## Process Intensification

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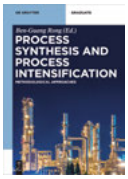


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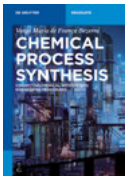


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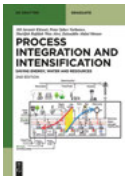


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# Process Intensification

Design Methodologies

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# 1 Generalities about process intensification

**Abstract:** Process intensification (PI) can bring significant reductions not only in the equipment requirement but also in the associated energy demands, the inventory of hazardous materials, and waste streams handling. Although most of these goals are not new to chemical engineering, PI goes beyond the traditional approach, since it focuses on designing innovative process and equipment, as miniaturized units, multifunctional systems, hybrid separations, as well as in the integration of alternative energy sources. This chapter introduces the general principles of PI, comparing the different types of intensified processes. It discusses the potential exploitation of these new technologies and seeks to identify the major barriers for its industrial application.

**Keywords:** process intensification, miniaturized units, process design, energy savings, sustainable processes

## 1.1 Introduction

During the past few decades, process intensification (PI) has been gaining interest in the academic and industrial fields, since the implementation of the related methodologies allows the development of more sustainable processes, by the reduction of several unit operations to intensified units in which the same process can be carried out. There is a great variety of definitions for PI and the concept has evolved over the years, from unit miniaturization to integrated approaches for process enhancement. PI can be defined in terms of process shrinking, as a *strategy of reducing the size of a chemical plant needed to achieve a given production objective* [1] or in terms of innovation, as *an integrated approach for process and product innovation in chemical research and development* [2].

PI can be considered as any activity that integrates one or more of the following: (i) smaller equipment for given throughput, (ii) higher throughput for given equipment size or a given process, (iii) less holdup for equipment or less inventory for the processing of certain materials for the same throughput, (iv) less usage of utility materials and feedstock for given throughput or equipment size, and (v) higher performance for given unit size [3].

Research efforts on PI can be categorized into two areas: (i) design of intensified equipment, which includes novel and miniaturized devices, and (ii) the

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development of process-intensifying methods, focused on the synthesis of integrated and/or multifunctional units, within whole processes. The design of new devices includes microreactors, supersonic reactors, rotating devices (reactors and mixers), and microchannel heat exchangers, among others. The development of new intensified processes has been focused on multifunctional units (reactive-separation or reaction-heat transfer) and hybrid separations. Moreover, the potential benefits of using alternative sources of energy are also an opportunity area in PI, for instance in those systems that make use of ultrasound, microwaves, or electric fields [4].

## 1.2 PI principles

The differences among PI, Process System Engineering (PSE), and Process Optimization (PO) have been described in literature [5, 6]. As stated in such reviews, even if there is a significant similarity among these areas, each of them involves particular aims. PO looks for performance improvement by implementing existing concepts, while PI and PSE involve the selection of design and processing methods. PI is based on the development of new concepts, including the synthesis of innovative process stages and the design of novel equipment. In order to clearly identify the PI fundamentals, four general principles of PI can be stated [6]:

1. Maximize the effectiveness of intra and intermolecular events.
2. Give each molecule the same processing experience.
3. Optimize the driving forces at every scale and maximize the specific surface area to which these forces apply.
4. Maximize the synergistic effects from partial processes.

Furthermore, during the PI design, the relevance of the scale level (molecular scale, mesoscale, and macroscale) has been emphasized by describing four approaches, associated with the following domains: spatial, thermodynamic, functional, and temporal.

1. Spatial domain refers to the importance of well-defined structures or environments that allow maximization of process synergy (i.e., activity and selectivity of a certain catalyst are highly dependent on its geometrical structure).
2. The thermodynamic domain is focused on the optimum use of energy, considering alternative forms of energy and/or ways for its transfer.
3. In the functional domain, PI looks to maximize the synergy from different units, processes, or forms of energy, bringing multiple functions within a single component (i.e., reactive distillation units).
4. Temporal domain considers the manipulation of time scales of different processes in order to significantly reduce the processing times or process periodicity. For

example, by using multitasking units or by switching from batch to continuous processing.

It is important to emphasize that during the synthesis of intensified process, the challenge is not only centered on the design of compacted units but also on how to guarantee their functionality. Taking into account process objectives, chemical processing can be described by the elementary process function of each unit operation or by the related process phenomena. These different phenomena can be classified into eight categories: (i) mixing, (ii) phase contact, (iii) phase transition, (iv) phase change, (v) phase separation, (vi) reaction, (vii) energy transfer, and (viii) stream dividing [7].

As a complementary perspective, PI might be categorized in two main groups: (i) local intensification and (ii) global intensification. Local intensification aims to use PI techniques to improve the efficiency of a single unit in isolation from the whole process. On the other hand, global intensification considers the performance of the whole process, taking into account the interactions among all units within the system [8].

## 1.3 Devices and equipment in PI

From its basic definition, PI is characterized by the development of novel equipment, wherein the miniaturization and multifunctionality are fundamental targets. PI equipment can be divided into two categories: (i) equipment involving chemical reactions and (ii) equipment for operation not involving reactions.

Tables 1.1 and 1.2 summarize the emblematic equipment in PI reported in literature [4, 5], their application, advantages, and disadvantages, aiming to illustrate their potential applications.

In addition, there is a great variety of multifunctional systems that, compared to those traditionally used, are expected to substantially improve the process performance in terms of processing time, energy requirements, or process selectivity. For instance, the implementation of internally heat integrated distillation columns and thermally coupled distillation systems allows high energy savings compared to conventional distillation columns [9]. Multifunctional and multiphase reactors that can incorporate not only reaction and heat transfer but also phase transition or separation, offer advantageous conditions for complex reactive systems [10]. Reactive distillation, a technology that incorporates both phase separation and chemical reaction in a single column, is, so far, the most important industrial application of PI [11]. Other hybrid systems such as reactive absorption, combining absorption of gases with chemical reactions in the liquid phase; reactive extraction, wherein the reaction enhances the capacity of the solvent; reactive crystallization, combining

**Table 1.1:** Equipment for PI for reacting systems [4, 5].

| Equipment | Applications | Advantages | Disadvantages |
|---|---|---|---|
| Static mixer reactor | Useful in the polymer industry for melt viscosity adjustments, among other applications. | Good mixing and radial heat transfer characteristics. | Low specific geometrical area and high sensitivity to obstruction by solids. |
| Monolithic reactor | For partial oxidations of hydrocarbons, catalytic combustion, and removal of soot from diesel engines. | Negligible pressure drop, high geometrical area, improves selectivity as reduces mass transfer resistances. | Difficult heat removal due to the absence of radial dispersion. |
| Microreactor | Different reaction systems as fluorination, chlorination, nitration, sulfonation, biodiesel production, enzymatic reactions, and vitamin precursor synthesis. | High heat transfer rates (recommended for highly exothermic processes). Very low volume/surface area ratios (suggested for process involving toxic or explosive components). Allow precise control of operating conditions. | In some operating conditions, catalyst deactivation may occur relatively fast. Formation of solids increases pressure drop and may block reactor channels. |

nucleation and crystal growth with chemical reactions, among others, are few examples of intensified technologies that may drastically transform the challenges in process engineering in the coming years [5].

## 1.4 PI methodologies

PI is focused on designing novel equipment or developing new conceptual processes, as well as on its implementation for retrofitting existing chemical plants. Designing intensified processes implies the definition of a number of degrees of freedom, which is not a straightforward task because of the large number of alternatives [12]. Given the complexity of the problem, several methodologies for designing intensified process have been developed during the past decade, including heuristic-based approaches for conceptual design, process screening via simulation, and sophisticated mathematical problem formulations.

Literature on the development of intensified process is wide-ranging, and different approaches aim to solve different problems. For instance, thermodynamic

**Table 1.2:** Equipment for PI for nonreactive systems [4, 5].

| Equipment | Applications | Advantages | Disadvantages |
|---|---|---|---|
| Static mixer | In plastic industry for blending of plasticizers, stabilizers, colorants, flame retardants, etc. In food factories can be used to mix food formulations. In chemical industry for gas mixing prior to processing. | Divide and redistribute streamlines using only the pumping energy of the flowing fluid. Produce a complex vortex system in which concomitant phenomena simultaneously enhance mass and heat transfer. | There is lack of information on the spatial mixing quality, which can result in underestimation or overestimation of mixing times. |
| Compact heat exchanger | As peripheral equipment in microreactors. | Exhibit high heat fluxes and convective heat transfer coefficients. | Limited choice, particularly for high pressure. Susceptibility to fouling. |
| Rotating packed bed | Deaeration of flooding water, separation processes, and reaction systems. | High centrifugal forces intensify momentum and mass transfer. | Compared to conventional columns requires additional power and maintenance for the rotating system within the range of power required by the feed and reflux pumps. |
| Centrifugal absorber | Ion exchange and absorption processes. | Centrifugal field enables use of very small absorbent particles with short contact times. | Significant PI is achieved only in the liquid side resistance, controlled by mass transfer. |

characteristics of the system may be utilized to generate feasible flowsheets to fulfill the design task. Holtbruegge et al. [13] presented a systematic procedure for the conceptual design of intensified processes, wherein the boundaries for the design task and the process indicators must be defined in terms of thermophysical properties. Their method uses thermodynamic insights to create a group of promising flowsheet options, and then use mathematical algorithms for their optimization. They divided process design into three steps: (i) system identification and analysis, (ii) generation of flowsheet options, and (iii) evaluation of flowsheet options. At the same time, generation of flowsheets considers three levels: (i) identification of reaction/separation techniques, (ii) detailed investigations of separation steps/techniques, and (iii) generation of flowsheets.

This approach allows the generation of a variety of promising flowsheet options, based on thermodynamic fundamentals, and provides a tool not only for the process synthesis but also for a deeper understanding of intensified techniques and processes.

Regarding the development of PI for process retrofitting, some synthesis techniques and design concepts have been evaluated, with the aim of guaranteeing the sustainability of existing plants. In this field, Niu and Rangaiah [14] presented a heuristic-based approach for retrofitting, via PI. It consists of four steps: (i) the first is to create a base case analysis, where the retrofit target is defined by using selected metrics, which can include utility costs, component losses, conversion of reactants, and selectivity of products. In this first stage, the objective is to identify the main contributors for each metric; (ii) the second step focuses on generating improved solutions, by optimizing the operating conditions, without capital investment (if no improved solution is attained, the original process remains as a basis); (iii) the third step considers the generation of integrated solutions; and (iv) the fourth step involves the comparison of the retrofit solutions for decision-making.

Currently, process retrofitting through PI usually involves the optimization of operating conditions or process integration, rather than replacing existing equipment with novel intensified units.

Besides, in order to quantitatively analyze the feasible alternatives, new modeling and computer-aided tools to perform multiobjective optimization have been developed by several authors. Ponce-Ortega et al. [3] proposed a general mathematical programing formulation for PI, considering the use of existing units and the implementation of additional units. These authors take into account two different PI cases: (i) unit intensification and (ii) plant intensification. In the first case the goal is to minimize the unit size for a given throughput or to maximize the performance for given size. For plant intensification, the objective is to simultaneously intensify the whole process, minimizing the process inventory, utilities, and feedstock, or maximizing the process throughput.

The methodologies previously discussed are a few examples among a number of contributions on PI development. It is evident that the field presents a high grade of development and that will certainly continue to grow in the coming years.

## 1.5 PI safety and control properties

As has been noted, the benefits of PI lie in cost reductions and compactness. In particular, it makes it possible to increase production capacity per unit of processing area, unlocking greater opportunities through sustainable growth and innovation. Furthermore, as PI may substantially reduce the process size, by implementing smaller equipment and inventories, process safety, and control properties can also been improved.

Several processes, mainly those in the chemicals and petrochemicals industries, involve the production, handling, and use of large quantities of hazardous materials. For hazardous processes, PI encourages the inventory of dangerous materials, and the consequences of processes failures, to be significantly reduced; thus, increasing intrinsic plant safety. From a simple point of view, the best way to deal with the problem is not to have it in the first place [15]. This has been also been pointed out by Kletz [16], through the phrase "what you don't have can't leak!". Significant approaches to the design of inherently safer processes and plants could be grouped into four major strategies [16, 17]:

1. Minimize, use small quantities of hazardous substances.
2. Substitute, replace material with a less hazardous substance.
3. Moderate, use less hazardous conditions, a less hazardous form of a material, or facilities, which minimize the impact of a release of hazardous material or energy.
4. Simplify, design facilities that eliminate unnecessary complexity and make operating errors less likely, and which are forgiving of errors which are made.

According to Etchells [18], some of the safety benefits that may arise from PI are:

- In some cases, the number of process operations can be reduced, leading to fewer transfer operations, and less pipework (which can be a source of leaks).
- It may be easier to design a smaller vessel to contain the maximum pressure of any credible explosion, so that further protective devices, such as emergency relief systems, are not needed (or the duties placed upon them are less onerous).
- Many incidents are associated with process transients such as startup and shutdown. These are reduced during continuous (and intensified) processes.
- For exothermic reactions, the heat evolution should be much less variable than in batch reactions, and should be easier to control. Furthermore, the enhanced specific surface area of intensified plant makes heat transfer easier. Certainly, very few runaway reactions occur in continuous processes (although there have been some notable exceptions [19]).

Thus, the applications and methods of PI are various, and therefore it is dangerous to assume that safety is always improved through intensification, even though this is true in many cases [20].

## 1.6 Sustainability

Sustainability has become a key concept for new processes and product development that requires a multidisciplinary approach, in which the sustainable development of energy systems accounts for six goals [21]:

1. Prosperity (economy) presenting a strong, inclusive, and transformative economy.

2. Justice, promoting safe and peaceful societies and strong institutions.
3. Partnership, to catalyze global solidarity for sustainable development.
4. Planet (environment), to protect ecosystems for societies and future generations.
5. People (social), to ensure healthy lives, knowledge, and the inclusion of women and children.
6. Dignity, to end poverty and fight inequality, which should definitely not be the last one.

Yong et al. [22] have summarized the future trends of the sustainable development of energy systems in three main areas: (i) higher efficiency and waste reduction of biofuel production, (ii) $CO_2$ removal and conversion, and (iii) process integration.

As discussed elsewhere [21, 22], the scope of PI is becoming much wider, considering the integration of not only heat and power but also water, safety, and other aspects of processes.

Environmentally, Reay et al. [15] have noticed that the most telling impact of PI is likely to be in the development of reactor designs; since the reactor dictates both the product quality and the extent of the downstream separation and treatment equipment, during any chemical process. Thus, the development of reactor designs enables PI to be beneficial for the energy use, impacting on the environment, through the delivery of a high-quality product, without extensive downstream purification sequences.

## 1.7 Main drawbacks for PI implementation

Stankiewicz and Moulijn [23] recognize some obstacles for PI implementation. Currently, the chemical industry is primarily focused on trade strategies, looking for improving their market visibility by merging complementary product portfolios of different industries, more than by implementing more fundamental changes in processing via R&D. Furthermore, most R&D efforts are focused on the development of new products (new materials and specialty products) rather than new processing methods. This last drawback is directly associated to the lack of familiarity of process engineers with the latest developments in PI and emerging technologies implementation. In addition, much novel equipment and many devices have not yet been assessed on an industrial scale, mainly because of the nature of emerging technologies and processing methods, with drastic differences between them, such that standard methodologies for their scaling up are still under development.

Furthermore, from a safety point of view, in some cases, hazards may remain, or new ones may be created, in the development of PI processes. According to Etchells [18], some potential problems may include:

- Some PI technologies require high-energy inputs, e.g., from microwaves, high voltages or electromagnetic radiation, or require to be operated at higher temperatures and pressures. Although expertise associated with the handling of high-energy sources is present in some industries, the new technology may also bring less familiar groups into contact with this hazard.
- The processes may be more complex or call for more complex control systems, and safety may suffer.
- As the residence time for many intensified processes will be of the order of seconds rather than hours, the subject of control and monitoring has to be addressed. It has been suggested that process control may become easier but more importantly, as the system is smaller, it may become more responsive to changes in process conditions. In some cases, it may mean that the process is unsuitable, or that new and novel techniques are needed to control them and these may not yet be available.
- In some cases, process pipework may be more complex, with a higher potential for equipment failure or operator error.
- Intensified reactors have the potential to significantly enhance reaction rates as a result of the improved mixing. This could lead to a much greater rate of energy release than in traditional reactors and, in some cases, may result in a change in the reaction chemistry.
- Rotating equipment may not be suitable for friction-sensitive substances (i.e., substances that can either deflagrate or detonate due to friction). Certainly the hazard of ignition needs to be addressed.
- Where fouling can occur on complex heated surfaces, then thermally unstable materials can overheat, possibly leading to high pressures being generated.

As previously discussed, PI has been considered as a strategy for reducing the inventory of hazardous chemicals contained inside the process, so that the safety and environmental consequences are reduced. However, as process robustness is defined in terms of process ability to tolerate significant disturbance from its surroundings, designing compacted plants may represent potential operational problems [17, 24].

## 1.8 PI assessment examples

It is clear that in order to replace conventional units with more efficient ones within the existing processes, it is necessary to verify their implementation feasibility, cost-effectiveness, controllability, and safety properties. Nowadays, several approaches are being developed to provide decision-making tools, considering both quantitative and qualitative elements. A couple of examples of “fast assessment” tools reported in literature are presented in this section [12, 20].

**Table 1.3:** Comparison of design variables for two intensified processes for obtaining biodiesel. Adapted from Rivas et al. [12].

| Design parameters | Reactive Distillation (RD) | Reactive Absorption (RA) |
|---|---|---|
| **Column** | | |
| Number of stages | 15 | 15 |
| HETP (m) | 0.5 | 0.6 |
| Column diameter (m) | 0.4 | 0.4 |
| Column volume ($m^3$) | 0.94 | 1.13 |
| **Heat exchangers duty (kW)** | | |
| Fatty acid heaters | 95 | 81 and 27 |
| Methanol heaters | 8 | 65 |
| Biodiesel cooler | 38 | 14 |
| Reboiler duty | 133 | 0 |
| Condenser/decanter duty | 72 | 77 |
| **Energy consumption as steam (E)** | | |
| Steam consumption (kg steam/ ton FAME) | 168 | 34 |

**Example 1.1** A simple method based on a weighted factor namely Intensification Factor (IF) can be used as decision-making element to compare different intensified processes [12]. Consider the Biodiesel production by integrated reactive technologies. In this case, biodiesel is produced by the reversible reaction of esterification of waste oils considering Reactive Absorption (RA) and Reactive Distillation (RD) processes. Table 1.3 summarizes the design variables of each intensified process [12].

It is clear that investment cost and energy requirements vary with the implemented technique. In order to compare both technologies, an intensification factor can be calculated as in Eq. 1.1.

$$IF = \prod_{i=1}^{n} \left( \frac{F_{bi}}{F_{ai}} \right)^{di} \tag{1.1}$$

Where $F$ is the evaluation criteria or factor, $b$ represents the new technology and $a$ the previous (or existing) technology. For instance, the $IF$ associated to the column cost is proportional to the ratio of columns volumes (V) with a scale exponent (Rivas et al. [12] reported a $d$ value of 0.85). Considering the sizing values reported in Table 3, $IF_{col}$ can be estimated as:

$$IF_{col} = \left(\frac{V_{RD}}{V_{RA}}\right)^{0.85} = \left(\frac{0.94}{1.13}\right)^{0.85} = 0.85 \tag{1.2}$$

The $IF_{hx}$ associated to the total exchangers cost is determined by the ratio of weighted heat load at power of 0.6

$$IF_{hx} = \frac{\sum_i^{RD} Q_i^{0.6}}{\sum_i^{RA} Q_i^{0.6}} = \frac{59.8}{51.8} = 1.15 \tag{1.3}$$

Where $Q_i$ is the heat load of each heat exchanger for the corresponding process (RD or RA). Finally, the *IF* for operating cost are computed as the ratio of steam consumption:

$$IF = \frac{E_{RD}}{E_{RA}} = \frac{168}{34} = 4.94 \tag{1.4}$$

Then, $IF_{total}$ can be calculated as

$$IF_{total} = \prod_{(i=1)}^{p} (IF_i)^{c_i} = (0.85)(1.15)(4.94) = 4.83 \tag{1.5}$$

Where p is the number of potential intensification strategies and the $c_i$ is a weigthening factor, if available info is limited or inexistent then $c_i$ takes a value of 1. For this case, as investment costs for columns and exchangers are relative similar for both processes and the operating cost are dominant, reactive absorption seems to be more cost-effective. Although this factor provides a simple method to evaluate different intensified processes, it must be weighted by experts in the field [12].

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**Example 1.2** Regarding safety on intensified processes, a simple way to evaluate how PI affects safety consists in developing a checklist using the concept of layers of protection [20]. Consider the case in which the oxidation reactor (bubble column) of the anthraquinone process is replaced by a tubular reactor with static mixers that enhance mass transfer.

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This unit replacement reduces the reaction volume to about one tenth of the conventional reactor. The main reason for this size reduction is the use of oxygen instead air. However, due to the fast oxidation, oxygen is rapidly consumed and it needs to be continuously fed to the reactor through several inlets. Furthermore, the reactor is very sensitive to certain process conditions. In order to compare both processes from a safety point of view, the criteria of the checklist are used and the obtained review is presented in Table 1.4 [20].

As can be observed from the check list, the intensified process are safer in three criteria, but become worse for five criteria. It is important to highlight that the final decision should consider that these criteria have different degrees of importance, such that, some additional quantitative measurements must be also considered [20].

Replace selected units in existing plants aiming intensifying the process, requires an in-depth analysis about the implications of its implementation. Different

**Table 1.4:** Effects on safety, if the bubble column is replaced by a tubular reactor. Adapted from Ebrahimi et al. [20].

| Safety criteria | Bubble column | Tubular reactor | Comparison between the systems | Effect |
|---|---|---|---|---|
| **1. Inherent safety layer** | | | | |
| Reaction route | | | | |
| Chemicals | Air | Oxygen | The flammable solvent has a lower ignition energy with oxygen than with air. | Negative |
| Process novelty | Traditional | Novel | Novelty reduces safety because of less experience. | Negative |
| **2. Passive layer** | | | | |
| Reactor type and geometry: | | | | |
| Complexity | Simple column | More complex | The intensified reactor has several gas feed points which makes it more complex. | Negative |
| Fluid hold-up | Liquid hold-up | Liquid hold-up about 10 times less. | Lower inventory reduces the risk. | Positive |
| Internal patterns | Channelling, axial dispersion | More regular | Flow pattern in the tubular reactor with static mixers is more regular with less axial dispersion. In the bubble column, channelling, axial dispersion, and irregular flow appear in a larger extent. | Positive |
| Surface to volume ratio | | Higher surface to volume ratio. | Intensified process has more capability to heat exchange. | Positive |
| Layout | Simple column | Tube elbows, several gas inlets. | Layout of the new reactor is more complex. The reactor tube has several elbows where liquid might be trapped at least in unusual conditions. | Negative |
| **3. Active layer** | | | | |
| Process control | | Several inlets to control | Control of several oxygen feed points has a risk of malfunction. | Negative |

criteria assessment for the process development decisions should be taken into account to guarantee that these new arrangements provide at least a similar performance than that the original.

## 1.9 Final remarks

Many advances have been made in terms of PI, engineering tools for innovative process design, and novel PI technology. Nevertheless, their industrial implementation is still limited, mainly due to the lack of standard methodologies for their scaling. As discussed previously, another important issue is the lack of familiarity of process engineers with the latest developments in PI and their implementation. To accomplish the skills necessary to design and implement PI for existing and new chemical plants, it is imperative that new chemical engineers embrace innovative approaches during their academic training; since, there is no doubt that PI will be an important key factor in supporting a sustainable future in the chemical engineering sector. In the following chapters, different PI strategies will be discussed in depth.

## References

[1] Cross, W. T., Ramshaw, C. Process intensification: laminar flow heat transfer. *Chemical Engineering Research and Design*, 1986, 64(4), 293–301.
[2] Becht, S., Franke, R., Geißelmann, A., Hahn, H. An industrial view of process intensification. *Chemical Engineering and Processing: Process Intensification*, 2009, 48(1), 329–332.
[3] Ponce-Ortega, J. M., Al-Thubaiti, M.M., El-Halwagi, M. Process intensification: New understanding and systematic approach. *Chemical Engineering and Processing: Process Intensification*, 2012, 53 63–75.
[4] Stankiewicz, A. I., Moulijn, J. A. Process intensification: Transforming chemical engineering. *Chemical Engineering Progress*, 2000, 96(1), 22–34.
[5] Keil, F., Process Intensification, *Reviews in Chemical Engeneering*, 2018, 34(2), 135–200.
[6] Van Gerven, T., Stankiewicz, A. Structure, Energy, Synergy, Time-The Fundamentals of Process Intensification. *Industrial & Engineering Chemistry Research*, 2009, 48(5), 2465–2474.
[7] Lutze, P., Babi, D. K., Woodley, J. M., Gani, R. Phenomena based methodology for process synthesis incorporating process intensification. *Industrial & Engineering Chemistry Research*, 2013, 52(22), 7127–7144.
[8] Portha, J. F., Falk, L., Commenge, J. M. Local and global process intensification. *Chemical Engineering and Processing: Process Intensification*, 2014, 84, 1–13.
[9] Vazquez–Castillo, J. A., Venegas–Sánchez, J. A., Segovia–Hernández, J. G., Hernández-Escoto, H., Hernandez, S., Gutiérrez–Antonio, C., Briones–Ramírez, A. Design and optimization, using genetic algorithms, of intensified distillation systems for a class of quaternary mixtures. *Computers & Chemical Engineering*, 2009, 33(11), 1841–1850.
[10] Utikar, R. P., Ranade, V. V. Intensifying multiphase reactions and reactors: strategies and examples. ACS *Sustainable Chemistry & Engineering*, 2017, 5(5), 3607–3622.

[11] Segovia-Hernández, J. G., Hernández, S., Petriciolet, A. B. Reactive distillation: A review of optimal design using deterministic and stochastic techniques. *Chemical Engineering and Processing: Process Intensification*, 2015, 97, 134–143.
[12] Rivas, D. F., Castro-Hernández, E., Perales, A. L. V., Van der Meer, W. Evaluation method for process intensification alternatives. *Chemical Engineering and Processing: Process Intensification*, 2018, 123, 221–232.
[13] Holtbruegge, J., Kuhlmann, H., Lutze, P. Conceptual Design of Flowsheet Options Based on Thermodynamic Insights for (Reaction–) Separation Processes Applying Process Intensification. *Industrial & Engineering Chemistry Research*, 2014, 53(34), 13412–13429.
[14] Niu, M. W., Rangaiah, G. P. Process retrofitting via intensification: a heuristic methodology and its application to isopropyl alcohol process. *Industrial & Engineering Chemistry Research*, 2016, 55(12), 3614–3629.
[15] Reay, D., Ramshaw, C., Harvey A., Process Intensificatio: Engineering for Efficiency, Sustainability and Flexibility. In: Process Intensification – An Overview. Butterworth-Heinemann Elsevier, Oxford UK, 2013, 27–55.
[16] Kletz, T. A., *Plant Design for Safety: A User-friendly Approach*. Taylor & Francis, NY, USA, 1991.
[17] Hendershot, D.C., (1997). Inherently safer chemical process design. *J. Loss Prev. Process. Ind*. 1997, 10, 51–157.
[18] Etchells, J.C., Process Intensification: Safety Pros and Cons. *Trans IChemE*, Part B, Process Safety and Environmental Protection, 2005, 83(B2): 85–89.
[19] Etchells, J.C., Why reactions run away. IChemE Symp. Series No 147, Hazards XIII Process safety-sharing best practice. IChemE, Rugby, UK, 1997, 361–366.
[20] Ebrahimi, F., Virkki-Hatakka, T., Turunen, I. Safety analysis of intensified processes, *Chemical Engineering and Processing: Process Intensification*, 2012, 52 28–33.
[21] Nemet, A., Varbanov, P.S., Kleme, J.J. Cleaner production, Process Integration and intensification, *Clean Techn. Environ. Policy*, 2016, 18: 2029–2035.
[22] Yong, J.Y., Kleme, J.J., Varbanov, P.V., Huisingh, D. Cleaner energy for cleaner production: modelling, simulation, optimization and waste management. J. *Clean Prod*. 2016, 111: 1–16.
[23] Stankiewicz, A. I., Moulijn, J. A. Process intensification. *Industrial & Engineering Chemistry Research*, 2002, 41 (8), 1920–1924.
[24] Luyben, W. L., Hendershot, D. C. Dynamic disadvantages of intensification in inherently safer process design. *Industrial & Engineering Chemistry Research*, 2004, 43(2), 384–396.

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# 2 Microreactors: Design methodologies, technology evolution, and applications to biofuels production

**Abstract:** In the past few years, the application of process intensification strategies has attracted attention, since it leads to the development of production processes with reduced energy consumption and increased efficiency. In the production processes, reactors constitute a key element for the conversion of raw materials to products; therefore, the efforts have been focused on the proposal of novel and improved equipment. In particular, microreactors have small size, minor residence times, an efficient mass and heat transfer, and high yields. This technology has been applied for the generation of several products, such as organic compounds, nanoparticles, polymers, among others. In particular, the application of microreactors for the production of biofuels is a powerful technology to obtain competitive carburant, both technically and economically. Thus, in this chapter, a revision of the design methodologies for microreactors is presented, along with the applications and technological advances of microreactors for biofuels production.

**Keywords:** microreactor, design methodology, biofuels production, microreactor technology

## 2.1 Introduction

Climate change and decline in oil production have driven the development of new processes to generate energy, fuels, and chemicals with renewable raw materials. In particular, the proposal of biofuels production processes has received a lot of attention, due to its importance for transportation and power and heat sectors. An important aspect to remark is that the carbon dioxide emissions generated during the combustion of the fuel are the ones captured by the crops during its growth. Therefore, a considerable decreasing in carbon dioxide emissions is obtained. Considering this fact, the development of conversion processes with reduced energy consumption and capital costs is necessary to minimize the carbon footprint of biofuels. In this context, process intensification is a potential mean for process improvement, to meet the increasing demands for sustainable production [1].

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According to Stankiewicz and Moulijn, process intensification consists of any chemical engineering development that leads to a substantially smaller, cleaner, and more energy-efficient technology [2], and it is one of the five principles to get an inherently safer design [3]. Thus, there is novel and multifunctional equipment, where mass and heat transfer are significantly improved. Respect to novel equipment, the development of reactors has attracted much attention.

Reactors are key equipment in any production processes because they perform the conversion of raw materials to products [4], especially for biofuels production. In conventional reactors, mass and heat transfer are limited, especially in heterogeneous reactions; due to this, reactants in excess and devices to create turbulence are needed to guarantee the contact between reactants along with a better heat transfer.

In the development of new and more efficient reactors, from process intensification point of view, there are important advances. According to Tian et al. [5], there are several intensified reactor technologies, which include structured catalytic reactors, oscillatory flow reactors, reverse flow reactors, catalyst that supply heat in endothermic reactions, and microreactors. In particular, microreactors, as the name suggests, are reactors with channel sizes of the order of micrometers, at which diffusion is the dominant mixing mechanism [6], as can be observed in Figure 2.1.

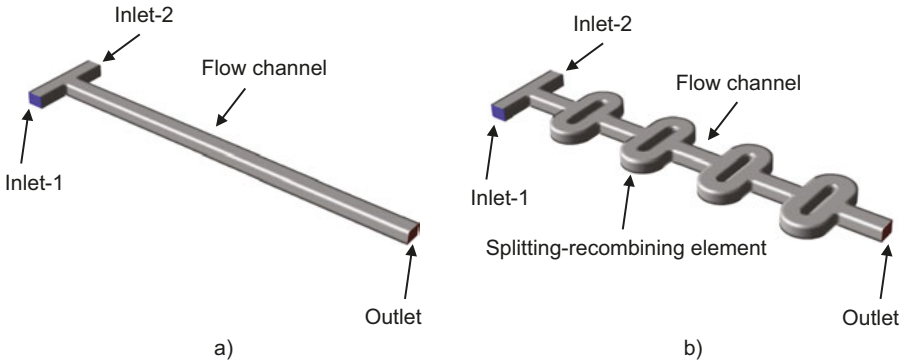


**Figure 2.1:** Main components in a microreactor with (a) a straight flow channel and (b) a flow channel with splitting-recombining elements.

As a consequence, little or no excess of reactants is required, and the safety increases due to the small residence times. An important advantage is that the desired total productivity is obtained simply by a linear increase in the productivity of individual microreactors, circumventing conventional scaling-up problems [7]. Microreactors have been used on the synthesis of nanoparticles, organics, polymers, and biosubstances [8], such as erythrulose [9], hydroxymethyl furan [10], nanocrystals of barium sulfate and boehmite [11], losartan potassium-loaded nanoparticles [12], palladium

nanoparticles [13], azo dyes [14], phenylethanol [15], hydrogenation of ethylpyruvate [16], oxidation of dibenzothiophene with hydrogen peroxide [17], cell lysis and DNA extraction [18], combustion [19], direct $H_2O_2$ synthesis [20], synthesis in liquid-liquid systems [20], and polymerization reactors [21].

Regarding microreactors, several reviews have been published focused on their applications on the synthesis of nanoparticles, organics, polymers, and biosubstances [8], methods and applications of heterogeneous catalysis [22], and microstructured catalytic reactors for gas-phase reactions [23]. Moreover, there are two reviews related to bioenergy area. One of them presented the use of microreactors for the production of biofuels (methanol and biodiesel considering Fischer-Tropsch technology) and electrical energy (hydrogen storage for fuel cells) [24]. That review includes a compilation of scientific developments reported until 2012. The other work was published in 2019, and it presents an analysis of the technical challenges for the development of microfluidic bioreactors for the production of biofuels (biodiesel and bioethanol) [25]. Both reviews are very interesting; in spite of none of these reviews include the production of gaseous biofuels. These reviews discuss the technical challenges to the development of microreactors for the production of biofuels; however, design methodologies are necessary to increase the implementation of intensified technologies in the industry, since they allow addressing the complexity and offering systematic solution procedures [26]. To the authors' knowledge, there is no available a compilation of design methodologies and applications to biofuels including a patent revision.

Therefore, this chapter focuses on the review of design methodologies for microreactors, mainly those where computational fluid dynamics (CFD) is used. Moreover, a revision of the applications of microreactors for production of biofuels along with technological advances of this technology are included.

The chapter is organized as follows. Section 2.2 includes the reported methodologies based on CFD for the design of microreactors. Later, the applications of microreactors for biofuels production are presented in Section 2.3. Finally, the technological advances for the production of biofuels are discussed in Section 2.4, while a recapitulation of these topics is addressed in Section 2.5.

## 2.2 Design methodologies

The design of microreactors requires extensive knowledge of the related phenomena such as fluid flow, chemical kinetics, and transport of heat and mass [27]. In this sense, CFD has been proposed as an attractive method for the design and optimization of these units [28].

A CFD study consists of obtaining the numerical solution of the equations that describe momentum, heat, and mass transfer in a system using computational

methods. One of the most interesting characteristics of techniques based on CFD is the possibility to model and represent the aforementioned phenomena in systems with both conventional and complex geometries. Therefore, the performance of microreactors with different geometric designs can be evaluated in terms of the described mechanisms.

Based on the previous discussion, the most common strategies based on CFD for the design of microreactors are presented in the following subsections.

### 2.2.1 Design based on the analysis of parameters of microreactors performance

Microreactors performance can be determined using the evaluation of mixing degree, mass and heat transfer, and reaction yield in these units [27]. Thus, the most commonly used strategy for the design of microreactors is described in the following lines:

a) First of all, different designs for the microreactors are proposed. These designs can be obtained by modifying some of the following geometric parameters: the shape of the flow channel, the shape of the channel cross-section, the shape and arrangement of the mixing elements located through the flow channel, the shape of the premixing elements at the inlet of the flow channel, the height of the flow channel, and the width of the flow channel. It has been demonstrated that the aforementioned geometric parameters have a significant effect on the performance of microreactors. Then, simulations are carried out for each one of these designs considering the operating conditions for the process to be represented (pressure, temperature, inlet velocities, concentrations of chemical species, etc.), the properties of fluids and materials involved (density, viscosity, heat capacity, etc.), and the boundary and initial conditions.
b) From the analysis of the results obtained, in terms of profiles for the mean values of velocity, temperature, concentration of chemical species, etc., the performance of each design is determined. In this case, the best microreactor design is the one that exhibits flow uniformity and the highest values for heat and mass transfer rate.
c) Additionally, some specific parameters such as mixing degree, figure of merit (FoM), and nonuniformity of flow can be estimated to support the findings obtained in the previous step. These parameters are defined in the following subsections. In this case, the best microreactor design is the one that offers the best compromise between reaction yield and energy consumption.
d) Finally, experiments with the best design can be carried out to validate the results obtained from the simulations through the comparison of the behavior of different variables (velocity, temperature, species concentration, etc.). Another usual way to validate the results obtained is the comparison with data reported in experimental works developed in similar conditions.

#### 2.2.1.1 Mixing index

Given the importance of an appropriate mixing between chemical species to improve heat and mass transfer in microreactors, the degree of mixing is a parameter used to evaluate the performance of these devices. The degree of mixing can be evaluated with the mixing index ($M_i$), which can be obtained from the standard deviation of species concentration for each cross-section in the direction of flow:

$$M_i = 1 - \sqrt{\frac{\tau^2}{\tau_{\max}}} \tag{2.1}$$

$$\tau^2 = \frac{1}{n}\sum_{i=1}^{n} (\omega_i - \omega_\infty)^2 \tag{2.2}$$

where $\tau$ indicates the variation of concentration for each cross-section, $\tau_{\max}$ is the maximum variance over the range of data, $n$ is the number of sampling points inside the cross-section, $\omega_i$ is the mass fraction at the sampling point $i$, and $\omega_\infty$ is the mass fraction at infinity. The mixing index has a value of 1 for complete mixing and 0 where there is no mixing.

#### 2.2.1.2 Mean variables

The mixed mean temperature is given by:

$$T_{\text{mean}} = \frac{1}{VA_c}\int_{A_c}^{0} T\mathrm{u}dA_c \tag{2.3}$$

while the mean mass fraction is written as:

$$\omega_{i,\text{mean}} = \frac{1}{VA_c}\int_{A_c}^{0} \omega_i \mathrm{u}dA_c \tag{2.4}$$

where $A_c$ is the cross-sectional area of the channel, u is the flow velocity, and $V$ is the mean velocity, which is given by:

$$V = \frac{1}{A_c}\int_{A_c}^{0} \mathrm{u}dA_c \tag{2.5}$$