a somewhat lower adiabatic temperature rise can be reacted autothermally. Overall, however, indirect gas-gas heat exchange is a weakness of this reactor concept.

5.2. Reaction Control with Periodic Flow Reversal

A major improvement was the autothermal reaction control with direct, regenerative heat exchange, developed by MATROS et al., in which the catalyst packing simultaneously acts as the regenerative heat exchanger [5.1]–[5.3]. Figure 5.2 A shows the basic arrangement. After the catalyst fixed bed has been heated to the reaction temperature, for example, with a pilot burner, the cold reaction gas flows into the packing, where it is heated by the hot catalyst packing and then reacts. At the same time the inflow part of the packing is cooled, so that the reaction front migrates into the packing (Fig. 5.2 B). Before the reaction front has reached the end of the bed, the flow direction is reversed by valves, so that the temperature front moves back again and heats the cooled part of the packing. In this way a periodic steady state is finally established, in which the temperature profile moves up a certain

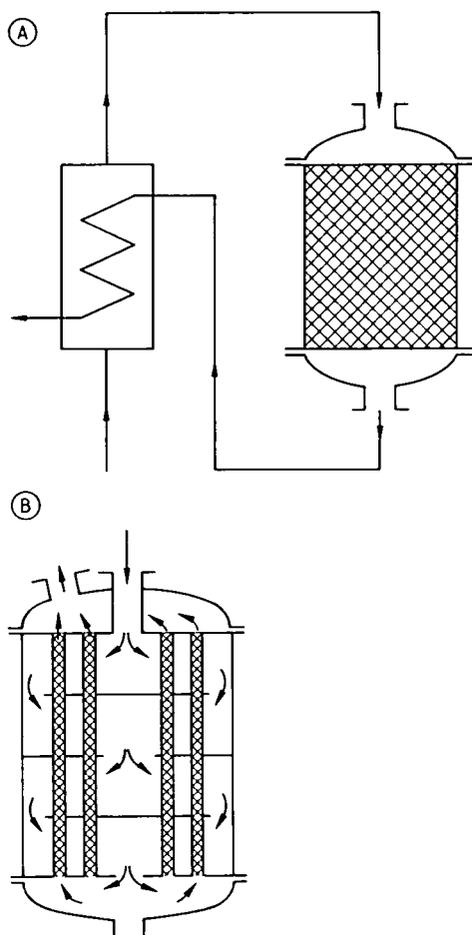


Figure 5.1. Reactor circuits for autothermal reaction control with indirect heat exchange
A) External heat exchange, B) Internal heat exchange

amount in one half cycle, and moves down by the same amount in the next half cycle. The upper and lower ends of the packing each serve as a regenerative heat exchanger, the hot reaction zone being maintained in each case in the interior of the packing.

If the fixed bed is adiabatically insulated, the heat of reaction can leave the reactor only via the outflow. This leads to the saw-toothed course of the outflow temperature T' with time shown in Figure 5.2 C. From the total energy balance it can easily be seen that the time-average value of the outflow temperature must lie exactly ΔT_{ad} above the inflow temperature. Nevertheless, the temperature peaks shown in Fig. 5.2 C may considerably exceed this mean value.

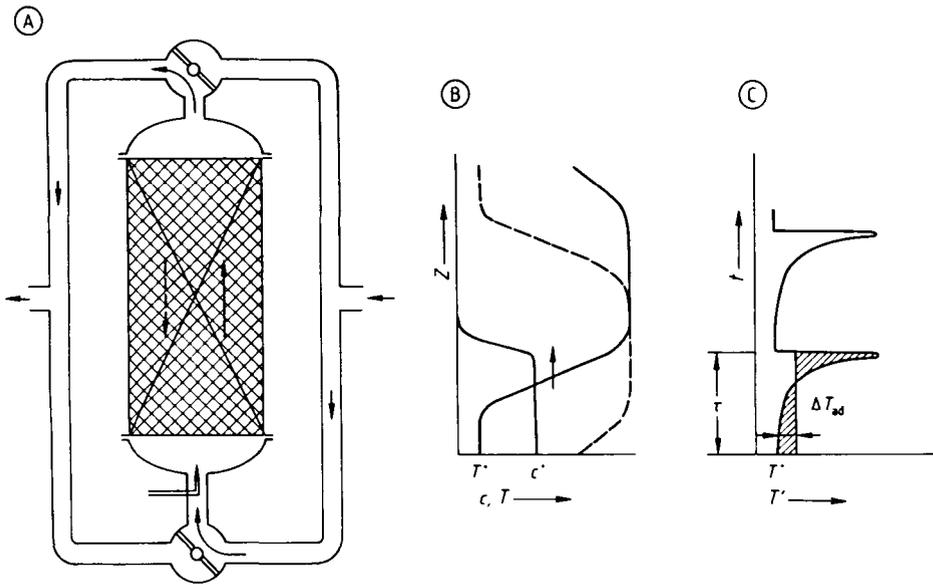


Figure 5.2. Autothermal reaction control with direct (regenerative) heat exchange for an irreversible reaction [2.11]
 A) Basic arrangement. B) Local concentration and temperature profiles prior to flow reversal in steady state. C) Variation of outlet temperature with time in steady state

The main advantage of this form of reaction control is the very effective regenerative heat exchange in the catalyst packing, which does not require any additional built-in components and permits autothermal reaction of gas mixtures with an adiabatic temperature increase of less than 20 K. The main application of autothermal reaction control with periodically varying flow direction is catalytic off-gas purification, in particular catalytic oxidation of small amounts of combustible substances in exhaust air [2.11]. In addition this form of reaction control has been tested by MATROS et al. for equilibrium-limited exothermic reactions such as SO_3 , methanol, and ammonia synthesis, and has in some cases been employed on an industrial scale [5.1]–[5.3].

In addition to the standard variants shown in Figure 5.2, a number of modifications have been proposed and applied (Fig. 5.3). For example, the bed shown in Figure 5.3 A can be designed as a radial flow system, so that the hot region insulates itself, and a multibed arrangement may be used to avoid flushing losses when reversing the flow direction, one bed being backflushed each time (Fig. 5.3 B). The arrangements of Figure 5.4 offer an elegant possibility of a valveless, continuous operation with an integrated flushing stage

[2.11]. Analogous to the Ljungström heat exchanger, the rotation of the segmented fixed bed with a stationary inlet, outlet, and flushing segment leads to a periodic change in the direction of flow through the bed, which can be either axial (Fig. 5.4 A) or radial (Fig. 5.4 B).

5.3. Reactor Behavior

Due to the direct coupling of the reaction with the heat exchange, autothermal reaction control exhibits some specific features as regards reactor behavior that distinguish it from the behavior of conventionally operated fixed-bed reactors. Firstly, the autothermal procedure presupposes the existence of several stationary operating states (see Section 6.3). The “ignited” operating state is the desired state, for only then is so much heat released that the cold inflow can be heated. In the “extinguished” state the reactor cools to the inflow temperature, so that no further detectable conversion takes place. The object of reaction control of autothermal reactors is to prevent extinction of the reaction, but also to limit the rise in the maximum temperature in the reactor due to the positive thermal feedback (see Section 6.3)

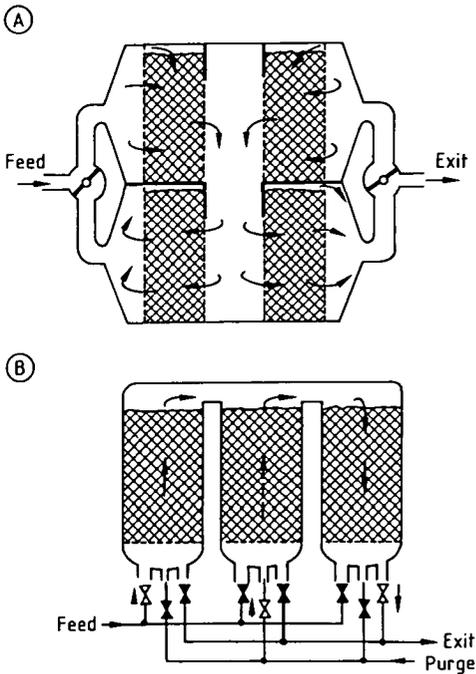


Figure 5.3. Alternative arrangements for autothermal reactor design with regenerative heat exchange
A) Radial flow concept, B) Multiple-bed arrangement

With regard to the combined handling of autothermal reaction control with indirect and direct (regenerative) heat exchange, it is convenient to consider the limiting case of a very rapid reversal of the flow direction [2.11]. For the sake of simplicity the discussion is restricted to a simple, irreversible exothermic reaction. A typical example is the catalytic oxidation of a combustible component in a waste air stream.

The mean gas temperature and mean catalyst temperature in the packing are considered separately. With a very frequent reversal of the flow direction, the catalyst temperature remains practically constant because the heat capacity of the packing is ca. 1000 times that of the gas, whereas the gas temperature is quasi-stationary compared to the packing temperature and therefore, depending on the flow direction, is somewhat below or above the packing temperature. To illustrate this, the principal temperature profiles are shown disproportionately far apart in Figure 5.5 B. These profiles are completely equivalent to those of a countercurrent heat exchange reactor

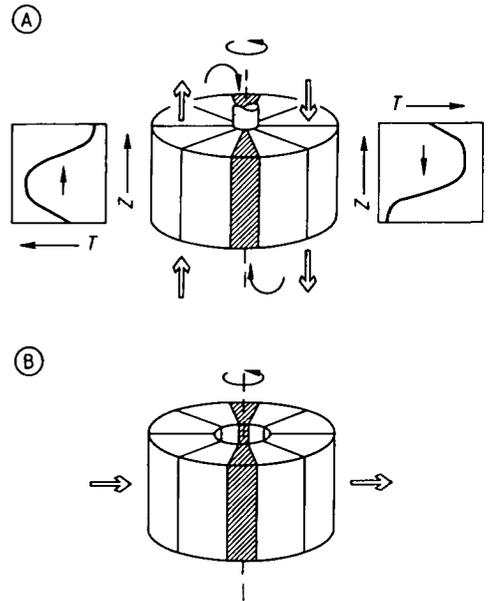


Figure 5.4. Schematic of flow control with a rotating catalyst bed [2 11]
A) Axial-flow reactor; B) Radial-flow reactor
The flushing segment is shaded.

in which the heat-exchanging partition is coated with catalyst (Fig. 5.5 C).

Since the stationary behavior of the countercurrent reactor can be calculated much more simply than the steady state of the reactor with periodic flow reversal, the equivalence model is suitable for rapid parameter studies. In addition, it permits straightforward assessment and interpretation of the somewhat unusual operating behavior of autothermal reactors. Considering the concentration profile corresponding to the temperature behavior in Fig. 5.5 D it can be seen that the reaction starts at an "ignition temperature" T_i and goes to rapid completion over a short section.

Thus it can be assumed to a first approximation that the temperature difference ΔT in Figure 5.5 D can be calculated from:

$$\Delta T = T_i + \Delta T_{ad} - T_0 \quad (5.1)$$

A detailed analysis shows that for more accurate estimates, heat exchange in the region of the reaction zone must also be included. In the following discussion the ignition temperature is therefore designated somewhat pragmatically as

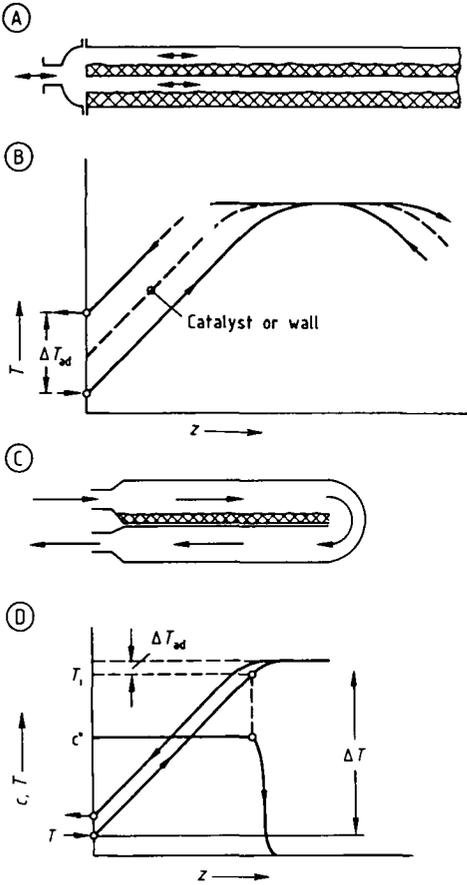


Figure 5.5. Equivalence of operating with periodical flow reversal and integrated countercurrent heat exchange. A) Matros reactor. B) Temperature profiles in the Matros reactor with rapid flow reversal. C) Countercurrent reactor with catalyst at the wall. D) Schematic concentration and temperature profiles in natros and countercurrent reactors [2.11]

the temperature that lies ΔT_{ad} below the maximum temperature.

The gradient of the temperature curves below the ignition temperature can be derived from the conditions of countercurrent heat exchange with axial thermal conduction [2.11]:

$$\frac{dT}{dz} = \frac{U_w \cdot a_p \cdot \varepsilon \cdot \rho_G \cdot c_{pG} \cdot v}{2 \cdot U_w \cdot a_p \cdot \lambda_{eff} + 4 \cdot (\varepsilon \cdot \rho_G \cdot c_{pG} \cdot v)} \Delta T_{ad} \tag{5.2}$$

This allows a simple graphical interpretation of the influence of the operating parameters on the reactor behavior.

Figure 5.6 A shows the change in the temperature and concentration profiles in the case of sufficiently quick reversal or countercurrent operation for gases with different ignition temperatures. The feed concentrations in each case are chosen such that the same adiabatic temperature increase occurs. The plateau region of the maximum temperature becomes increasingly narrow with rising ignition temperature. If the ignition temperature lies above the point of intersection T_i of the two lateral straight lines, then operation in the ignited state is not possible. Accordingly, the narrower the plateau region of the maximum temperature, the closer the operating point is to the stability boundary; the wider the maximum temperature plateau, the more stable is the operation.

In this connection, the influence of catalyst deactivation can also be illustrated. Deactivation means a rise in the ignition temperature. In this case autothermal operation exhibits a fortunate tendency to self-stabilization: the maximum temperature adapts quasi-automatically to the rising ignition temperature, so that total conversion is ensured over a large activity range. If the catalyst activity is too low, then extinction from a state with highest maximum temperature occurs rather abruptly. In the case where the catalyst is deactivated by excess temperature, the self-stabilization of course leads to a vicious circle: the higher the maximum temperature, the greater the deactivation, and the higher the maximum temperature, etc.

The influence of inert front and end zones, which are frequently used with this type of reactor, can also easily be explained by means of Figure 5.6 A. If the ignition temperature is T_{i1} and the fixed bed of the reactor is inert up to the point z_2 , then the catalytic reaction can be initiated at the earliest at z_2 , the maximum temperature is thus raised from T_{i1} to T_{i2} , compared to the case of a continuously active catalyst.

Figure 5.6 B shows the influence of the feed concentration in the form of the adiabatic temperature rise on the temperature profile in the steady state. According to Equation (5.2), an increase in ΔT_{ad} broadens the temperature profile and raises the maximum temperature, whereby the increase in the maximum temperature above the ignition temperature is roughly proportional to ΔT_{ad} .

The above discussion refers to countercurrent operation and to the limiting case of a very-rapid reversal of the flow direction. Normally

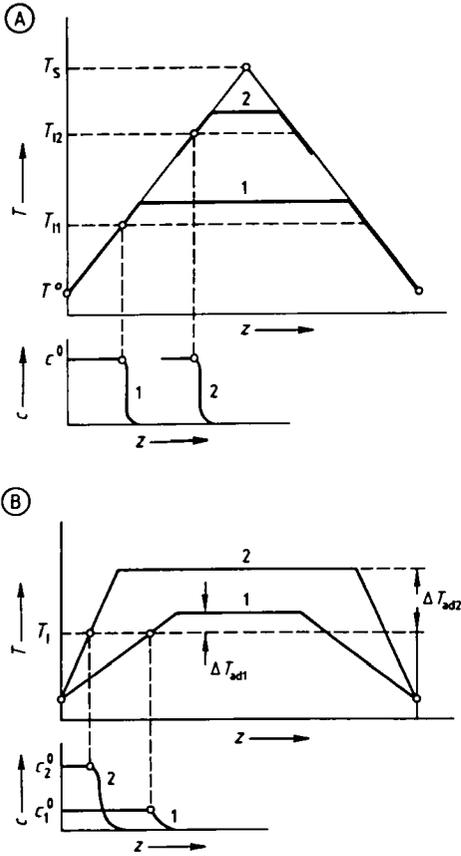


Figure 5.6. The influence of operating parameters on reactor behavior
 A) Temperature and concentration profiles for gases with different ignition temperatures T_{11} , T_{12} ; B) Influence of the feed concentration c_1 , c_2 , in the form of an adiabatic temperature rise ΔT_{ad} [2.11]

during operation with periodic flow reversal, the reaction zone first migrates a certain extent into the reactor. As shown in Chapter 6, a relationship for the front migration velocity w can be derived from the total energy balance around the moving reaction front, and in the case of a large temperature rise ΔT and a small adiabatic temperature increase ΔT_{ad} , w can be approximated as follows:

$$w = \frac{\varepsilon \cdot \rho_G \cdot c_{pG}}{\varepsilon \cdot \rho_G \cdot c_{pG} + (1 - \varepsilon) \cdot \rho_s \cdot c_s} \cdot v_G \quad (5.3)$$

w from the above equation also corresponds to the migration velocity of a temperature front in a packing without reaction traversed with a ve-

locity v_G . The influence of the period duration on the reactor behavior with periodic alternation of the flow direction can easily be estimated by using Equation (5.3). For stable, ignited operation the maximum temperature and full conversion must be reached during the entire period. A semi-period may only be so long that the temperature profile after reversal changes to the gradient specified in Equation (5.2), without the maximum temperature falling below the ignition temperature. Thus, a conservative estimate of the maximum semi-period duration τ_{max} is

$$\tau_{max} = \frac{\Delta l_{max}}{w}$$

with

$$\Delta l_{max} = L - 2(T_i - T_0) \cdot \frac{dT}{dz} \quad (5.4)$$

with catalyst bed length L as well as w , ΔT , and dT/dz from Equations (5.3), (5.1), and (5.2). The behavior of autothermal combustion reactors with periodically alternating flow direction or integrated countercurrent heat exchange can be estimated by using the above equations [2.11]

6. Stability, Dynamics, and Control of Industrial Fixed-Bed Reactors

6.1. Introduction

Stability, dynamics, and control of fixed-bed reactors with strongly exothermic reactions has been studied in great detail since the early 1970s. The numerous publications could give the impression that this is a particularly critical reactor type with a large potential risk. In fact, the opposite is true. Compared to a liquid-phase reactor of the same size, a fixed-bed reactor with a gas-phase reaction contains a mass of reactants several orders of magnitude smaller. There is therefore no danger of a runaway exothermic reaction due to reactants accumulating in the reactor, especially as the heat capacity of the catalyst mass additionally damps the uncontrolled temperature rise.

Nevertheless, instabilities can arise in fixed-bed reactors, particularly with strongly exothermic reactions, and can lead to excess temperatures that can damage the catalyst and the reactor construction materials. Some causes of this are discussed below.

Fixed-bed reactors for industrial syntheses are generally operated over a long production period with almost constant operating parameters. The task of process control engineering is simply to keep these parameters optimal. In contrast, for supply or disposal plants that have several users or suppliers in a production network, there are frequent changes of feed material and throughput which require fast, automatic reaction control. Examples are fixed-bed reactors for synthesis gas production or off-gas treatment.

6.2. Parametric Sensitivity

Parametric sensitivity is the property typical of all highly exothermic reactions with high activation energy: small changes in the operating parameters can lead to large changes in the maximum temperature and yield. The reason is the exponential dependence of the reaction rate on temperature (Arrhenius law). Figure 6.1 shows calculated temperature profiles for partial oxidation in a wall-cooled, fixed-bed reactor tube of typical dimensions. In Figure 6.1 A only the main reaction is considered, while in Figure 6.1 B the total combustion to CO_2 and water is additionally taken into account. Since considerably more heat is liberated in the total combustion than in the desired main reaction, the sensitivity is increased considerably. As a measure of the parametric sensitivity, Figure 6.1 C shows the change in the maximum temperature via the cooling temperature for case B. The sensitivity is only moderate at low cooling temperatures, whereas above $T_c = 343 \text{ C}$ small changes in T_c and also in other parameters such as throughput, feed concentration, or pressure lead to large changes in reactor behavior. Due to the unavoidable differences between individual tubes, multitubular reactors cannot be operated in the range of high parametric sensitivity. In this case the cooling temperature must be lowered to ca. 340 C , and the tubes made longer to give a good conversion. This example emphasizes the requirement, discussed in Chapter 4, for making the conditions in the tubes of the tube bundle and in the cooling circuit as uniform as possible to avoid premature runaway reaction in individual tubes.

In the literature there are numerous runaway criteria with which operating ranges of high parametric sensitivity can be precalculated for known reaction kinetics [6.1] [6.3]. In prac-

tice, however, these parameters are of only limited importance because they rarely take into account the peculiarities of individual cases. Sensitive reactions such as partial oxidation and partial hydrogenation are therefore generally tested in single-tube reactors of the same dimensions as those in the subsequent multitubular reactor. This allows the range of parametric sensitivity to be determined directly. Recalculation of the results for other tube diameters is only possible to a limited extent due to the uncertainties in the quantification of the heat-transfer parameters (see Section 2.3).

An operating fixed-bed reactor can enter the region of high parametric sensitivity through changes in the catalyst properties or operating conditions. Initially a few particularly sensitive tubes of the bundle will runaway, i.e., the reaction changes, for example, from a selective partial oxidation to a total combustion, and the temperature rises rapidly. In a multitubular reactor with thousands of tubes every tube cannot be equipped with temperature-profile measurements; it is therefore likely that this runaway will remain undetected, especially if it involves only a few tubes. Although temperatures $> 1000 \text{ C}$ can often be reached in the catalyst during such runaways, they are generally safe provided the tube is surrounded by heat-transfer medium. Because of the good heat transfer to the fluid the tube temperature remains close to that of the heat-transfer medium, and melting of the tube does not occur. The most certain method of detecting a runaway is on-line analysis of a product formed in the runaway reaction. For example, CO_2 can be monitored in the off-gas during the runaway-sensitive synthesis of ethylene oxide. If its concentration increases above a specified limit, the reactor must be shut down and for a certain period cooled to a lower cooling temperature before operation is recommenced. The reason why lowering the cooling temperature during operation does not extinguish the runaway reaction is discussed below.

6.3. Multiple Stationary States

The term parametric sensitivity applies when, according to Figure 6.1 D, a state quantity (T_{max}) is a single-valued function of a control quantity (T_c). However, in the runaway examples discussed in Section 6.1 this dependence can also be multiple valued. Then the runaway occurs not in

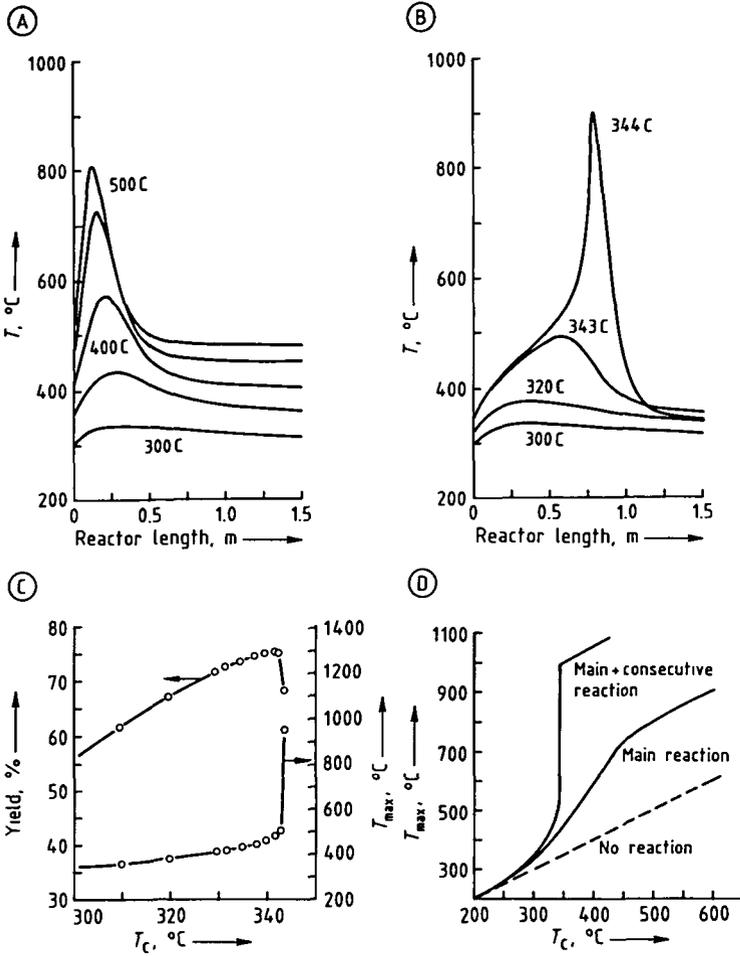


Figure 6.1. Parametric sensitivity of a partial oxidation reaction in a fixed-bed reactor of typical dimensions as a function of the coolant temperature T_c with $T(z = 0) = T_c$. A) Temperature profile over reaction length (main reaction only); B) Temperature profile including total oxidation as side reaction. C) Maximum temperature T_{max} , and yield as a function of coolant temperature T_c in case B; D) T_{max} as a function of T_c for both cases

a finite range of the control quantity, but on exceeding a fixed limit T_{ci} , often referred to as the ignition limit (Fig. 6.2). Between ignition and extinction of the runaway reaction (at $T_c = T_{ce}$), there is a hysteresis region in which two stable stationary states are possible; at least one unstable intermediate state must lie between them. Various causes of multiple stationary states in fixed-bed reactors are known [6.4], [6.5]. Here, only the so-called thermal instabilities are discussed. They occur in exothermic reactions and arise because the evolution of heat increases exponentially with increasing temperature, while the heat removal at constant cooling temperature in-

creases only linearly. Thus on exceeding a certain temperature limit, the heat release increases more rapidly than the heat removal, and the reaction ignites. On dropping below a second, lower temperature limit, the heat release becomes less than the heat removal, and the reaction is extinguished. In fixed-bed reactors, this process of ignition and extinction is associated with a local displacement of the main reaction zone. This can be most readily demonstrated by the example of an exothermic reaction in an adiabatic fixed-bed reactor.

Figure 6.3 shows the temperature profile for the catalytic total oxidation of ethane as a func-

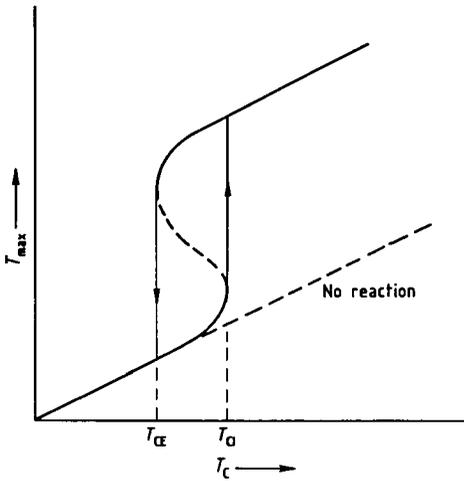


Figure 6.2. Ignition-extinction hysteresis in the region of multiple steady states
Ignition occurs at $T_c = T_{ci}$ and extinction at $T_c = T_{ce}$.

tion of feed temperature. If this temperature is raised only slightly above the value for profile I, the reaction ignites in the rear portion of the reactor. Due to the axial thermal conduction in the developing steep temperature front, the main reaction zone moves slowly towards the entrance and is stabilized in position II a. The feed temperature must be lowered considerably to the value of position II b before the reaction extinguishes completely to profile III upon a further slight lowering of the feed temperature. A similar ignition-extinction behavior can also arise on changing the throughput or the feed concentration. The multiple stationary states I-II a and II b-III are partly a result of the axial backward conduction of heat in the reaction front. This represents a positive feedback which stabilizes either the ignited or the extinguished state. Mechanisms that transport heat from the end of the bed to its beginning stabilize multiple stationary states in a similar manner. These include the axial thermal conduction in the tube wall [6.7] and especially the influence of countercurrent cooling when the temperature of the coolant rises significantly [6.8]. In autothermal reaction control (see Chap. 5), countercurrent cooling is used to stabilize the ignited state, which is desired in this case. However, in the case of strongly exothermic reactions with a risk of runaway, countercurrent cooling should generally not be used. The destabilizing effect of countercurrent cooling is demonstrated by the examples discussed in Fig-

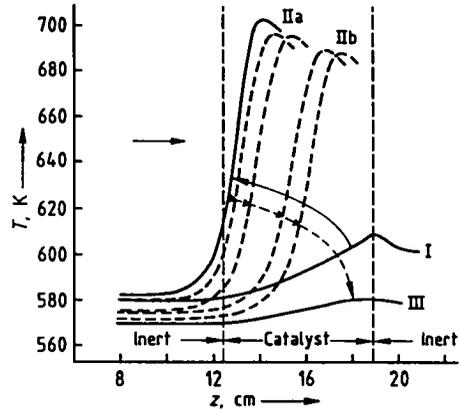


Figure 6.3. Measured axial temperature profile in the region of multiple steady states in an adiabatic fixed-bed reactor for the oxidation of ethane [6.6]
Ignition from profile I to II a, extinction from II b to III

ure 4.9 (see p. 221). Another effect that can result in multiple stationary states is single-grain instability (see → Principles of Chemical Engineering, p. 75–82), which in fixed-bed reactors is always coupled with the effect of the reverse axial backward thermal conduction of heat [6.9] and intensifies the above-mentioned hysteresis behavior.

Whether a fixed-bed reactor goes runaway due to high parametric sensitivity or whether the reaction ignites on passing from a lower to a higher stationary state, the results in practice are the same: the maximum temperature increases rapidly to an unacceptably high value. However, in the case of parametric sensitivity, decreasing the cooling temperature or feed concentration during operation results in the maximum temperature returning to the safe range, whereas when multiple stationary states are present, this need not be the case. If a certain limit is exceeded on ignition, then the runaway reaction proceeds towards the ignited stationary state, even if the feed concentration or cooling temperature is lowered considerably. Extinction of the reaction occurs only on passing below the extinction limits, which particularly for strongly exothermic reactions lie far below the ignition conditions. In this case, the best strategy is to switch off the feed followed by inert gas purging, until all temperatures have fallen to uncritical values.

6.4. Migrating Reaction Zones

The discussion in the previous sections refers exclusively to the stationary state, i.e., the tem-

perature and concentration profiles established after a sufficiently long operating time. However, in practice it is often more important in which way and with which velocity these profiles approach the next stationary state. This dynamic behavior of fixed-bed reactors with exothermic reactions exhibits several special features which are connected with the axial displacement of the main reaction zone in the form of a so-called migrating or moving reaction zone. The behavior can be most easily discussed by using the example of an adiabatic fixed-bed reactor.

Figure 6.4 shows measured temperature profiles for the methanation of traces of CO and CO₂. This reaction is carried out in an adiabatic fixed-bed reactor during ammonia synthesis gas production. If the feed concentration is increased, a new main reaction zone forms in the front part of the reactor, and the temperature rises here to a new maximum value. At the same time, the reactor outlet temperature initially drops below the original value before increasing to the new final value. This temporary reaction in the wrong direction is known as wrong-way behavior. More surprising is the wrong-way behavior in the examples of Figure 6.4 B (decrease in feed concentration) and Figure 6.4 C (decrease in feed temperature). Particularly in the latter case, the maximum temperature in the fixed bed initially increases rapidly while the main reaction zone moves slowly backwards out of the reactor. An explanation for this behavior in terms of the heat balance around a migrating combustion zone was first derived by WICKE and VORTMEYER [6.11]. In a migrating reaction zone that moves through an adiabatic fixed-bed reactor with velocity w due to lowering of the feed temperature to T^0 (Fig. 6.5), gas flows from the left into the reaction zone with velocity $v - w$ and temperature T^0 (v = gas velocity), while from the right catalyst enters the reaction zone with velocity w and temperature $T^0 + \Delta T$ and reacted gas leaves with velocity $v - w$ and the same temperature. The energy balance for the migrating reaction zone is thus:

$$\varepsilon \cdot A \cdot (v - w) \cdot \varrho_G \cdot c_{pG} \cdot \Delta T_{ad} =$$

Heat of reaction introduced and released with the gas $\varepsilon \cdot A \cdot (v - w) \cdot \varrho_G \cdot c_{pG} \cdot \Delta T$
 Latent heat taken up by the gas

$$+ (1 - \varepsilon) \cdot A \cdot w \cdot \varrho_s \cdot c_s \cdot \Delta T$$

Latent heat released by the packing (6.1)

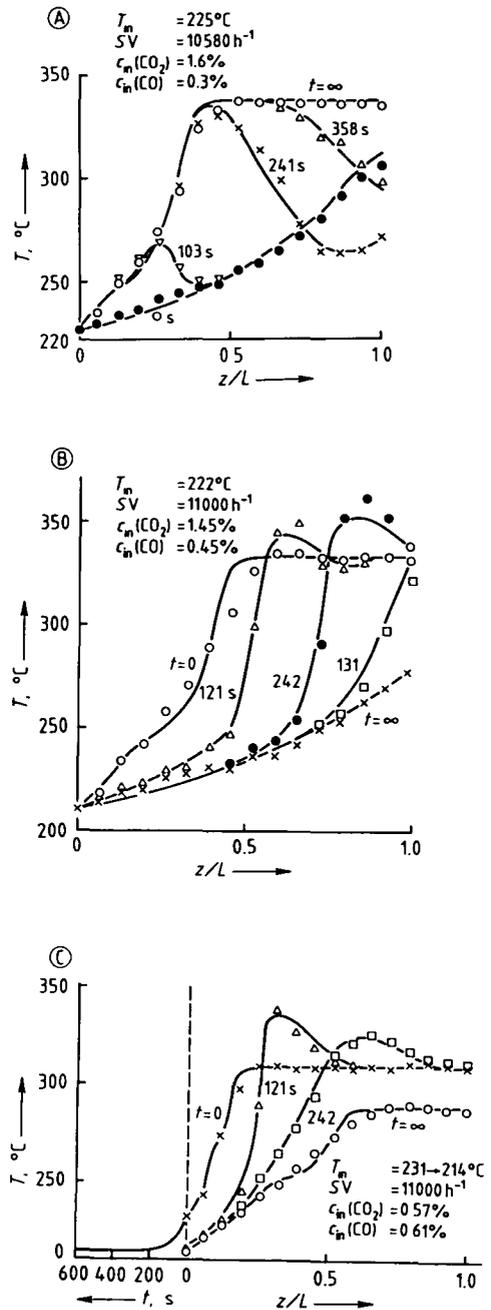


Figure 6.4. Measured (points) and calculated temperature profiles showing the transient of an adiabatic fixed-bed reactor for the methanation of CO and CO₂ [6.10]
 A) Transition after increase in feed concentration; B) Transition after decrease in feed concentration; C) Transition after decrease in feed temperature
 SV = \dot{V}_R / V_R (space velocity)

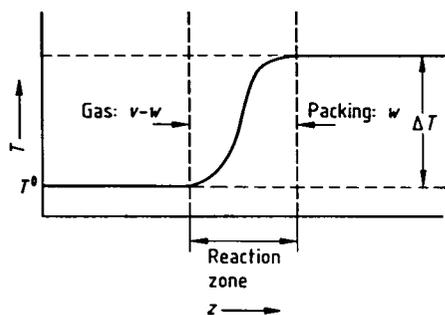


Figure 6.5. Derivation of the energy balance in a quasi-stationary migrating reaction zone in a fixed-bed reactor

It follows that for the temperature increase ΔT at the reaction front:

$$\Delta T = \frac{\Delta T_{ad}}{1 - \frac{(1 - \epsilon) \cdot w \cdot \rho_s \cdot c_s}{\epsilon \cdot (v - w) \cdot \rho_G \cdot c_{pG}}} \quad (6.2)$$

Thus for $w > 0$ (i.e., reaction zone moving downstream), the temperature increase of the reaction front is always larger than the adiabatic temperature rise because the entering gas is heated by the hot catalyst (which is cooled) and because of the liberated heat of reaction.

The examples of autothermal reaction control with periodic reversal of the flow direction (Section 5.2) show that the temperature increase of the combustion zone can be considerably higher than the adiabatic temperature rise. According to Equation (6.2), the temperature increase in the combustion can even rise to arbitrarily high values when the denominator approaches zero; i.e., the migration velocity reaches the critical limit W_{crit} :

$$W_{crit} = \frac{\epsilon \cdot \rho_G \cdot c_{pG}}{\epsilon \cdot \rho_G \cdot c_{pG} + (1 - \epsilon) \cdot \rho_s \cdot c_s} \cdot v \quad (6.3)$$

In this case, the reaction front moves with exactly the velocity of a temperature front without reaction. If dispersion effects such as thermal conduction are neglected, the liberated heat of reaction can no longer be transported out of the reaction zone and thus accumulates there.

The migration velocity w of a reaction front can generally not be preset from outside, but is instead a result of the complex interaction of material and heat transport with the reaction, as is approximately described by fixed-bed reactor models. However, there is one noteworthy ex-

ception, which occurs when the catalyst in the main reaction zone is deactivated with exactly the critical velocity.

In the example of Figure 6.6, this deactivation was carried out deliberately by adding a catalyst poison (thiophene) to the feed at time $t = 0$. This results in a deactivation of the nickel catalyst by irreversible adsorption of thiophene, whereby the adsorption front moves through the bed with velocity w , pushing the reaction front before it. The accidental addition of a catalyst poison can thus lead to migrating combustion zones with very high maximum temperatures in both adiabatic and nonadiabatic reactors, if a migration velocity in the critical range is initiated.

Particularly problematic is catalyst deactivation due to excess temperature deactivation of the catalyst because it results in a vicious circle: the catalyst is deactivated in the region of the main reaction zone due to an excessive maximum temperature. This leads to a migrating combustion zone in which the maximum temperature rises further, and so on. Impressive examples of this behavior in wall-cooled reactor tubes have been described by BLAUM [6.13] and EMIG [6.14].

Figure 6.7 shows measured profiles in a bed of thermally unstable nickel catalyst in the case of CO oxidation. Figure 6.8 shows the temperature profile for vinyl acetate synthesis over zinc acetate. Since the zinc acetate catalyst decomposes above 500 K, the result is a reaction front that moves downstream. The dip in the temperature profile (d) clearly indicates deactivation at the position of the original temperature maxi-

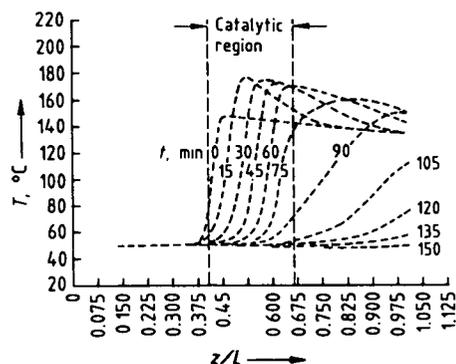


Figure 6.6. Migrating reaction front in an adiabatic fixed-bed reactor due to intentional catalyst poisoning (hydrogenation of benzene over nickel) [6.12]

At $t = 0$, a catalyst poison thiophene is added to the feed

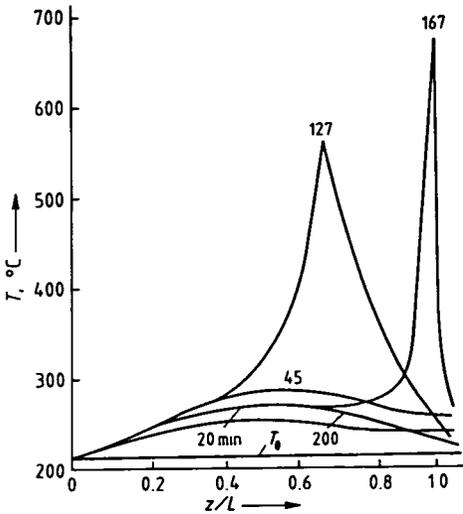


Figure 6.7. Migrating combustion zone in the case of CO oxidation over nickel, caused by thermal deactivation of the catalyst [6.13]

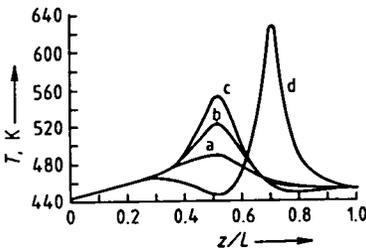


Figure 6.8. Migrating reaction front during the synthesis of vinyl acetate over zinc acetate, caused by thermal damage to the catalyst [6.14]

a) 60 min; b) 75 min; c) 100 min; d) 165 min

imum. In the past, this was sometimes cited as a good example of parametric sensitivity. The above discussion, however, shows that the cause of the "runaway" reaction should rather be attributed to the dynamic influence of the migrating combustion zone.

6.5. Safety Aspects

Because of the small mass storage capacity compared to liquid-phase reactors, the danger of sudden reaction of accumulated reactants in gas-phase fixed-bed reactors is low. Leaving out the peculiarities of individual cases, the following

safety risks can be assumed for fixed-bed reactors:

- 1) Leaks which result in the release of large amounts of gas or vapor and the formation of explosive clouds
- 2) Leaks resulting in release of large amounts of liquid heat-transfer media (oils, salt melts)
- 3) Occurrence of ignitable or decomposable gas mixtures in the reactor
- 4) Melting of the reactor due to a runaway reaction

The safety aspects of liquid heat-transfer media are discussed in Section 4.3.1. Ignitable gas mixtures can arise particularly during partial oxidation reactions. They are especially critical where large packing-free volumes are present. This is the case in the inflow and outflow hoods of the reactor, while in the reactor tubes the catalyst packing dampens the propagation of a flame front due to its heat capacity. Complete avoidance of ignitable mixture is generally not possible in partial oxidations because at least during mixing of the gas streams prior to the reactor the ignition limit is exceeded locally. Nevertheless, in the past, operation of fixed-bed reactors with ignitable mixtures was avoided, either by dilution with inert gas or by operating in the nonstoichiometric range. The former requires additional efforts for heating, cooling, and separation of the inert gas, while the latter gives only low conversions of the reactants in a single pass. New developments in partial oxidation therefore aim for stoichiometric operation in the ignitable range [6.17]. A prerequisite for this is pressure-resistant construction with check valves and flame barriers so a possible that ignition is confined to the interior of the reactor.

Melting of reactor tubes during runaway reaction is only to be feared in multitubular reactors if the respective tube is not surrounded by heat-transfer medium. Thus, appropriate design must ensure that running dry of reactor tubes cannot occur. In the case of corrosive reaction gases, apparatus for the detection of leaks caused by corrosion must be provided, particularly when pressurized or boiling water is used as coolant.

If the coolant circulation is interrupted during an exothermic reaction, the reactor must be shut down. Nevertheless, the heat storage capacity of the catalyst and the heat-transfer medium surrounding the tubes allows sufficient reaction time for controlled shutdown of the reactor.

This is shown by simulation calculations for a multitubular reactor (Fig. 6.9) with a partial oxidation reaction. It was assumed that at $t = 0$ either the circulating pump fails or that the regulating valve in the pipe to the steam generator closes. As can be seen in Figure 6.9, there is a time span of 200 or 350 s, respectively before the maximum temperature in the catalyst reaches unpermissibly high values.

In large-volume adiabatic fixed-bed reactors, local temperature maxima (hot spots) can form due to nonuniform distribution of the flow or inhomogeneities in the catalyst packing. They

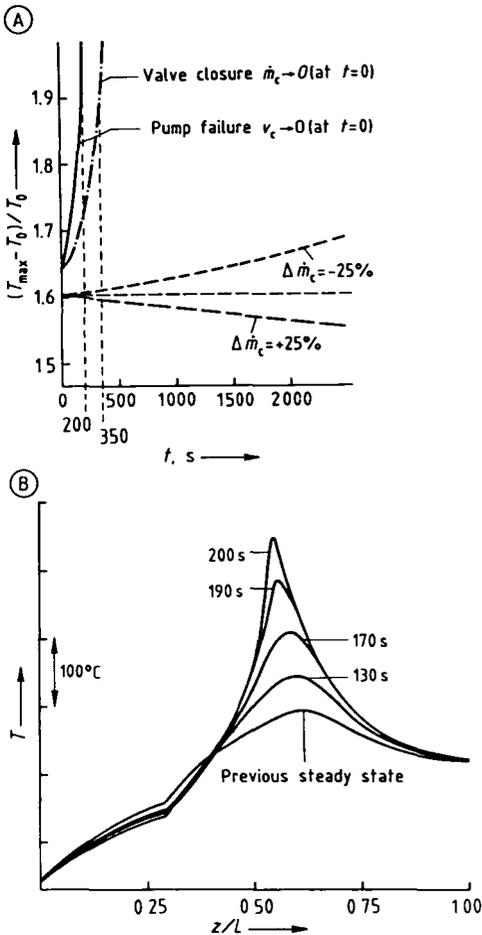


Figure 6.9. Effect of disturbances in the coolant circuit of a multitubular reactor (Fig. 6.10) with a partial oxidation reaction [6.15]

A) Profile of maximum temperature with time after change of the valve position ($\Delta \dot{m}_c$), after pump failure ($t_c \rightarrow 0$), and after valve closure ($\dot{m}_c \rightarrow 0$); B) Temperature profile after failure of the coolant circulation pump

can be intensified by front migration phenomena (Section 6.4) and can lead to thermal damage of the reactor. This is particularly true of runaway-prone reactions such as partial hydrogenation with a large excess of hydrogen, which can change from selective hydrogenation to complete methanation. This can be detected by on-line analysis of methane in the product.

6.6. Control of Fixed-Bed Reactors

The control of fixed-bed reactors for chemical synthesis generally only involves maintaining the operating conditions at the optimum values. For runaway-prone reactions, this is supplemented by an extensive measurement and control system with built-in redundancy for giving alarm and shutting down the reactor. Slow changes in catalyst activity during multistage adiabatic reactors are corrected by "manual" adjustment of the set value for the feed temperature of each stage in multitubular reactors or by the adjustment of the heat-transfer medium temperature. The target is usually to keep the desired conversion constant. Mass flow control, feed stoichiometry control, control of the total pressure (generally in the reactor outlet), as well as feed temperature and heat-transfer medium temperature control are therefore the most important automatic control circuits in fixed-bed reactors.

In the following, some special points concerning the cooling temperature control of multitubular fixed-bed reactors are considered. In a multitubular reactor with molten-salt cooling (Fig. 6.10) the cooling temperature is controlled by a control unit in the connecting channel to the steam generator. In this way, varying amounts of colder salt melt can be introduced into the circulation system, with effective mixing taking place in the circulating pump. This cooling circuit can be unstable [6.3]. Since the reaction rate or liberated heat \dot{Q}_E increases exponentially with increasing cooling temperature, while the heat removed in the steam generator \dot{Q}_A increases only linearly, the conditions shown in Figure 6.11 may occur in the desired state. On a slight increase of the cooling temperature above $T_{C, set}$, the cooling circuit warms up since $\dot{Q}_E > \dot{Q}_A$, and on dropping slightly below $T_{C, set}$ cools down because $\dot{Q}_A > \dot{Q}_E$. Because of the large thermal inertia, however, the unstable operating point can easily be stabilized via the control TC (Fig. 6.10).

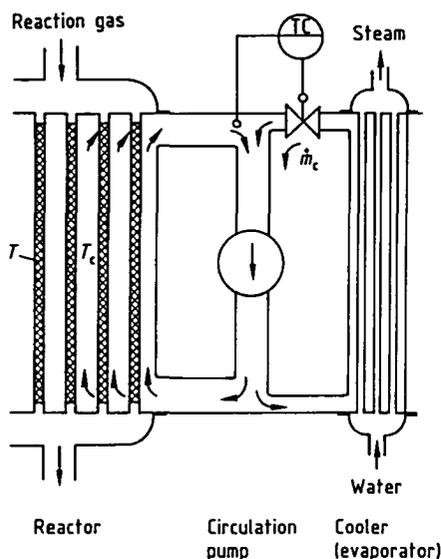


Figure 6.10. Temperature control in a fixed-bed reactor with molten-salt cooling

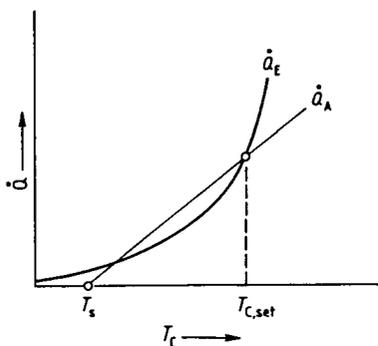


Figure 6.11. Heat generation \dot{Q}_E and heat removal \dot{Q}_A for the cooled multitubular reactor of Figure 6.10 as a function of coolant temperature [6.3]

To obtain optimum conversion, attempts are usually made to operate with a cooling temperature so high that a previously determined maximum temperature in the reactor is just reached but not exceeded. The maximum temperature can be measured by equipping several tubes of the bundle with multiple thermoelements which allow simultaneous measurement of, for example, 10–20 temperatures along the tube length. This allows regulation of the maximum temperature, which influences the set point of the cooling temperature in a cascade circuit. However, determining the maximum temperature from various

discrete measurement points is not trivial [6.16]. Therefore, methods for the model-based measurement techniques should be used here.

In the case of cooling with a boiling medium, a multitubular reactor generally has the structure shown in Figure 6.12. The cooling temperature here corresponds to the boiling temperature in the vapor drum, which is controlled by a control unit in the saturated vapor line. The cooling temperature control is thus performed by controlling the saturated vapor pressure in the vapor drum. The dynamics of the natural convection cooling circuit has a particular effect on the behavior of this control loop. Thus rapid lowering of the cooling temperature via the drum pressure by opening the saturated vapor valve leads to increased boiling of the coolant in the circuit. If the liquid boils into the downpipe, the natural circulation is temporarily interrupted. Furthermore, the increase in volume associated with boiling pushes liquid into the vapor drum, which can result in liquid entering the vapor line. This is discussed in detail in [6.15].

If the fixed bed to be regulated is part of a supply or off-gas treatment plant that is subject to large variations in feed concentration and throughput, then a fixed control is difficult,

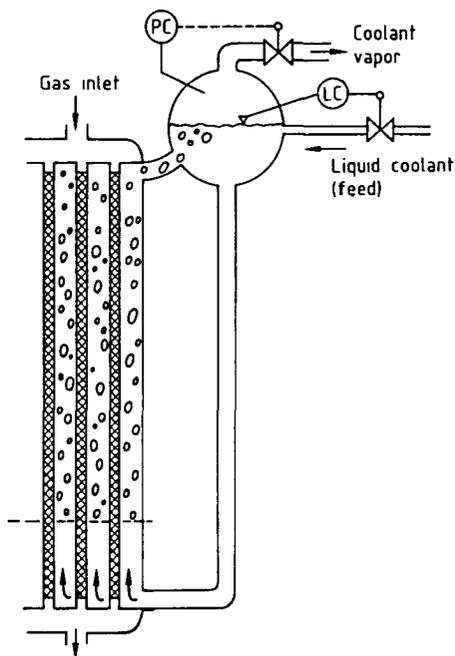


Figure 6.12. Multitubular reactor with evaporative cooling

mainly because of the complex wrong-way behavior (see Section 6.4). Hence, in practice a catalyst with a wide operating range is used and the reactor is made larger.

7. References

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