1   Introduction

1.1   Process Intensification

Process intensification (PI) is the term used to describe the means by which a process manufacturing stage can be rendered more compact than the conventional standard. This implies a lower inventory and a corresponding increase in manufacturing rate compared with the standard for that stage. Process intensification is important because its application can lead to: novel or enhanced products, better use of chemistry, improved processing (higher efficiency), distributed manufacturing; energy and environmental benefits; process flexibility, improved product quality, reduced footprint, improved inherent safety and energy efficiency, capital cost reduction, and reduced material inventories. Process intensification also encapsulates a novel design philosophy that aims to revolutionize process engineering by revisiting the fundamentals of fluid dynamics and transport phenomena.

The concept of process intensification has been around for a number of years and the adoption of ground-breaking applications of recent, innovative process intensification techniques in industrial processing has been relatively slow. One of the principal reasons is the risk-averse approach taken by manufacturing companies (Tsouris and Porcelli, 2003) toward the application of entirely new technologies. However, as greater understanding of the fundamentals is forthcoming and with the refinement of modeling techniques, some of the major risks can be reduced at relatively low cost. In addition, by its very nature process intensification often involves scale-up using multiple equipment modules, which singly or in small numbers can be rigorously tested and evaluated prior to implementation at full scale.

Intensification technologies and the associated research and development focus mostly on multiphase processes: gas/liquid, gas/solid, liquid/solid, and liquid/liquid. In the case of both gas/liquid and liquid/liquid, the fluid mechanics are the most complex because of the fact that gas bubbles and liquid droplets are dynamic entities whose shapes and sizes are time dependent. For example, gas bubbles oscillate, which influences internal circulation, exhibiting variable shear conditions at the gas–liquid boundary and time-dependent interfacial area values. Gas bubbles in a swarming system may collide and coalesce, thus experiencing large hydrodynamic disturbance, and experiencing a change in shape and size. This not only complicates the understanding of the fluid mechanics, but also complicates our understanding of the interrelated processes of heat and mass transfer across the phase boundary. Recently developed

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concepts in intensification inevitably include novel equipment designs, some with complex geometries that further complicate rigorous description and fundamental understanding of the fluid mechanics of the system. The key to the success of the majority of intensification techniques, which will be discussed in later chapters of this book, is the control of the fluid mechanics.

In the case of liquid–liquid processes, complexities similar to those already briefly mentioned for gas–liquid systems also apply, including complex drop size behavior, shape dynamics, and coalescence phenomena. In addition, knowledge of the physics of the drop surface and the interface is also a vital consideration for understanding intensification of liquid–liquid contacting.

A number of definitions of intensification have been articulated. An overall definition may be described as follows: "The reduction in size of a process or element of a process by improved design, choice of better reagents or materials, and improved control of fluid mechanics." The above overarching result may be achieved in many different ways. These include achievement of higher heat and mass transfer fluxes, improved reaction selectivity, development of new solvents and materials for improving separation efficiency, and improved physical geometries of reactors and contactors. There are a number of important underpinning reasons why intensification techniques are of on-going interest among designers, researchers, and innovators. Energy saving is a major reason why intensification techniques are considered (Baird and Rao, 1995; Baird and Stonestreet, 1995; Qiu, Zhao, and Weatherley, 2010; Ramshaw, 1999). There is substantial evidence of demonstrated savings in energy utilization through the adoption of process intensification principles through improvements in mechanical efficiency, through the application of better catalysts, through the application of intensification principles to heat exchanger design, and through the use of reaction and separation media that enable more efficient and easier product separation. A second basic reason for the adoption of process intensification is the reduction in size and process plant footprint that the application to equipment design affords. The intensification of reaction rates and heat and mass transfer fluxes results in reduction of equipment size for a given throughput and thus the space required to accommodate the plant hardware is correspondingly reduced. Another potential benefit of reduction in plant size is the possibility of a distributed manufacturing approach being adopted. Distributed manufacturing involves organizing production in a larger number of smaller plants that are located close to sources of raw materials and the market, rather than in a series of larger plants in a central location. There are economic and environmental benefits to be gained from distributed manufacturing due to reduction of transportation costs of both raw materials and products. A further positive feature of intensification is the reduction in inventory due to smaller equipment size and reduced residence times. Inventory reduction is not only economically beneficial but also is a huge safety feature of PI, especially when processing highly toxic, explosive, or flammable materials.

Modularization of process plant is also made possible by reducing equipment size resulting from more intensive reaction rates and higher material and energy fluxes. Building plants in modular form can be achieved off-site with cost benefits and improved flexibility for the configuration of multipurpose plants. Modularization is

also a major consideration in the design of offshore oil and gas processing facilities where space costs are extremely high, with a necessity for plant of the smallest possible footprint.

Traditionally, process intensification has been strongly identified with the development of new or improved devices for processing. These include devices whose design exploits phenomena such as cavitation, centrifugal forces, electrical fields, magnetic fields, creation of thin films, high shear, cyclic dispersion and coalescence, pulsatile flows, and others. Another emerging view of process intensification is strongly based on the development of new materials and fluids. These include new catalysts, new reaction media and solvents for separation, and the application of biological processes.

Of special relevance to liquid–liquid systems is the development of two new families of solvents, ionic liquids and solvents based on near-critical carbon dioxide. Much of the interest in these groups of solvents has focused on the possibilities they offer as reaction and extraction media in terms of higher rates of reaction, high reactant solubilities, and easier separations. The availability of ionic liquid media (ILM) at near-ambient temperatures has stimulated many possibilities for their use as media for organic reactions involving gas, liquid, and solid reaction substrates. The principal process advantages of ILM center on their very low vapor pressure and relatively low toxicity. These address the major concerns surrounding volatile organic compound (VOC) emissions and toxic exposure within the chemical and process industries, which currently use very large amounts of conventional organic solvents both as reaction media and as extractants. Another key advantage of ILM is their excellent performance as solvents for a wide range of compounds. The extensive work of Seddon and co-workers and others (Earle and Seddon, 2000; Holbrey, Rooney, and Seddon, 1999; Welton, 1999; Wilkes, 2004) has confirmed the potential of ILM for catalysis at laboratory scale for a range of systems. However, there has been less attention paid thus far to the issues of contacting, mixing, and phase separation in liquid–liquid systems involving ionic liquids. A detailed understanding of these key process phenomena is required if a fuller appreciation of the performance of ionic liquids as solvents in liquid–liquid processes is to be obtained.

Another "clean" solvent of importance to intensification is carbon dioxide (CO_2), which may be used either as a subcritical or supercritical fluid functioning as a benign solvent or as a reaction medium. The ability to control solvent properties, both the solvation properties and the physical properties, offers significant flexibility for process applications. Advantages include: relatively low cost; low toxicity; properties that are well understood; for separations, product isolation is straightforward; wide control of solvation and selectivity behavior (via temperature and pressure control, and addition of entrainers); high diffusion coefficients that offer potential for increased reaction rates; potential for homogeneous catalytic reactions; high gas miscibility; nonoxidizable; nonflammable; excellent medium for oxidation and reduction reactions; and further tunability can be obtained by combination of near-critical CO_2 with conventional solvents (CXLs) and entrainers. The potential for using CO_2-expanded liquids (CXLs) as reaction media has received increased attention in recent times. These are compressible media that are synthesized by mixing dense-phase CO_2 with an organic solvent to produce a liquid having properties that are

substantially different from either of the constituents. The physical and chemical properties of the mixture are highly tunable through variation of the chemical composition and the temperature and pressure of the system. One of the significant features of CXLs is the intensification of gas solubility (Bezanehtak, Dehghani, and Foster, 2004; Hert et al., 2005) as this accrues potential enhancements in reaction conditions. Similarly, some catalytically significant transition metal complexes, many of which are only sparingly soluble in conventional organic solvents, also demonstrate enhanced solubility, resulting in improved reaction conditions.

Knez et al. (2014) highlight the interesting possibility of conducting environmentally benign enzymatic catalytic reactions in a liquid–liquid system comprising an ionic liquid and a supercritical fluid. It is shown that reactions may be successfully conducted in the resulting two-phase liquid–liquid environment that effectively facilitates simultaneous reaction and separation (Fan and Qi, 2010; Paljevac, Knez, and Habulin, 2009). In a significant review article, Keskin et al. (2007) showed how ionic liquid solvents have become the "partner" solvents with supercritical CO_2 in many applications, based on a significant literature focus on the interaction of these two green solvents.

The drawbacks of CO_2 as a processing fluid include the constraints associated with high-pressure processing, high capital cost for large-scale applications, and lack of good design data.

Developments in these areas are part of the strong nexus between intensification technologies, "green engineering" and "green chemistry," sometimes also referred to as subsets of "sustainable engineering." Sustainable engineering could be defined as the multidisciplinary integration of sciences and engineering for the restoration and preservation of the environment and for the sustainable use of resources. The associated process engineering is crucial for the success of clean technology. The principles of waste minimization which have been articulated for several years have a direct bearing on the goals of sustainable engineering. The continuum of goals may be put simply as: treatment > reduction > minimization > zero emission.

It is useful to quote the 1995 definition of sustainable development from the UK Engineering Council:

Sustainable development [is] ... development, which has as its goal the maximization of human well-being within the constraints necessary for conserving the integrity of the environment.

Making the transition to a sustainable model for human activity will be an extremely complex and long term task ... It will require considerable technological innovation and many other skills which engineers are uniquely placed to offer ...

It may be argued that sustainable development can be described as the "goal" – and sustainable engineering as the "means." We can consider some modified definitions of sustainable engineering and we can use analogies with some of the definitions of process intensification, for example:

The term used to describe the means by which a process manufacturing element, or entire process can be rendered more sustainable than the conventional standard. This implies a lower inventory and usage of hazardous and non-renewable material in manufacturing compared with the standard. (Jones, 1996)

Sustainable engineering may be considered to be the adoption of a novel approach to process development, plant design, operation, and control that aims to minimize environmental impact at every stage. A related goal is a sustainable environment for chemical processing that results in safer and less polluting products in compact, highly efficient equipment at low cost.

The sustainable engineering approach, in addition to leading to the replacement of inefficient processes, can also provide opportunities for new chemical products, distributed manufacturing, and higher profitability. A design philosophy underpinned by the principles of sustainability can result in improved energy efficiency, lower carbon footprint, reduced hazard, lower capital and inventory costs, and reduction in plant size and footprint.

In considering the actualities of moving toward sustainable engineering, there are a number of key questions to be examined. Can the goals behind sustainable engineering be achieved and delivered through: (i) novel or enhanced products; (ii) better use of chemistry; (iii) reduced inventories; (iv) enhanced safety and control systems; (v) improved processing (higher efficiency); (vi) distributed manufacturing; (vii) energy and environmental benefits; or (viii) capital cost reduction? It can be argued that most of the above include the design and operational goals of good process engineering and have done so for many years. It can also be argued that there are a host of specific examples already in place, such as recycle reactors, renewable energy (wave, wind, solar, tidal), waste water treatment and recycling, and biofuels (biodiesel, bioethanol, gasified wood and other cellulose). A difference observed in recent developments is the importance of fundamental knowledge in addressing the challenge of sustainable development. New science and deeper understanding of engineering principles are making a positive impact and contributing to the implementation of sustainable engineering. Process intensification is a crucial part of that implementation, bringing not only economic advantages but also environmental benefits to manufacturing processes. This applies to processes involving liquid–liquid mixtures as much as to any other multiphase system.

The evolution in the design of liquid–liquid processes has occurred over many years, as shown in the improvements in equipment performance and reliability, and in the development of solvents with improved chemical and physical properties. Deeper understanding of hydrodynamics, advances in computational modeling of equipment behavior, novel approaches to equipment geometry, and innovations in solvent chemistry have been the main driving forces behind development of improved liquid–liquid processes.

The design of liquid–liquid contacting equipment has evolved over many years, covering a wide range of applications. The major application that has underpinned the majority of developments in design has been for extractive separations, product purification, and recovery. These range from purification and separation processes in high-volume industries, such as petrochemicals, to separations in the metals and mining industry, to the stringent separation requirements of the nuclear industry and the pharmaceutical industry. The underpinning principles in all cases are concerned with ensuring high mass transfer efficiency, tight control of hydraulic conditions during

contact, and effective phase separation. In the case of certain industries other factors also have influenced design. These include product stability, which is a major factor in certain pharmaceutical separations where rapid extraction and product stabilization are paramount requirements for process efficiency and economic operation. Another industry-specific factor is the need for hygienic process conditions and the avoidance of contamination, the ease of cleaning, and sterilization, which is again the case in the pharmaceutical industry but also in the food, perfumery, and ingredients industries. The nuclear industry also has additional special conditions required for the design of liquid–liquid contact equipment. Here the need for maintenance-free equipment throws up challenges for equipment designers, added to which is the need to ensure equipment design takes into account criticality safety criteria in cases where fissile nuclear fuel compounds are processed.

In general the design of separation process equipment is governed largely by requirements to achieve the desired separation reliably, safely, and economically, requirements that continue today to dominate decision making regarding equipment design and choice for a particular application. Other considerations have also become important with the emergence of green chemistry, the drive for greater process efficiencies and product yield, and increased emphasis on process safety and inventory reduction. Exploitation of new catalysts and innovative solvent media will depend in some cases on the development of new equipment technology in order to make the application of new materials feasible at industrial scale. The high cost of homogeneous catalysts and novel solvent media such as ionic liquids, aqueous-based solvents, and complexing agents such liquid ion-exchangers, have led to new developments in equipment design and operations. The reasons include the need to maximize solvent recovery and recycle, to ensure phase separations are highly efficient, and that extractions are conducted to minimize solvent degradation and loss. As discussed earlier, these are major driving forces behind process intensification.

Liquid–liquid processes involving interfacial transport must ensure that the hydrodynamic conditions of the contact create an environment for high mass transfer rates. For all types of equipment this involves breaking up or dispersing one phase into the second phase, generating small but unstable drops, achieving high rates of interfacial shear, and minimizing back-mixing, dead space, and short-circuit flows. These considerations are paramount in stagewise equipment, column contactors, batch or continuous contact, and in high-intensity contactors such as centrifugal devices. The fundamentals of the liquid–liquid behaviors that govern the meeting of these requirements are considered in Chapters 2 and 3.

The overarching requirement can be simply described in two steps; contacting followed by phase separation. Figure 1.1(a)–(f) shows a sequence of shots in which the static liquid–liquid mixture proceeds to a complete dispersion after the onset of agitation. Frames (b) and (c) show the onset of interfacial breakup, followed by the dispersion of the droplet phase as discrete drops in frame (d), and then to complete dispersion in frame (e). Frame (f) show the progress toward phase disengagement after approximately 20 s from the discontinuation of agitation.

Frame (f) illustrates one of the fundamental conflicts in liquid–liquid mixing and the design and operation of mixer settlers. On the one hand, high levels of drop break-up,
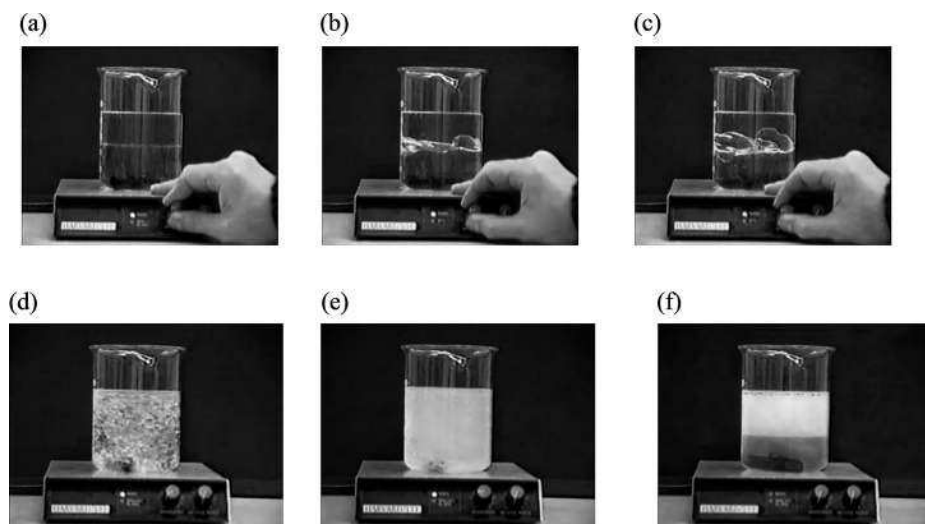
Figure 1.1 Stages of mechanical dispersion of a liquid–liquid mixture.
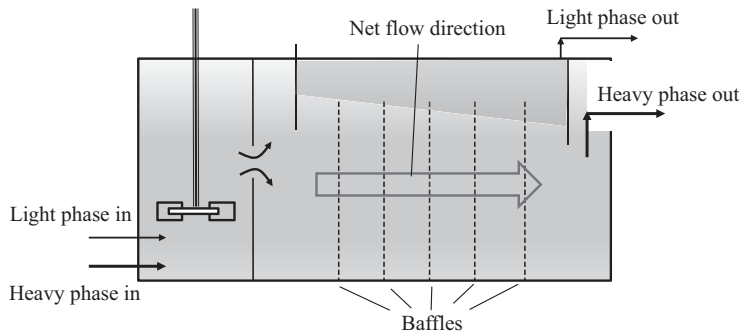
Figure 1.2 Mixer settler arrangement with baffled settling chamber.

mixing, and dispersion are required for high rates of mass transfer and efficient mixer compartment utilization. On the other hand, high rates of phase disengagement and coalescence are also an essential requirement. As can be seen in frame (f), in the light phase there is strong evidence of fine drops of the heavy phase remaining that may be slow to settle on account of their very small size. Therefore the degree of agitation must be carefully controlled to ensure that settling can be realized efficiently while at the same time maintaining high mass transfer rates.

Innovations in liquid–liquid contacting equipment design are mainly focused on enhancing the fluid dynamics and interfacial phenomena that govern mass and energy transport, and that govern physical phase separation. To recap, Figure 1.2 shows the principle of mixing and settling for liquid–liquid extraction or solvent extraction. This may be defined as the selective transfer of a desired solute for recovery and purification from a feed liquid phase into a second partially or totally immiscible liquid phase whose

physical and chemical thermodynamic properties are designed for the separation required. There are many texts that describe liquid–liquid extraction technologies in detail, for example Logsdail and Slater (1993). The principle features of the process are physical contacting of the two liquid feed phases to achieve high interfacial area and efficient interfacial mass transfer between the phases. The promotion of interfacial shear between the surface of droplets of one phase and the surrounding continuum of the second phase together with droplet instability are important for good mass transfer. The second major part of liquid–liquid processes is the efficient separation of the liquid phases after mass transfer has approached completion. This is important in order to ensure high efficiency and to avoid contamination of each exiting liquid stream with traces of the other phase as much as possible.

These fundamental requirements strongly impact the design and operation of industrial liquid–liquid contacting equipment. The intensification of liquid–liquid processes and future developments of this approach require not only clear understanding of the relevant fluid mechanics and transport phenomena in existing equipment designs but also innovation in equipment design and geometries. The intensification of liquid–liquid processes through improved equipment design therefore must be based on better understanding of the fluid mechanics and how these may be better controlled. Improved equipment performance through intensification opens up avenues for the viable commercialization of new chemistry and biotechnology for new and improved chemical products, and for the manufacture of existing products with lower environmental impacts. The nexus between equipment innovation and new chemistry, for example in the development of new pathways, solvent media, and catalysts, is an essential component driving development of new equipment technologies.

The technologies for industrial-scale liquid–liquid contacting processes are traditionally categorized as follows:

  (i)   mixer settler (stagewise) equipment;
 (ii)   continuous column (differential) contact equipment;
(iii)   centrifugal contact equipment.

The majority of modern, high-performance contact devices use externally applied mechanical energy to achieve good dispersion and use turbulence of the liquid–liquid mixture in order to ensure high rates of mass transfer. The proportion of total energy supplied to the contactor that is actually utilized to enhance mass transfer rates is small in the majority of cases and a major proportion is dissipated through frictional loss. Thus there is significant scope for improvements in efficiency.

As we review both traditional liquid–liquid contacting technologies and new, emerging technologies we see that a number of well-established equipment designs already embrace many of the tenets of process intensification. As already stated, liquid–liquid contacting equipment design falls into three broad categories: (i) stagewise equipment, for example mixer settler trains; (ii) continuous countercurrent column contactors; and (iii) centrifugal contactors. Equipment that falls into any of these three categories to a greater or lesser degree contain design features to increase kinetics, improve phase separation, and enhance hydraulic capacity. In new and emerging

equipment technology we see a move toward miniaturization with equipment having smaller footprints, modular design, and incorporation of novel methods of intensification such as microwaves, ultrasonic fields, and electrical fields. Another factor that has enabled improved optimization of equipment design is the availability of highly accurate mathematical modeling tools that allow us to study the performance of new equipment geometries without the expense of building and experimental testing until design choices are significantly narrowed down. Such tools also provide valuable insights into the fluid dynamics inside liquid–liquid contacting equipment hitherto unavailable to designers.

1.2 Review of Current Equipment Technologies

1.2.1 Mixer Settlers

Mixer settlers have provided the mainstay of many large-scale industrial liquid–liquid extraction processes. A typical arrangement is shown in Figure 1.2.

The two immiscible liquid phases are fed to the mixing compartment at the left-hand end, where mixing of the phases is conducted. The main objectives required in the mixing compartment are as follows:

- To increase the interfacial area per unit volume in order to enhance overall mass transfer rates. This is achieved by efficient breakup and dispersion of one phase into the other phase.
- To reduce the diffusion boundary layer around individual droplets to minimize mass transfer resistances in the continuous phase surrounding the dispersed droplets.
- To promote good mass transfer within the droplet phase by reducing internal concentration gradients. Promotion of cyclic dispersion and coalescence processes to enhance convection inside individual droplets within the mixing chamber can result in significant internal hydrodynamic disturbances thus intensifying mass transfer.
- To ensure that the entire volume of the mixing chamber is used for effective mixing of the two phases, avoiding dead space and short-circuit unmixed flow of either of the phases.
- To produce a mixed phase that can be readily separated in the coalescence section of the mixer settler.

The above requirements have a fundamental influence on the design and operating conditions of the mixing chamber. Understanding the interactions between the fluid dynamics, geometry, and transport rates is critical for intensification of the liquid–liquid interaction.

With reference to Figure 1.2, the mixing chamber is shown on the left-hand end of the unit and is shown as being equipped with an impeller on a vertical drive shaft. The speed, depth, and shape of impeller, together with the volume of the mixing

compartment, are all considerations in determining the optimum mixing and dispersion conditions as listed. Early work on liquid–liquid mixing focused on establishing the minimum agitator speed required to obtain a well-mixed dispersion. For example, Skelland and Seksaria (1978) proposed the following correlation for the minimum agitator speed N_{cd} for complete dispersion in terms of physical properties (viscosities of continuous and dispersed phases μ_c and μ_d respectively, interfacial tension σ, and density difference $\Delta\rho$)

$$N_{cd} = C_0 D^{\alpha_0} \mu_C^{1/9} \mu_d^{-1/9} \sigma^{0.3} \Delta\rho^{0.25} \tag{1.1}$$

where C_0 and α_0 are constants depending on the type of impeller, the location of the impeller, and dimensions (height : width ratio).

In later work, Skelland developed another correlation for minimum agitator speed $(N_{Fr})_{min}$ in baffled vessels (Skelland and Ramsey, 1987):

$$(N_{Fr})_{min} = C^2 \left(\frac{T}{D}\right)^{2\alpha} \phi^{0.106} (N_{Ga} N_{Bo})^{-0.084} \tag{1.2}$$

$$N_{Bo} = \frac{D^2 g \Delta\rho}{\sigma} \qquad \text{(Bond number)}$$

$$N_{Ga} = \frac{D^3 \rho_M g \Delta\rho}{\mu_M^2} \quad \text{(Gallileo number)}$$

C = a shape factor
T = tank diameter (m)
D = impeller diameter (m)
ϕ = volume fraction of the dispersed phase
μ_m = mean viscosity (N s m^{-2})
ρ_m = mean density (kg m^{-3})

Another major requirement of mixer design is the need to ensure well-mixed conditions in the mixing chamber while achieving uniform flow. Here the design of mixing impeller, the rotation speed, the positioning of the impeller relative to the base of the mixing chamber, the design and positioning of baffles in the mixing chamber, and conditions of operation are critical to achieving uniform mixing. One of the conflicts in liquid–liquid mixing is, on the one hand a need to generate interfacial area for high mass transfer through dispersion, on the other hand avoidance of stable emulsion formation. There is a significant literature on the subject of mixing, so the coverage here is necessarily concise and we will review the main concepts and governing relationships relevant to liquid–liquid systems, and in particular the nexus between understanding mixing and intensification.

The type of impeller exerts a significant influence on the nature of the flows within the mixing chamber, although all three regimes are present to a greater or lesser extent (Figure 1.3). Flat-bladed turbine impellers are associated with strong radial flows, where angled turbine impellers tend to be associated with dominant axial flows. Flat-bladed paddle impellers tend to be associated with more dominant tangential flows. The latter