Reactors with flexible mixing characteristics: A key aspect in the design and operation of low tonnage processes

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Abstract

The progress of fast chemical reactions is often governed by the mixing characteristics of a reactor if their reaction time is smaller than or of the order of the mixing time of the reactor. The definition of the mixing characteristics of the reactor here includes its ability to match the heat transfer, mass transfer and uniformity of properties to the level required for the best outcome of chemical reactions. The reactive mixture resulting from inefficient mixing causes stoichiometric imbalance, temperature variation and non-uniformity of properties at a molecular scale. Profound adverse effects of such in-homogeneities existing at molecular scale environment on the product distribution of complex multiple reactions have been observed in all sectors of chemical process industry (CPI).

Novel Process Intensification (PI) reactors are being developed to carry out such complex multiple reactions in a more efficient manner compared to conventional reactors. However, most of them are custom designed to carry out one particular reaction at fixed operating conditions. This makes them highly inflexible and unacceptable for a large sector of CPI having multiple products and fluctuating demands. The overwhelming majority of low tonnage processes are of this nature and most of the reactions involved are complex multiple reactions. A key aspect for the selection of reactors for these processes is their ability to closely match the demands of a wide range of chemical reactions. Reactors having flexible mixing characteristics are more likely to possess this ability and hence more likely to be a successful candidate for these processes.

This paper proposes a novel approach to design and operate PI reactors with flexible mixing characteristics to help widen their acceptance for chemical process industries having multiple products and fluctuating demands, in particular low tonnage process industries. A pragmatic mathematical model has been proposed to assist in the design and operation of such reactors. Results obtained with this approach and model have been compared to industrial examples from the literature. The approach and the model proposed in this paper are equally valid for conventional reactors. Their use for scale up of the conventional reactors have also been highlighted. An experimental programme has been designed to prove application of this approach and model.

Introduction

Mixing can be defined as the reduction of inhomogeneity in concentration, temperature, phase and properties. Chemical reaction is a molecular scale phenomenon and requires uniform molecular scale environment to proceed at its intrinsic rate. Any deviations from the homogeneous molecular scale environment can result in to the reduction of the reaction rate and unacceptable product distribution for complex multiple reactions. The role of the mixing in such cases is to provide a homogeneous reactive environment at the molecular scale at the rate demanded by the chemical reaction. This consideration about the role of mixing in the progress of chemical reaction applies to both homogeneous and heterogeneous reactions. It is often very difficult to achieve the homogeneous reactive environment at the rate demanded by the fast and exo- / endo-thermic multiple reactions at production scale using the conventional reactors. Examples of the profound adverse effects of the inefficient mixing on the conversion, product distribution and costs have been observed in all the sectors of chemical process industry (CPI). Design and scale-up of reactors for carrying out such reactions is still regarded as an extreme challenge for the development and design engineers (Paul, Atiemo-obeng, & Kresta, 2004).

Fast and exo-/ endo-thermic reactions coupled with complex chemistry are often encountered in low tonnage CPI. This very fact makes mixing an important factor for low tonnage process reactor design and operation. The mixing requirements can vary over the full mixing spectrum, from simple blending to high-shear specialty designs due to the wide range of chemistries used and and multiproduct nature of this industry. This adds an important additional criterion of flexible mixing to be considered while designing and selecting the reactor for low tonnage process industry. One solution often proposed to overcome this flexible mixing requirement is to have a jacketed stirred tank reactor (STR) equipped with a variable speed drive mixing system and the facility to use different types of impellers. In accordance with this notion of flexibility, majority of the reactions in the low tonnage chemical industry are run in the batch or semi-batch mode in the STR. Other reasons often highlighted for the choice of stirred tank reactor include complete conversion, accuracy of charge and low productivity. However, the STR fails to provide the essential uniform molecular scale environment for fast, multiple and exo-/ endo-thermic reactions and also pose a major hazard due to the presence of large reactive inventories (Jones, 1996). A number of other factors including the change in business models, stringent environmental regulations, change in the acceptable levels of safety and availability of options are forcing the low tonnage chemical industry to resort to more efficient reactors than STR. Use of high mixing efficiency continuous tubular flow reactors with good control of reaction temperature profiles and contact times for carrying out such reactions can prove to be useful in alleviating the limitations of the batch and semi-batch STR to a large extent. In certain cases, it would be inappropriate to use conventional tubular reactors due to their comparatively large throughput and lack of precise control of the progress of the reaction compared to the requirement of the low tonnage industry. However, recently introduced meso- and micro-scale process intensification (PI) reactors hold great promises in both overcoming the limitations of the STR and to suit majority of the requirements of the low tonnage industry.

Need for the reactor with flexible mixing characteristics

It is worthwhile to understand the needs for the reactor with flexible mixing characteristics for low tonnage chemical industry before exploring the flexibility of the PI

reactors. In this industry, one product is made, often in a campaign for a period that may last for days or few months. Then, the same plant with addition or deletion of a few of the processing components is used to manufacture another product. Reaction conditions and demands, reactants and also the inter-connection between the processing components may change drastically compared to that of the previous product. Also, to add to the complexity of the situation, new products with different processing requirements are continually added to the product portfolio due to short life cycle of the existing products.
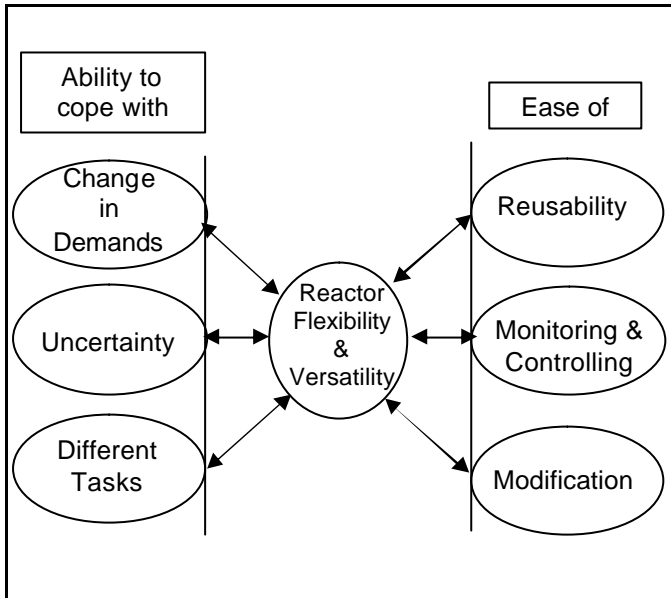

Figure 1 Flexibility and versatility criteria for reactor
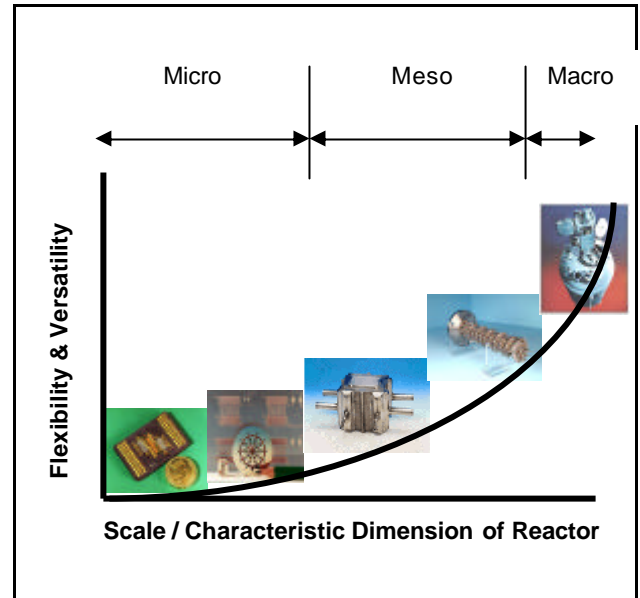

Figure 2 Notion of flexibility and versatility of reactor as function of its scale*

      The overwhelming majority of low tonnage processes are of this nature, that is, a single reactor and upstream or downstream processing system components producing a portfolio of final products in a short time span. A major problem in the design and selection of the system components is that the substantial part of the demand that they are required to meet is often unknown at the start. In such cases, a variety of process task sequences and poorly defined process requirements have to be considered. Similarly, the allocation of process tasks and sequencing of the components need to be changed frequently to match the new process requirements. In such situations, flexibility and versatility of the components including the reactor becomes an important criterion for selection. The flexibility of any given reactor has been defined here as its ability to cope with the changes in the demands for different reactions, capability to handle the uncertainty inherent in the characterisation of the reaction and the capability to carry out other tasks than the reaction. The versatility of the reactor has been defined here as the ease of design modification to suit to the requirements of different reactions, the facility to monitor, control and adjust the reactions and also the reusability of the reactor for other purposes. The criteria summarized above can be used to judge the flexibility and versatility offered by the PI reactors under consideration compared to that of the conventional STR (Figure 1). Criteria listed on the left in Figure 1 are more relevant to the term flexibility and the ones on the right to the term versatility. Apart from these flexibility and versatility criteria, the ability of exercising them quickly to match the demands of different reactions is also an important criterion for the selection of reactors in low tonnage process industry.

PI Reactors and Flexibility

A wide range of novel PI reactors such as spinning disk-, spinning cone-, oscillatory baffled-, heat exchanger-, monolith-, static mixer-, rotating packed bed-, micro-reactors and a large number of their variations have been designed and made available to CPI in the last few years. Suitability and even superiority of PI reactors for industrially relevant reaction schemes over conventional reactors have also been demonstrated at different levels. However, despite all the potential advantages associated with them, industrial applications of PI reactors have been very limited so far. Normally, lack of experimental evidence, awareness, familiarity, standardisation, reliability and conservatism are cited as barriers hindering the acceptance of PI reactors at wider scale in the industry. However, one of the major reasons frequently highlighted by the industry is the lack of flexibility of the PI reactors to cope with changes in process demands. This is partly true in a way that most of the PI reactors so far have been designed and operated keeping in view very specific needs of the process and throughput, neglecting the flexibility aspects required of them. This could be a key factor in spreading the perception about their inflexibility and making them unacceptable in the low tonnage industry where the flexibility holds prime importance. It is also a notion in the industry that the flexibility and versatility offered by the reactor decreases with scale of the reactor (Figure 2).
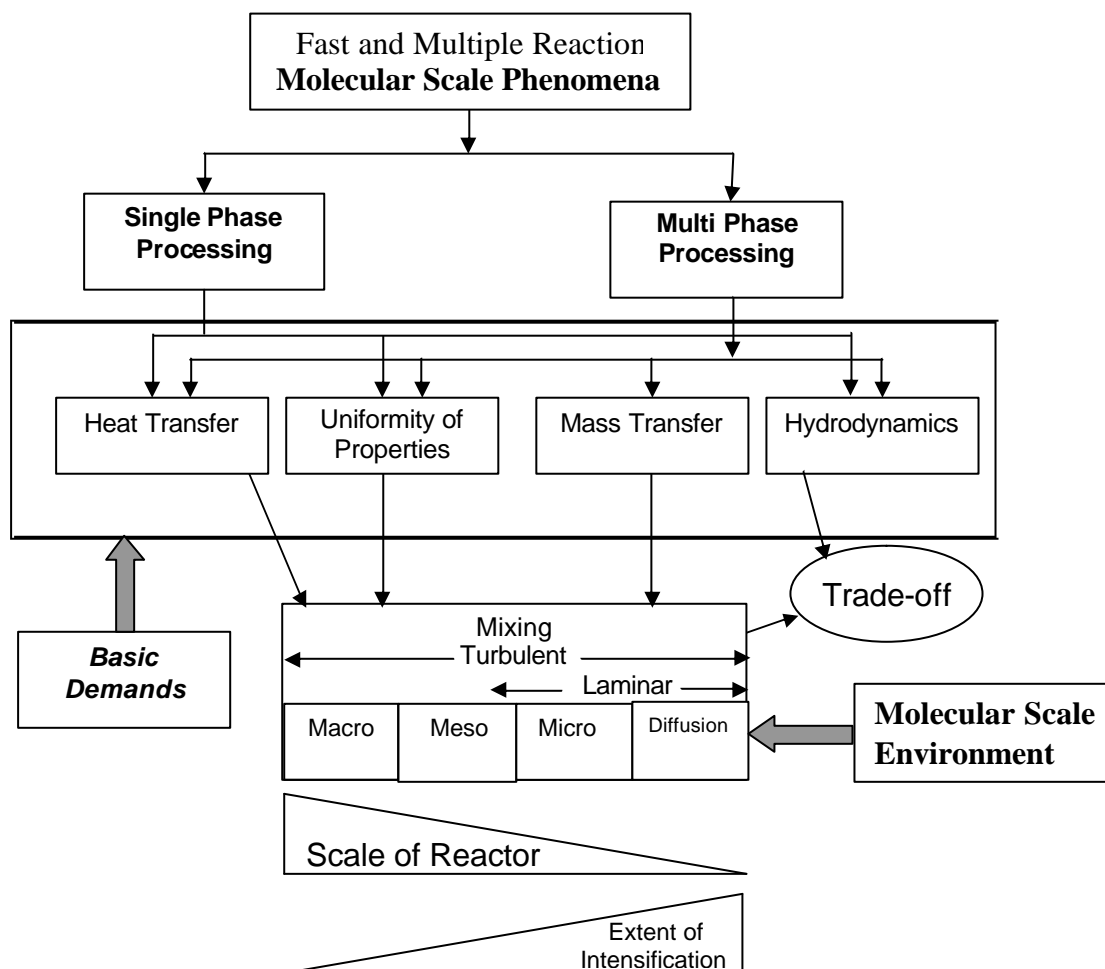

Figure 3 Interrelationship between basic demands of a typical chemical reaction and advantages offered by PI reactors over conventional reactors

PI reactors would be accepted more widely in low tonnage industry if the perception about their inflexibility could be abolished and proved to match the flexibility and versatility

criteria dictated by the inherent nature of the industry. This paper addresses the advantages offered by the PI reactors over conventional reactors in terms of fulfilling the basic demands of fast, exo-/ endo-thermic multiple reactions and also explores the additional dimensions of flexibility offered by the PI reactors. Figure 3 depicts inter-relationship that exists between the basic demands for a typical chemical reaction and improvements offered by using PI reactors over conventional reactors. Scale of the reactor and the characteristic mixing length scales decrease with the increase in intensification. This reduced characteristic mixing length scales could prove to be immensely helpful in creating the homogeneous molecular scale environment at the rate demanded by the chemical reaction. A trade-off between the intensity of mixing offered by the PI reactor and favourable hydrodynamics for the multiphase reactions might be required in some cases.

Drastic reductions in the throughput and the size achieved with the PI reactors compared to conventional reactors can be utilized favourably to achieve higher degree of flexibility by configuring and operating them in novel ways. PI reactors can be configured in a number of different ways which is not conceivable with conventional reactors. The PI reactors can also be operated in regimes impossible with conventional reactors due to substantially small reacting inventories and much more robust construction. These two novel and additional flexibility dimensions over and above the flexible design bears great potential to make PI reactors as flexible or probably more compared to conventional reactors. However, these three aspects of flexibility are not independent of each other and are likely to have a major influence on the overall flexibility. The importance of flexible design for PI reactors can still not be underestimated and suggestions have been made to design them in more flexible ways. Suggestions have also been made about exploiting the additional configuration and operation flexibility to improve the overall flexibility of PI reactors having tubular/ in-passage flow channels of meso- or micro-scales. They are also equally applicable to any PI reactor.

Flexibility by Design

PI reactors with inherent flexibility are highly desirable as they could adjust themselves to cope with change in demands and tasks. They could also offer higher degree of tolerance to disturbances or uncertainties associated with the processing. Some of the degrees of freedom available to design flexible PI reactors are listed in Figure 4. It could also be possible to design PI reactors that can be readily tailored to meet requirements of the given reaction with the use of adjustable parameters. Level of independency to adjust these parameters is important as the effects are very much interwoven. This independence could also achieve decoupling between heat transfer, mass transfer and hydrodynamic regime to suit the needs of certain reaction schemes.

Flexibility by Configuration

It is possible to derive different types of useful configurations using similar or different types of PI reactors to meet specific demands of reaction schemes over and above offered by the flexible design. Two of such plausible configurations have been illustrated in Figure 5.
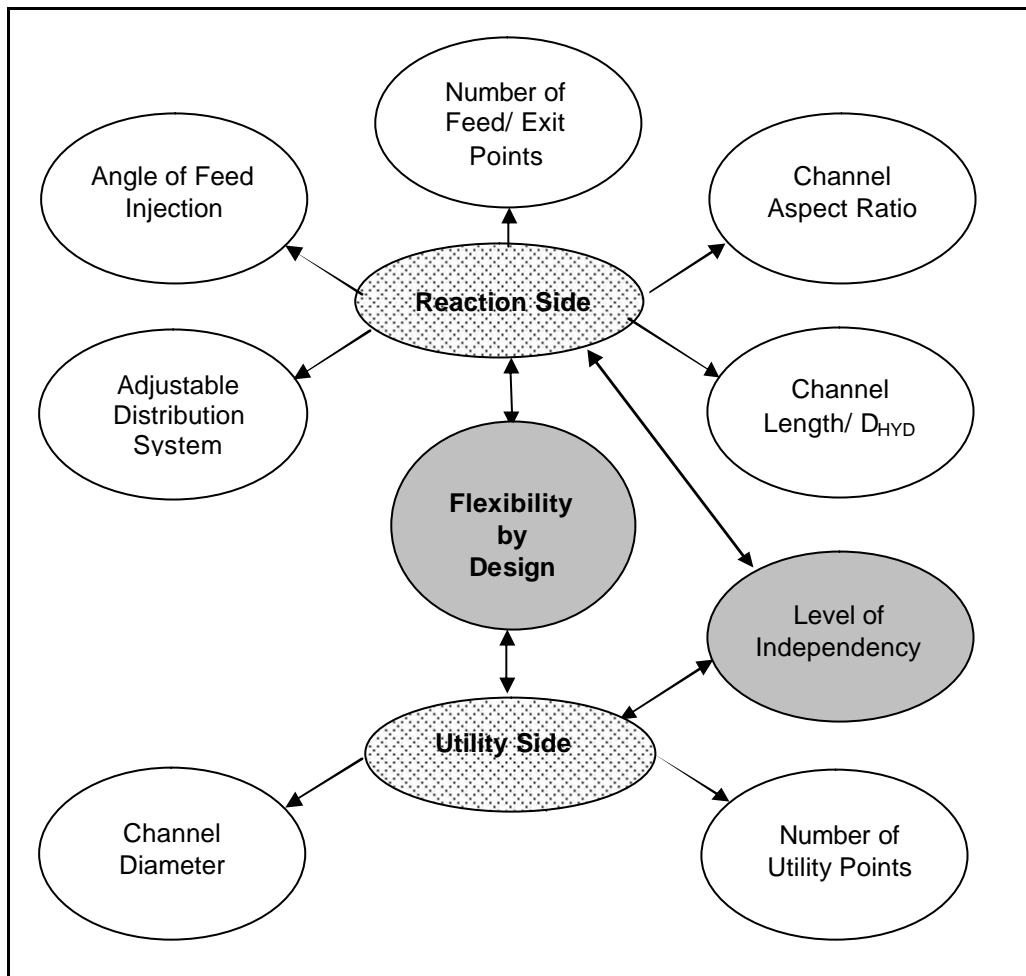
Figure 4 Flexibility by design

The configuration shown in Figure 5a could be used to carry out reactions requiring smaller mixing time compared to that offered by the reactor itself. This can be achieved by configuring the reactors to offer simultaneous hydrodynamic and geometric focusing and thus reduced mixing time. Both hydrodynamic and geometric focusing are regarded as common means to reduce the mixing time in laminar mixers (Hessel et al., 2003). The method of reducing the width of one fluid at the expense of increasing the width (flow) of the other is known as the hydrodynamic focusing. The method of reducing the width of one fluid by means of geometry restriction is called the geometric focusing. Hessel and co-workers (2003) and Knight and co-workers (1998) have achieved mixing times in the range of milliseconds down to microseconds using the combination of hydrodynamic and geometric and the hydrodynamic focusing, respectively. This is often required for reactions involving viscous and non-Newtonian fluids where viscosity increases with the progress of reaction and the mixing time has to be maintained same along the length of the reactor. The method of achieving focusing by configuration compared to the use of focused equipment provides greater degree of adjustability to suit the reaction requirements by using or bypassing the intermediate layers. By using the configuration shown in Figure 5b any variable residence time could be achieved while retaining the same flow pattern. Phoenix Chemicals, UK has successfully built a continuous equipment to carry out hydrolysis of ester product in aqueous environment using similar arrangement (Crystal Window, Issue No. 8, December 2003).

Another important flexibility offered by these arrangements is about introduction of the reactants and the capability to intensify mixing. All the reactants can be introduced at once at the first reactor layer or one of the reactant can be divided into number of portions and introduced separately at each layer to meet the concentration & temperature profile or hydrodynamics criteria depending on the reaction under consideration. Multi-step reactions involving use of different reactants can also be carried out in one go using the availability of multiple feed positions.
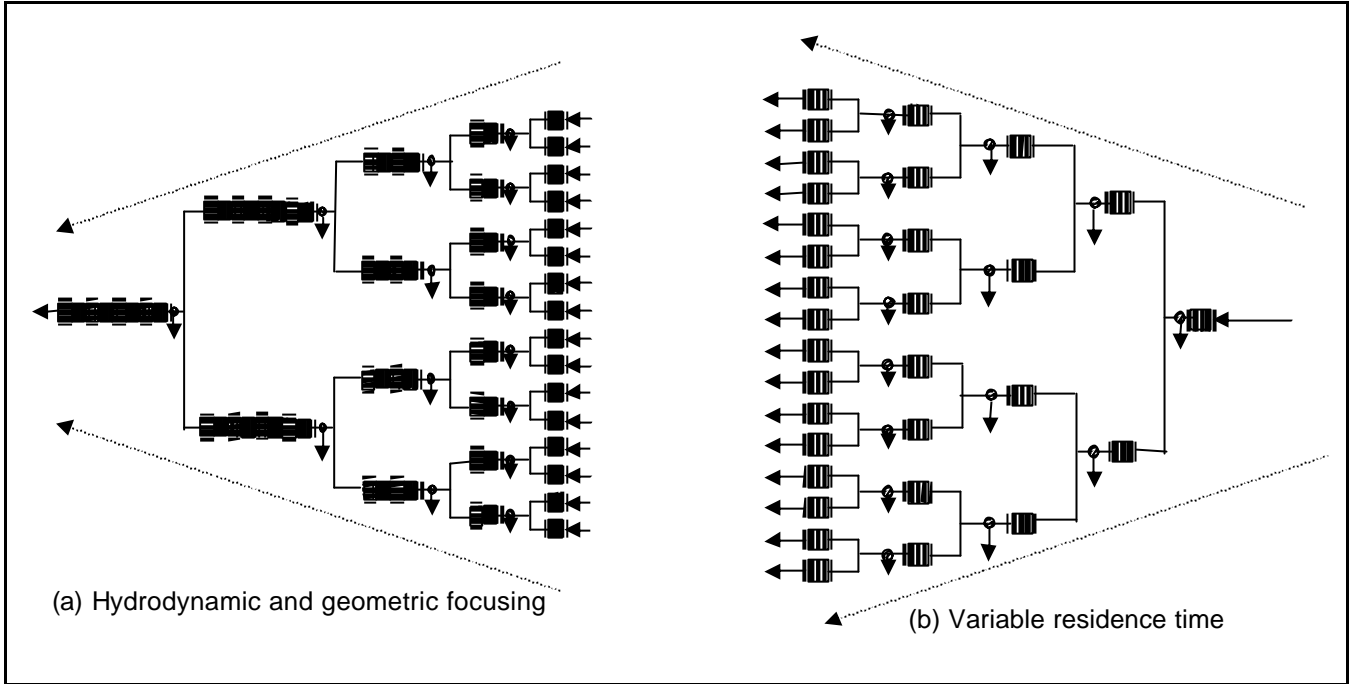

(a) Hydrodynamic and geometric focusing

(b) Variable residence time

Figure 5 Flexibility by configuration

Flexibility by Operation

Increased level of flexibility compared to that offered by the flexible design and configuration can be obtained by operating the equipment in different ways. Comparatively very small reactive inventories and ability to precisely control the progress of the reaction offers an extended range of process variables such as temperature, concentration and pressure compared to that offered by conventional reactors. Diverse conventional modes of operation such as semi-batch, continuous operation with or without recirculation can readily be obtained with PI reactors configured and operated in appropriate manner.

Figure 6a illustrates the use of adjustable volume recycle loop and addition of one of the reactants in multiple portions. The operation in this way could transform the reactor with single feed position into a reactor almost equivalent to one with multiple feed points. This method of operation can provide flexibility of hydrodynamic focusing, mixing and control over hydrodynamic regime. As shown in Figure 6b the reactant B can be added at the predetermined positions and more than one utility can be used to control the concentration and temperature profiles along the length of the reactor.
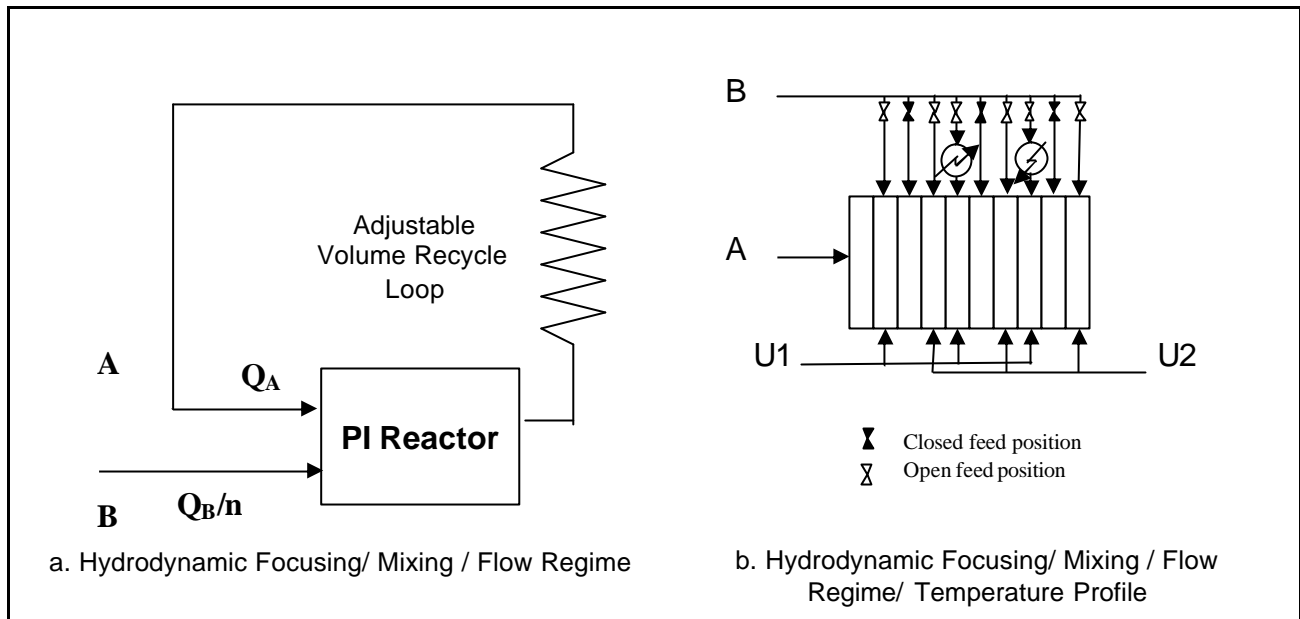
a. Hydrodynamic Focusing/ Mixing / Flow Regime

b. Hydrodynamic Focusing/ Mixing / Flow Regime/ Temperature Profile

Figure 6 Flexibility by Operation

Pragmatic Mixing Model

As discussed above, it is possible to achieve flexible and improved mixing characteristics with the PI reactor. However, close match between the mixing characteristics of the PI reactor and the demands of the reaction is still the most important factor determining the product distribution for the complex multiple reactions. In order to achieve the best possible product distribution for the given reaction, it is of prime importance to identify the possible design, configuration and operating regime options offered by the PI reactor beforehand. Without having this capability of identifying the options in the early stages of decision making process, the flexibility and improved mixing characteristics offered by the PI reactor can not be utilised at the maximum and the results thus obtained could undermine the true potential of the PI reactor. To assist in the process of identifying the options at the early stages of decision making, it is vital to have a consistent and established mixing model.

A pragmatic mixing model based on the analysis of the experimental results reported in the literature so far for the fast multiple reactions with both the turbulent and laminar flow reactors has been developed for this purpose. Another purpose of this model is to present experimental results reported in the literature in a concise and more understandable manner. This model does not involve any quantitative prediction of the product distribution unlike many other mixing models available in the literature; however, it does use the correlations proposed for estimating the meso- and micro-mixing time scales for the reactor (Baldyga & Bourne, 1989; Baldyga, Bourne, & Hearn, 1997; Ottino, 1994; Rozen, Bakker, & Baldyga, 2001; Villermaux, Falk, & Fournier, 1994). The model can be used to explain the results obtained by different mathematical models proposed in the literature. The model can identify the controlling mixing mechanism, namely micro-, meso- or macro-scale mixing, for the given reaction, reactor and operating conditions. The model can then be used to explore the possibilities that exist to shift the given reaction to micro-

scale controlled mixing for the given reactor and reaction in order to achieve better product distribution.

The key suggestion of this model is that the use of multiple feed points either across the cross section or the length of the reactor without intermingling of the reaction zones can have major improvement in the product distribution. According to the model the overall mixing time (τ_M) is inversely proportional to the number of feed points used to introduce the second reactant(s) (n_F) in to the primary reactant flow.

$$t_M \, a \, \frac{1}{\left(n_F\right)^K}$$

Where, K is the constant dependent on the mixing mechanism and geometry of the reactor.

This dependence of the overall mixing time on the number of feed points has been observed in the cases of both the turbulent as well as laminar reactors and have been reported in the literature. The availability of the multiple feed points and also their independent control to feed the second reactant(s) can have positive influence on the reactor's flexibility to cope with the mixing requirements of different reactions. However, the upper limit on the number of feed points that can be used is highly dependent on the geometry of the reactor; second reactant feed point location and orientation, apart from the mixing mechanism. Use of the multiple feed points could also provide the flexibility towards maintaining desired concentration and temperature profiles across the length of the reactor as discussed before. Feed points located along the length of the reactor could be used to introduce different reactants as the reaction progresses for multiple sequential reactions in a single piece of reactor or as exit points to match residence time requirements of some of the reactions.

Some of the key observations from the literature that suggest the validity of the proposed mixing model have been discussed here. Use of multiple feed points across the cross section of the reactor for single and multiphase multiple reactions have been widely studied for semi-batch (Baldyga & Bourne, 1992; Baldyga, Bourne, & Yang, 1993; Bourne & Hilber, 1990; Paul & Treybal, 1971) and turbulent tubular reactors (Baldyga & Bourne, 1989; Baldyga, Bourne, & Hearn, 1997; Bourne & Maire, 1991; Bourne & Tovstiga, 1988; ETSU, 2001; Li & Toor, 1986; Phillips, Lauschke, & Peerhossaini, 1997; Toor, 1975). These studies have shown improvements in the product quality with the use of multiple feed points over a single feed point, mainly due to intensified mixing. The critical feed time was reduced by the same factor as number of feed points for semi-batch STRs. Apart from the above reactions many multiple reactions such as, co-dimerization of propene and butane, chlorination of propene to allyl chloride, sulfuric acid alkylation of iso-butane, hydroprocessing of oils and polymerisation of ethene are being carried out in reactors with multiple feed injections at industrial scale to achieve better selectivity or conversion (Krishna & Sie, 1994). For laminar reactors, use of multiple feed points to feed the secondary reactant(s) has the potential to result into hydrodynamic focusing of the second reactant and thus intensified mixing (Hessel et al., 2003).

The main objective of any scale-up exercise is to achieve constant product distribution at the production scale. Even small increase in the impurity levels in the product

distribution on scale-up might make the product unacceptable for many of the products in low tonnage industry. The primary function of the development chemist or engineer, therefore, is to determine for each reaction whether or not special design considerations are required. Availability and the use of multiple feed points to achieve efficient mixing and to match the overall mixing time with the reaction demands provides an additional degree of freedom to achieve successful scale-up of the given reaction scheme. However, as stated before the upper limit on the use of number of feed points depends on number of factors including the geometry of the reactor.

Conclusion

Benefits of using PI reactors over conventional reactors such as STR to carry out fast, exo-/ endo-thermic and complex multiple reactions have been highlighted. The term flexibility in context of low tonnage process industry and the necessity of the flexible PI rectors to match the demands of processes carried out in such industry has been explained. Factors responsible for the lack of enthusiasm about PI reactors in general at the industrial scale have also been outlined. Some of the key aspects of flexibility for PI reactor at large and tubular/ in-passage flow PI reactors in specific have been identified here.

As has been shown, it is possible to configure and operate PI reactors to derive additional flexibility over and above that offered by its design. However, designing flexible or adjustable PI reactors is the most important step, as the flexibility offered at this level is likely to determine the level of flexibility that can be achieved at other two levels. A judicious blend of these three levels of flexibility can enable PI reactors to carry out a range of complex multiple chemical reactions having different basic demands. However, important questions including how to use flexible design, configuration and operation offered by the PI reactors to meet the demands of the given set of reactions still need to be addressed.

Importance of a reliable mixing model for PI reactors has been stressed upon. Development of a pragmatic mixing model based on experimental evidence has been discussed. Its validation with the help of experimental results reported in the literature for both turbulent and laminar reactors have been exhibited. Its usefulness for the scale-up of the conventional reactors has also been highlighted.

An experimental setup have been designed and constructed at the chemical engineering department, UMIST, UK to verify the proposed mixing model and exhibit the different levels of flexibility for the range of PI reactors. Experimental proof of both the aspects is likely to pave a way in increasing the acceptance level of PI reactors in low tonnage industry.

Reference

Baldyga, J. & Bourne, J.R. (1989). Simplification of micromixing calculations. II. New applications. *Chemical Engineering Journal (Amsterdam, Netherlands)*, 42(2), 93-101.
Baldyga, J. & Bourne, J.R. (1992). Interactions between mixing on various scales in stirred tank reactors. *Chemical Engineering Science*, 47(8), 1839-1848.

Baldyga, J., Bourne, J.R., & Yang, Y. (1993). Influence of feed pipe diameter on mesomixing in stirred tank reactions. *Chemical Engineering Science*, 48(19), 3383-3390.

Baldyga, J., Bourne, J.R., & Hearn, S.J. (1997). Interaction between chemical reactions and mixing on various scales. *Chemical Engineering Science*, 52(4), 457-466.

Bourne, J.R. & Tovstiga, G. (1988). Micromixing and fast chemical reactions in a turbulent tubular reactor. *Chemical Engineering Research and Design*, 66(1), 26-32.

Bourne, J.R. & Hilber, C.P. (1990). The productivity of micromixing-controlled reactions: Effect of feed distribution in stirred tanks. *Chemical Engineering Research and Design*, 68(A1), 51-56.

Bourne, J.R. & Maire, H. (1991). Micromixing and fast chemical reactions in static mixers. *Chemical Engineering and Processing*, 30(1), 23-30.

ETSU (2001). Compact integrated reactor heat exchangers for process intensification future practice report 82. Harwell, Didcot, Oxfordshire.

Hessel, V., et al. (2003). Laminar mixing in different interdigital micromixers: I. Experimental characterization. *AIChE Journal*, 49(3), 566-577.

Jones, D.O. (1996). Process intensification of batch, exothermic reactors: 1-29. Surrey: Complied by W S Atkins Safety and Reliability for Health and Safety Executive, UK.

Knight, J.B., et al. (1998). Hydrodynamic focusing on a silicon chip: Mixing nanoliters in microseconds. *Physical Review Letters*, 80(17), 3863-3866.

Krishna, R. & Sie, S.T. (1994). Strategies for multiphase reactor selection. *Chemical Engineering Science*, 49(24A), 4029-4065.

Li, K.T. & Toor, H.L. (1986). Turbulent reactive mixing with a series-parallel reaction: Effect of mixing on yield. *AIChE Journal*, 32(8), 1312-1333.

Ottino, J.M. (1994). Mixing and chemical reactions. A tutorial. *Chemical Engineering Science*, 49(24A), 4005-4027.

Paul, E.L. & Treybal, R.E. (1971). Mixing and product distribution for a liquid-phase, second-order, competitive-consecutive reaction. *AIChE Journal*, 17(3), 718-724.

Paul, E.L., Atiemo-obeng, V.A., & Kresta, S.M. (Eds.) (2004). Handbook of industrial mixing-science and practice: Wiley Interscience.

Phillips, C.H., Lauschke, G., & Peerhossaini, H. (1997). Intensification of batch chemical processes by using integrated chemical reactor-heat exchangers. *Applied Thermal Engineering*, 17(8-10), 809-824.

Rozen, A., Bakker, R.A., & Baldyga, J. (2001). Application of an integral method to modeling of laminar micromixing. *Chemical Engineering Journal (Amsterdam, Netherlands)*, 84(3), 413-428.

Toor, H.L. (1975). Chapter 3, The non-premixed reaction: A + B = Products. In R.S. Brodkey, *Turbulence in mixing operations* (p. 121-166). New York: Academic Press.

Villermaux, J., Falk, L., & Fournier, M.C. (1994). Potential use of a new parallel reaction system to characterize micromixing in stirred reactors. *AIChE Symposium Series*, 299(INDUSTRIAL MIXING TECHNOLOGY), 50-54.

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[*] Pictures have been used here only to represent the scale of equipment more clearly and have been taken from the websites http://www.bhrgroup.co.uk/pi/flexreactor.htm, http://www.bhrgroup.co.uk/pi/hexreactor.htm, http://www.imm-mainz.de.