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Process Intensification: An Overview of Principles and Practice

Kamelia Boodhoo and Adam Harvey

School of Chemical Engineering & Advanced Materials,
Newcastle University, UK

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

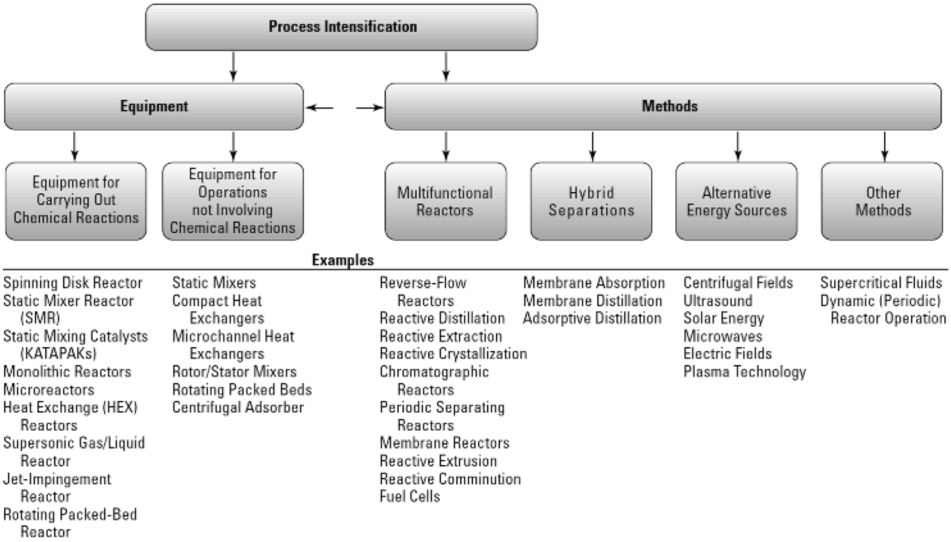

Figure 1.1 *Classification of PI equipment and methods. Reproduced from [ref 2] with permission of American Institute of Chemical Engineers copyright (2000).*

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

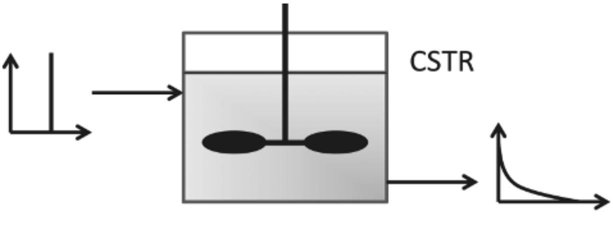

Figure 1.3 RTD for an ideal CSTR.

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

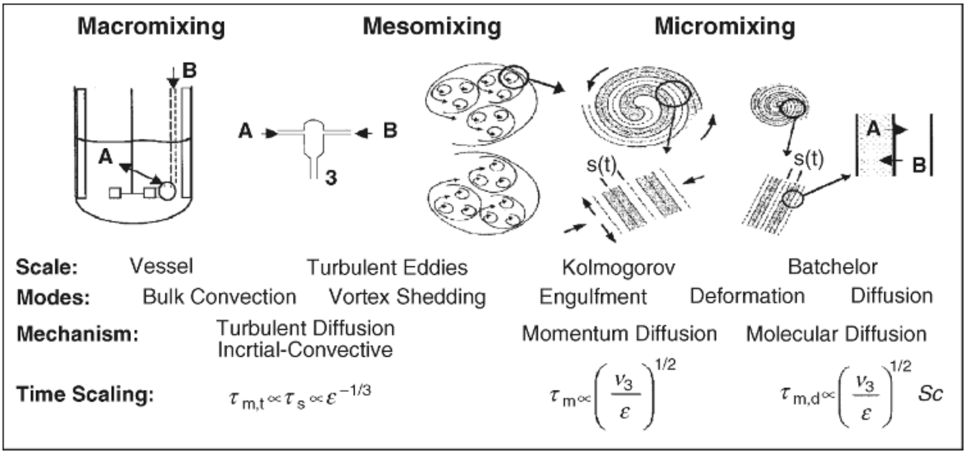

Figure 1.4 *Turbulent mixing mechanisms across various length scales. Reproduced from [ref 7] by permission of John Wiley & Sons. © 2003.*

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)	≤6000	[12]
Thin-film spinning disc reactor (10 cm disc diameter, range of disc speeds 200–2400 rpm)	≤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, $\mathrm{Sc}\left(=\frac{v}{D_1}\right)$, 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]:

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

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

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:

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

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':

$$\mathrm{q} = \mathrm{UA_s \Delta T_{lm}} \tag{1.12}$$

It is also clearly a function of the heat-transfer surface area $\mathrm{A_s}$. 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

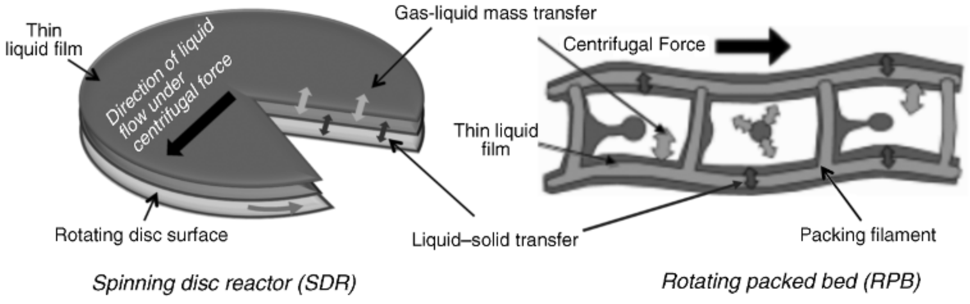

Figure 1.5 *Thin-film processing in an SDR and a RPB, illustrating the short diffusion/conduction path lengths and high surface area for enhanced heat and mass transfer.*

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

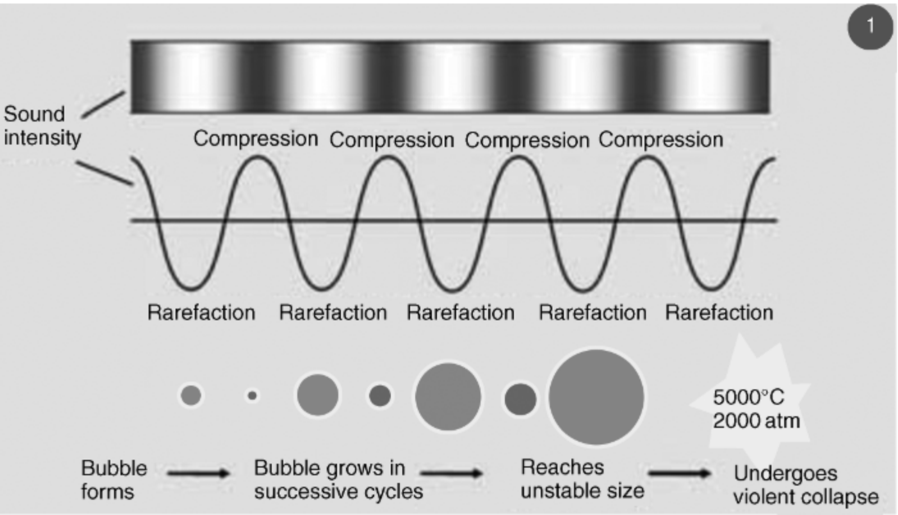

Figure 1.6 *Generation and collapse of an acoustic cavitation bubble. Reprinted from [ref 29] © 2010, with permission from Elsevier.*

referred to as ‘sonolysis’) under the very intense local temperatures attained in the bubble cavities. The literature has many documented examples of sonolysis [26,30,31]. Such chemical effects are usually reflected in changes in mechanisms and product distributions [32]. The well-documented influence of ultrasound on crystallization processes illustrates the latter effect most appropriately [33].

In summary, ultrasonic processing for intensification of chemical processes is associated with the following benefits, all of which have wider implications for greener processing [26,29]:

- Increases in both reaction speed and yield in an extensive range of heterogeneous and homogeneous systems, as highlighted by Thompson and Doirasawmy [28].
- Waste minimization through increased selectivity.
- Changes in and simplification of reaction pathways, which can lead to milder processing conditions (e.g. ambient temperatures and pressures, reduced solvent use) and higher energy efficiency.
- The use of environmentally benign reactants and solvents while retaining or even enhancing the reaction rate under ultrasonication.

Chapter 7 explores these concepts in more detail.

Electric Fields. High-intensity electrical fields have long been known to have a destabilizing effect on dispersed systems containing polar molecules, such as water, and to enhance mass-transfer processes via promoted coalescence of the dispersed phase. The removal of dust from air in the Cottrell precipitator [34] and the dehydration of crude oil emulsion in oilfields were among the first industrial processes developed almost a century ago to harness the beneficial effects of electric fields in such phase separations. The essential features of the mechanism involved in such electrostatic separations are [35]:

- Charging of a liquid droplet – this can be by either (a) induced charging of polar molecules via polarization and reorientation of molecular-dipoles charging by the applied electric field or (b) direct or contact charging of nonpolar molecules by contact with a DC-charged electrode
- Aggregation, coalescence and settling under gravity of electrically charged droplets, in order to achieve complete phase separation

Intensification of electrical field separations has focused on improved designs for the coalescing vessel and the electrodes, enhanced hydrodynamics to promote electrically charged droplet interactions through turbulence and higher electric field strengths [35].

The large interfacial areas formed due to small droplet formation in electric fields can also be beneficially applied to enhance overall rates of reaction in immiscible liquid systems, whereby a higher degree of stable emulsification is achieved [36,37]. In one such process involving the enzymatic hydrolysis of triglyceride esters to yield free fatty acids and glycerol, studied by Weatherley and Rooney [38], electrostatic fields were used to intensify the dispersion of the aqueous phase into the oil substrate by creating large interfacial areas between the reacting species and thus enhancing the overall rate of reaction at relatively modest temperatures and pressures.

Electric field effects on intensification of heat-transfer processes in general and of boiling in particular are also well documented [39–42], and the mechanisms are generally well understood [43–45]. In nucleate boiling, for instance, not only are more bubbles released from the surface when an electric field is applied but also they are smaller than in its absence [44].

The combined effects of electric and centrifugal fields on hydrodynamics in thin-film flow in an SDR have been analysed via numerical simulations by Matar and Lawrence [46]. The applied electric field was shown to induce turbulence on the film surface through the formation of an increased intensity of large-amplitude waves. These simulation results suggest that electric fields have the potential to further enhance heat and mass transfer and reaction rates in thin-film processing.

Electromagnetic Fields. The electromagnetic spectrum covers a wide range of energy fields, such as microwaves, light, X-rays and γ-rays. Here only microwaves and light will be considered with respect to the intensification of chemical processes.

Microwaves. Microwaves are a form of electromagnetic energy, with frequencies in the range of 300 MHz to 300 GHz. The commonly used frequency for microwave heating and chemical processing is 2.45 GHz. Microwave heating of materials is quite distinct from conventional heating, where conduction and convection are the main mechanisms for the transfer of heat. Under microwave exposure, on the other hand, either dipole interactions or ionic conduction come into play, depending on the chemical species involved [47,48]. Dipole interactions occur with polar molecules that have high dielectric constants, such as water and alcohols, while migration of dissolved ions in the electric field takes place in ionic conduction. Both mechanisms require effective coupling between components of the target material and the rapidly oscillating electrical field of the microwaves. Heat is generated by molecular collision and friction.

Microwave-assisted processing is associated with many features that have positive implications for intensification of processes. In particular, the more rapid, controlled and uniform heating rates afforded by microwave exposure result not only in higher rates of reaction than conventional heating methods but also in better product quality, through improved selectivity. Recent publications by Toukoniitty *et al.* [27] and Leonelli and Mason [29] provide good reviews of these aspects, with the former focusing on heterogeneous catalytic systems.

There are a number of examples of the industrial use of microwave heating in the food, rubber and wood industries, as highlighted by Leonelli and Mason [29]. Although small-scale batch and continuous reactor systems with microwave irradiation capabilities are commercially available [47], there is still much scope for further development of industrial-scale microwave reactors, with continuous flow systems that have microwave irradiation or indeed coupled microwave and ultrasound irradiation capabilities being ideally suited for this purpose [25,29].

Light Energy. The observation that certain compounds could be affected by sunlight to give materials with the same chemical composition but very different physical properties was first made in 1845, when Blyth and Hofmann [49] noted that styrene was converted from a liquid to a glassy solid when exposed to sunlight. Since then, the industrial potential of photochemistry has been widely demonstrated in a number of reactions, such as the production of caprolactam, used in the manufacture of nylon 6, and the formation of vitamins D_2 and D_3 [50].

Photoinitiation is an attractive alternative to thermal activation of reactions for a number of reasons. It is an inherently clean process, requiring only the reacting molecules in order for the reaction to be activated. Additional and often expensive and environmentally unfriendly reagents and catalysts can be minimized. The irradiation by a specific wavelength, and therefore a well-defined energy input in the form of photons, allows only certain reactions to be targeted, thereby reducing byproduct formation and costly downstream separation processes. Since activation is by light, ambient operating temperatures can be utilized, which not only reduce thermal energy consumption but can also result in better control of the process, especially if side reactions can be minimized at lower temperatures. This is particularly relevant for polymer processing, where low temperatures generally result in (1) better tacticity control of the polymer, (2) reduced transfer effects, which can be a cause of excessively branched macromolecules, and (3) minimal thermal degradation risks for the polymer formed.

In spite of the clear advantages offered by photochemistry as a reaction-initiation technique, its use in industry is surprisingly rather limited. This is mostly because of the technical problems associated with the uniform irradiation of large reaction volumes, such as those encountered in conventional batch set-ups. Batch reactors, especially those at commercial scale, possess particularly low surface area to volume ratios. This poses enormous processing challenges in that the photons emanating from the light source have extremely limited penetration depths into the fluid (a few centimetres at most), resulting in quite ineffective and non-uniform initiation of reactions in conventional stirred tank reactor configurations. These issues have been addressed to a certain extent by the development of the falling film reactor, but other reactor configurations such as the thin-film SDR or microreactor might potentially be applied for more efficient processing of photochemical processes. This will be dealt with in more detail in Chapter 3, where the SDR is considered.

1.4.1.2 Enhanced Surface Configurations

The influence of well-defined structures or enhanced surface configurations on the increased efficiency of chemical processes, in terms of heat/mass transfer and mixing rates, is well established. Such structures can be classified according to the time and length scales at which they function. For example, molecular-scale structures such as zeolite supports, which are termed 'molecular reactors' [6], have been used to improve chemical transformations at molecular scales. A range of examples of such molecular reactors applied in chemical reactions is provided in a recent paper by Van Gerven and Stankiewicz [6]. At the meso- and macroscales, structures such as channel reactors (including milli- and microchannels), monoliths, foams and static mixers have all been used to improve process performances such as yield and selectivity. A brief overview of these areas is given in this subsection; a selection of them will form the subject of later chapters in the book.

Micro/millichannel Reactors. The use of micrometre- or millimetre-scale (typical dimensions of 10–100 μm and 0.5–2.0 mm, respectively) reaction spaces in the form of channels of various shapes (Figure 1.7) allows for much more precise control of diffusion, heat exchange, retention/residence times and flow patterns in chemical reactions [51]. Although flow in these types of reactor systems tends to be mainly laminar (Re $<$ 100, typically), effective mass transfer can be achieved via the very short diffusion path lengths, determined by the diameter of the channels. Thus, given that the characteristic diffusion time, t_D, is expressed as:

$$t_D = \frac{l^2}{D_l} \tag{1.15}$$

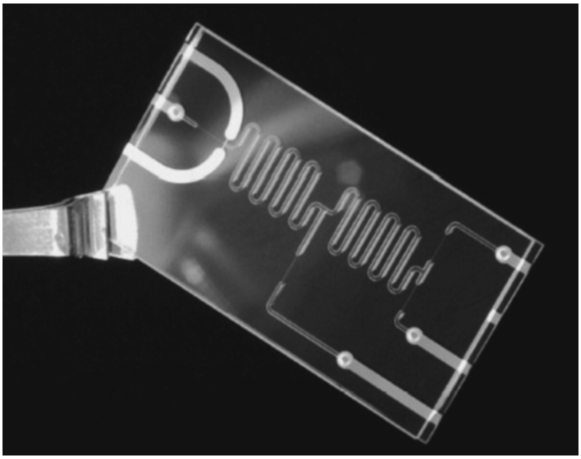

Figure 1.7 A glass microreactor. Reproduced from [ref 52] by permission of John Wiley & Sons. © 2005.

the diffusion time across a macroscale channel (of the order of 1 cm diameter) versus a microchannel of 100 μm diameter can vary dramatically from 10^5 to 10 s, respectively, for solvated molecules of typical diffusivity 10^{-9} m^2/s. Although the diffusion timescale is greatly reduced in the microchannel, it is nevertheless still a slow process for efficient micromixing in fast reactions where micromixing times of the order of milliseconds are required. In such cases, it is therefore important to also provide very large interfacial areas for efficient contact between reacting streams in the channel, which can be achieved through a number of ‘passive’ techniques, as described by Hessel *et al.* [53] – for example, the use of miniaturized static inserts, which continuously split and recombine the flow streams, or of turbulent collision of injected streams, among many other techniques – albeit at the expense of greater pressure drop. Moreover, when more than one phase is present, vortex motions generated by the shearing motion within the slug flow are also known to enhance the mixing within the slugs and improve mass-transfer rates across the interface [54,55]. Near-plug flow behaviour that gives control of RTDs in micro-/millichannel reactors can be achieved by introducing segmented flow via a second phase in the flowing system [53]. Very good control of highly exothermic reactions in small-diameter channel reactors is also possible, due to the extremely high surface area to volume ratios, of up to 50 000 m^2/m^3, when compared with conventional stirred tank reactor geometries.

As a result of these admirable traits, much attention has been given to micro- and mesoscale channel reactors as alternative systems for a host of reactions that are typically limited in some way (mass transfer, heat transfer or mixing) when conducted in conventional batch reactors. Mason *et al.* [56] offers an extensive review of the current literature in this area, but specific examples worthy of note include hydrogenations reactions [57], a nitration reaction [58] and a simple acid–base reaction [54], all of which require rapid mass transfer in order to keep pace with the inherently fast reaction kinetics.

The characteristics of microreactor technologies and their processing advantages will be covered in greater depth in Chapter 4.

Monolithic Structures. Monoliths represent a type of structured packing unit consisting of a large number of parallel, straight capillary channels, separated from each other by walls. The ‘honeycomb’ channels come in various shapes and sizes, with rectangular channels being most commonly used. They are usually made from ceramic or metallic materials and they have traditionally been used as catalyst supports in the treatment of NOx and CO emissions in the automotive industry [59]. Monolithic catalyst structures are characterized by several features that make them highly attractive for use in multiphase catalytic reactors [59,60]. In brief, flow in the channels is uniformly distributed, with relatively low pressure drops. The large catalyst-coated surface areas presented by the monolith arrangement, which can be further augmented by the provision of fins in the channel walls, are conducive to extremely good contact between the gas/liquid phase and the catalyst. Combined with the short diffusion path length offered by the thin catalyst coating, the large contact areas between the catalyst and the reacting phases give rise to intense mass transfer to and from the catalyst.

Other structures include porous meshes [61,62] and metal foams [63]. These have been shown to enhance gas–liquid mass transfer and uniformity of mixing, respectively.

Monolith catalytic reactors will be covered in more detail in Chapter 6.

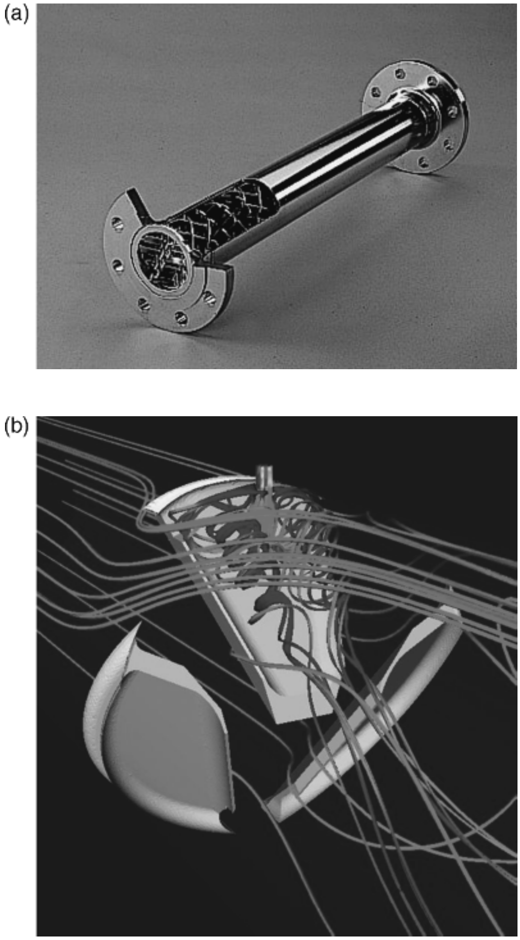

Figure 1.8 *(a) SMX static mixer for laminar mixing; (b) CompaX static mixer for turbulent mixing. Reproduced with permission from Sulzer ChemTech © 2012.*

Static Mixers. Static mixers are motionless pipeline inserts designed to promote mixing. Various static mixer designs are available for a range of applications, including blending of viscous materials and laminar or turbulent mixing in single-phase liquids or multiphase systems. For laminar mixing, the mixer elements such as those of the SMX configuration (Figure 1.8a) are designed to repeatedly split the incoming flow into many layers, which are redistributed around the mixer structure in the transverse direction relative to the net flow. This gives rise to greater uniformity of component distribution across the flow cross-section of the pipe and increased interfacial area for enhanced diffusion. On the other hand, static mixers designed for turbulent mixing seek to enhance the formation of turbulent eddies in the flow stream (Figure 1.8b).

Several benefits of static mixers can be exploited, including homogenous mixing, narrow RTD, low cost and low maintenance due to lack of moving parts. One of their limitations is

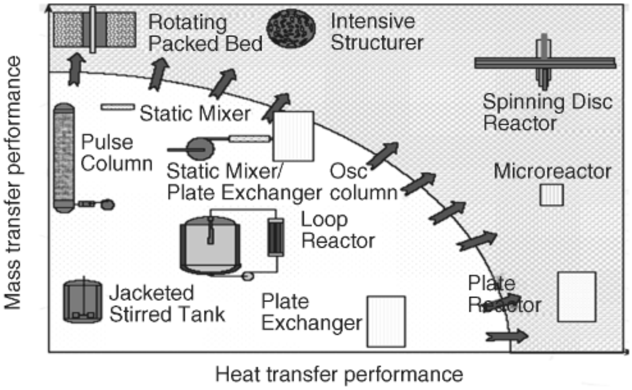

Figure 1.9 *Heat- and mass-transfer performance of several intensified units compared to the jacketed stirred tank. Reproduced from [ref 69] with permission from Britest © 2000.*

related to the handling of very viscous materials, which may result in extremely high pressure drops, although new designs such as the SMX plus mixer have been introduced to alleviate such processing difficulties [64]. Moreover, unless the structures are very open, static mixers can be prone to blockages by suspended solids (e.g. catalysts).

Static mixers have found wide applications in many industrial mixing operations involving gas–liquid dispersion and liquid–liquid extraction for enhanced mass transfer [65], and they have long been regarded as one of the successful applications of PI in industry. They can also be employed as an in-line mixer in multifunctional heat-exchanger reactors, where they not only facilitate rapid mixing between reacting species but also provide additional surfaces for efficient heat transfer [66–68].

The heat- and mass-transfer intensification abilities of the various technologies described in this section are neatly summed up in Figure 1.9. The comparatively poor performance of the workhorse of the chemical industry that is the jacketed stirred tank reactor sits in stark contrast with the intensified systems.

1.4.2 Integrating Process Steps

One of the most important intensification strategies is combining process steps, thereby reducing the overall number in a process. This can have a range of benefits:

- Reduction in capital cost
- Reduction in running cost
- Reduction in duty of downstream unit operations

One of the most familiar integrations is between reaction and separation. Examples include:

- *Membrane Reactors:* Membranes that are permeable to only one of the products are used to remove this product in situ, thereby overcoming equilibrium constraints. In this way, membrane reactors have often been used to bring equilibrium reactions to completion.

- *Reactive Extraction:* This is a separation process in which reaction is used to cause a product to move into a different phase. This is usually between two liquid phases, normally organic and aqueous, although it can be between solids and liquids. Again, this is often a way of overcoming equilibrium limitations.
- *Reactive Distillation (RD):* In this method, the distillation column has a second function as a reactor, which removes the reactor from the flow-sheet. The greatest advantage usually lies not in reducing the number of unit operations (although this can be a significant benefit) in the plant, but in overcoming the equilibrium limitations of a reaction, by removing the product through distillation.
- *Supercritical Operation:* A key advantage of performing reactions in supercritical carbon dioxide, for example, is that separation of the solvent (the CO_2) from the reaction mixture becomes facile, and does not require a separate unit operation. Instead, all that is required is that the pressure be released to the necessary degree for the reaction mixture to come out of solution.

There are many other examples of combined reaction and separation: these are simply a selection to illustrate the range and the possibilities for process improvement.

To focus on one example, RD, in the 200 kte[1]/yr Eastman process for methyl acetate production, the following reaction takes place:

$$\text{acetic acid} + \text{methanol} \leftrightarrow \text{methyl acetate} + \text{water} \tag{1.16}$$

Eastman successfully used RD to replace 11 distillation vessels (with associated condensers and reboilers) with just 3 RD vessels [70], resulting in significant running and capital cost savings (as distillation columns are among the most energy-intensive unit operations in any process). This intensification was shown to be successful because the reaction fitted the requirements of RD, the most important of which was that one of the products (the methyl acetate itself) had a significantly lower boiling point (57 °C) than any other species present.

When integrating process steps, as with any other intensification, the effects on the whole process should be assessed. It may be that the effects on the process as a whole are minimal or even undesirable, or that the economics are not significantly affected by the new design. However, there is a wide range of process steps that can be combined, and with any process it is worth taking the time to assess the scope for intensification by integrating steps.

1.4.3 Moving from Batch to Continuous Processing

Generally, continuous processing is more efficient than batch processing. Continuous reactors are usually smaller than equivalent batch reactors for two reasons:

1. *Greater Occupancy:* Batch vessels are tied to the ‘batch cycle’, meaning that much of their time is spent on processes such as filling, emptying, cleaning, heating and cooling, all of which reduce their space-time yield, as during these processes the reactor is not generating product.

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[1] Kilotonnes

2. *More Effective Mixing:* The more efficient mixing observed in continuous reactors often leads to higher rates of reaction, which lead to smaller reactors (for the same production rate). This is only the case when the reaction is 'mixing-limited', but it often occurs at larger scales, because good mixing is difficult to achieve at scale, which limits the reaction rate. Batch-stirred vessels 'do not scale up well', which essentially means that their performance at laboratory scale/pilot scale may not be a reliable guide to their performance at industrial scale. A particular problem is that energy densities that are easily achieved at laboratory scale are practically unattainable at the scale of 10s of m^3, as the power scales up on the diameter of the impeller to the power 5. Continuous reactors often have better mixing simply because the length scales are smaller, the diameter of a tubular reactor being considerably less than that of an equivalent tank. Beyond this, there may well be different mixing patterns in continuous reactors that are more effective than those of typical batch agitation.

The reduced scale and improved mixing patterns lead to a range of benefits of continuous operation, such as:

- Improved control
- Better product quality
- Less hazardous operation, due to the reduced volumes of hazardous material
- Reduced capital costs: this is due to the smaller size of the equipment, although in some instances this can be somewhat counteracted by costs associated with the mixing mechanisms or pumps
- Reduced running costs: better control of the temperatures in a reactor usually means that less energy is required to run the process, as the reaction mixture will not need to be overheated to allow for inhomogeneities. When reaction times are reduced by conversion from batch to continuous, the reaction mixture has to be held at the correct temperature for a shorter period of time, which reduces the heating duty overall

It should be noted that these are generalities, so are not all true for all cases of batch–continuous conversion.

In practice, however, batch processing is often used, and there are a range of reasons for this:

- *Flexibility:* Batch vessels can be used for a range of different reactions, and indeed different process steps, whereas continuous equipment needs to be purpose-designed.
- *Batch Integrity:* In pharmaceutical processing, every operation undergone by a specific batch of reactants must be clearly defined, and this is achieved much more easily when there is a well-defined batch of material.
- *Small-Scale Operation:* At very small scales of production, the benefits of moving to continuous operation can be minimal. Continuous processing is usually one of the main economies of scale in chemicals manufacture.
- *High-Added-Value Products:* When the value of a product is high, the processing costs can be immaterial, and other process qualities will become more important. Often the time-to-market will be critical, and in such cases it is often perceived as being less risky to rely on known batch processes, or to scale up in batch, as the processes will have been developed in that way in the laboratory.

- *Long Residence Times:* When reaction times are more than a few minutes, conventional reactors start to become increasingly impractical or expensive if tight control of product specification (achieved by 'plug flow') is to be realized. Very few reactions that take hours are performed continuously. This is the main 'niche' of the oscillatory baffled reactor (OBR): converting 'long' batch processes to more efficient continuous processing.

1.5 Merits of PI Technologies

PI is associated with several business-, process- and environment-related benefits, as summarized in Figure 1.10.

1.5.1 Business

Cutting down the size of the main plant items such as reactors, heat exchangers and separators in a process entails not only a reduction in individual equipment cost but also – and to a more appreciable extent – huge savings in installation costs as a result of reduced pipework, civil engineering and support structure, to name but a few factors. Furthermore, it is envisaged that smaller-sized plants will become more 'mobile' and hence be capable of being transported to the customer or to resources such as an oil field, for instance, for processing of flare gas into methanol. In this distributed manufacturing scenario, the logistics associated with such small, portable plants will be greatly simplified. Another benefit, especially relevant to the pharmaceutical industry, is the ability to introduce new products to the market more rapidly than is currently possible. With PI, a lab-scale continuous reactor can become the manufacturing unit, if the throughput matches the

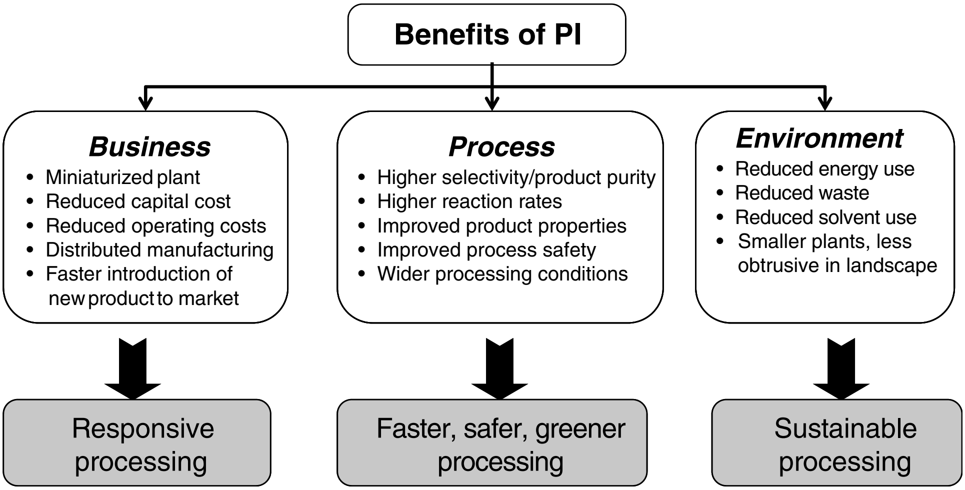

Figure 1.10 Business, process and environmental benefits of PI.

desired production rate. This concept has been demonstrated in a feasibility study undertaken by SmithKline Beecham in the SDR [71], where a lab-scale reactor could match the production capacity of a batch process giving 8 tonnes of product per annum. Cutting down on the process development stages can avoid lengthy delays, as these stages alone can take up to 3 years when scaling up batch processes, which is a considerable amount of time in a product lifespan of 20–25 years before patent expiry.

1.5.2 Process

The process benefits of higher selectivity, faster reaction rates and better product properties were explored in great detail under the various technologies considered in Section 1.4.

Safety in the chemical industry is one of the highest priorities for health-and-safety regulatory bodies following a number of fatal incidents involving large inventories of hazardous materials and exothermic runaways in batch reactors, such as the Bhopal disaster in 1984 [72]. Adopting the PI approach can substantially improve the intrinsic safety of a process as there will be a significantly reduced volume of potentially hazardous chemical at any one time, in a smaller intensified unit. In addition, one of the objectives of PI is to move away from batch processing to small continuous reactors, which have a more efficient overall operation, especially in the case of hugely exothermic reactions, in which the heat can be removed continuously as it is being released. It is to be borne in mind, however, that when intensifying a process, for example by integrating process steps, the process will be prone to becoming more complex, and overall safety considerations on the basis of a number of parameters need to be properly assessed, as highlighted in a recent study [73].

Another major advantage of PI technologies is that by virtue of their greatly improved heat and mass transfer, they allow process conditions to be employed which would previously have been impossible with conventional technologies. These are what Hessel refers to as the 'novel process windows' offered by PI [74]. Several applications, particularly related to microreactors [74–76] and SDRs [77,78], in which these more intense operating conditions – such as highly concentrated reaction systems, higher temperatures and higher pressures – have been investigated, are documented in the literature.

1.5.3 Environment

PI technologies have tremendously appealing environmental implications, whereby a small, compact, highly intensified plant is more likely to be below the tree line, making it far less of an eyesore for the general public than the unsightly and massive steel works characterizing our present chemical plants. Furthermore, novel reactor designs based on the PI concept will enable clean technology to be practised by enabling waste minimization at source. In other words, high-selectivity operation in intensified reactors will reduce or eliminate altogether the formation of unwanted byproducts, which, if not removed from the effluent before discharge, can cause irreversible damage to the environment. High-purity product – which is hence of improved quality – will thus be obtained without incurring enormous downstream purification costs.

The improved energy efficiency foreseeable in intensified unit operations constitutes yet another highly attractive benefit of PI in a world where there is overwhelming concern about the ever-growing demand on non-renewable energy resources. In order to address this concern, there is a great and urgent need for new process technologies that can utilize energy in an efficient manner. In this respect, PI is a positive step for the chemical industry. Great enhancements in heat and mass transfer, two of the most fundamental and frequently encountered operations in chemical engineering processes, can be achieved in intensified units, as has been described in this chapter. Such improvements mean that process times and therefore energy consumption can be dramatically reduced for a given operation. Furthermore, alternative energy sources such as microwave and light energy, which can be targeted to desired process chemistries, can result in less energy waste than is usually encountered with conventional thermal energy sources. A case study highlighting the energy-saving potential of a PI technology is presented in Chapter 15.

1.6 Challenges to Implementation of PI

PI was first developed as a coherent philosophy by Ramshaw *et al.* in the 1970s, so it might be surprising that it has not had more impact by now. There are manifold reasons for the lack of implementation in industry. Some are:

- *Perception of Risk:* Most chemical/pharmaceutical companies are (understandably) risk-averse, and for new technologies the risk is difficult to assess. There is typically a lack of data and a lack of previous case studies on which to base designs and operation, and therefore economic calculations. This results in a so-called ‘rush-to-be-second’ mentality. The lack of risk and cost data makes it difficult to assess the risk–reward balance and perform a reliable cost–benefit analysis for the process change.
- *Lack of ‘Champions’ within Industry:* For any given change in an organization, there is an associated individual with responsibility for it. When this change is substantial and technical, such as the change to a novel unit operation in a chemical plant, the ‘champion’ will have a lot of inertia to overcome, and must be dedicated and well-informed.The champion has to fully understand the technology and its benefits. It is the responsibility of technology developers to inform possible users of the benefits of their technology, but changes cannot be effected without a substantial ‘pull’ from the users.
- *Control/Monitoring:* The greatly enhanced rate of some intensified processes leads to problems in monitoring, as the response times of the instruments become significant in comparison to the process time. This can be an important added technical development step, and as such an obstacle to commercialization. To address these issues, a large body of research work has been undertaken on control of more established PI technologies, such as RD and dividing wall columns, as highlighted in a recent review of control aspects in PI [79]. Work is currently ongoing to develop appropriate control strategies for newer developments such as the SDR [80].
- *PI’s Limitations:* Sometimes PI is not the solution. Any technology has a specific problem or set of problems that it can solve, and these need to be clearly identified and explained. The greatest danger of not doing so is that feasibility studies/pilot-scale trials

are performed that fail because the premise was incorrect (i.e. it was the wrong technology from the start), rather than because of any technical failing, and the technology itself is then labelled as inadequate. A number of technologies developed have been characterized as 'solutions seeking problems', and these problems will sometimes be found. However, sometimes the question that is asked is, 'Can this technology be used for this application?', when it should be, 'Does this technology have realizable economic benefits for the process overall?'

Many of these challenges are familiar to anyone who has had a new technology of any sort to promote. The key issue is simply that the new process/technology must have a *provable and significant* economic advantage. It must be borne in mind that an economic advantage is not only achieved by reducing the size of a piece of process equipment (or, preferably, the entire plant), but can be brought about in a variety of ways:

- *Safer Operation:* Accidents are a cost. Some function of the risk and consequent cost of an accident should be factored into the economic evaluation of any project. Intensified technologies in general will significantly reduce the hazard, and therefore cost, of any incident. More effective monitoring, which is more likely with smaller intensified equipment, should help to reduce the rate of incidence of accidents.
- *Product Quality:* Improved product quality reduces the load on downstream separations, perhaps allowing a reduction in size, or alternative technologies to be used, or process steps to be removed altogether, thereby reducing capital and running costs in other areas of the plant. The higher product quality produced in intensified processes due to the enhanced effectiveness of heat and mass transfer reduces the amount of waste produced, thereby lessening the amount that has to be disposed of. In some industries, where the wastes are highly toxic, for instance, disposal and/or treatment is one of the largest running costs. This will become more of a driver in the future, as environmental legislation becomes more stringent worldwide.
- *Reduced Running Costs:* The greater efficiency of intensified plants reduces energy costs. In a fossil fuel-based energy supply system, as most currently are, this equates directly to reduced CO_2 emissions. Such issues should become increasingly important as carbon trading becomes more standard.

1.7 Conclusion

As a revolutionary approach to chemical processing, PI has gained remarkable momentum in the last 2 decades. It was described more than 10 years ago as 'the key to survival of the fittest in international competition' [81]. It is not surprising, therefore, given the intensely competitive environment in which businesses in the chemical industry operate, that great strides have been made in the research and development of PI technologies over the last few years.

With greater emphasis being placed on sustainable development nowadays, PI can be an important element in making future chemical and pharmaceutical industries greener. This is because it can be used to greatly reduce the size of many unit operations, and in doing so reduce not only the energy required to run them but also the surrounding infrastructure and the energy and materials used in their manufacture. In an intensified environment, higher selectivities and yields can result in improved atom efficiency and waste minimization at source, leading to reduced downstream processing.

There is no doubt that PI is here to stay and that it will continue to play a major role in the development and growth of the chemical and processing industry in the years to come. Whether or not large plants should be considered ‘dinosaurs’ that will be extinct within the next 50 years remains to be seen, but it is a vision that is not altogether unrealistic. There are still many challenges ahead, which will require a concerted effort from both the academic community and industry partners before PI is more widely implemented and practised. It is also worthy of note here that how successful PI is in its application to a given process is very much dependent on the characteristics of that process. An inherently slow process will not be made any faster by intensifying heat- and mass-transfer characteristics. Thus, it is important to clearly understand the fundamentals of a process before any attempt at intensifying it is made. There are a few other process-related limitations to the general application of PI, such as:

- Some processes operate at too small a scale for PI to be economically worthwhile.
- Various plants require a flexibility of operation that is difficult to achieve in a continuous plant, which is usually purpose-designed.

However, in spite of these application limitations and challenges, the potential for PI remains largely untapped, but the economic rewards for those companies that do introduce PI are likely to be substantial – and this will have environmental benefits for a more sustainable future for generations to come.

Nomenclature

A	Constant
A_s	Heat-transfer surface area (m^2)
C_1, C_2	Constants in Nusselt number and Sherwood number correlations, respectively
C_D	Coefficient of discharge of impeller (−)
C_p	Specific heat capacity (J/kg K)
D	Pipe or channel diameter (m)
$\mathbf{D}$	Diffusivity (m^2/s)
D_i	Impeller diameter (m)
D_l	Liquid diffusivity (m^2/s)
D_{turb}	Turbulent diffusivity (m^2/s)
h	Heat-transfer coefficient (W/m^2 K)
k	Thermal conductivity (W/m K)
k_m	Mass-transfer coefficient (m/s)
l	Characteristic length for diffusion (m)
L	Characteristic length scale of large eddies (at macroscale) (m)
L_c	Integral length scale of turbulence (m)
L_D	Characteristic length scale for turbulent dispersion (m)
N	Impeller rotational speed (Hz)
Nu	Nusselt number (= hD/k)
Q	Heat-transfer rate (W)

Q_c	Impeller pumping capacity (m^3/s)
Q_f	Flow rate of injected fluid (m^3/s)
r_{pipe}	Radius of pipe for feed introduction (m)
Re	Reynolds number ($= \rho uD/\mu$)
Sc	Schmidt number ($= \nu/\mathbf{D}$ or ν/D_l)
Sh	Sherwood number ($= \mathrm{km}l\,/\mathbf{D}$)
t_D	Characteristic diffusion time (s)
ΔT_{lm}	Logarithmic mean temperature difference (K)
u	Average velocity (m/s)
U	Overall heat transfer (W/m^2 K)
V	Vessel volume (m^3)

Greek Letters

ε	Turbulent energy dissipation rate (W/kg)
η_K	Kolgomorov length scale (m)
η_B	Batchelor length scale (m)
ν	Kinematic viscosity of fluid (m^2/s)
τ_c	Circulation time (s)
τ_D	Characteristic mesomixing timescale for turbulent dispersion (s)
τ_{DS}	Characteristic micromixing time for shear deformation and diffusion at Batchelor scale (s)
τ_e	Characteristic micromixing time for engulfment (s)
τ_{mac}	Macromixing time (s)
τ_s	Inertial-convective mesomixing time (s)
μ	Viscosity (Pa.s)
ρ	Density (kg/m^3)

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