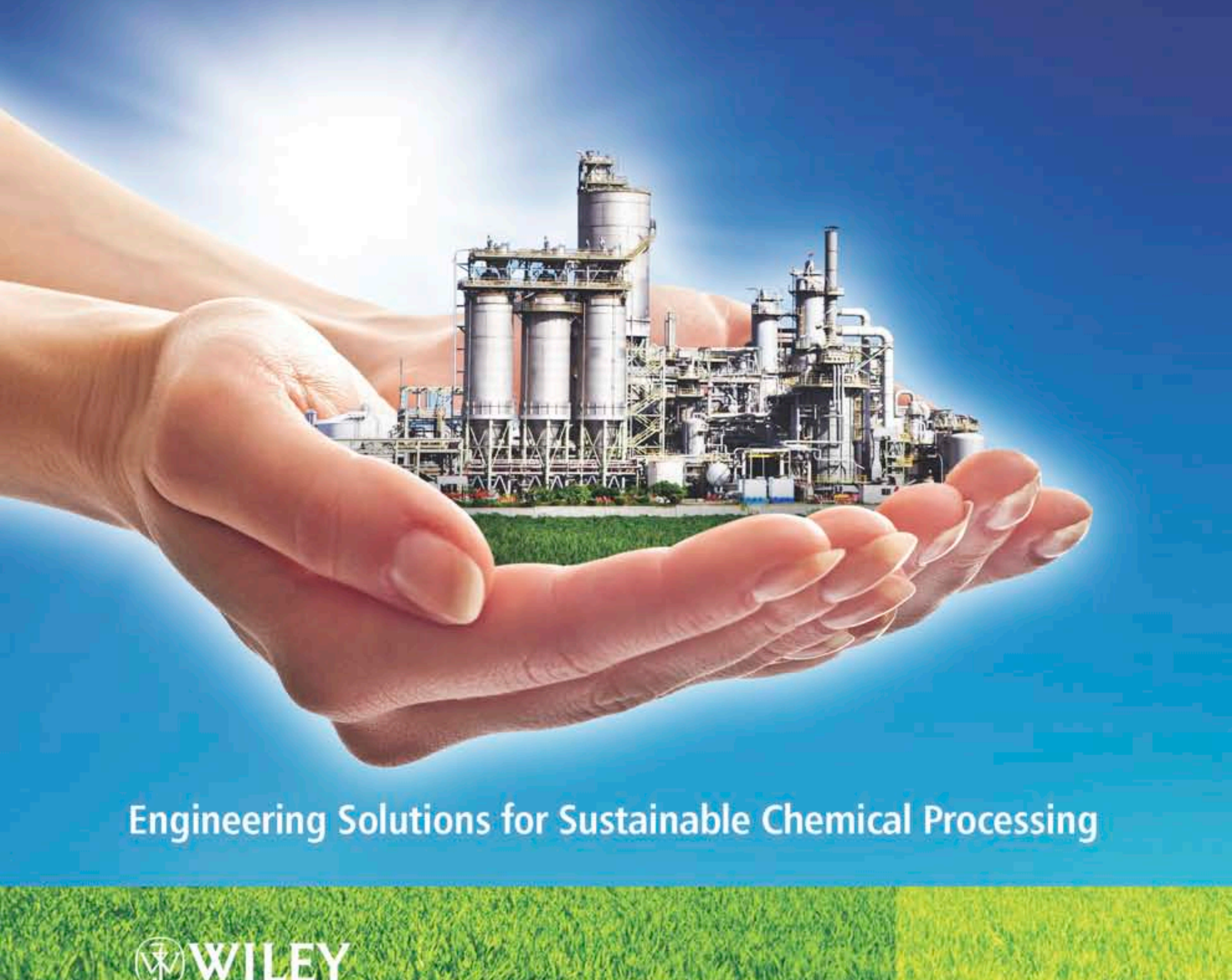
Kamelia Boodhoo and Adam Harvey

Process Intensification For Green Chemistry



Engineering Solutions for Sustainable Chemical Processing

WILEY

Process Intensification for Green Chemistry

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Engineering Solutions for Sustainable Chemical Processing

Edited by

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WILEY

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Preface

Of late, a tremendous effort has been made to implement more sustainable and environmentally friendly processes in the chemical industry. Increased legislation on emissions and waste disposal and the need for businesses to remain highly competitive and to demonstrate their social responsibility are just some of the reasons for this drive towards greener processing. The successful implementation of greener chemical processes relies not only on the development of more efficient catalysts for synthetic chemistry but also, and as importantly, on the development of reactor and separation technologies that can deliver enhanced processing performance in a safe, cost-effective and energy-efficient manner. In some sectors, particularly those related to pharmaceuticals and fine chemicals processing, separations is often the stage at which the most waste is generated, through large amounts of solvents for purification, and this must therefore be addressed at the outset when novel green reactions are explored. The ideal process is one in which byproducts are reduced or eliminated altogether at the reaction stage, rather than removed *after* they are formed – a concept referred to as *waste minimization at source*.

Process intensification (PI) has emerged as a promising field that can effectively tackle these process challenges while offering at the same time the potential for 'clean' or 'green' processing in order to diminish the environmental impact presented by the chemical industry. One of the ways this is made possible is by minimizing the scale of reactors operating ideally in continuous mode so that more rapid heat/mass-transfer/mixing rates and plug flow behaviour can be achieved for high selectivity in optimized reaction processes.

This book covers the latest developments in a number of intensified technologies, with particular emphasis on their application to green chemical processes. The focus is on intensified *reactor* technologies, such as spinning disc reactors, microreactors, monolith reactors, oscillatory flow reactors and so on, and a number of combined or *hybrid* reactor/separator systems, the most well known and widely used in industry being reactive distillation (RD). PI is about not only the implementation of novel designs of reaction/separation units but also the use of *novel processing methods* such as alternative forms of energy input to promote reactions. A notable example here is ultrasonic energy, applications for which are also highlighted in this book. Each chapter presents relevant case studies examining the green processing aspect of these technologies. Towards the end of the book, we have included four chapters to emphasize the industry relevance of PI, with particular focus on the general business context within which intensification technology development and application takes place; on process economics and environmental impact; on the energy-saving potential of intensification technologies; and on practical considerations for industrial implementation of PI.

The book is intended to be a useful resource for practising engineers and chemists alike who are interested in applying intensified reactor and/or separator systems in a range of industries, such as petrochemicals, fine/specialty chemicals, pharmaceuticals and so on. Not only will it provide a basic knowledge of chemical engineering principles and PI for chemists and engineers who may be unfamiliar with these concepts, but it will be a valuable tool for chemical engineers who wish to fully apply their background in reaction and separation engineering to the design and implementation of green processing technologies based on PI principles. Students on undergraduate and postgraduate degree programmes which cover topics on advanced reactor designs, PI, clean technology and green chemistry will also have at their disposal a vast array of material to help them gain a better understanding of the practical applications of these different areas.

We would like to thank all contributors to this book for their commitment in producing their high-quality manuscripts. Our heartfelt gratitude goes to Sarah Hall, Sarah Tilley and Rebecca Ralf at Wiley-Blackwell, whose support and encouragement throughout this project made it all possible.

Kamelia Boodhoo
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August 2012

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Process Intensification: An Overview of Principles and Practice

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1.1 Introduction

The beginning of the 21st century has been markedly characterized by increased environmental awareness and pressure from legislators to curb emissions and improve energy efficiency by adopting ‘greener technologies’. In this context, the need for the chemical industry to develop processes which are more sustainable or eco-efficient has never been so vital. The successful delivery of green, sustainable chemical technologies at industrial scale will inevitably require the development of innovative processing and engineering technologies that can transform industrial processes in a fundamental and radical fashion. In bioprocessing, for example, genetic engineering of microorganisms will obviously play a major part in the efficient use of biomass, but development of novel reactor and separation technologies giving high reactor productivity and ultimately high-purity products will be equally important for commercial success. Process intensification (PI) can provide such sought-after innovation of equipment design and processing to enhance process efficiency.

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1.2 Process Intensification: Definition and Concept

PI aims to make dramatic reductions in plant volume, ideally between 100- and 1000-fold, by replacing the traditional unit operations with novel, usually very compact designs, often by combining two or more traditional operations in one hybrid unit. The PI concept was first established at Imperial Chemical Industries (ICI) during the late 1970s, when the primary goal was to reduce the capital cost of a production system. Although cost reduction was the original target, it quickly became apparent that there were other important benefits to be gained from PI, particularly in respect of improved intrinsic safety and reduced environmental impact and energy consumption, as will be discussed later in this chapter.

Over the last 2 decades, the definition of PI has thus evolved from the simplistic statement of '*the physical miniaturisation of process equipment while retaining throughput and performance*' [1] to the all-encompassing definition '*the development of innovative apparatus and techniques that offer drastic improvements in chemical manufacturing and processing, substantially decreasing equipment volume, energy consumption, or waste formation, and ultimately leading to cheaper, safer, sustainable technologies*' [2]. Several other definitions with slight variations on the generic theme of innovative technologies for greater efficiency have since emerged [3].

The reduction in scale implied by intensification has many desirable consequences for chemical engineering operations. First, the lower mass- and heat-transfer resistances enabled by the reduced path lengths of the diffusion/conduction interfaces, coupled with more intense fluid dynamics in active enhancement equipment, allow reactions to proceed at their inherent rates. By the same token, the more rapid mixing environment afforded by the low reaction volumes should enable conversion and selectivity to be

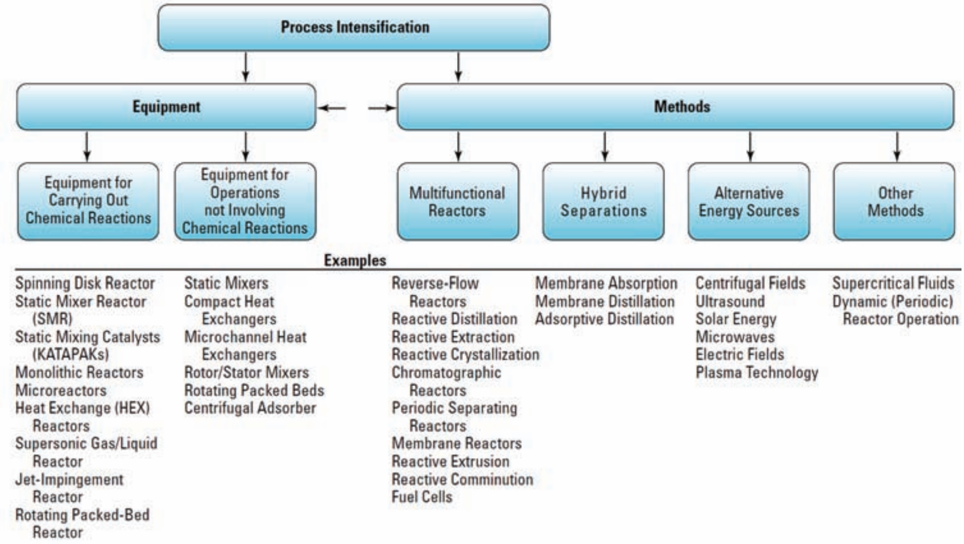

Figure 1.1 *Classification of PI equipment and methods. Reproduced from [ref 2] with permission of American Institute of Chemical Engineers copyright (2000).*

maximized. Residence times of the order of minutes and seconds may be substituted for the hour-scale processing times associated with large conventional batch operations, with beneficial consequences for energy consumption and process safety.

PI covers a wide range of processing equipment types and methodologies, as aptly illustrated in Figure 1.1 [2]. Many of the equipment types classed as 'intensified technologies' have long been implemented in the chemical industry, such as compact heat exchangers, structured packed columns and static mixers. More recent developments include the spinning disc reactor (SDR), oscillatory baffled reactor, loop reactor, spinning tube-in-tube reactor, heat-exchange reactor, microchannel reactor and so on. Lately, it has become increasingly important for the chemical processing industries not only to remain cost competitive but to do so in an environmentally friendly or 'green' manner. It is fitting, therefore, that many of the processes based on the PI philosophy also enable *clean technology* to be practised. For instance, high selectivity operations in intensified reactors will on their own reduce or ideally eliminate the formation of unwanted byproducts. Combining such intensified reactors with renewable energy sources such as solar energy would give even greater impetus to achieving these green processing targets.

1.3 Fundamentals of Chemical Engineering Operations

1.3.1 Reaction Engineering

Reactor engineering starts with the simple mass balance:

$$\text{In} + \text{Made} = \text{Out} + \text{Accumulated} \tag{1.1}$$

Where 'Made' is the rate at which a species is created or lost by reaction. The rate of this reaction in a well-mixed system is governed by the reaction kinetics, which depend only upon the concentrations of species and temperature. However, not all systems are well mixed, particularly at larger scales, and mixing can be rate-determining. The different degrees and types of mixing are introduced in Section 1.3.2. The 'Accumulated' term will be zero for continuous reactors running in steady state, but will be of interest during start-up or shut-down. Determining the rate at which species are created or destroyed in a reactor requires knowledge of mixing, reaction kinetics and heat transfer. Once these are known they can be input into a reactor model. An important part of this model for continuous reactors (as most intensified reactors are) is the residence time distribution (RTD), which is the probability distribution for the length of time elements of fluid will spend in a given reactor design. It can be envisaged as the response to the input of an infinitely narrow pulse of a tracer. All real reactors fall between two extreme cases: the plug flow reactor (PFR) and the continuously stirred tank reactor (CSTR).

1.3.1.1 Plug Flow Reactor

'Plug flow' refers to fluid flowing in discrete 'plugs'; that is, without interaction between the elements. The RTD of a perfect PFR is infinitely thin. Any input tracer pulse to the reactor will remain unchanged, as shown in Figure 1.2.

Real PFRs have symmetrical Gaussian RTDs centred on the mean residence time, the breadth of the RTD decreasing with increasing proximity to ideal plug flow. In practice, this

Figure 1.2 *A perfect PFR, showing the response to a perfect input pulse.*

is usually achieved by ensuring a high level of turbulence in the flow, as this produces a flat velocity profile. The most conventional form of PFR is a tubular reactor in very turbulent flow. However, there are many variations on this basic form, and other ways of achieving plug flow. Chapters 3 and 5 cover examples of unconventional, intensified PFRs.

1.3.1.2 Continuously Stirred Tank Reactor

The CSTR is, at its simplest, a batch-stirred tank to which an inflow and outflow have been added (of equal flow rate, when at steady state). To determine the RTD of such a reactor, we must picture a pulse of fluid entering it. A ‘perfect’ CSTR is perfectly mixed, meaning that fluid is uniformly dispersed the instant it enters the reactor. The outflow is at the same concentration of tracer as the bulk of the reactor. Tracer will initially flow out at this concentration, while being replaced with fluid containing no tracer; that is, the tank gradually becomes diluted, and the concentration in the outflow decreases. This leads to a monotonic decrease in concentration, which can be shown to follow an exponential decay (Figure 1.3).

1.3.1.3 The Plug-Flow Advantage

A CSTR’s RTD is generally not desirable, as, for a given desired mean average residence time:

- Much of the material in the reactor will spend too long in the reactor (due to the long tail in the RTD) and will consequently be ‘overcooked’. The main problem with this is that it allows competing reactions to become more significant.
- Much of the material will be in the reactor for less than the desired residence time. It will therefore not reach the desired level of conversion.

The CSTR can thus lead to increased by-product formation and unsatisfactory conversion. In contrast, plug flow means that each element of fluid experiences the same processing history: each spends exactly the same amount of time in the reactor as every other, and is subject to exactly the same sequence of conditions. This reduces by-product formation and

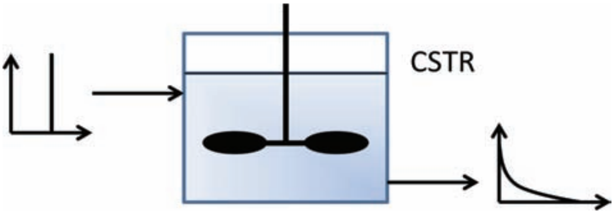

Figure 1.3 *RTD for an ideal CSTR.*

ensures that the desired conversion is achieved. Furthermore, in practice a PFR will have a smaller volume than an equivalent CSTR, for the following reasons:

- The reactor will be the correct size. CSTRs are usually oversized to compensate for the poor RTD.
- No headspace is required, as is the case in any tank reactor.
- For most reaction kinetics (the most notable exception perhaps being autocatalytic reactions), simply following the design equations will lead to a PFR design that is smaller than a CSTR. For an explanation of this, the reader is advised to consult Sections 5.2 and 5.3 in reference [4].
- Stirred tanks do not scale up in a predictable manner. Uniform mixing becomes difficult to achieve, which can reduce the rate of reaction, necessitating a larger reactor. This is less of an issue with tubular reactors.

For these reasons, PFRs are often preferred in principle. In practice they are difficult to use at long residence times (above a few minutes) and multiphase reactions can be difficult.

1.3.2 Mixing Principles

Mixing is the process of bringing separated fluid elements into close proximity, in a system which, in the simplest case, aims to reduce non-uniformity in a particular property, such as concentration, viscosity or temperature. Most mixing processes occur alongside heat- and/or mass-transfer operations and chemical reactions.

1.3.2.1 Influence of Mixing on Reactions

Mixing is a particularly important process in reactor design, especially in continuous-flow reactors. Designing the mixing process to yield a much shorter mixing time in comparison to the mean residence time of the reactants in the reaction vessel is of paramount importance for good operation of the reactor. If mixing is slow, large and varying concentration gradients of reactant species will exist in different parts of the reactor, resulting in wide variations in product concentrations and properties, which may be deemed off-spec in many applications. In fact, the rate of mixing often determines the rate of these processes and may have a significant impact on the product distribution obtained, especially if many competing reaction steps are involved.

1.3.2.2 Turbulent Mixing: Mixing Scales, Mechanisms and Mixing Times

In a single-phase turbulent flow system, there are three distinct mixing scales that influence a chemical process: macromixing, mesomixing and micromixing [5,6]. These are defined on the basis of their characteristic length scale, as depicted in Figure 1.4, and are directly correlated with the turbulent energy dissipation rate, ε.

The intensity of mixing at each of these scales is significantly influenced by the mechanical energy input into the system by the mixing device. It is generally assumed that higher energy input translates into a higher energy dissipation rate for better mixing – but this is not always the case, as energy may be wasted, for example, in vortex formation at a higher agitation rate in an unbaffled vessel. The energy input causes the fluid to undergo motion across the cascade of length scales described in this section, so that any

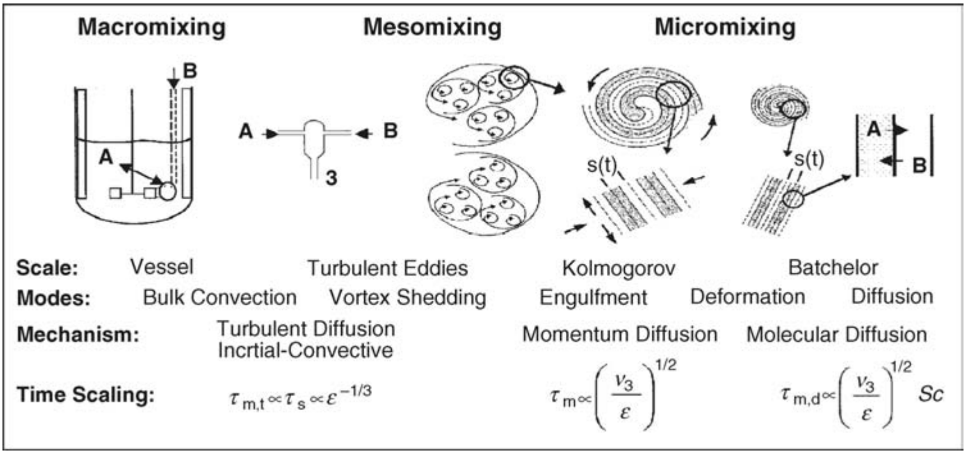

Figure 1.4 *Turbulent mixing mechanisms across various length scales. Reproduced from [ref 7] by permission of John Wiley & Sons. © 2003.*

concentration inhomogeneities are gradually reduced and eliminated. The kinetic energy thus imparted to the fluid is ultimately dissipated as internal energy, which occurs at the smallest length scales of turbulence; that is, at the Kolgomorov scale.

Various mixers/reactors have been characterized in terms of their energy dissipation rates, as shown in Table 1.1. This illustrates the potential capability of intensified systems such as static mixers, rotor-stator mixers and the SDR, among others, to provide a higher level of mixing intensity than the conventional stirred tank reactor. It is important to remember, however, that higher energy input will be a penalty incurred in terms of energy consumption, and the benefits from the mixing process under these conditions have to demonstrate significant process improvement.

Macromixing. Macromixing involves mixing on the macroscopic scale, which refers to the scale of the vessel or reactor. The process is often referred to as 'distributive mixing' [6,14], which is achieved by bulk motion or convective transport of the liquid at the macroscopic scale, resulting in uniform spatial distribution of fluid elements within the

Table 1.1 *Comparison of energy dissipation rates in a range of mixers/reactors.*

Reactor/mixer type	Energy dissipation rate (W/kg)	References
Stirred tank reactor	0.1–100	[8,9]
Static mixers	1–1000	[9,10]
Impinging jet reactor	20–6800	[11]
Rotor-stator spinning disc reactor (27 cm disc diameter, 240–2000 rpm)	$\leq$6000	[12]
Thin-film spinning disc reactor (10 cm disc diameter, range of disc speeds 200–2400 rpm)	$\leq$2000	[13]

reactor volume. In a continuous flow reactor, the macromixing process directly influences the RTD of a feed stream introduced into the contents of the vessel.

The macromixing time in a mechanically stirred, baffled tank, τ_{mac}, is a function of the mean circulation time, τ_{c}, in the vessel. In a vessel configured for optimized mixing, $\tau_{\mathrm{mac}} = 3\tau_{\mathrm{c}}$, while in a non-optimized system, $\tau_{\mathrm{mac}} = 5\tau_{\mathrm{c}}$ [6].

The mean circulation time, τ_{c}, is generally expressed in terms of the impeller pumping capacity, Q_{c} [14]:

$$\tau_c = \frac{V}{Q_{\mathrm{c}}} \tag{1.2}$$

or

$$\tau_c = \frac{V}{C_{\mathrm{D}} N D_{\mathrm{i}}^3} \tag{1.3}$$

where C_{D}, the discharge coefficient of the impeller, is a constant, which typically varies between 0.7 and 1.0, depending upon the impeller used [14].

Mesomixing. Mesomixing refers to coarse-scale, dispersive mixing via turbulent eddies. It is typically characterized by two different mechanisms [5,15]: (1) turbulent dispersion of a fresh feed introduced to a vessel which mixes with its local surroundings; and (2) inertial-convective break-up of large eddies that are larger than the Kolgomorov length scale.

The characteristic timescale associated with turbulent dispersion, τ_{D}, can be defined by either equation 1.4 or equation 1.5, depending on the radius of the feed pipe, r_{pipe}, with respect to the characteristic length scale for dispersion, L_{D} [5,15]:

$$\tau_{\mathrm{D}} = \frac{Q_{\mathrm{f}}}{u D_{\mathrm{turb}}} \quad (\text{if } r_{\mathrm{pipe}} << L_{\mathrm{D}}) \tag{1.4}$$

$$\tau_{\mathrm{D}} = \frac{{r_{\mathrm{pipe}}}^2}{D_{\mathrm{turb}}} \quad (\text{if } r_{\mathrm{pipe}} \approx L_{\mathrm{D}} \text{ or } r_{\mathrm{pipe}} > L_{\mathrm{D}}) \tag{1.5}$$

where $D_{\mathrm{turb}} = 0.12\varepsilon^{1/3} L_{\mathrm{D}}^{4/3}$ [5,16].

Baldyga *et al.* [15] have expressed the inertial-convective mesomixing timescale, τ_{s}, as:

$$\tau_s = A\left(\frac{L_C^2}{\varepsilon}\right)^{1/3} \tag{1.6}$$

where A is a constant having a value between 1 and 2, depending on the turbulence level in the system.

Micromixing. Micromixing represents the final stage of the turbulent mixing process, which proceeds at much finer length scales than macro- and mesomixing, referred to as the

Kolgomorov or Batchelor length scale. At the microscale level, the Kolgomorov length scale, η_K (representing smallest scales of *turbulence* before viscosity effects dominate), and Batchelor length scale, η_B (representing smallest scales of fluctuations prior to *molecular diffusion*), are defined as [17–19]:

$$\eta_\mathrm{K} = \left(\frac{v^2}{\varepsilon}\right)^{1/4} \tag{1.7}$$

$$\eta_\mathrm{B} = \left(\frac{vD_1^2}{\varepsilon}\right)^{1/4} = \frac{\eta_\mathrm{K}}{\sqrt{Sc}} \tag{1.8}$$

where the Schmidt number, Sc$\left(=\frac{v}{D_1}\right)$, for liquids is typically of the order of 10^3, so that $\eta_B << \eta_K$. For aqueous solutions in turbulent regimes, η_K is of the order of 10–30 μm.

The physical phenomena of the micromixing process include engulfment, deformation by shear and diffusion of the fine-scale fluid elements. The relevant mixing times associated with these processes are [5]:

$$\text{Engulfment} : \tau_e = 17.2\left(\frac{v}{\varepsilon}\right)^{0.5} \tag{1.9}$$

$$\text{Shear deformation and diffusion} : \tau_\mathrm{Ds} \approx 2\left(\frac{v}{\varepsilon}\right)^{0.5} arc\,\sinh\,(0.05\,Sc) \tag{1.10}$$

More often than not, $\tau_{\mathrm{D_S}} << \tau_\mathrm{e}$, resulting in the overall micromixing process being dictated by the progression of the engulfment phenomenon taking place at the Kolgomorov length scale.

Although the actual molecular mass transfer process before the reaction is ultimately achieved by molecular diffusion, enhancing the rates of macro- and mesomixing through turbulent hydrodynamic conditions enables faster attainment of the fluid state, where micromixing and therefore molecular diffusion prevail.

1.3.3 Transport Processes

Understanding transport processes is at the heart of PI, as the subject can be defined as a search for new ways of enhancing or achieving transport of mass, heat or momentum.

Transport processes – heat, mass and momentum transfer – are generally governed by equations of the same form. They are all flows in response to a ‘driving force’ – a temperature difference, a concentration difference and a pressure difference, respectively – opposed by their respective resistances. Brief overviews of the intensification of mass, heat and momentum transfer follow.

1.3.3.1 Heat Transfer

Heat transfer – the transport of energy from one region to another, driven by a temperature difference between the two – is a key consideration in the design of all unit operations. Unit operations have defined operating temperatures, so the heat flows in and out must be understood in order to maintain the temperature within a desired range. Reactors, for instance, must be supplied with heat or must have it removed at a rate that depends upon the exo/endothermicity of the reaction, the heat-transfer characteristics of the reactor and the heat flows in and out, in order to ensure that the reaction takes place at the correct temperature and therefore the correct rate.

Furthermore, the streams into and out of unit operations must be maintained at the correct temperatures. This is usually achieved using heat exchangers: devices for transferring heat between fluid streams without the streams mixing. It was always been a given in heat exchanger design that they must operate in turbulent flow wherever possible, as turbulent flow results in considerably higher heat-transfer coefficients than laminar. Hence, heat exchangers were not designed with narrow channels, as the achievement of turbulence depends upon exceeding a certain Reynolds number, which is directly proportional to the diameter of the channel:

$$\mathrm{Re} = \rho \mathrm{v} \mathrm{D}/\mu \tag{1.11}$$

Reassessing such assumptions about heat and mass transfer is at the heart of PI, and has led to the development of 'compact heat exchangers', which have extremely narrow channels.

This only makes sense if the heat transfer itself rather than just the heat-transfer coefficient is considered. The rate of heat transfer in a heat exchanger is not only a function of the heat-transfer coefficient, as can be observed in the 'heat exchanger design equation':

$$\mathrm{q} = \mathrm{U}\mathrm{A}_\mathrm{s}\Delta \mathrm{T}_\mathrm{lm} \tag{1.12}$$

It is also clearly a function of the heat-transfer surface area A_s. Compact heat exchangers have very narrow channels (sub-mm), so the flow is laminar (as Re depends upon channel width, D) and therefore has a significantly lower heat-transfer coefficient than a turbulent flow. However, this is more than compensated for by the increase in heat-transfer surface area per unit volume, giving a higher heat-transfer rate per unit volume than conventional heat exchanger designs (such as 'shell-and-tube'). A concise overview of compact heat exchangers is given by Reay *et al.* [20].

There are also a range of devices ('turbulence promoters') that are designed to perturb flow in order to bring about the onset of turbulence at lower Re. These promoters allow the higher heat- and mass-transfer coefficients associated with turbulence to be accessed at lower velocities, thereby reducing the associated pumping duties. They can also be classified as intensified devices, although the degree of intensification is nowhere near as great as that in the compact heat exchanger. They suffer less from fouling, however, which is one of the main drawbacks of compact heat exchangers: their applications are limited to 'clean' fluids, as they are very easily blocked by fouling. As with most technologies, the strengths and weaknesses of intensified technologies must be assessed so as to define a 'niche' or parameter space within which they are the best-performing.

1.3.3.2 Mass Transfer

An appreciation of mass transfer is required for the intensification of separation processes. Common separation unit operations are distillation, crystallization, ad/absorption and drying.

In many processes, the heat and mass transfer are interrelated. Generally, what enhances one enhances the other. Indeed, the mechanisms for transfer are often the same or are closely related. Experiments in heat transfer have often been used to draw conclusions about mass transfer (and vice versa) through analogies. Various equations describing one or the other are based upon analogy. Compare for instance the Dittus–Boelter equations for heat and mass transfer:

$$\text{Heat: Nu} = \text{C}_1.\text{Re}^{0.8}.\text{Pr}^{0.33} \tag{1.13}$$

$$\text{Mass: Sh} = \text{C}_2.\text{Re}^{0.8}.\text{Sc}^{0.33} \tag{1.14}$$

An example of an intensified mass-transfer device is the rotating liquid–liquid extractor. The conventional design of liquid–liquid extractors was based on using the density difference between the liquids to drive a countercurrent flow, by inputting the denser fluid at the top of the column and the lighter at the bottom. One of the variables, although it may not appear to be a variable initially, is g, the acceleration due to gravity. This can of course be increased by applying a centrifugal field, in which case the lighter fluid is introduced from the outside and travels inward countercurrent to the denser fluid. The first example of this kind of device was the Podbielniak liquid–liquid contactor, originally developed in the 1940s for penicillin extraction. There are currently hundreds of Podbielniak contactors in use worldwide for a range of applications, including antibiotic extraction, vitamin refining, uranium extraction, removal of aromatics, ion exchange, soap manufacture and extraction of various organics [21]. This illustrates that there are many successful examples of PI in industry today, although they are not viewed as such, as they are not a new technology (and the term ‘process intensification’ did not exist when they were invented). Indeed, any continuous process is an example of an intensified process.

1.3.3.3 Momentum Transfer

Momentum transfer occurs due to velocity gradients within fluids. Many of the technologies listed above to enhance mass and heat transfer, also involve enhanced momentum transfer. Again, as illustrated by the equations in section 1.3.3.2 (between heat and mass transfer), there are analogies between this transfer process and others that lead to meaningful quantitative relationships. Theories such as the Reynolds analogy (see Ref [22] for a concise explanation), and its more sophisticated and accurate descendants, are based on heat, mass and momentum transfer processes having the same mechanism: in this particular analogy, the mechanism for all is the transport of turbulent eddies from a bulk medium to a surface.

Essentially, any technology that enhances the flow increases momentum transfer. The rotational fields applied to flows in section ‘Centrifugal Fields’ (see section 1.4.1.1) and the turbulence promoters mentioned in 1.3.3.1 are just two examples of enhanced momentum transfer (along with enhancement of other transfer properties). It should be noted that enhancement of momentum transfer is often not performed for its own sake, but rather to promote other transfer properties.

1.4 Intensification Techniques

Intensification of a process may be achieved through a variety of means, including enhancing mixing and heat/mass transfer by additional energy input via external force fields or via enhanced surface configurations, transforming processes from batch to continuous mode in order to achieve smaller process volume and integrating process steps in hybrid technologies. Each of these will be discussed briefly in this section.

1.4.1 Enhanced Transport Processes

Heat and mass transport rates are largely influenced by the fluid dynamics, which directly affect the heat/mass-transfer coefficients and the available area on which the transfer of energy/mass can occur. Mixing rates are similarly affected by these parameters. Therefore, any attempt at intensifying these processes should focus on enhancing the turbulence in the system and/or increasing the transfer surface area. One way of achieving this is by subjecting the reaction environment to external force fields, such as centrifugal, electric and ultrasonic fields.

1.4.1.1 Enhanced Force Fields

Centrifugal Fields. Surface rotation as a technique for intensification has stimulated keen interest from academic workers for many years. As early as the 1950s, Hickman's research efforts into two-phase heat transfer on spinning disc surfaces culminated in the development of the first successful centrifugal evaporator used in sea water desalination [23].

The benefits that can be extracted from the exploitation of high centrifugal fields created by rotation are as follows:

- The rotational speed of the spinning surface provides an additional degree of freedom, which can be readily manipulated for optimum equipment performance.
- The extremely high gravity fields thus generated are capable of producing very thin films, in which heat transfer, mass transfer and mixing rates are greatly intensified. The short path lengths and the high surface area per unit volume provide the opportunity for rapid molecular diffusion and enhanced heat transfer, even on scale-up (Figure 1.5). The

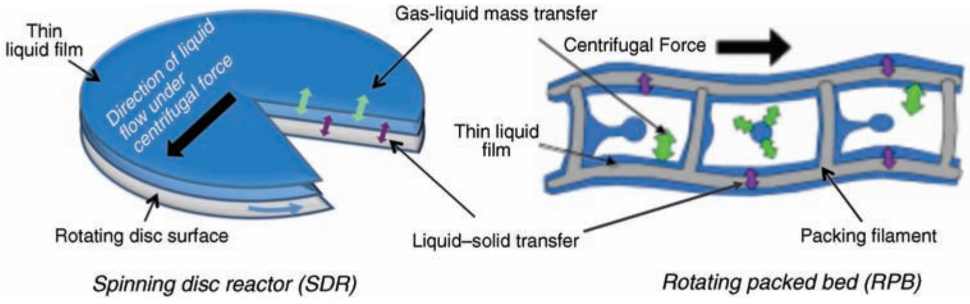

Figure 1.5 *Thin-film processing in an SDR and a RPB, illustrating the short diffusion/conduction path lengths and high surface area for enhanced heat and mass transfer.*

performance of multiple phase processes in particular stands more chance of being enhanced under the influence of high gravitational forces as a result of increased interphase buoyancy and slip velocity [24].
- Applications in which the solid content of a process fluid poses problems with regard to fouling in conventional devices can, in principle, be handled by the rotating equipment. The rotating action in itself provides a scraping or 'self-cleaning' mechanism strong enough to shift most solid deposits away from the surface of revolution, thereby ensuring maximum exposed area at all times during operation.
- The very short and controllable residence times achieved under the centrifugal action enable heat-sensitive materials to be processed with minimal risk of degradation.

Several unit operations have been identified in which the centrifugal acceleration generated on the surfaces of revolution presents remarkable potential for intensification. Typical operations include distillation, extraction, boiling, condensation, crystallization, precipitation and gas–liquid reactions.

The SDR and the rotating packed bed (RPB) are two well-known examples of centrifugal field processing equipment. The SDR will be treated in more detail in Chapter 3.

Alternative Force Fields. Alternative force fields commonly employed to intensify processes include ultrasound, electric fields and energy of electromagnetic radiation, whose applications to chemical and biochemical processes in the context of PI have been reviewed by Stankiewicz [25].

Ultrasonic Fields. 'Ultrasound' refers to sound waves beyond the audible range of the human ear, with a frequency of approximately 20 kHz to 500 MHz. The frequency typically applied to chemical processing is generally no higher than 2 MHz [26]. Ultrasound is propagated through a liquid medium in alternating cycles of compression and stretching, or rarefaction. These induce an effect known as cavitation, whereby microbubbles are generated, expand and are subsequently destroyed in successive compression cycles, releasing a large amount of heat and pressure energy in the local environment of the bubbles (Figure 1.6). Local temperatures and pressures after the collapse of microbubbles can reach as high as 5000 °C and 2000 atmospheres, respectively, depending on the power input [26]. Mechanical or chemical effects can arise from such extreme conditions in the system, as discussed in many review articles on the subject [27,28]. Thus, for instance, the mechanical effects are characterized by the pressure waves or shock waves resulting from the collapse of cavitation bubbles. These waves generate intense mixing conditions and enhanced transport rates throughout the bulk of the liquid medium in homogeneous systems and at liquid/liquid or liquid/solid interfaces in heterogeneous systems, which have a direct, positive influence on a chemical reaction. Furthermore, in immiscible liquid systems much finer droplets can be formed under ultrasound exposure than by mechanical agitation, creating a greater surface area for mass transfer. These mechanical or physical effects are generally thought to be responsible for the rate enhancements and improved product properties observed in many chemical processes subjected to ultrasonic irradiation [28,29].

Chemical effects due to ultrasound arise if the chemical compounds in the processing medium can fracture into reactive intermediates such as free radicals (a process often