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Reaction and Process System Analysis, Miniaturization and Intensification Strategies

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2.1

Introduction

The concepts of process miniaturization and process intensification have developed considerably in chemical engineering since the 1990s, in relation to the principle of sustainable development. These concepts often appear as potential solutions not only to meet the societal demand concerning a “smaller, cheaper and safer” chemical industry, but also to satisfy an ever more dynamic market in search of portable, distributed and responsive process solutions.

Whereas “miniaturization” can be easily understood as the volume reduction of a fixed-performance production system, “intensification” can be interpreted in several ways. As defined by Stankiewicz and Moulijn [1], process intensification refers to “apparatuses and techniques that [...] are expected to bring dramatic improvements in manufacturing and processing, substantially decreasing equipment size/production capacity ratio, energy consumption or waste production”. This definition may lead to very different objectives, such as: improvement of reactor selectivity by appropriate control of operating conditions, decrease in the reactants/intermediates/products inventory for safety reasons, decrease in the process energy consumption by heat integration or reaction/separation coupling, operation under aggressive or solvent-free conditions for simplified separation steps and high-throughput development tests/protocols for shorter time-to-market delay.

For each of these intensification challenges, the objective to be reached (volume reduction, reduced size/capacity ratio, etc.), and also the constraints (fixed productivity, fixed performance, quality specifications, etc.) can be identified and quantified with respect to technical and economic data. Unfortunately, the means to tackle these issues are much more complex to define since they can be of very different natures: operating conditions (temperature, pressure, concentrations, etc.), physical or chemical parameters (solvents, catalysts, etc.), equipment (heat exchangers, mixers, columns, etc.), process parameters (reflux ratio, feed strategy of semi-batch reactors, separate unit operations or multi-functional reactors, separator types, etc.). In

addition to this variety of potential solutions offered to chemical engineers, process intensification also includes new technologies, enabling one to work under radically different operating conditions: spinning disk reactors, microstructured reactors, centrifugal field reactors, supercritical systems, periodic operating conditions and so forth.

Such a large number of potential answers to a single well-defined question require a choice of methodology, which until now has been mainly empirical. If such a methodology could be defined, it would only yield to a fully-adapted solution if the base problem is properly understood. What is the limitation to be broken in order to reach the objective? Which phenomenon must be modified?

The aim of this chapter consists in identifying tools to answer these questions. By performing an analysis of the various phenomena involved in a system and comparing these individual phenomena with the global behavior of the system, the limiting phenomenon that restricts the performance can be identified. Then, a strategy can be defined to act selectively on this phenomenon in order to reduce this limitation and intensify the process. Whereas the strategies presented below are applied to microstructured reactors, the different steps of this analysis are of a general nature and may be adapted to various processes.

2.2

Reactor Analysis for Further Intensification

As stated above, intensification can be applied to a large number of parts of a given process and appropriate strategies depend on the specific features of the problem under consideration. The scale of the problem (chemistry scale, equipment scale, process scale or development scale), and also the moment the problem occurs (modification of an existing process or construction of a new process) will make particular strategies necessary [2]. Developing all the possible strategies to solve these various problems falls beyond the scope of the present chapter [3]. For that reason, this chapter will focus on reactor miniaturization/intensification. In spite of this restriction, reactor analysis enables one to cover a large set of phenomena that can also be involved in other intensification problems, thus keeping the general aspect of the approach described below.

2.2.1

Analysis of the Limiting Phenomenon

Specialists in heterogeneous catalysis and process control are used to observing how a complex system involving various coupled phenomena can exhibit global characteristics that seem to be under the influence of only one of these phenomena. The rate-limiting step in heterogeneous catalysis and approximate system orders in process control are the consequence of a limiting phenomenon that imposes its rate or inefficiency on the global system. That can also be observed in the performance of chemical reactors and will serve as a base principle for the analysis detailed below.

In the case of chemical reactors, a large number of fundamental phenomena are likely to interact and influence the global performance of the system. The following phenomena are the most commonly studied:

- homogeneous and heterogeneous reactions
- heat and mass transfer in fluid phases
- mass transfer between immiscible fluids or with walls
- physical effects that can also influence the hydrodynamic behavior of the fluid phases (gravity, surface tension, electric forces, etc.).

Taking into account all these phenomena to quantify their specific influence on the global performance of a reactor would require either the development of very complex and hard to validate models or the experimental realization of cost- and time-consuming measurements dedicated to each of these phenomena. Instead of these fine but complex approaches, the methodology used thereafter proposes a simpler characterization of the phenomena involved, based on the comparison of their characteristic times.

Whereas this simple approach does not enable one to identify systematically a unique solution, it makes it possible to eliminate various dead-end solutions and has the advantage of being physically meaningful without requiring complex calculations.

The general principle of this method consists in characterizing all the phenomena involved in the system by a common feature: their own characteristic times. Thus, the phenomena can be compared on a single scale: the time scale. Discussion of the couplings and final comparison of these fundamental time scales with the global dynamic performance of the system will enable one to identify the limiting phenomenon to which further intensification strategies should be applied.

2.2.2

The Reference Time

The first characteristic time of interest for this reactor analysis will serve as a basis to describe the reactor efficiency. This reference time must be carefully chosen as a function of the type of reactor under consideration. As detailed below, this “reference time” could be also denoted “flow time”, “convection time” or “residence time” to enforce its physical meaning. Nevertheless, to avoid some confusion, it will be called “reference time” in the present chapter.

For purely batch reactors, the reference time is naturally the residence time, as a function of which the conversion in the reactor is usually described. This batch time can also be used for analysis of semi-batch reactors. Nevertheless, as the reactant introduction in semi-batch reactors can have a drastic influence on the reactor performance, the feed time is more preferably used as the reference time [4].

As far as the majority of chemical reactors are concerned, their continuous behavior implies that the most commonly used reference time is the usual fluid space time. Nevertheless, particular attention must be paid to systems involving catalytic

heterogeneous reactions. Indeed, the modified space time should be preferred since it includes the quantity of catalytic sites where the reaction occurs [5, 6].

In contrast to the process fundamental times described below, the reference time is an operational parameter of the system. It can be experimentally modified, which generally leads to a change in the reactor performance. Subsequent steps of this analysis will consist in relating these performance variations to the reference time and the characteristic times of the phenomena involved.

2.2.3

The Fundamental Characteristic Times

Regardless of the reference time, all usual physical and chemical phenomena can be described by a fundamental characteristic time, which is peculiar to it. From a general point of view, a characteristic time can be defined as the time required for a physical/chemical system governed by this phenomenon to evolve from a non-equilibrium state to its equilibrium. In practice, they can often be considered as the ratio of a quantity of extensity to the exchanged flux or the transformation rate of this extensity. For example, a reaction time relates a mole quantity to the molar transformation rate and can be simplified as the ratio of the concentration [mol m^{-3}] to the reaction rate [$\text{mol m}^{-3} \text{s}^{-1}$]. Similar relations can be developed for the heat-transfer time and mass-transfer time, where the extensities considered are the heat and the mass, respectively.

As a result, the value of the characteristic time of a phenomenon is a property of the rate of this phenomenon. Particular attention must be paid to the counter-intuitive fact that a fast phenomenon exhibits a small characteristic time, whereas large characteristic times correspond to slow phenomena.

Table 2.1 presents a non-exhaustive list of expressions of the characteristic times corresponding to the most commonly used phenomena involved in chemical reactors. The previous definitions unfortunately do not always enable one to build the expressions presented in Table 2.1. Various methods can be used such as a blind dimensional analysis, similar to the Buckingham method used for dimensionless numbers [7], which can be applied to the list of fundamental physical and chemical properties. Nevertheless, the most relevant method consists in extracting the expressions from a mass/heat/force balance.

The expressions presented in Table 2.1 illustrate first clues for further intensification strategies. Indeed, the characteristic times exhibit dependencies with respect to a large variety of parameters (fluid properties, operating conditions, etc.), among which the geometric dimension R appears as a practical solution to adapt the reactor geometry to the desired effect.

2.2.4

Relation Between System Efficiency and Characteristic Times

In order to relate these different phenomena to the reactor performance, it is first necessary to define their efficiency η . For example, the heat-transfer efficiency of

Table 2.1 Expressions of various elementary characteristic times and their dependence on the characteristic dimension R .

Phenomenon	Characteristic time expression	Order of the dependence law on the dimension R	Examples of characteristic dimension R	Description
n th-order homogeneous reaction	$t_{\text{hom}} = \frac{C_0}{r_0} = \frac{1}{kC_0^{n-1}}$	0	–	Characteristic time required to reach full conversion if the reaction rate is constant and equal to the initial rate
Gravity	$t_{\text{grav}} = \sqrt{\frac{2R}{g}}$	$\frac{1}{2}$	Height, channel radius	Characteristic time required to travel a height R in free fall with no initial velocity
Apparent first-order heterogeneous reaction	$t_{\text{het},1} = \frac{R}{2k_s}$	1	Reciprocal of the surface-to-volume ratio	Characteristic time required to reach 63% conversion
General heterogeneous reaction	$t_{\text{het}} = \frac{C}{r}$	Varies	–	
Surface tension	$t_{\text{surf}} = \sqrt{\frac{\rho R^3}{2\sigma \cos(\theta)}}$	$\frac{3}{2}$	Droplet radius, channel radius	Characteristic deformation time of non-viscous droplets
Viscosity	$t_{\text{visco}} = \frac{\rho R^2}{\mu}$	2	Channel radius, droplet radius	Characteristic time required to establish a momentum effect over a distance R
Diffusive mass transfer	$t_{\text{diff}} = \frac{R^2}{D_m}$	2	Diffusion length	Characteristic time required to travel a distance R with Brownian motion
Convective mass transfer at constant Sherwood number	$t_{\text{mass}} = \frac{R^2}{Sh D_m}$	2	Channel radius	Characteristic time required to transfer a mass quantity between a wall and a flowing fluid
Heat conduction	$t_{\text{cond}} = \frac{\rho C_p R^2}{\lambda}$	2	Length of heat conduction, wall thickness	Characteristic time required to establish a conductive temperature profile
Convective heat transfer at constant Nusselt number	$t_{\text{heat}} = \frac{\rho C_p R^2}{\lambda Nu}$	2	Channel radius	Characteristic time required to transfer a heat quantity between a wall and a flowing fluid

a system is usually defined as the ratio of the heat quantity actually transferred by the system to the maximum heat quantity that the system could transfer. For chemical reactions, whose extensity is the mass, the efficiency is the ratio of transformed mass to the mass available for reaction, which is simply the definition of the reaction conversion. Similar definitions can be used for physical phenomena and hydrodynamics. Thus, concerning the liquid ascension of a liquid through a vertical capillary, the ascension efficiency can be defined as the ratio of the actual height reached by the liquid at time t to the equilibrium height reached after a long time.

For the phenomena presented in Table 2.1, efficiency can be related to characteristic times by writing a balance of the extensity concerned. For a chemical plug-flow reactor (with an apparent first-order reaction or with heat/mass transfer at constant exchange coefficient), the quantity of this extensity is linearly related to its variation with respect to the reference time, yielding ordinary differential equations such as

$$\frac{dC}{d\tau} = -kC \quad \text{and} \quad \frac{dT}{d\tau} = -\frac{HS}{\rho VC_p}(T - T_{\text{ext}}) \quad (2.1)$$

where C denotes the reactant concentration [mol m^{-3}], τ the reference time [s], k the apparent first-order rate constant [s^{-1}], T the temperature [K], H the heat-transfer coefficient [$\text{W m}^{-2} \text{K}^{-1}$], S the heat-exchange surface [m^2], ρ the density [kg m^{-3}], V the volume [m^3], C_p the specific heat [$\text{J kg}^{-1} \text{K}^{-1}$] and T_{ext} the external temperature [K].

For these “first-order” cases of plug-flow reactors, the efficiency can be more precisely expressed as a function of the ratio of the reference time τ to the concerned characteristic time of the phenomenon t_{op} as

$$\eta = 1 - \exp\left(-\frac{\tau}{t_{\text{op}}}\right) \quad (2.2)$$

For comparison, if the same phenomena are considered in a continuously stirred tank reactor (CSTR), the relation takes the form

$$\eta = \frac{\frac{\tau}{t_{\text{op}}}}{1 + \frac{\tau}{t_{\text{op}}}} \quad (2.3)$$

For the plug-flow examples considered above, developing the analytical solutions of the differential Equations (2.1) enables us to isolate two operational characteristic times of chemical reaction and first order as

$$t_{\text{op}} = t_{\text{hom}} = \frac{1}{k} \quad \text{and} \quad t_{\text{op}} = t_{\text{heat}} = \frac{\rho VC_p}{HS} \quad (2.4)$$

respectively. These simple relations, applicable for first-order systems, demonstrate the dependence of the efficiency of a phenomenon on its intrinsic properties (the characteristic time t_{op}) and operating parameters (the reference time τ). The example of heat transfer can be used to discuss the physical meaning of this relation. Indeed, when the reference time (in this case, the space time) is small

compared with the heat-transfer time t_{heat} , the efficiency is very low, since the fluid does not stay long enough in the system to exchange heat. In contrast, if the space time is large compared with the heat-transfer time, efficiency is close to unity, since the fluid stays long enough in the system so that thermal equilibrium with the external medium can be reached.

This ratio of characteristic times represents, in fact, a classical feature used in chemical engineering: the number of transfer units (NTU) in heat-transfer processes and Damköhler number in a reactor. Here, this number is generalized as a number of operation units (NOU), including operations such as heat/mass transfer, reactions, physical phenomena or their combination:

$$\text{NOU} = \frac{\tau}{\tau_{\text{op}}} \quad (2.5)$$

When the behavior of the studied system departs from a first-order behavior, which is the case for numerous chemical reactions, more complex relations can be developed between the efficiency and the NOU, whose expressions will not be detailed here. In a plug-flow system, and also in a CSTR, a direct relation, either explicit or implicit, exists between the efficiency and the NOU. Figure 2.1 presents the evolution of the efficiency as a function of the NOU for reaction orders between -1 and 2 . The shape of the curves clearly depends on the reaction order, therefore enabling identification of the system order by comparison with experimental data and estimation of the operation time.

2.2.5

Times Grading and Scale Dependence of the Phenomena Hierarchy

As stated above, chemical reactor performance is the result of a number of coupled phenomena. Depending on the relative rates of these phenomena, one phenomenon can dominate the others and impose its efficiency on the system. This predominant phenomenon is the limiting one.

In order to identify the limiting phenomenon, the phenomena involved must be distinguished, which is made possible by comparison of their characteristic times. Nevertheless, before discussing these differences and the potentials for process intensification, attention must be paid to the fact that a small characteristic time represents a fast phenomenon: a second-responding system runs faster than a minute-responding system. The smallest characteristic time therefore corresponds to the fastest phenomenon.

The various phenomena involved in a given reactor can be sorted with respect to their characteristic times, which enables one to define the times grading. This times grading does not depend on the couplings between phenomena since it depends only on the values of the fundamental characteristic times. The combination of this grading with the couplings between phenomena (see the next section) is the base that makes it possible to define the phenomena hierarchy that sorts them in order of predominance. The phenomena hierarchy enables one to isolate the limiting phenomenon, which can be either the fastest or the slowest one depending on the

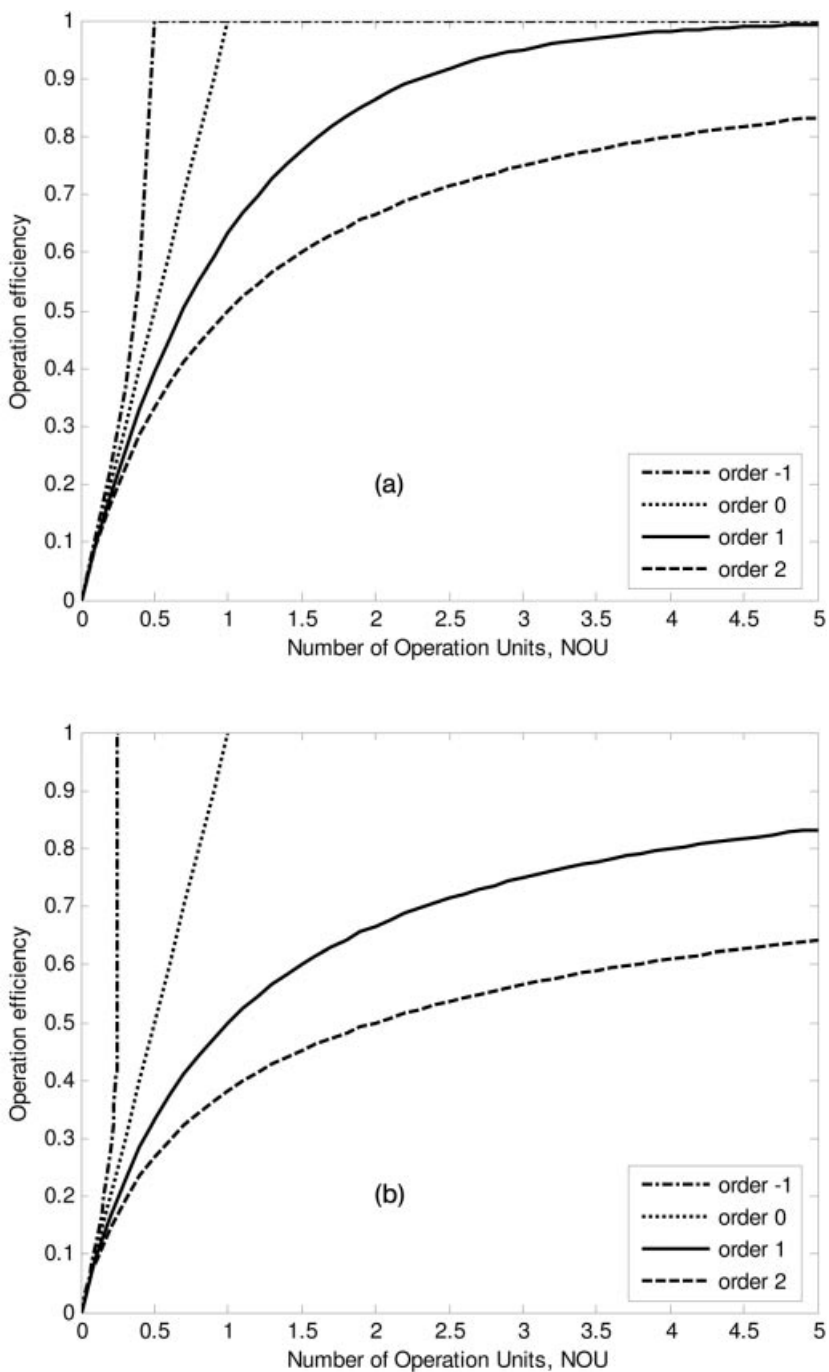


Figure 2.1 Evolution of the operation efficiency η as a function of the number of operation units NOU for system orders ranging from -1 to 2 in batch and plug-flow reactors (a) and in continuously stirred tank reactors (b).

way in which they are coupled. Controlling this hierarchy therefore enables one to control the reactor performance.

Whereas the couplings are not scale dependent, the times grading can be adjusted since the phenomena involved exhibit various dependencies with respect to the characteristic dimension. Indeed, the characteristic times presented in Table 2.1 are sorted in ascending order of their power dependence on the characteristic geometric dimension. What should be noticed first is the large variation of the scale dependence with respect to the phenomenon. Homogeneous reactions exhibit no dependence on the characteristic dimension whereas transfer phenomena are strongly influenced by the presence of walls and obstacles.

As a result, for a given operation involving a set of coupled phenomena, performing this operation in reactors of different geometric scales enables one to modify the characteristic times of these phenomena and change the times grading. The direct consequence of that is a change in the predominance hierarchy and a potentially new dominant phenomenon. This effect is well known as the major difficulty encountered in traditional “scale-up” from the laboratory scale to the production scale, where thermal effects can become detrimental whereas they could be neglected in smaller systems.

Appropriate reactor structuring therefore appears as a relevant intensification strategy: by offering new dimensions for operation, microstructured reactors can be used to modify selectively the hierarchy and choose the phenomenon that should impose its efficiency on the system. For example, reducing the characteristic dimension accelerates transfer phenomena with respect to homogeneous reactions, enabling one to eliminate detrimental temperature effects.

2.2.6

The Global Operation Time as a Result of the Couplings

To adapt the above-mentioned hierarchy properly to the desired performance, interactions between the phenomena involved must be taken into account. Indeed, the fundamental phenomena presented in Table 2.1 can exhibit strong couplings that radically change the system efficiency: a heterogeneous reaction is coupled to a mass transfer of reactants from the bulk fluid to the catalyst, multiphase reactions combine multiphase transfer and reactions and so forth.

In all cases, the global efficiency is a function of the couplings between the fundamental phenomena. As a result, the global performance of the system can be characterized by a characteristic time that is a function of the times of the elementary processes under consideration. The simplest couplings are serial and parallel couplings. To illustrate how the fundamental times of coupled first-order phenomena combine, two examples are considered:

- The conversion of a reactant A undergoing two simultaneous homogeneous reactions towards B and C illustrates the case of a parallel coupling.
- The conversion of a reactant D undergoing a heterogeneous reaction, requiring previous mass transfer from the bulk fluid to the catalyst support, illustrates a serial coupling.

For parallel and serial coupling of two fundamental phenomena of characteristic times t_1 and t_2 , the global operation time t_{op} can be expressed as follows:

$$\text{For a parallel coupling : } \frac{1}{t_{glob}} = \frac{1}{t_1} + \frac{1}{t_2} \quad (2.6)$$

$$\text{For a serial coupling : } t_{glob} = t_1 + t_2 \quad (2.7)$$

These expressions can be physically explained for both examples. In the case of a parallel coupling, the global operation time is dominated by the smallest fundamental time, i.e. the fastest phenomena. For the parallel reactions, the conversion of reactant A evolves as fast as the fastest reaction. In this case, the fastest phenomenon dominates. In contrast, for serial phenomena, the slowest phenomenon dominates: the conversion rate of reactant D submitted to mass transfer and heterogeneous reaction proceeds at the rate of the slowest phenomenon, leading to a possible diffusion regime or chemical regime.

Whereas the fundamental characteristic times are scale dependent, the structure of the couplings between these phenomena does not change with the geometric scale. However, changing the hierarchy of these phenomena enables one to control the dominating phenomenon and control the global efficiency of the system.

In practice, serial and parallel couplings are the most common in chemical engineering, but some other complex couplings can also appear. To ease the readability of this chapter, these complex couplings, and also couplings of phenomena departing from first-order behavior, will not be developed here [7].

2.2.7

Comparison of the Global Time with the Fundamental Times

First, the value of the global operation time can be identified from experimental or simulation data: this is made possible by fitting the efficiency as a function of the reference time using expressions such as Equations (2.2) or (2.3) or appropriate expressions corresponding to the apparent system order. For example, for first-order systems, the operation time is the time required to reach 63% efficiency. Then, using appropriate literature results or correlations enables to estimate the fundamental times involved in the studied system, using expressions presented in Table 2.1.

Sorting the fundamental times on the time scale and comparing this times grading with the observed global operation time make it possible in most cases to identify the dominating phenomenon, which is the clue to the performance limitations. As demonstrated by the second example presented in the next section, since serial and parallel couplings are the most usual, the global operation time is often very close to the slowest or fastest of the phenomena involved. Deviations between the global operation time and the fundamental times indicate that complex orders and/or couplings (not presented here) should be taken into account.

As soon as the limiting phenomenon has been identified, different strategies (presented further) can be designed to modify the hierarchy in the sense of a performance increase.

2.2.8

Effects Related to the Control of the Phenomena Hierarchy

The main effects that can be reached by appropriate control of the phenomena hierarchy have already been demonstrated by the use of microstructured reactors [8]. They are summarized here in the frame of the previous analysis:

- Selective intensification of heat transfer with respect to reaction. The scale dependence of heat transfer and reactions being different, it is possible to accelerate heat transfer selectively compared with reactions. As a result, more homogeneous temperature conditions or even isothermal conditions can be reached. That enables one not only to control temperature conditions for determination of kinetic parameters, but also to control fast exothermic reactions and prevent thermal runaway.
- Selective intensification of mass transfer with respect to reaction. With a similar scale dependence to heat transfer, one can preferentially improve the selectivity of competing reactions, in either single- or multi-phase systems. For reasons of readability, the mixing times are not discussed in this chapter but would enter this category.
- Selective intensification of heterogeneous reactions with respect to homogeneous reactions. This effect, often called “the grid effect”, can be advantageously exploited to control the radical chain reactions leading to explosions so as to operate microstructured reactors in the explosion regime.

2.3

Examples

The following two examples are intended to show how the performance of a system involving given phenomena can be improved by adapting the characteristic dimensions to the limiting phenomenon that should impose its efficiency. They also indicate the combination of the couplings with the phenomena hierarchy.

2.3.1

Scales of Homogeneous Chemistry

Figure 2.2 presents the evolution of the main characteristic times of interest with respect to the characteristic dimension. The dimensions studied range from $10\ \mu\text{m}$ up to 1 m and enable one to cover successively the microscale (from $10\ \mu\text{m}$ to 1 mm), the mesoscale (from 1 mm to 1 cm), the laboratory scale (from 1 cm to 10 cm) and the pilot scale (from 10 cm to 1 m). As a function of this dimension, Figure 2.2 presents the evolution of several characteristic times (calculated using properties of aqueous solutions and water/air surface tension):

- two homogeneous reactions with times equal to 1 min and 1 s. Since homogeneous reactions are not scale dependent, these evolutions are reduced to horizontal lines
- the diffusion time of mass

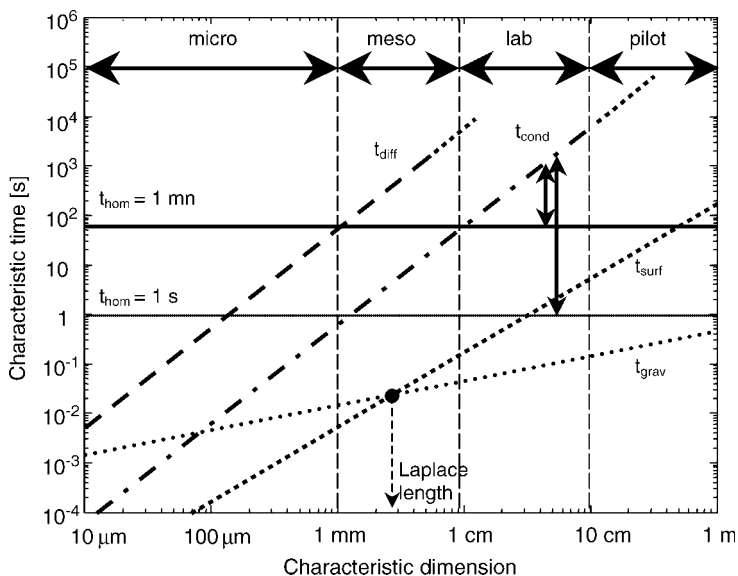


Figure 2.2 Evolution of the homogeneous reaction time, diffusion time, conduction time, surface tension time and gravity time with respect to the characteristic dimension from the microscale up to the pilot scale (properties of aqueous solutions and water/air surface tension).

- the conduction time of heat
- the surface tension time
- the gravity time.

Before describing the influence of the scales on the operation of homogeneous reactions, it is interesting to discuss the combination of the lines corresponding to the surface tension time and the gravity time. As can be seen in Table 2.1, these times exhibit different scale dependencies and therefore appear in Figure 2.2 as lines with different slopes. For water/air systems, these lines cross each other for a characteristic dimension around 3 mm, which is known as the Laplace length. This characteristic dimension is usually considered as the dimension under which surface tension effects become predominant over gravity effects. This particular change in hierarchy has been observed for gas–liquid flow regimes in microchannels [9, 10].

To discuss the influence of scale on the operation of a homogeneous reaction, we can consider two different reactions (with times equal to 1 min and 1 s), assuming that they are exothermic. If the slow reaction ($t_{\text{hom}} = 1 \text{ min}$) is performed in a 5-cm system, the conduction time is 20 times larger than the reaction time, indicating a very slow heat transfer, which may induce detrimental local hot spots or even thermal runaway. Fortunately, this 20-fold factor can be drastically reduced by mechanical stirring of the 5-cm vessel, permitting the acceleration of heat transfer and prevention of detrimental temperature effects. However, in the case of a faster reaction (1 s) performed in the

same 5-cm vessel, the ratio of the conduction time to the reaction time is larger than 1000. Such a factor is too large to be reduced by usual mechanical agitation so that operating this reaction in this system may induce detrimental effects.

Now, considering the same reactions in microstructured reactors enables one to see the impact of a change in the hierarchy. Indeed, for dimensions below 1 mm, the conduction time is always lower than the reaction time for both slow and fast reactions. That indicates that heat transfer is always so fast that it allows operation without detrimental thermal effects. Moreover, since the heat-transfer time considered here is the conduction time, which is always larger than the convective heat-transfer time, still faster homogeneous reactions can be safely studied in these systems. Similar analysis can be performed by comparison of the reaction times with the mass-transfer time.

2.3.2

Competitive Reactions and Mass-transfer Effect

In order to understand properly how coupled phenomena may interact and modify the global behavior of a chemical system, the example schematically described in Figure 2.3 is considered. The goal product C is obtained by the heterogeneous reaction of the main reactant A with a catalyst coated on the walls of a plug-flow reactor. In the same time, reactant A can undergo an undesirable homogeneous degradation reaction in the fluid phase to form a by-product B. The conversion of reactant A, and also the selectivity towards product C, will therefore be a result of the coupling between:

- the homogeneous reaction of A to B, with a first-order rate coefficient k_{hom}
- the apparent first-order heterogeneous reaction of A to C, with a rate coefficient k_{het}
- and the mass transfer of reactant A from the bulk fluid to the catalytic wall, with a convective Sherwood number Sh and a mass-transfer coefficient k_d .

The characteristic time analysis presented above indicates that these phenomena exhibit different dependencies with respect to the characteristic dimension R :

$$t_{\text{hom}} = \frac{1}{k_{\text{hom}}}, \quad t_{\text{het}} = \frac{R}{2k_s} \quad \text{and} \quad t_{\text{mass}} = \frac{R^2}{ShD_m} \quad (2.8)$$

where $Sh = 2k_dR/D_m$.

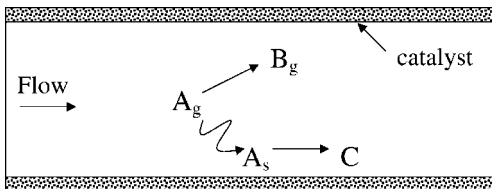


Figure 2.3 Schematic view of a reactant A undergoing competitive homogeneous and heterogeneous catalytic reactions towards the by-product B and the goal product C.

Solution of the mass balance over reactant A in the gas phase enables one to demonstrate that the conversion of A is related to the space time τ and an operation time t_{op} by the relation

$$X_A = 1 - \exp\left(-\frac{\tau}{t_{op}}\right) \quad (2.9)$$

where

$$t_{op} = \frac{1}{t_{hom}} + \frac{1}{t_{het} + t_{mass}}$$

This expression of the global operation time could have been predicted since the homogeneous reaction acts in parallel with the serial combination of mass transfer and heterogeneous reaction.

The consequence of this multiple coupling is presented in Figure 2.4, where the global operation time (thick line), that could have been identified experimentally, is compared with the three independent characteristic times (thin lines), with respect to the characteristic scale. To ease the readability, both time and dimension scales are normalized with respect to arbitrary reference values, but could have been presented with their original units. This comparison shows the influence of the characteristic dimension on the couplings and on the hierarchy of the involved phenomena. Four large domains can be distinguished in Figure 2.4 defined by the changes in the phenomena hierarchy:

- At large scales (domain 1), the homogeneous reaction is the fastest phenomenon and therefore dominates the hierarchy. This reaction imposes the conversion and the global operation time is equal to the homogeneous reaction time.
- For intermediate scales (domain 2), the heterogeneous reaction becomes faster than the homogeneous reaction. Unfortunately, the mass transfer still remains very slow: reactant A does not have time enough to reach the wall before being consumed by the homogeneous reaction. As a consequence, the homogeneous reaction remains dominant and the global operation time is still equal to the homogeneous reaction time.
- At lower scales (domain 3), the mass transfer runs faster than the homogeneous reaction but remains slower than the heterogeneous reaction. The conversion should be imposed by the heterogeneous reaction, but the reactant consumption still remains limited by the mass transfer from the bulk fluid to the catalytic wall. The global operation time is then equal to the mass-transfer time.
- Finally, at small scales (domain 4), the mass transfer has become faster than both reactions. The heterogeneous reaction dominates and the global operation time is equal to the heterogeneous reaction time.

This example highlights the possibilities offered by appropriate choice of the characteristic dimension. Indeed, modifying the characteristic dimension enables one to switch between the homogeneous and the heterogeneous reactions to control the selectivity. In addition, this example shows how the fastest or slowest phenomenon dominates depending on the serial or parallel coupling between fundamental

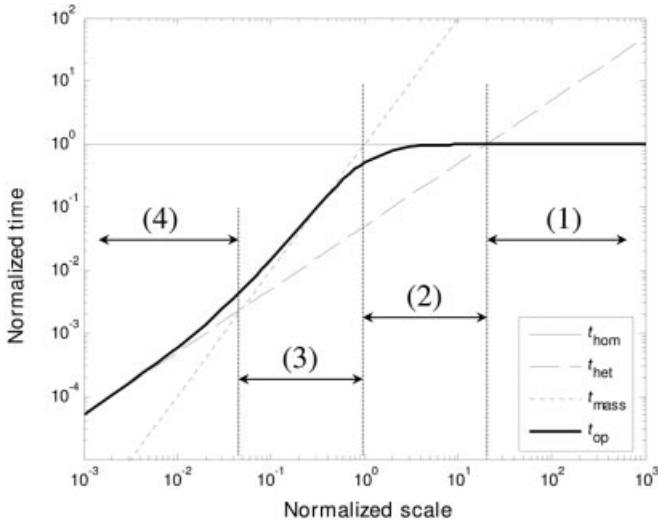


Figure 2.4 Evolution of the homogeneous reaction time t_{hom} , heterogeneous reaction time t_{het} , mass-transfer time t_{mass} and global operation time t_{op} with respect to the normalized geometric scale of the reactor. The thick line corresponds to coupling Equation (2.9).

phenomena. Finally, it shows how the limiting phenomena can be identified if the variation of the operation time with respect to the characteristic dimension can be determined experimentally.

2.4 Miniaturization and Intensification Strategies

Whereas process intensification may aim at different objectives, these goals can generally be reformulated as productivity increase or equipment miniaturization. These two aspects are shown to converge towards one goal using the idea of reference time described above. Indeed, for batch and semi-batch processes, productivity increase is reached by reduction of the batch time or feed time. For continuous processes, miniaturization requires the volume reduction, but is also constrained by the fact that the production flow rate must be maintained. This constraint implies that the space time must be reduced. As a result, in all continuous and discontinuous cases, miniaturization and intensification both require to reduce the reference time τ .

As demonstrated above, the efficiency of a system increases with the NOU, i.e. with the ratio of the reference time to the characteristic operation time. So as to satisfy the constant productivity constraint, this time ratio must be maintained. Therefore, the characteristic operation time must be reduced by the same factor as the reference time.

The various expressions of characteristic times presented in Table 2.1 show that most phenomena can be accelerated by reducing the system dimension.

Nevertheless, the various scale dependencies imply design difficulties that must be taken into account to accelerate phenomena while controlling the hierarchy. As detailed below, the main difficulty in designing intensified reactors lies in changes in the phenomena hierarchy.

2.4.1

Miniaturization without Hierarchy Change

The objective here consists in reducing the system volume V [m^3] while operating with the same flow rate Q [$\text{m}^3 \text{s}^{-1}$] and the same NOU.

To keep the present study as general as possible, miniaturization is performed by designing a group of N_c parallel cylindrical channels of radius R [m] and length L_c [m], each of them exhibiting plug-flow behavior. The total flow rate Q is uniformly distributed to each channel. The operation efficiency η is related to the space time τ and operation time t_{op} as presented in Equation (2.2). In this case, the phenomena hierarchy is considered to be unchanged in spite of the reduction in the characteristic dimension. Therefore, the global operation time has a constant scale dependence m with respect to the dimension R :

$$t_{\text{op}} \approx R^m \quad (2.10)$$

To maintain the system efficiency η , the number of operation units is constant:

$$\text{NOU} = \frac{\tau}{t_{\text{op}}} = \frac{V}{Qt_{\text{op}}} \approx \frac{N_c L_c R^2}{QR^m} \approx N_c L_c R^{2-m} = \text{constant} \quad (2.11)$$

This condition relates the design parameters N_c , L_c and R and immediately shows a first design constraint:

$$N_c L_c \approx R^{m-2} \quad (2.12)$$

Considering that the reactor volume is proportional to the channel volume, substituting this constraint in the expression for the reactor volume yields

$$V \approx N_c L_c R^2 \approx R^m \quad (2.13)$$

This relation highlights the miniaturization potential that can be reached by adapting the channel radius: a decrease in the dimension R implies a decrease in the reactor volume as soon as the scale dependence of the limiting phenomenon m is positive. Almost all the phenomena presented in Table 2.1 enable one to apply this strategy since their scale dependences are positive. Only homogeneous reactions make it impossible since they are not scale dependent, and other strategies are required for these reactions. For transfer phenomena, the miniaturization potential can be very large, since a two-fold decrease in the channel radius implies a four-fold decrease in the reactor volume.

Whereas this miniaturization factor seems very attractive, design possibilities related to the previous constraint must be carefully considered. Indeed, maintaining $N_c L_c R^{2-m}$ constant has strong consequences for the possible reactor geometries, and also process characteristics. For that reason, it is useful to calculate the reactor

cross-section S and the laminar pressure drop through the reactor, which are related to R , N_c and L_c as

$$S \approx N_c R^2 \quad (2.14)$$

$$\Delta P \approx u_m \frac{L_c}{R^2} \approx \frac{Q}{N_c R^2} \frac{L_c}{R^2} \approx \frac{L_c}{N_c R^2} \approx \frac{R^{m-6}}{N_c^2} \quad (2.15)$$

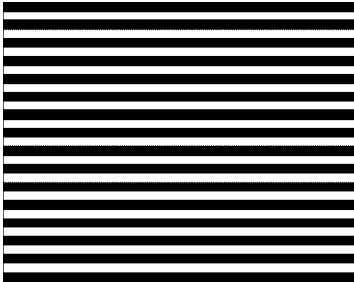
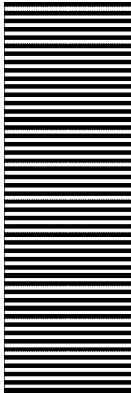
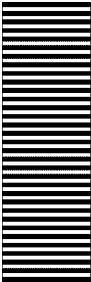
Table 2.2 presents the evolutions of these quantities for three types of scale dependence of the operation time: $m = 0, 1$ and 2 . For heterogeneous reaction and heat/mass transfers, maintaining either the channels number or their length while reducing the radius induces systematically an increase in the reactor pressure drop that can even become prohibitive. However, by choosing an appropriate channel number and channel length, the pressure drop for these reactors can be maintained or even reduced. However, this is generally combined with an increase in the reactor cross-section.

Table 2.3 illustrates the changes in the apparatus shape permitting a volume reduction while maintaining the pressure drop constant. Two phenomena exhibiting different scale dependencies are successively considered. In the first case, the operation time is proportional to the radius, which may represent an apparent first-order heterogeneous reaction: a two-fold decrease in the radius R can create a two-fold decrease in the reactor volume, which is mainly due to the increase in the surface-to-volume ratio. In the second case, the operation time is proportional to R^2 , which represents a heat or mass transfer: a two-fold decrease in the radius R then

Table 2.2 Variation in the channel number N_c , channel length L_c , reactor cross-section S and pressure drop ΔP as a function of the channel radius R when one of these parameters is fixed, for characteristic times varying as R^m ($m = 0, 1, 2$).

Scale dependence m	Operation time t_{op}	Reference time τ	Volume V	Channel number N_c	Channel length L_c	Cross-section S	Pressure drop ΔP
0	Constant	Constant	Constant	Constant	$\approx \frac{1}{R^2}$	$\approx R^2$	$\approx \frac{1}{R^6}$
				$\approx \frac{1}{R^6}$	Constant	Constant	$\approx \frac{1}{R^6}$
				$\approx \frac{1}{R^3}$	$\approx R$	$\approx \frac{1}{R}$	Constant
1	$\approx R$	$\approx R$	$\approx R$	Constant	$\approx \frac{1}{R}$	$\approx R^2$	$\approx \frac{1}{R^5}$
				$\approx \frac{1}{R}$	Constant	$\approx R$	$\approx \frac{1}{R^3}$
				$\approx \frac{1}{R^6}$	$\approx R$	Constant	$\approx \frac{1}{R^6}$
				$\approx \frac{1}{R^3}$	$\approx R^3$	$\approx \frac{1}{R^3}$	Constant
2	$\approx R^2$	$\approx R^2$	$\approx R^2$	Constant	Constant	$\approx R^2$	$\approx \frac{1}{R^4}$
				$\approx \frac{1}{R^6}$	$\approx R^2$	Constant	Constant

Table 2.3 Variation in the shape of a structured monolith following reduction of the channel radius, at constant efficiency and pressure drop, for the operations considered

		Shape and parameters after channel radius reduction	
		$t_{op} \approx R$	$t_{op} \approx R^2$
Initial shape			
Radius of a channel	$R = R_0$	$R = \frac{R_0}{2}$	$R = \frac{R_0}{2}$
Number of channels	$N_c = 100$	$N_c = 560$	$N_c = 400$
Apparatus cross-section	$S = S_0$	$S = \sqrt{2} \cdot S_0$	$S = S_0$
Channel length	$L = L_0$	$L = \frac{L_0}{2\sqrt{2}}$	$L = \frac{L_0}{4}$
Total volume	$V = V_0$	$V = \frac{V_0}{2}$	$V = \frac{V_0}{4}$
Shape of the reactor			

creates a four-fold decrease in the reactor volume. However, this volume reduction is constrained by the previous equations and the reactor shape evolves towards a micro-perforated plate, since the channel length becomes small compared with the channel radius. If a decrease in pressure drop is desired, the channel length can become very small in comparison with the reactor cross-section, leading to a configuration similar to a membrane. The flow distribution in such cases may become highly non-uniform, requiring totally new concepts for flow distribution and manifold design.

2.4.2

Miniaturization with Hierarchy Change

Whereas this second case considers the same objective and the same constraints as the case above, it includes a new difficulty. Indeed, due to the scale dependence of the phenomena considered, a large reduction in the volume reactor is generally

coupled with a change in the phenomena hierarchy. The rules presented in Table 2.2 can no longer be used on the whole dimension domain, since they assume a fixed hierarchy. Nevertheless, they can be used on each sub-domain where the hierarchy is maintained. For that reason, a similar approach can be used by paying particular attention to the transition dimensions where the hierarchy changes.

2.4.3

Other Intensification Strategies

As explained in the Introduction, no general methodology for process intensification is yet available. The characteristic times analysis presented above is not exhaustive but can be used as a first tool to analyze a problem and identify possible strategies related to geometric structuring. Nevertheless, geometric structuring does not enable one to eliminate all possible limitations, therefore requiring other strategies. The following points indicate some of these strategies.

- *Kinetic effects.* As a first example of limitation, the previous sections demonstrated that homogeneous reactions cannot be intensified by geometric structuring since they are not scale dependent. Nevertheless, their characteristic times can be accelerated, since they depend on a kinetic constant and on the reactant concentration. As a result, intensification of homogeneous reactions requires either a temperature increase (when additional selectivity or thermal sensitivity problems do not prevent this possibility) or a concentration increase.
- *Thermodynamic effects.* Many performance limitations are related to a thermodynamic equilibrium, which is the case for numerous reversible reactions. Existing solutions consist in coupling the reaction with a separation system (reactive distillation, reactive chromatography, etc.) and can even be coupled to geometric structuring [11].
- *Safety and hygiene effects.* Limitations related to process/product safety can in some cases be solved by the use of microstructured reactors. For example, very exothermic reactions and explosive gas mixtures have been demonstrated to operate safely in structured reactors [12]. The transport of hazardous chemicals could also find sustainable solutions in the development of distributed production in miniaturized plants [13]. In the frame of product engineering, micromixers allowed the quantity of emulsifiers and preservatives required to stabilize emulsions for pharmaceutical applications to be reduced [14].
- *Effects of non-uniformity.* The performance of chemical processes can also be altered by non-uniform operating conditions: flow distribution, photonic activation, electrochemical current densities and so forth. Geometric structuring, even at the microscale, can help in solving these non-uniformities by improving local control [15]. Some of these problems are even the basis of the constructal theory [16, 17].
- *Saturation effects.* Either by active sites blocking or catalyst poisoning, saturation effects may induce large limitations and can generally be solved by periodic

operation of the reactor, alternating reaction and regeneration phases. In particular cases, microstructured reactors offer the possibility of high-frequency periodic operations [18, 19].

Finally, when enlarging the view of a process not only to the equipment but also to its development, specific limitations may occur, concerning for example the time required to formulate properly a catalyst or the scale-up phase from the pilot scale to the production scale. These steps, which can make the time-to-market longer, can be reduced by strategies such as high-throughput screening [20] or numbering-up [21].

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