Catalytic cleaning of polluted air: reaction engineering problems and new solutions

Integration of regenerative heat exchange into a catalyst bed enables autothermal operation of catalytic purification of polluted air with a low content of combustible pollutants. Concentrations corresponding to an adiabatic temperature rise of less than 20 °C can be handled without introduction of additional fuel. For higher concentrations, a technique involving side-stream withdrawal allows utilization of the total heat of combustion at the highest reactor temperature. Heat recovery by integrated heat exchange gives rise to an unusual behavior of the reactor. Based upon an analogy to fixed-bed reactors with integrated countercurrent heat exchange, simple equations are derived for reactor design and operation. Substantial reduction in pressure loss and in the volume of the packed bed can be obtained by replacing conventional catalyst packings by monolithic catalysts. The corresponding relationships are briefly discussed.

1. Introduction

Air purification by catalytic oxidation of the pollutants is the most appropriate method for many problems in praxis. In the following, a process will be discussed, which is relatively simple and energy-efficient, and permits an almost complete utilization of the liberated heat of combustion at a high temperature level.

In contrast to adsorption, absorption, and membrane separation, no residues exist, requiring further processing or disposal. By comparison with biological air cleaning, besides heat recovery, the packed-bed volume is much less, and, in contrast to thermal combustion, the lower temperature in catalytic oxidation permits a more favorable energy economy and the absence of NOx emission. Thus, catalytic oxidation of polluted air is particularly suited for such pollutants which require no further waste-gas cleaning following the oxidation, and whose separation and recycling for economical reuse is not feasible. An important condition for application of catalytic oxidation is the availability of a durable catalyst. However, a wide selection of catalysts is available for a large variety of applications.

In a typical application, the task is to purify large volumetric flows of air, containing low pollutant concentrations, with the least possible energy input, to concentration levels below the legal limits. The required energy input is partly determined by the loss of pressure encountered when the gas flows through the reactor, and partly by the amount of additional fuel required if the concentration of the pollutant is too low. In order to facilitate comparisons, the pollutant concentration is stated in the form of the adiabatic temperature rise $\Delta T_{ad}$ experienced for complete oxidation. The adiabatic temperature rise is related to the pollutant concentration $c_G$ and to the heat of combustion $\Delta h_v$ as follows:

$$\Delta T_{ad} = \frac{c_G \Delta h_v}{\rho G c_p G}$$  \hspace{1cm} (1)
For example, air containing 0.13 wt% toluene has an adiabatic temperature rise of 50 °C.

New developments in autothermal operation of fixed-bed reactors made it possible to catalytically oxidize polluted air with a pollutant concentration corresponding to $\Delta T_{ad} = 10-20$ °C, i.e., without the use of any additional fuel. New catalyst structures allow a significant reduction of the pressure loss in comparison with conventional random packings. This subject matter and special features of these developments are described in the present paper.

1.1. Introductory example

Figure 1 shows two current standard arrangements of catalytic oxidation reactors with external heat exchange. In autothermal operation (see Figure 1a), the amount of heat transferred from the exit gases to the input must be sufficient to heat up the input at least to the ignition temperature of the oxidation. The conditions of autothermal operation are illustrated by the following typical example of an actual air-cleaning problem, namely, 10,000 m$^3$/hr of air is to be cleaned, containing toluene vapors, originating from a spray-paint plant, and characterized by an adiabatic temperature rise of 50 °C. The temperature and concentration profiles in the reactor and in the heat exchanger may be calculated by means of the corresponding balance equations, if the reaction kinetics and the equipment geometry are known. At this point, only a rough approximation will be used under the above specified conditions. This approximation is based on the assumption that, above the ignition temperature, the rate of reaction is so high that it is controlled by the product of the outside gas-catalyst surface mass transfer coefficient $k_G$ with the available specific catalyst surface area $a_v$. For a given gas flow-rate, the required catalyst volume $V_R$ is then inversely proportional to $(k_Ga_v)$ under these conditions.

As explained in more detail in section 2.3, and depending on the type of catalyst used, a catalyst volume on the order of 1-2 m$^3$ follows for this example. The flow of heat required for heating the gas to the temperature of ignition at 350 °C is 1,130 kW. This rate is to be compared with the rate of heat liberation of 175 kW by the reaction. If oxidation is supposed to be carried out without additional heat input, a heat exchange surface area of ~ 1,000 m$^2$, corresponding to a heat exchanger volume of about 20 m$^3$, must be made available. The energetics and the temperature profiles in the equipment are sketched in Figure 1a.

The heat exchange surface area can be drastically reduced if a part of the required heat is supplied in the form of additional heating. The conditions shown in Figure 1b are based on an assumed 50% recycled heat, i.e., a heat exchanger performance of 565 kW. The driving temperature difference in the heat exchanger is now more than four times as great, and, as a result, the volume of the heat exchanger is reduced to about 1/10th of the original size. However, an additional 565 kW have to be supplied through a supporting burner.

2. Reactors with integrated heat recycling

On the basis of the example presented, the conclusion may be drawn that autothermal operation of a conventional catalytic combustor, using recuperative heat exchange, is technically possible only above pollutant-concentration levels corresponding to $\Delta T_{ad} = 150-200$ °C. Much more favorable is regenerative heat exchange, particularly, if it is integrated in the fixed bed of catalyst.

An interesting coupling of regenerative heat exchange with fixed-bed reaction is present in the type of reactor operation developed by Matros et al. [1-3], using periodic flow reversal. Figure 2a shows the reactor schematically. As with all autothermal reactors, the reactor must be started with the help of an ignition burner $Z_B$. After a sufficient portion of the
packing has been heated to temperatures higher than the ignition temperature, the burner can be turned off. Thereafter, cold polluted air enters into the packing, where the air is heated by the hot bed so that catalytic oxidation takes place. The introduction of cold air leads to a progressive cooling of the inlet portion of the bed, and, as a result, to a continuous displacement of the temperature front, a so-called migrating combustion zone. Without further action, the temperature front would move out of the reactor after a certain time, and, thereafter, the reaction would be extinguished. To prevent extinction, the direction of flow through the fixed bed is periodically reversed with the help of valves. As a result, the portion of packing which has cooled down is heated up again by the combustion zone moving in the opposite direction. Hence, the two end regions of the packing act as regenerative heat exchangers.

After a considerable number of flow reversals, a periodically steady state is established in the fixed bed in which, in one half period, the zone of reaction moves a distance upward, whereas, in the next half period, the zone moves the same distance downward (see Figure 2b). Only this periodically steady state, characterized by temperature and concentration profiles immediately before a reversal in flow, is discussed in more detail below. Since the reaction in the fixed bed is adiabatic, the heat liberated can leave the reactor only with the exhaust. Figure 2c shows the periodic rise of exit air-temperature as a function of time $t$. From an overall energy balance, for the rise of the exhaust temperature $T^e$ above the inlet temperature $T^0$ in a half period of length $\tau$,

$$\int_{0}^{\tau} \frac{T^e(t) - T^0}{\tau} \, dt = \Delta T_{ad}$$

In the arrangement shown in Figure 2a, the air present in the previous inlet is discharged without purification after every reversal in flow. In order to avoid this discharge, a purging cycle is required, that can only be applied without interruption of the exit air-stream if a multiple-bed arrangement is used.

An elegant possibility for operating in a continuous manner without using valves and with an integrated purging step consists of using rotating catalyst beds, as shown in Figure 3. In analogy to the Ljungström heat exchanger, the rotation of the segmented fixed bed leads to a periodic reversal of the flow direction through the bed. In this operation, one or two sections of the bed are continuously purged with clean air, and the flow through the rotor can take place either in axial or in radial direction. The latter arrangement has the advantage that the hot inner region isolates itself to some extent, from the outer region.

An indirect recuperative heat exchanger can, in principle, also be integrated into the reactor. Figure 4 shows a possible solution which is analogous to the constructions used in ammonia synthesis reactors.

2.1. Reactor behavior

Air-cleaning problems are often characterized by strongly fluctuating pollution concentrations.
Therefore, a danger exists that, in periods of high emissions, the catalyst is overheated and is thermally damaged, whereas, in periods of low concentrations, the temperature inside the bed drops below the ignition temperature and, as a result, the reaction extinguishes. In the latter situation, controlled introduction of additional fuel is a necessary and practical solution. Catalyst overheating proves to be a much more difficult problem to take care of. The obvious possibility of changing the length of a period has not been successful under the conditions typical of cleaning polluted air. Figure 5 shows results of simulations, obtained by varying the period length between very short times and the longest times possible for stable operation in a specific example. As before, only the profiles in the periodically steady state are shown immediately before reversal in flow. The result that the maximum temperature reached is practically independent of the period length is typical of these simple irreversible reactions in which the inlet temperature lies considerably below the temperature for ignition. The maximum temperature reached corresponds to the value obtained in a moving combustion zone in a sufficiently long fixed bed [1,4].

2.1.1. Approximate model

From the time of the first detailed research of Wicke and Vortmeyer [5], the phenomenon of a migrating combustion zone has formed the subject of many publications. Besides the work of Gilles et al. [6–8], recent results of the research groups of Matros [1,4] and Luss [9–11] should be mentioned. Both groups developed correlations for the determination of the maximum temperature and the rate of migration as a function of the process parameters. If the increase in temperature $\Delta T'$ is known, then, the rate of migration $w$ may be determined from the overall energy balance around a migrating combustion zone,

$$\frac{dT}{dz} = \frac{G_z C_p \Delta T'}{\rho c_v} - \frac{Q}{\rho c_v}$$

where $G_z$ is the gas flow rate, $C_p$ is the specific heat capacity of the gas, $\rho$ is the density of the gas, $c_v$ is the specific heat capacity at constant volume, $Q$ is the heat generated in the reactor, and $z$ is the axial distance.

![Fig. 3. Schematic diagram of pattern of flow in a rotating catalyst bed; a) axial flow reactor, b) radial flow reactor. The segments being purged are shown cross-hatched.](image1)

![Fig. 4. Fixed-bed reactor with integrated countercurrent heat exchange; a) tube-bundle reactor, b) pattern of flow, c) stationary temperature and concentration profiles.](image2)

![Fig. 5. Temperature and concentration profile as a function of length of period. Simulation calculations for propene with $\Delta T_{ad} = 25^\circ C$ on monolithic catalyst with noble metal coating $G_z = 1.3$ kg/(m$^2$ s); 1) $\tau = 0$ s, 2) $\tau = 30$ s, 3) $\tau = 60$ s, 4) $\tau = 90$ s, 5) $\tau = 120$ s.](image3)
introduced first by Wicke and Vortmeyer [5]. In the present notation, this relationship is as follows [12]:

\[
\Delta T = \frac{v - w}{v - \left(1 + \frac{(1 - \epsilon) \rho_G c_p}{\epsilon \rho_G c_p G}\right) w} \Delta T_{ad}
\]

From this, for \( w \),

\[
w = \frac{\left(1 - \frac{\Delta T_{ad}}{\Delta T}\right) \epsilon \rho_G c_p G v}{\left(1 - \frac{\Delta T_{ad}}{\Delta T}\right) \epsilon \rho_G c_p G + (1 - \epsilon) \rho_S c_S}
\]  

(3)

For reactions at normal pressure and where the adiabatic temperature rise is small in comparison with the total temperature rise \( \Delta T \), the rate of migration approaches that of a temperature front without reaction:

\[
w \approx \frac{\epsilon \rho_G c_p G}{\epsilon \rho_G c_p G + (1 - \epsilon) \rho_S c_S} v
\]  

(4)

For an estimation of the total temperature increase \( \Delta T \), an analogy can be used between the autothermal reactor with frequent periodic reversal in flow and the autothermal reactor with indirect countercurrent heat exchange [14]. The limiting case of very frequent reversals in flow is shown as profile 1 in Figure 5. For the purpose of a more detailed analysis, a distinction should be made between gas and catalyst temperature. Under the conditions of a periodic reversal in flow, the temperature of a gas can be considered to be in quasi steady state with respect to the catalyst temperature, due to a factor of 700 in the respective heat capacities. If the switching frequency is sufficiently high, the temperature of the catalyst remains almost constant, while the temperature of the gas either follows a profile above or below the temperature of the catalyst. For the sake of illustration, the qualitative temperature profiles are shown, not to scale, in Figure 6b. The behavior is equivalent to the stationary conditions in a countercurrent heat-exchange reactor in which the heat exchange surface is covered with catalyst (see Figure 6c).

Since the stationary behavior of the countercurrent reactor (see Figure 6c) can be calculated much more simply than the periodically oscillating behavior of the Matros reactor, the equivalent model may be used to carry out rapid parametric studies. In addition, this model permits a simple estimation and interpretation of the somewhat unusual operation of the autothermal reactors under consideration. From the conversion profiles shown in Figure 5, which are typical of catalytic oxidation, it can be deduced that the reaction rapidly starts after a certain ignition temperature \( T_I \) if the catalyst is exceeded. The schematic conversion and temperature profiles are plotted in Figure 6d. Hence, the assumption can be postulated, to a first rough approximation, that the rise in temperature \( \Delta T \) is the sum of the rise to the ignition temperature \( T_I \) and the adiabatic temperature rise \( \Delta T_{ad} \):

\[
\Delta T = T_I + \Delta T_{ad} - T_0
\]  

(5)

A more detailed analysis shows [14] that the heat exchange in the region of the reaction zone must also be taken into consideration. Hence, for the purpose of subsequent discussion, the temperature at ignition will be somewhat pragmatically defined as the temperature lying under the maximum temperature by an amount \( \Delta T_{ad} \).

The slope of the temperature profile below the temperature at ignition may be obtained from the conditions of countercurrent heat exchange with axial heat conduction [14]:

\[
\frac{dT}{dz} = \frac{U_d \alpha \epsilon \rho_G c_p G v}{2 U_d \alpha \lambda_{eff} + 4(\epsilon \rho_G c_p G)^2} \Delta T_{ad}
\]  

(6)
With the help of this equation, a simple graphical interpretation of the effect of operating parameters on the reactor behavior becomes feasible. This feasibility is discussed in conjunction with Figure 7 and, subsequently, confirmed through experimental and simulative results.

Figure 7a shows the resulting temperature and concentration profiles for the limiting case of frequent flow reversals or for countercurrent operation. Pollutants with different ignition temperatures are considered in this figure. The pollutant concentration has always been chosen so as to correspond to the same adiabatic temperature rise. Note should be made that the length of the plateau region decreases with increasing ignition temperature. If the ignition temperature lies above the point of intersection of the two inclined boundary lines, then, operation in the ignited state is not possible. Hence, the narrower the plateau region of the maximum temperature the closer is the operating point to the limit of extinction; and the broader the maximum temperature shoulder the more stable is the entire operation.

In this context, by similar arguments, the effects of catalyst deactivation can also be explained. Deactivation indicates an increase of the ignition temperature. One of the advantages of this type of autothermal operation is a tendency for selfstabilization, e.g., the maximum temperature automatically follows the rising ignition temperature, resulting in complete conversion over a wide range of catalyst activities. Then, with continuing catalyst deactivation, extinction takes place rather abruptly from a state of the highest maximum temperature. However, for temperature-induced deactivation of the catalyst, selfstabilization leads to a vicious circle: the higher the maximum temperature the greater is the degree of deactivation and, in turn, the higher is the maximum temperature.

Figure 7b shows the effect of the inlet concentration in the form of adiabatic temperature rise on the temperature profile. Increase of $\Delta T_{ad}$, according to Equation (6), results in a broader temperature profile and in a higher maximum temperature. However, the maximum temperature increases only by about the same amount as the adiabatic temperature rise.

The above-mentioned estimates were made for the limiting case of very rapid reversal in direction of flow. With the help of Equation (3) for the migration velocity of the temperature front, the effect of the period length can also be estimated. For a stable, ignited operation, complete conversion must be attained throughout the entire period, and, after reversal in flow, the temperature of the catalyst must not drop below the temperature of ignition. According to Figure 7c, the maximum half period length $\tau_{max}$ can be conservatively estimated as

$$\tau_{max} = \frac{\Delta l_{max}}{w} \quad \text{with} \quad \Delta l_{max} = L - 2(T_f - T_0) \frac{dz}{dT} \quad (7)$$

Here, $L$ is the length of the catalyst bed; $w$, $\Delta T$, and $\Delta T/dz$ are given by Equations (3), (5), and (6), respectively.

With the help of the equations given here, the behavior of autothermal combustion reactors with periodic reversal in flow or integrated countercurrent heat exchange may be estimated. In the next section, this will be verified by a comparison with experimental results and with some simulations. Systematic simulations with parametric studies may be found in [13,14,15], along with details of the models used.

2.1.2. Experimental results

The experimental setup used is schematically shown in Figure 8. Instead of a packed catalyst bed,
ceramic automobile exhaust monoliths of 5 cm in outer diameter, manufactured by Degussa Corporation, Federal Republic of Germany, were used. The entire bed length was 84 cm. The heat losses which were unavoidable with these dimensions were compensated for by additional electric heating.

Figure 9 shows the effect of the ignition temperature. For inlet concentrations corresponding to the same adiabatic temperature rise, the experimental results obtained with propane and propene as pollutants were compared at identical air flow-rates. In agreement with the graphical interpretation given in Figure 7a, the more readily oxidizable component, which is propene with an ignition temperature of approximately 190°C, led to a lower temperature profile than propane with an ignition temperature of approximately 450°C. The slope of the temperature profile is about the same in both situations, as predicted by Equation (6). Methane, which is the most thermally stable hydrocarbon with an ignition temperature on noble metal catalysts of approximately 600°C, leads to an even higher maximum temperature.

Since the end zones of the catalyst bed only serve for regenerative heat exchange, these zones may also consist of inert materials. Figure 10 shows the results of simulations performed to predict the effect of inert end-zones of different size. As long as the material used is inert, the reaction cannot start before the point where the active catalyst begins, resulting in an apparent shift of the ignition temperature to higher values (see Figure 10). The simulation results shown, however, are more of academic interest, since, for the situations taken into consideration, detectable homogeneous combustion already exists at temperatures in excess of 500°C, and, for this reason, the reaction already ignites in the inert zones.

2.2. High-temperature oxidation

At this point, a discussion of thermal combustion, i.e., catalyst-free oxidation of polluted air, seems appropriate. The autothermal reactor concepts, discussed before, are equally suitable for this purpose if inert material instead of the catalyst is used for regenerative heat exchange. Here, the ignition temperature is equal to the temperature necessary for homogeneous combustion. Commercial plants have been successfully operating, using this process [16]. In contrast to catalytic oxidation, however, the reaction kinetics of thermal oxidation are complicated. Reaction normally starts as a free radical chain reaction at temperatures over 300°C, i.e., cool flames; however, the reaction is rapid enough only at temperatures in excess of 700 to 800°C to obtain significant conversion. Orientation experiments using catalyst-free monolithic supports (Cordierite) in the experimental setup shown in Figure 8 yielded incomplete conversion under the same inlet conditions which were used in catalytic oxidation, even though the maximum temperature rose to about 1,000°C. Therefore, in the commercial equipment mentioned before, slow flow is maintained through the inert packing so that complete conversion can be attained, and the period of reversal in flow can be extended on the order of magnitude of one hour. If, by keeping the maximum temperature below certain limits, NO formation can be prevented, homogeneous combustion in the autothermal reactors described is an alternative worth consideration for many applications.

2.3. Utilization of heat of reaction by side-stream withdrawal

At times of high air pollutant loadings, to withdraw the heat of oxidation liberated at the highest possible temperature level and to put it to some practical use is desirable. Ideally, the maximum temperature should be limited in order to avoid catalyst damage and/or NO formation. To this end, Matros et al. [1,2] recommended the integration of heat exchangers into the middle of the reactor. In contrast to this, the side stream withdrawal of hot reaction gas proposed in [15] will be considered. From a point of view of design, this proposition is much simpler than the first-mentioned solution, and leads to more
stable operating conditions. Since conversion is already complete before the middle of the reactor, the side stream withdrawn consists of purified air at the highest temperature level. According to an overall energy balance, the maximal withdrawable rate of flow \( \dot{m}_M \) is

\[
\dot{m}_M = \dot{m}^0 \frac{\Delta T_{ad}}{\Delta T}
\]  

(8)

If the heat of reaction liberated is removed in this manner by side stream withdrawal, inlet and exit air are at ambient temperature, and the entire heat of reaction liberated can be utilized at the highest temperature attained in the reactor. Figure 11 shows relevant experimental results obtained with the setup shown in Figure 8. Here, the observed lowering of the maximum temperature is not a consequence of the side stream withdrawal, but can be mostly explained by the incompletely adiabatic operating conditions of the experimental setup. However, if a structured packed bed is used [14], the maximum temperature can be influenced by side-stream withdrawal under completely adiabatic operation.

3. Catalyst shapes

 Whereas the integration of the heat exchanger into the reactor is of decisive significance for the efficient utilization of heat, the external geometry of the catalyst determines the required bed volume, the total conversion, and, by pressure loss, the required blower performance.

As has already been mentioned at the outset, for reactor temperatures attained with the help of integrated heat recycling, the reaction rate is essentially controlled by external mass transport. Therefore, the available external catalyst surface-area \( a_e \) and the attainable value of the mass transfer coefficient \( k_G \) play an important role. The pressure loss is a decisive cost factor, particularly for purification of large polluted air flows. Pressure loss and external mass transfer are usually closely correlated with one another. Nevertheless, for a given problem, to optimize the conditions is possible; this will be shown next where conventional catalytic packed beds of spherical particles are compared with ordered packings in monolithic form.
3.1. Monolithic catalysts

Since the great success in car-exhaust purification, catalyst structures in monolithic form have increasingly been considered also in other segments of reaction engineering. Three main shapes exist to choose from:

1. monoliths with straight parallel channels of different cross-sectional areas;
2. stacks of parallel, often slightly embossed plates;
3. stacked plates with a pattern of diagonal corrugational waves, similar to the Sulzer SMV-mixers (Sulzer KATAPAK).

The effectiveness of a catalyst packing can be visualized very nicely by using a method developed by Kottke and Blenke [17]. This method is based on the reaction of traces of NH3 present in an air stream with a wet surface containing manganese chloride to form manganese dioxide. The reaction is so fast, even at ambient conditions, that its rate practically depends only on the diffusional resistance in the boundary layer. As a result, the conditions correspond to those present in catalytic oxidation at much higher temperatures. The intensity of brown discoloration is a measure of the amount of reaction product formed, and, thus, directly corresponds to the local rate of reaction.

Figure 12 shows, as a result of such a visualization, the local distribution of the rate of reaction in a pack consisting of corrugated plates [18]. In the experiment, corrugated plates were covered with filter paper soaked with manganese chloride solution. The upper part of Figure 12 shows a corrugated plate, and the lower part the filter paper removed from its surface. The intensity of discoloration shows fast reaction at the inlet end on the left-hand side. Toward the exit, NH3 has completely disappeared from the gas stream.

The conditions in a monolith with square channels of the same hydraulic diameter, obtained under identical conditions, are shown in Figure 13. Again, the color intensity decreases rapidly from the inlet to the outlet. Visualization in a short corrugated plate package after the end of the monolith reveals, however, that the reactant was still present in a high concentration at the exit. Hence, the decrease of reaction rate is caused here, in contrast to the previous example, not by complete consumption but by dilution in the laminar boundary layer above the surface.

Figure 13 shows another characteristic of monolithic catalysts with angular cross section: at the inlet only those areas appear white on which the vertical slats are located. Downstream, the white streaks become increasingly broad. The reason for this is that two reaction surfaces meet in corners, resulting in a fast depletion of the material introduced at the inlet. Additional material is only slowly supplied from the core of the stream, due to the long diffusional path. This corner effect appears in all monolith channels which have angular cross-section, and results in a reduction of the effective surface area to a value corresponding approximately to that of an inscribed circular channel.

The qualitative results show, for identical dimensions, significantly better mass transfer in the corrugated package than in the channel-type monolith. This has also been confirmed by quantitative tests.

Considering the pressure loss encountered in the gas flow, it is well known that an improvement in mass or heat transfer can usually be obtained only at the expense of a more than proportional increase of pressure loss. Among all known shapes, at the same value of the hydraulic radius, the straight smooth tube of circular cross-section has the most favorable ratio of mass or heat transfer rate to pressure loss. Next, these effects will be quantitatively estimated for the example presented at the outset.
3.2. Estimate of catalyst-bed volume and pressure loss

Using the approximate assumption that the external mass transport is the rate-determining step for the oxidation, the material balance for the concentration \( c_G \) of the component to be oxidized along the path of flow \( z \) is as follows:

\[
\epsilon v \frac{dc_G}{dz} = -k_G a_v (c_G - c_S) \quad \text{with} \quad c_S = 0 \quad (9)
\]

If 99% conversion, i.e., a final concentration of 1% of the inlet concentration, is required, then, integration gives for the length of the reaction zone \( z_L \)

\[
z_L = -\frac{\ln(0.01) \epsilon v}{k_G a_v} = 4.6 \frac{\epsilon v}{k_G a_v} \quad (10)
\]

With a reactor cross-sectional area of \( A \), the following result is obtained for the required reactor volume \( V_R \):

\[
V_R = z_L A = 4.6 \frac{V}{k_G a_v} \quad (11)
\]

i.e., \( V_R \) is directly proportional to the gas volumetric rate of flow \( V \), and inversely proportional to the specific mass transfer \( k_G a_v \). From the literature, e.g., the VDI-Heat-Transfer Handbook [19], correlations for \( k_G \) and \( a_v \) may be taken. These correlations are particularly simple for straight channels and laminar flow. Past the startup region, visible in Figure 13, corresponding to about 10 channel diameters, the dimensionless mass transfer coefficient (Sherwood number \( Sh \)) becomes constant. For square channels with an hydraulic diameter \( d_h \),

\[
Sh = \frac{k_G d_h}{D} = 3 \quad (12)
\]

where \( D \) is the diffusivity of the pollutant present in the air; for toluene in air at 600 K, \( D = 0.28 \times 10^{-4} \) m²/s. The specific surface can be expressed as

\[
a_v = \frac{4}{d_h \epsilon} \quad (13)
\]

Hence, neglecting the startup region, for monolithic catalysts with square channel cross-section,

\[
k_G a_v = \frac{12 D}{d_h^2 \epsilon} \quad (14)
\]

and

\[
V_R = 0.38 \frac{V d_h^2 \epsilon}{D} \quad (15)
\]

Here, the Hagen-Poiseuille equation applies [20] for the pressure loss:

\[
\Delta p = \frac{32 \eta v_G z_L}{d_h^2} \quad (16)
\]

whence, by Equations (10) and (14),

\[
\Delta p = \frac{12.25 \eta}{D} v_G^2 \epsilon^2 \quad (17)
\]

For random catalyst packings, similar trend predictions are obtained, even though the Sherwood number \( Sh \) (Equation (12)) depends, in a more complicated manner, on the geometry, the physical properties, and on the rate of flow. In addition, in contrast to Equation (16), the loss in pressure increases with the velocity \( v \) at a greater than linear rate.

The general conclusions, however, remain the same. Hence, from Equation (15) follows that, for a given volumetric rate of flow of air, \( V \), the catalyst volume which is required varies quadratically with the hydraulic diameter; on the other hand, the geometrical arrangement, i.e., small flow cross-sectional area \( A \), and a great bed length \( z_L \), or large flow cross-sectional area and short bed, has no effect on \( V_R \). Furthermore, the pressure loss depends, via flow velocity \( v_G \), on the square of the flow cross-sectional area, while the hydraulic diameter plays no role. Hence, minimum catalyst volume at minimum pressure loss is attained by using a very shallow bed with a high flow cross-sectional area and a small hydraulic diameter.

The discussion up to this point was limited to the catalyst contained in the reaction zone. Entirely analogous relationships apply, according to the equivalence between heat and mass transport, also to zones of regenerative heat exchange. The necessary length of the heat exchange zone depends, as shown in Figure 6d, on the ignition temperature \( T_i \), and on the slope, Equation (6), of the two sides of the temperature profile.

For an order of magnitude estimate, in the following it will be postulated that the heat exchange zone is four times as long as the reaction zone \( z_L \), given by Equation (10). Since in a Matrosov reactor, both zones are present twice, a multiplicative factor of 10 follows. These conditions were used in the example given at the outset for a comparison between a sphere packing and a monolithic catalyst with square channels. In Figure 14, the total pressure loss is plotted as a function of the reactor length. The parameter is the hydraulic diameter, given in millimeters, at a given superficial velocity of the gas \( v_s \), corresponding to a given inlet cross-sectional area \( A \). Note should be made that the required packing
length, or, equivalently, the catalyst volume, increases faster than linearly with $d_h$, whereas the total pressure loss is affected by $d_h$ only to a negligible extent. By choosing a higher superficial gas velocity, the flow cross-sectional area can be correspondingly less, and the bed length greater. The loss in pressure, however, increases with the square of the velocity. For other catalyst shapes such as, e.g., Raschig rings or corrugated plate packages, the curves lie between the limiting curves plotted in Figure 14.

3.3. Flow-through monoliths

The result that a minimum catalyst-bed volume with minimum pressure loss can be obtained by using a shallow bed with a large cross-sectional area and small hydraulic diameter, is not directly applicable in practice. One reason for this is the tendency of very fine channels to become clogged by suspended matter. Hence, the values of $d_h = 1$ mm, customary in present-day automobile catalysts, already seem to be close to the lower limit (also for manufacturing reasons). The second difficulty lies in uniformly distributing the polluted air from the inlet pipe over a large cross-sectional area.

Figure 15 shows the measured velocity profiles immediately before entry into the monolith for a ready-to-use catalyst for an automobile. As shown in Figure 15, for constructional reasons, the inlet flow is eccentric, and the cross-sectional area expands over a short distance by a factor of 4.5. Here, the entering gas reaches the catalyst surface as a free jet, and flows through about 1/3 of the entire cross-sectional area with a correspondingly high velocity. Since the region through which the flow is rapid determines the total conversion, it can be estimated that the catalyst cross-sectional area can be reduced by almost 50% if the flow through the bed is uniform.

In this respect, crossed corrugated plates used as catalyst supports display a much more favorable behavior. For correctly chosen parameters, the supports also assure fast transverse mixing for nonuniform inflow. This is shown in Figure 16 on an example where, with the visualization technique described before, a point tracer pulse was introduced [18]. How fast this pulse was distributed over the entire width of the package is apparent.

4. Summary and conclusions

Due to the usually low pollutant concentrations, the standard way of catalytic oxidation with external heat exchangers requires either additional fuel or very large heat-exchange surface areas. In contrast, the integration of heat exchange into the catalyst bed, using direct, i.e., regenerative, heat exchange,
permits a great deal of heat recovery while requiring only a small packed-bed volume. Two different variants, using either fixed beds and periodic reversal in flow, which is the Matros-type operation [1,2], or rotating fixed beds, have been discussed. In both situations, a side-stream withdrawal allows utilization of almost the total heat of combustion at the highest temperature level in the reactor.

As a result of heat integration, the reactor behavior is very different from that of standard fixed-bed reactors. Using an analogy with the behavior of a fixed-bed reactor with integrated countercurrent heat exchange, however, simple relationships can be derived by which the reactor behavior can be estimated.

Since the packing of the catalyst also acts as a regenerative heat exchanger, a larger amount of catalyst is used than in the conventional processes. This drawback can be minimized by using high-frequency flow reversal, and inert end-zones. If the inert end-zones are too long, however, high reaction temperatures unnecessarily result. In principle, this process is also suitable for homogeneous high temperature oxidation, if both the residence time in the hot region is sufficiently long to achieve complete oxidation, and the maximum temperature can be kept below a certain value, to avoid NOx formation.

Either conventional, random packings, or ordered structures can be used as packings. The pertinent relationships between catalyst volume, bed length, pressure loss, and channel diameter have been given for monolithic catalysts with straight parallel channels, based on the assumption of a mass-transfer-controlled reaction rate. A comparison shows the advantages of monolithic catalysts over sphere packings. However, for parallel-path monolithic catalysts, great care must be exercised to ensure uniform distribution of flow.

Nomenclature

\begin{align*}
A & \quad \text{cross-sectional area} \\
a_v & \quad \text{specific surface, m}^2\text{m}^{-3} \\
c & \quad \text{concentration} \\
c_{pG} & \quad \text{heat capacity (gas)} \\
c_S & \quad \text{heat capacity (solid)} \\
d_h & \quad \text{hydraulic diameter} \\
D & \quad \text{pollutant/air molecular diffusivity} \\
g & \quad \text{mass fraction of oxidizable components} \\
G_z & \quad \text{cross-sectional mass velocity} \\
\Delta h_v & \quad \text{molar heat of combustion} \\
k_G & \quad \text{mass transfer coefficient} \\
l & \quad \text{length} \\
L & \quad \text{catalyst bed-length} \\
\dot{m} & \quad \text{flow rate of mass} \\
\dot{m}_M & \quad \text{side-stream withdrawal mass flow-rate} \\
Sh & \quad \text{Sherwood number} \\
\Delta p & \quad \text{loss in pressure} \\
t & \quad \text{time} \\
T & \quad \text{temperature} \\
T_i & \quad \text{ignition temperature} \\
\Delta T_{ad} & \quad \text{adiabatic temperature rise} \\
\Delta T & \quad \text{total temperature rise in reactor} \\
U_w & \quad \text{heat transfer coefficient} \\
v & \quad \text{flow rate in channel} \\
v_\tau & \quad \text{superficial velocity} \\
V & \quad \text{volume} \\
V & \quad \text{volumetric rate of flow} \\
w & \quad \text{moving velocity of the temperature front} \\
X & \quad \text{conversion} \\
z & \quad \text{axial coordinate} \\
z_L & \quad \text{length of reaction zone} \\
\end{align*}

Greek letters

\begin{align*}
\epsilon & \quad \text{void fraction of fixed bed} \\
\kappa & \quad \text{thermal conductivity} \\
\eta & \quad \text{viscosity} \\
\rho & \quad \text{density} \\
\tau & \quad \text{half period length} \\
\end{align*}

Subscripts

\begin{align*}
eff & \quad \text{effective value} \\
\sigma & \quad \text{gas phase} \\
1 & \quad \text{exit} \\
\max & \quad \text{maximum value} \\
\text{r} & \quad \text{reactor} \\
\text{s} & \quad \text{solid} \\
0 & \quad \text{inlet} \\
\end{align*}

Literature cited


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