

Chapter 12

The Place of Intensified Processes in the Plant of the Future

12.1. Process intensification in the context of sustainable development

In a January 2000 article, George Keller and Paul Bryan [KEL 00] estimated in line with the predictions of the “Technology Vision 2020” [TEC 96] report that the chemical plant of 2020 had to meet several important challenges, including the reduction of costs associated with the consumption of raw materials, energy and investments, the improvement of safety conditions, the best product quality, increasing environmental performances of (CO₂), the reduction of stocks, and a greater flexibility of the production capacities.

In reality, these challenges are not different from those of nowadays, but we can consider that they will take a more and more significant place in the future plant.

The question is to know whether the technologies and current production methods can meet these major challenges. Currently a very significant part of the global chemical production in volume, and even more significant in value, is made in batch stirred reactors and this proportion does not seem to be decreasing [RIP 83]. According to Thomas Schwalbe [SCH 06], approximately 97% of organic syntheses are made in batch processes. This major share by batch processes is explained by several reasons. There are numerous syntheses of small annual capacities for which the conventional agitated tank offers great flexibility and versatility of process units. This is also the production tool that seems the easiest to adapt from manufacturing recipes developed in laboratories (apparent ease of extrapolation). Finally, the capital intensity

of the equipment is relatively reasonable and, in the case of fine chemicals, the cost of equipment changes according to the volume at the power 0.3, well below the commonly accepted value of 0.6 for other types of continuous processes [ROB 05].

However, it is striking to note that some high-tech products with high added values are derived from the manufacturing process units that are using relatively inefficient pieces of equipment. The latter have many disadvantages detrimental to both the quality of the synthesized products, to the environment by excessive consumption of energy or solvents, and also to the safety of installations and people.

Currently, we realize more and more in fine chemical industries that the manufacturing methods are in fact less efficient for a rather high operating cost. This is particularly true for intermediate chemical products, where the limitations induced by medium- and large-sized stirred tanks lead to potential losses of products by a low selectivity. Stirred tanks have limited thermal performances. This is why the implementation of rapid exothermic reactions in such systems often requires the dilution of reactants, which in turn necessitates a separation stage. The use of solvents is detrimental on many levels. A high consumption of solvents, whose recycling cannot be complete and which induces direct or indirect environmental discharges, is of course a first element. The need for separation processes of reaction products and the recycling of solvents are also stages requiring energy consumption, that become greater as the amount of solvent gets higher.

In addition, the rates of chemical reactions are directly related to the concentration of reactants, the dilution contributes *de facto* to a slowdown of kinetics and to longer synthesis durations that induce increased costs, and also increased energy consumptions.

Finally, extrapolation stages between the laboratory and the production unit, especially for new products, are particularly complicated. Using inefficient equipment, which is difficult to be extrapolated increases the durations of the industrialization and product marketing phases. The associated costs may be particularly penalizing in the context of high economic competition.

For many years, there has been a major attraction for the significant improvement of manufacturing methods through the replacement of conventional equipment by intensified equipment and by transforming the discontinuous process units into batch process units, where the operating conditions are more strictly controlled.

Process intensification consists of, through the development of suitable methods, techniques and devices, designing more efficient, more compact, and more economic processes, whose production capacity is several times greater than that of a conventional process. The implemented technical principles aim at getting rid of

the limitations of heat transfer (outflow and inflow), more generally of energy flows and material transfer, and also to change the thermodynamic limitations (solubilities, reaction equilibria), which slow down the overall kinetics of transformation and/or separation of a process.

The above applicable objectives are not new and evidently come under the general mission of the process engineer, but they appear in a constantly evolving context. Thus, the industrial accident of the Union Carbide plant at Bhopal in December 1984, now listed as the most significant industrial disaster to date (between 20,000 and 25,000 casualties according to victim associations), has raised awareness by putting the emphasis on the need to reduce risk factors by avoiding the massive handling of dangerous intermediate products. Let us note that already in the same year, T. Kletz [KLE 84] had indicated that process intensification was a way of reducing chemical hazards.

The intensification thus ensues from an essential need for the evolution of process engineering, particularly in the current context of trade globalization, of increased competition, and of a genuine concern related to sustainable development [CHA 07].

The answer to these objectives requires an integrated and complex vision of all the three principal components of sustainable development called the “3Ps” (process, people, and planet) or 3Es (environment, economy, and ethics):

- environmental component by the development of safer processes that are less consuming in energy, raw materials and solvents (resource conservation), which are less polluting;
- economic component mainly due to the gains in raw materials and energy and also due to the miniaturization that helps to reduce the capital intensity of processes (volume of installations and buildings), the duration, and thus the cost of design (high-output screening) and extrapolation phases (using the numbering-up technique);
- societal component coming from the technical and economical advantages that contribute to the competitiveness of the chemical industry. The decrease in the design and industrialization stages accelerates the marketing of new molecules and new products and can preserve the competitiveness of the companies. The intensified technologies also contribute to the improvement of the quality of life by small, clean and safe plants located close to dense urban areas.

The concept of intensification is closely linked to the concept of miniaturization of the pieces of equipment. In fact, the increase in transfer and processing rates enables us *de facto*, by reducing the residence time of fluids, to design more compact and equally efficient pieces of equipment. It is from this purely technical concept, developed in the 1980s by Colin Ramshaw [RAM 83], that process intensification [REA 08, STA 09] is seen nowadays as one of the founding concepts of the plant of

the future by developing new production methods that generate new business models (onsite production and production on demand, reduction of the stocks, reduced transportation of raw materials and products, and flexibility by the modular plant).

In this chapter, we will present the main technical principles of intensification and more especially the relationship between the intensification and size of installations. We will consider some examples of applications and developments, without, however, drawing an exhaustive list. In the context of sustainable development, economical aspects are essential. This is why it seems to be necessary to also address the problem of the real impact of intensification in economic terms, but also of business models, although this subject is generally difficult to deal with in a few lines, partly also because of the few published data.

12.2. Main principles of intensification

The first works on process intensification in the industrial world, date back to the late 1970s, when the ICI company had been the first to highlight that the concept of intensification was an effective way to reduce the investment costs of a production system by developing the HiGee technology thus enabling the separation of mixtures by centrifugation (the intensification of transfers helps to concentrate the equivalent of a large number of theoretical stages in a small volume). A very large-scale application of this technology has enabled the replacement of 30 m splitters operating under vacuum by rotary devices of 1.5 m in diameter for a single separation efficiency. However, the order of magnitude of this dramatic reduction has raised many questions among distillation specialists; Colin Ramshaw [RAM 95], one of the pioneers of process intensification was announcing reduction of factors 100 times or even more. According to Stankiewicz and Mouljin [STA 00], a factor 2 is considered to be within the scope of process intensification.

The basic idea of process intensification thus opens the way to many and diverse applications. Stankiewicz and Mouljin [STA 00] classify them according to the two lines of approach (methods and equipment) as detailed on the organization chart in Figure 12.1.

We have the following:

- the *methods* relative to process intensification represent a vast field of study and include multifunctional reactors (reactive distillation), hybrid separations (membrane distillation, etc.), alternative energy sources (microwaves), or different methods for measurement and control. The use of hybrid processes, and especially the multifunctional reactors, implement most of the time, in a single device, the reaction stages followed by the separation of products. In addition to the significant savings in operating costs and to the reduced installation size, these methods have one major advantage of overcoming the limitations of thermodynamic equilibrium by separating the reaction products as and when they are formed;

– the *equipment* that make up the alternative strategy of process intensification. Particularly, it involves playing on the structuring of flows, by adapting for example the geometric dimensions of the system to the characteristic times of the limiting processes. Microreactors and microswitches are part of these pieces of equipment, as well as static mixers, rotating disks, and exchangers reactor (HEX).

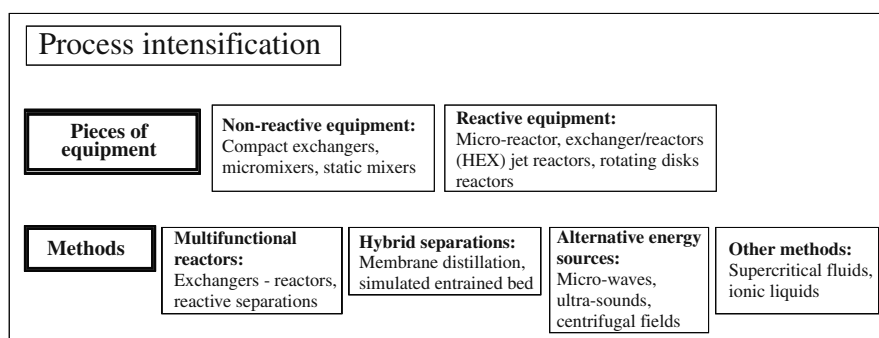


Figure 12.1. *Process intensification and its components: classification according to Stankiewicz and Mouljin [STA 00] following the methods and pieces of equipment*

This classification has the disadvantage of not being completely clear because the pieces of equipment are technological solutions obtained from the intensification methods. Therefore, intensification is best addressed through the methods that can remove some limitations, from where technologies and equipment originate. The processes of material and energy transformation involves multiple phenomena coupled at different spatial and temporal scales. The slowest processes have the highest characteristic times. This reflects the influence of the limiting phenomena. The means of action of intensification therefore vary depending on the nature of the limiting processes. These limitations are of four types: material and heat transfer limitations, thermodynamic limitations, energy limitations, and kinetic limitations.

12.2.1. Mass, heat and mixing limitations

In practice, these limitations can be partially removed by a transfer intensification, which is obtained by degrading a surplus of mechanical energy. However, this form of intensification is very penalizing. Let us consider a chemical reactor consisting of an stirred tank, in which we wish to increase the cooling capacities for better temperature maintaining. To increase the heat transfer coefficient in the stirred tank by a factor 2, approximately a 15 times greater mechanical power should be used by increasing the rotating speed of the agitator. An attractive alternative of intensification is to use microstructuration, where the stirred tank reactor is replaced by a continuous multitubular heat exchanger reactor

cooled by an external fluid. To simplify things, this heat exchanger-reactor can be seen as a simple heat exchanger, whose reactive fluid flows in laminar regime in straight cylindrical channels and is cooled by contact with the wall at constant temperature. In this case, the heat transfer coefficient is inversely proportional to the diameter of the flow channel. As the exchange area per unit reactor volume is also inversely proportional to the diameter, the cooling flow per volume unit becomes inversely proportional to the square of the channel diameter. The intensification effect is thus very significant as the decrease of the channel diameter by a factor 10 is enough to increase the bulk exchange flux by a factor 100!

We show [COM 04] that this major intensification effect is found in many other processes such as mass mixing and transfer.

With the considerable development of microtechniques, it is possible to produce microstructured reactors, mixers, and contactors of very small dimensions from about a few microns to several millimeters. By better controlling the conditions of flow and transfer, the secondary parasitic reactions can be removed, thus enabling the manufacture of very pure products with a high selectivity [LOM 06]. These objects provide new opportunities for transformation processes by allowing a selective intensification of physical and chemical processes: new synthesis possibilities producing less non-recyclable effluents, safer production units, lower solvent rates, new materials and products, etc.

12.2.2. Thermodynamic limitations

The first class of thermodynamic limitations appeared in balanced chemical reactions. To shift the reaction equilibria, stoichiometric surplus of reactants are used, which induce several problems in conventional equipments. This leads to the acceleration of reaction kinetics, as well as to higher adiabatic temperature rise that can be difficult to manage if the cooling capacities of the reactors are inadequate. In addition, excessive reactants require the separation of downstream products and recycling, which can lead to sophisticated separation equipments that are costly in terms of investment and operation (separation and recycling energy). The multifunctional equipment, in which the reaction and separation are performed simultaneously, has the advantage of a potential significant decrease in equipment cost and of a reduced energy consumption thanks to heat integration [SAD 01, STA 03]. The most symbolic example is that of the production of methyl acetate by reactive distillation developed by Eastman Chemical Inc., which not only reduces the capital intensity of equipment by 5 (reducing the number of pieces of equipment from 28 to 3), but also the energy costs by the same factor [SII 95, STA 04]. There are many other principles such as reactors coupled with adsorption and absorption, membrane reactors, reaction-crystallization couplings, and precipitation [STA 03].

The second class of thermodynamic limitations is related to the solubility of the reactants and products that can lead to a decrease in reaction rates and selectivity rates or separation efficiency rates. The use of ionic liquids, whose scope is much broader than that of simple solvents (e.g. catalytic activity [FRE 07, MAR 00]), comes under this framework. For example, the Difasol process for olefin dimerization [FAV 05] proposed by IFP-Axens is a two-phase process using an ionic liquid phase and the organic phase. In comparison with the homogeneous Dimersol process, the ionic liquids of the two-phase process have the advantage of a lower solubility rate for octenes than for butenes. The significant reduction in consecutive octene reactions provides an increase in selectivity from 68% to 75%. The Difasol process also has the advantage, over the Dimersol process, of a 10-fold reduction in catalyst consumption, high compactness (four 120 m³ reactors for one 50 m³ reactor), i.e. an economic gain of 15% on capital expenditures (CAPEX) and 20% on operating expenses (OPEX).

Supercritical processes are also considered to be intensified processes, particularly due to the high solvent power of the media used. Supercritical CO₂ is thus an interesting alternative to many organic solvents and can be easily separated by simple expansion. Many reaction applications have been implemented [HYD 05], such as Friedel-Crafts alkylations, hydroformylations, oxidations, etherifications, and especially hydrogenations where, on the one hand, mass transfer limitations are eliminated as the supercritical medium is monophasic and, on the other hand, the solubility of hydrogen is infinite, thereby leading to substantial gains in selectivity (synthesis of 3-ethyl-cyclohexene by catalytic hydrogenation in supercritical CO₂) [STE 03].

12.2.3. Limitation by energy input

Another method of intensification aims at providing energy to the system unconventionally by playing on the modes of supply (microwaves, acoustic waves), the location, and the type of energy or dissipation.

In some processes using diphasic fluids, the gravitational force is an important parameter that determines the mixing, flow, or separation of phases. It is sometimes necessary to have large pieces of equipment to achieve higher efficiencies. One way to reduce the size of the pieces of equipment is to increase the field of gravitational acceleration by rotating the fluids, as it is done by centrifugation. But the application of these centrifugal fields can also be very beneficial to intensify mass and heat transfers by obtaining very thin liquid films, or very high specific interfacial areas. There are many uses of the rotating disk technology for reactive applications and for absorption, extraction, or distillation processes [REA 08b].

In some cases, the energy input by generation of microwaves also provides significant gains in efficiency and selectivity of reactions [LOU 06]. There have been studies in this field for many years but it is often the combined approach of microwaves and continuous processes (flow chemistry), which offers a significant gain compared to batch processes [HES 11, RAZ 10]. Microwave generators are also used for localized energy inputs in separation processes such as distillation [ALT 10].

Let us also note the intensification by acoustic generation, which by a very high energy contribution of several million of kw/m^3 , enables a local increase of pressures and temperatures or the formation of radicals, which are favorable to transfer between phases and reaction kinetics [GOG 03].

12.2.4. Kinetic limitations

There are some reactive systems whose kinetics are relatively slow (characteristic time of reaction of several hours) and therefore not limited by mass or heat transfer. High residence times are hardly compatible with intensified reactors and very small microreactors. These classes of reactions have been, for some time, removed from the operating range of intensification [ROB 05]. Conventionally, we can of course accelerate the reaction rates by higher temperatures or working pressures, or even by increasing the concentrations. However, these activation modes are either difficult to control in conventional agitated reactors because the heating or cooling rates are limited (long durations to heat up or cool down the reactor which are detrimental to productivity), or because the equipment costs become prohibitive (high pressure). On the other hand, complex syntheses often involve thermally activated secondary reactions that are detrimental to the selectivity and efficiencies, and that are difficult to control.

The transition from the batch production mode to the continuous mode opens new routes because it is possible to work in new operating windows (high pressure and temperature) without bringing on a significant cost overrun of equipment, while significantly improving the reaction efficiencies [HES 05, HES 09a, KOC 09, LOM 06]. The principle of thermal activation of two parallel reactions is illustrated in section 12.3 on Figure 12.2.

12.3. Connection between intensification and miniaturization

In all of these means of action, the internal and external geometrical structure of the device plays a significant role, as it allows a better local piloting of phenomena by controlling the flow conditions, and heat (energy) and mass transfer conditions. This is an important problem of intensification, which conditions the possibility of extrapolation for high capacity processes.

The performance of any equipment (reactor, heat exchanger, mass exchanger, separator) can be represented by its efficiency, η . In a reactor, it is similar to the conversion, which can be defined as the ratio of the flow rate or the amount (mass or mole) of processed material to the flow rate or as the amount of material available for processing. In a heat or mass exchanger, in a separator, this efficiency is the ratio of the amount (the flow rate) of heat or material transferred to the amount (or to the flow rate) of potentially transferable material or heat.

As a first approximation in many cases of continuous processes, the efficiency η is an asymptotic relation of the ratio between the space time τ (ratio of the volume of fluid in the equipment by the volume flow rate of fluid) and the global characteristic time t_{op} of the processes governing this process. The characteristic time is an indicator of the speed at which the transformations or transfers occur in the equipment; it is all the more short as the kinetics or the transfer rate is high.

Thus, in the simple case of a first-order process, the effectiveness, according to the type of flow considered (perfect mixer or plug flow), is given by the following relationships:

$$\begin{aligned} \text{Perfect mixer: } \eta &= \left(\frac{\tau}{t_{op}} \right) / \left(1 + \frac{\tau}{t_{op}} \right) \\ \text{Plug flow: } \eta &= 1 - \exp\left(-\frac{\tau}{t_{op}} \right) \end{aligned} \quad [12.1]$$

We deduce from these relationships that for a given efficiency, the volume V of the equipment is directly proportional to the characteristic time of the process t_{op} and to the fluid flow rate Q :

$$\begin{aligned} \text{Perfect mixer: } V &= t_{op} Q (\eta / (1 - \eta)) \\ \text{Plug flow: } V &= t_{op} Q (-\ln(1 - \eta)) \end{aligned} \quad [12.2]$$

This simple idea shows that process intensification, which consists of increasing process rates or, in other words, of reducing the characteristic times, especially by reducing the limiting phenomena, involves reducing the volume of equipment and/or increasing the processed flow rates.

In the case of processes limited by mass or heat transfer, the characteristic times are highly dependent, often by a quadratic relation of the characteristic dimension of

the channels in which the fluids circulate. That is why microreactors, micromixers, and microexchangers have amazing efficiencies for particularly low volumes.

To illustrate the close relationship between intensification and miniaturization, let us consider an example of exothermic synthesis, for which we seek to maximize the selectivity of one of the reaction products. Figure 12.2 shows the influence of the temperature and residence time in the reactor on the selectivity of an intermediate product B in the simple case ($A \xrightarrow{1} B \xrightarrow{2} C$); the main reaction $A \xrightarrow{1} B$ is exothermic and the secondary reaction $B \xrightarrow{2} C$ is favorably activated by the temperature with respect to the first reaction.

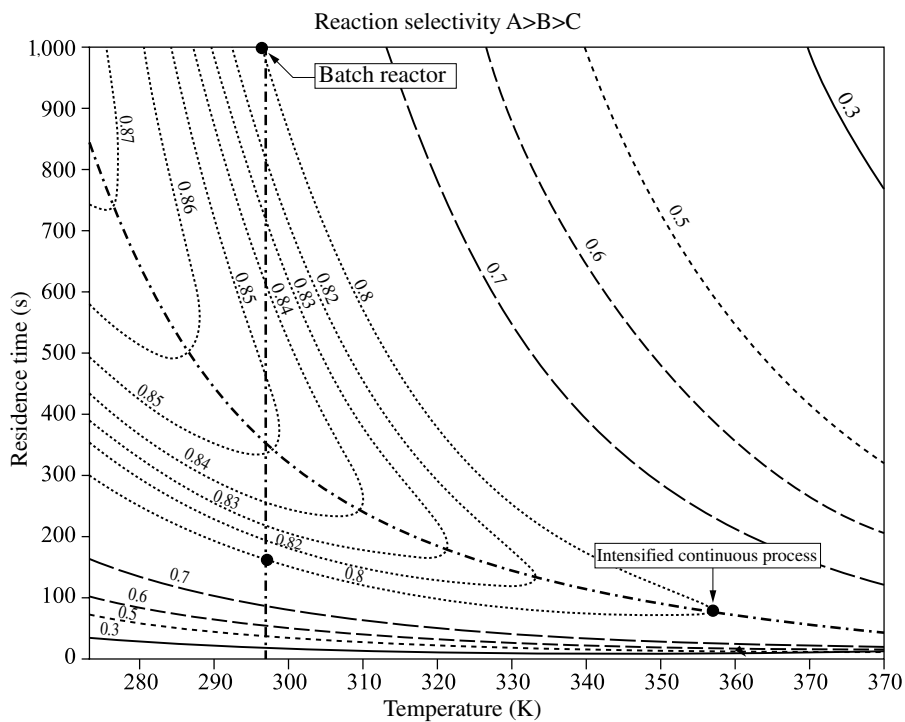


Figure 12.2. Selectivity chart based on the temperature and residence time. Comparative analysis of operating points of a conventional batch process and an intensified continuous process

In a conventional agitated batch reactor whose cooling capacities are quite limited, the flows of reactants are slowly carried out so as to work at low temperature and prevent any thermal runaway detrimental to the selectivity

(e.g. Grignard reactions). In the example, the operating point of the semi-batch reactor at 297 K requires a long residence time of about 20 minutes (1,000 s) to achieve a maximum selectivity (selectivity $S_B = 80\%$), which is detrimental to productivity. By using an intensified reactor with very good cooling capacity, it is possible to control the temperature of the medium and work at 357 K. The reaction kinetics being strongly accelerated, the residence time can be considerably reduced to a few dozen of seconds (70 s). This makes it possible to maintain the high value of selectivity ($S_B =$ nearly 90%). For a similar production flow rate, the intensified equipment can be almost 15 times more compact than a standard stirred tank.

This equipment miniaturization, involves however several significant challenges, such as the risk of clogging by the introduction or formation of solid products and a very high pressure drop, which have long been seen as major obstacles to the industrialization of these compact piece of equipment.

The internal flows in these pieces of equipment are often in laminar regime. The impedance loss ΔP can be estimated from Poiseuille's equation, which shows that ΔP is inversely proportional to the diameter D of the flow channel at a power 4:

$$\frac{\Delta P}{L} \approx \frac{Q}{D^4} \quad [12.3]$$

This equation indicates that sending the entire flow rate Q to be processed in a single channel of length L , is done at the cost of an impedance loss and thus of a very high energy consumption, on the contrary to the objectives of sustainable development in which the principle of intensification fits. An alternative would be to use multiple channels in parallel in order to subdivide the main flow rate into very low elementary sub-flow rates, thereby compensating for the increase of the impedance loss due to the reduction of the channel diameters.

In some cases (limitation by heat or mass transfer), the reduction of the channel diameter is accompanied with a significant intensification that reduces the length of the channels. This leads to very short multichannel equipment with an impedance loss much lower than that of a conventional piece of equipment [COM 04].

The chart (a) of Figure 12.3 shows, in the case of heat transfer intensification, the evolution in the energy overconsumption (energy factor) to be implemented in order to increase the heat transfer coefficient by an intensification factor F . In this chart, several possible strategies are shown: the "power increase" curve corresponds to the laws of heat transfer in stirred tanks, for which it is found that the increase in the heat transfer by a factor 2 requires close to 13 times more mechanical power. In the case of a laminar flow in a single channel, we obtain a very similar behavior that show that intensification is very energy consuming.

By choosing to subdivide the flow into N parallel channels, it is possible to significantly reduce this overconsumption. Thus, for an intensification factor $F = 2$, the separation of the flow into three channels ($N = F^{1.5} \cong 3$) leads to an energy overconsumption by a factor 2 when compared with a single channel; the four-channel separation ($N = F^2$) does not require any overconsumption and the separation into six channels ($N = F^{2.5}$) even allows a reduction by a factor 2. This flow structuring strategy however requires designing a distributor and a collector that ensure a perfect flow distribution.

Figure 12.3(b) illustrates the problem of the size reduction of a multichannel catalytic reactor, while maintaining the same effectiveness and impedance loss at identical flow rate. The decrease in the internal channel diameters by a factor 2, reduces the volume of the monolith by a factor 4 [COM 04].

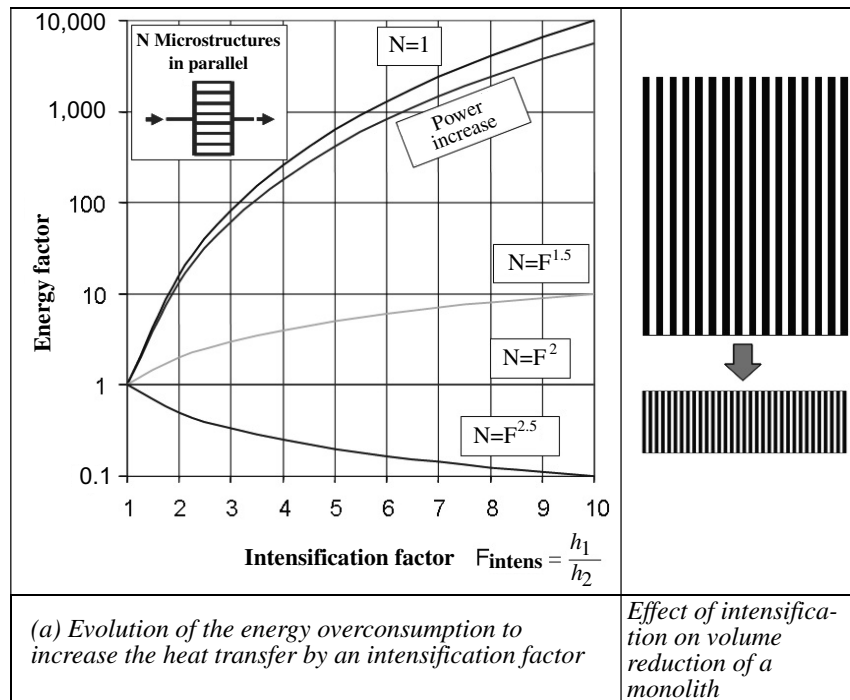


Figure 12.3. Intensification by microstructuring. Relationship between intensification, energy consumption, and equipment volume

This principle of flow structuring has given rise to the concept of micro- or multistructured equipment, which corresponds to large pieces of equipment for handling high flow rates, in which the internal flow structuring allows intensification,

miniaturization, but a moderate impedance loss. The typical example is the plate reactor-exchanger; an industrial example proposed by Degussa is the DEMIS (*Demonstration Project for the Evaluation of Microreaction Technology in Industrial Systems*) process of catalytic epoxidation of propene [MAR 05] which is illustrated in Figure 12.4.

The important potential innovation brought by process miniaturization lies in the possibility to extrapolate by multiplication and parallelization of equipment, all the while avoiding the various problems of conventional extrapolation by scaling up. This concept of ideal parallelization, which requires, however, a perfect equidistribution of the flow down to the smallest geometric scales [LUO 05, SAB 09], infers that if the optimum operating conditions at the smallest scale (elementary channel) of an equipment can be determined in laboratories, then the operating conditions of the industrial reactor are identical. It is then enough to optimize the operating conditions in laboratories or on a small pilot scale to define the operating conditions of the industrial system. This underlies the complete review of the classical methodology of process engineering, where we proceed in steps (determination of chemical and physical intrinsic kinetics, characterization of coupled transfers, etc.), so as to build a model enabling extrapolation by calculation.

We can foresee that this extrapolation technique (known as scaling out or numbering-up) would contribute to significant savings in the costs and development times of an industrial process.

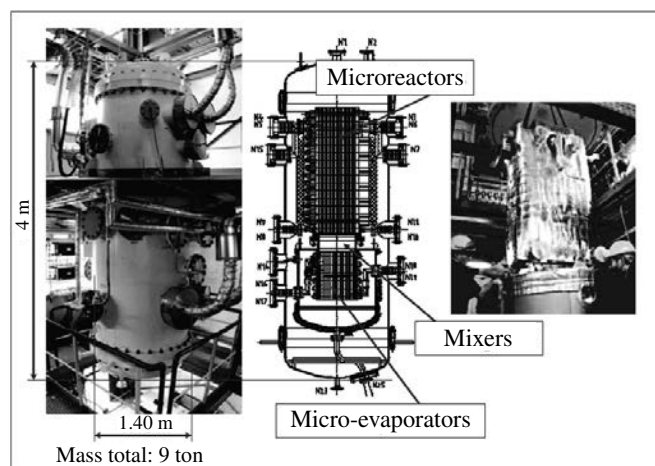


Figure 12.4. Presentation of the multistructured reactor of the DEMIS project [MAR 05]

However, it is necessary to modulate this advantage by the fact that, in reality, the network of multiple scales in large structures creates new couplings depending

on the size of the system (e.g. heat transfer). In addition, the distribution of flows in a network of channels of different sizes, especially in two-phase flow, is not yet a fully resolved problem.

12.4. Applications

12.4.1. Intensification for safer processes

Intensification is involved in many ways to improve process safety. Initially, the significant increase in heat transfers can very efficiently cool the chemical reactors and prevent the formation of hot spots and the runaway of reactions [ANX 08, BEN 08, ETC 97]. Equipment miniaturization is also one of the key elements in improving the safety provided by process intensification. As Trevor Kletz [KLE 91] very simply puts it, “What you don’t have, can’t leak!”. The reduction in volumes reduces the severity of impacts in the case of leakages or accidents. This volume reduction results in lower storage volumes of reactants and products, smaller reactors and pipes, thereby reducing the potentially stored energy, and facilitating containment.

For example, a batch reactor producing an organic intermediate can contain a potential energy by thermal degradation of the equivalent of several tons of TNT. A small continuous intensified reactor, which is nearly a thousand times smaller than the batch reactor, reduces this TNT equivalent to a few kilograms.

The reduction of the pipe diameters also reduces the size of toxic clouds. For example, the rupture of a chlorine pipe of 2 inches diameter requires setting up a blast area (20 ppm of chlorine in the atmosphere) of 5.5 km; with a diameter of 1 inch, the distance is reduced to 700 m and 0.5 inch to 80 m [HEN 00]. For small installations, the solution of containment in a bunker becomes possible as the building costs are considerably reduced. This ensures a very high passive safety and that is why intensified processes are often associated with intrinsically safe processes.

Another application of intensification and miniaturization involves the production on site and the demand for hazardous intermediate products used in the manufacture of secondary products. It thus eliminates the need for any storage and transportation of hazardous materials. This concept is not entirely new, but the volume reduction of installations provides an additional important element. Let us quote the example of the synthesis of Caro’s acid used as a powerful oxidizing agent, formed from sulfuric acid and hydrogen peroxide, in a tubular reactor of 20 ml volume at a rate of 1 ton per day [WHI 92]. Alternatively, the direct synthesis to the demand for phosgene that has reduced the amount of storage from 25 tons to only 70 kg [HEN 00]. The AET Group has developed a small synthesis unit of 4 kg/h phosgene for applications in fine chemicals [AET 10], which are illustrated in Figure 12.8.

However, the intensified processes often operate under higher conditions of temperature, pressure, concentration, or energy density than conventional processes, thereby increasing the potential hazard. It can therefore be a contradiction in stating that the intensified processes are inherently safer. Etchell [ETC 05] thus lists some of the important elements which in some cases show that intrinsic safety is not ensured. An important point concerns the human factors to be considered in risk analyses of intensified processes. The new operating conditions may be unusual for untrained operators. Similarly, the complexity of processes can be greater (multifunctional equipment, start-up and shutdown procedures, more complex control systems).

The reaction rates are often higher because of strict operating conditions (pressure, temperature, concentrations), or because of the removal of limitations on mixing, heat and mass transfer. The phenomena are thus very fast and there is a need for rapid and sophisticated online measurement and control systems. In risk analysis, it is therefore important to consider these specific dynamic aspects. Finally, despite the small size of the equipment, fluid flow rates can be high; if the process does not operate in normal operating conditions, off-spec products or hazardous by-products may be formed. It is necessary to store them rapidly at the line output and then to reprocess them. We are confronted again with the problems associated with some batch processes with high material accumulation.

Another important point is that in some cases, only one of the piece's of equipment of the process is intensified, whereas the other devices are conventional. This is particularly true during the rearrangement of batch processes to continuous processes in fine chemicals, where we replace the conventional stirred tank with an intensified reactor operating at a higher pressure. We were able to identify [FAL 10, MAC 10], in a HAZOP comparative analysis between an intensified process and a conventional process, that the risk lies in the phase downstream to the reactor (separation device in glass that cannot withstand high pressure). This shows that if intensified equipment can be intrinsically safer, this is not necessarily the same for the entire process.

12.4.2. Intensified processes for energy

The intensification of heat and mass transfer phenomena by the microstructuring of flows (structured monolith or plates) and catalytic depositions (thin film depositions by wash-coating) potentially allows a considerable reduction of the reactor size. In some applications, the limiting process becomes the chemical reaction itself and it is necessary to improve the formulation and the catalyst deposition. Velocys and Oxford Catalysts have therefore developed new Fischer–Tropsch catalysts for microstructured reactors that accelerate the kinetics by a factor 10–15 in comparison to conventional reactors, and that enable conversions of about 70% per

pass (against 50% for a conventional reactor). The size of the Fischer–Tropsch installations may be reduced by almost 90% over a conventional installation [LER 10]. A direct application involves the GTL (*Gas to Liquid*) installations established by the TOYO and MODEC companies on the offshore FPSO (Floating Production Storage and Offloading units) platforms in 2012 [GER 10].

The miniaturization of catalytic processes opens, due to the equipment cost reduction, completely new perspectives of distributed small capacity units, in order to meet the local energy requirements (production, valorization, and storage) but also for the production of synthetic gas and hydrogen for chemistry and processing industries.

There are many potential applications and it is impossible to provide an exhaustive list here. The following can be cited as examples:

– *valorization of flare gases*: according to the World Bank, the discharges of flare gases were about 100 billion m³ per year in 2002 [WBG 04]. The costs of different gas valorization techniques (liquefaction, gas pipes, electrical energy generation, etc.) can help us to define, for each of them, a field of application based on the gas flow rates and on the distance between the production site and the use site. Velocys [LER 10] thus estimates that conventional GTL methods are economically viable only from a production of 10,000 barrels per day, which covers only 6% of the total emissions. The profitability of small GTL valorization units based on microstructured reactors would be demonstrated for productions between 10,000 and 2,000 barrels per day, representing nearly 40% of the gas sources;

– *hydrogen production*: the hydrogen market for energy and chemical applications is rapidly developing but is also complex. A study by the European project Roads2HyCom [HYG 09] shows that there is an onsite production market with a demand for hydrogen of a capacity ranging between 30 and 800 Nm³/h. In the case of production by methane reforming (SMR process), it is, however, still necessary to reduce the costs by a factor 2 with respect to the high capacity units; a hypothesis that seems to be realistic. Currently, the costs for onsite hydrogen production by reforming are not competitive with those for transportation.

12.5. New economic models implied by process intensification

Process intensification offers new perspectives for a cleaner and safer sustainable chemical plant of the future. Improved performances in terms of efficiency and selectivity also lead to economic gains in operation (raw materials and energy), which can be significant, depending on the sector.

In addition, miniaturization equipment, underlying the intensification, naturally leads to the concepts of chemical and modular mini-plants which, thanks to units

with a greater flexibility, can further enhance economic performances. Although not entirely new, the concept of modularity, encountered in the oil industry, is reinforced by compactness equipment and opens up new economic perspectives for the chemical industry.

12.5.1. Assessment of operation cost reduction

The fields of applications of intensification are very vast and the disparities among the various examples are sometimes significant. It is therefore difficult to draw general laws on the economic operational gains.

It is, however, possible to approach the problem in a simple way by estimating the return on investment time coming from the financial gain brought by the productivity gain associated with the technological change (transition from the conventional process to the intensified process). This estimation can be made by the following simple calculation:

$$\text{ROI Time} \cong \frac{\text{Total amount of investment (€)}}{\text{Annual financial gain (€ / year)}} \quad [12.4]$$

with:

$$\left(\begin{array}{c} \text{Annual financial} \\ \text{gain (€ / year)} \end{array} \right) = \left(\begin{array}{c} \text{Annual nominal} \\ \text{production (tons / year)} \end{array} \right) \times \left(\begin{array}{c} \text{Price of the} \\ \text{product (€ / ton)} \end{array} \right) \times \left(\begin{array}{c} \text{Productivity} \\ \text{gain (\%)} \end{array} \right)$$

From this relationship illustrated in Figure 12.5, we show the production gain necessary to amortize an investment of 100 k€ in 3 years depending on the price of the manufactured product and for different production capacities (in tons/year).

We can notice that technological innovation mostly favors pharmaceutical processes (products with high added value and low tonnage), because even with a small overall gain in the productivity by a few percent, we obtain a short return on investment (ROI) time. The innovation for intermediate products at a few dollars per kilogram and of higher annual tonnage requires a substantially higher overall productivity gain. For a higher investment of several hundreds of k€ (to use the figure, the value of the nominal productivity at constant gain, or the gain at constant nominal productivity must be multiplied accordingly), we find that the expected gain on the entire production line should not be incremental, but must at least reach several dozens of percents, which is a much more difficult objective. The simplifying assumption made here, which considers that the financial gain is entirely supported by the productivity gain, shows the need to find other gains on operating costs in order to reduce the ROI time.

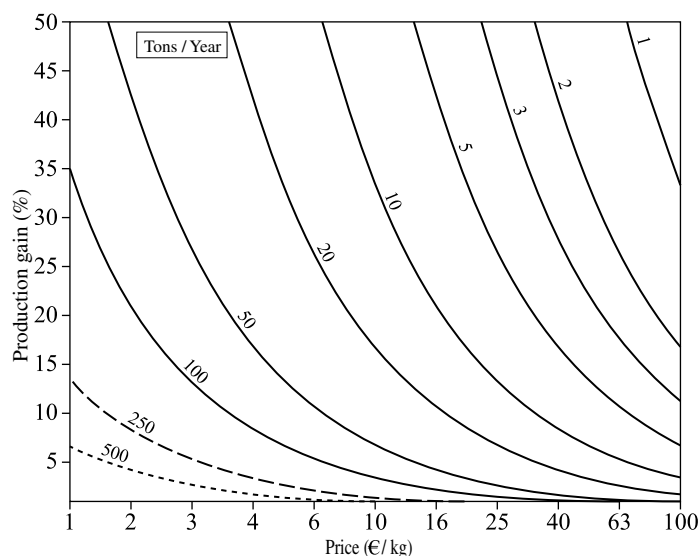


Figure 12.5. Production gain required to amortize an investment of 100 k€ in 36 months based on the price of the manufactured product and for different production capacities (tons/year)

The gain in operating costs brought by intensification is not evenly distributed over all the items and the impact can be very different based on the type of product. Figure 12.6 shows the distribution of different items in fine chemical and pharmaceutical products, according to two different proportions of the raw material cost in the total cost (average values taken from [HES 06, KRT 06, ROB 05, ROB 08]).

For these high added value products, the impact of intensification of the reaction conditions may be significant due to the gain in raw materials provided by the increased reaction efficiencies and selectivities.

In addition, intensification often requires the transformation of fine chemicals plants from the batch mode to the continuous mode and allows de facto a greater automation of production modes. It is thus estimated that the cost of workforce per mass of product manufactured by a highly automated continuous process, can be reduced to about 50% in comparison to a batch process unit [PET 03, ULR 88]. The intensification can also help us to reduce the number of synthesis steps: this is also a factor for reducing material handling costs [PIS 11, ROB 08]. Corning, producer of intensified processes, estimates that the rate of reduction in labor costs can reach about 20% [PIS 11]. Following the various examples reported in fine chemicals, the gains provided by intensification are on average about 15–25% [HES 09b, PIS 10, ROB 08, ROB 10].

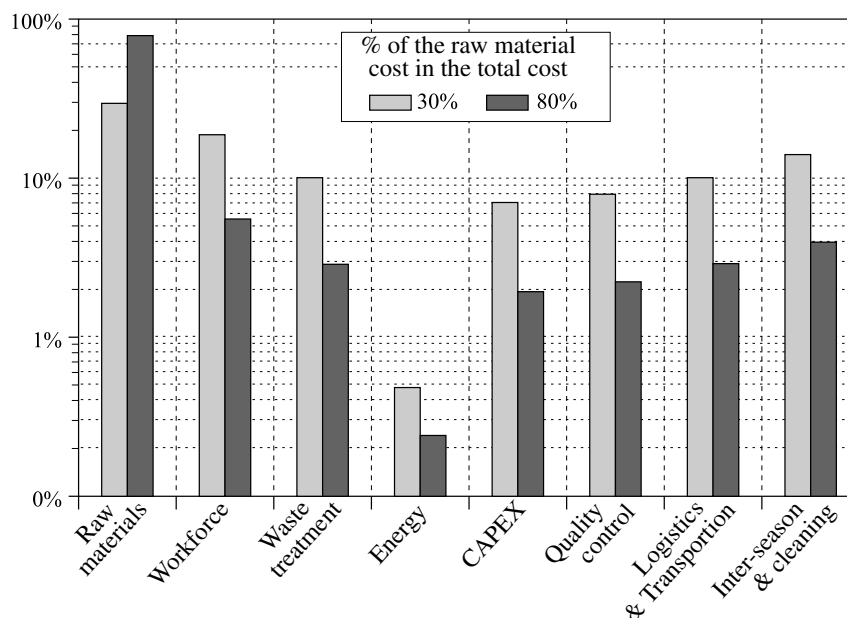


Figure 12.6. Distribution of different items in the total cost of a fine chemical and pharmaceutical product according to two proportions of raw material costs (30% and 80%)

For the other sectors of chemical industry, the proportion of energy in the operating costs can be much higher. Thus, for the Dow Chemical company, energy costs represent about 50% of the incomes (\$54 billion in 2007) [PRI 10]. Intensification comes as a support of other methods such as heat integration (pinch method), management and organization of production methods, thermal insulation, and equipment improvement and renovation (burners, compressors, etc.).

According to the recent studies conducted in the United Kingdom and the Netherlands [REA 08], it is estimated that the reduction potential of the energy consumption in the chemical industry and subsidiaries, thanks to intensification reaches 40 PJ per year, i.e. about 1 million of ton oil equivalent/year (1 PJ = petajoule = 10^{15} J = 2.38×10^4 TEP). The projections for the chemical and food industries will provide figures of about 50–100 PJ/year by 2050 for the Netherlands.

The modes of action offered by intensification primarily focus on two points. The first point concerns the improvement of reaction efficiencies with a better control of operating conditions for efficiency and selectivity gains [MOH 11,

WAL 03]. These gains in efficiency lead to reduced energy consumption during the downstream separation operation. To illustrate this case, the impact of the conversion gain of the reactor over the specific energy consumption in Joule per mole of output product in a fine chemicals plant has been considered.

The hypotheses correspond to the classical case of a process unit where the column is currently in existence and unchanged (20 theoretical plates) and the degree of purity of the product at the head of the column is fixed at 99%. Depending on the input composition of the column (reactor outlet), the power of the boiler and the rate of recycling R are adjusted to satisfy the constraints of composition at the column outlet. We examine two cases, depending on whether the separation (ideal mixture) is easy (relative volatility $\alpha = 3$) or difficult (relative volatility $\alpha = 1.5$).

The results illustrated in Figure 12.7 show that the energy gain is significantly different depending on the separation “difficulty”. For an increase of about 30% of the reaction conversion, the gains in separation energy are about 25–40%.

The second point concerns the intensification of separation processes such as reactive distillation and distilling columns with partitions for which we can achieve energy savings up to 30–40% in comparison to the conventional units [EMT 01, HO 11, SCH 02, TRI 92, WOL 95].

12.5.2. Assessment of the investment costs of intensified processes

The concept of chemical and modular plant miniplant opens up new economical perspectives for the chemical industry.

The economic advantage of small, modular production units is however contradicted by the traditional rules of the industrial development, where it is commonly accepted that the investment costs are proportional to the production capacity, i.e. equipment volume at the 0.6 power [PET 03], or less in some cases (0.3 power for a fine chemicals batch process unit [ROB 05]). This promotes the development of high capacity units and disadvantage *de facto* the use of intensified technologies that cannot profit from this scaling law.

In fact, in this comparative approach, it is necessary to consider the fact that the production capacity of a conventional piece of equipment is not always proportional to its volume, as is the case, for example, for a reaction limited by heat transfer, where the productivity of a batch stirred tank is only proportional to the $\frac{2}{3}$ power of the volume. In this case, the equipment cost becomes proportional to the 0.9 (0.45 in the case of a fine chemicals batch unit) power of the productivity,

thereby indicating a less marked scale effect. Figure 12.8 compares the extrapolation rules in size (scaling law) and number.

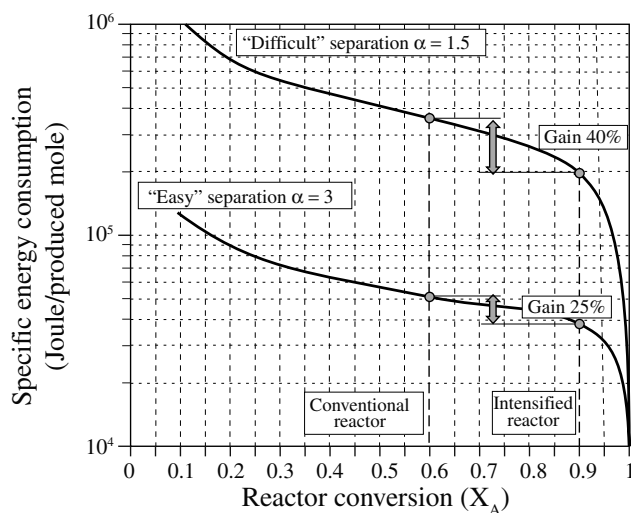
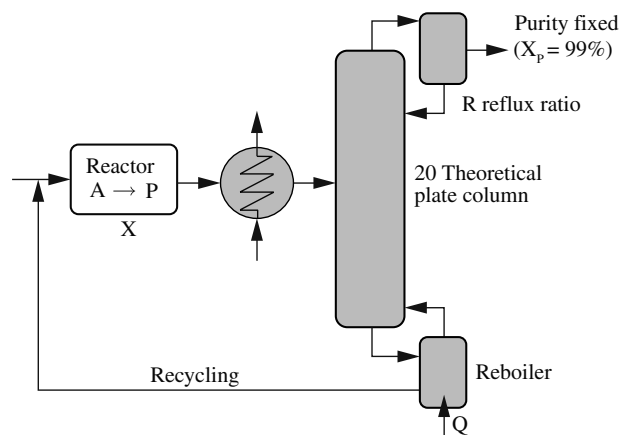


Figure 12.7. Impact of the intensification of a reactor on the downstream separation energy consumption by distillation. Influence of the “difficulty” of separation (relative volatility $\alpha = 1.5$ and $\alpha = 3$) (fixed data: 99% purity, 20 theoretical plate column, enthalpy of vaporization $L_v = 25$ kJ/mole)

The duplication in number by paralleling the equipment and peripheral systems (pumps, sensors, and actuators) is detrimental to high capacities and shows that the intensified units are kept for low production capacities; the limit depending on the type of manufactured products can be estimated at several dozens of tons/year.

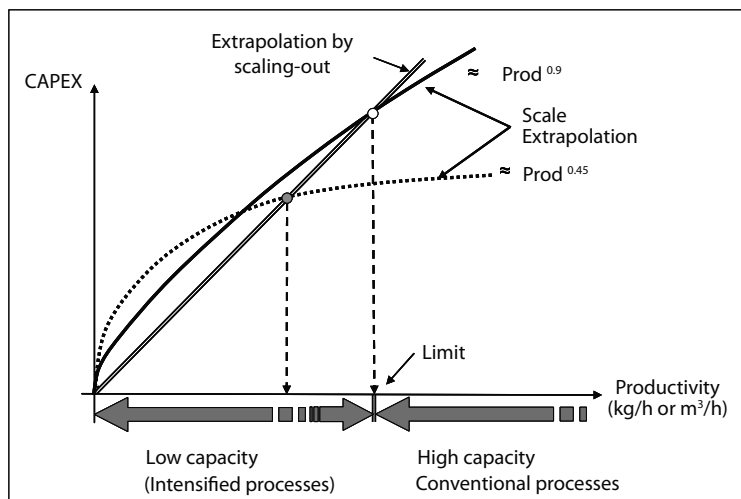


Figure 12.8. Evolution of the investment costs according to the production capacity. Comparison of approaches of extrapolation of size and of extrapolation by duplication in number



Figure 12.9. Comparison of a continuous intensified reactor RAPTOR[®] with a batch stirred tank with the same productivity (AET Group)

In reality, this approach needs to be revised significantly as the productivity per volume unit of intensified equipment is often higher by several orders of magnitude in comparison to conventional equipment (see example of selectivity). The AET

Group has thus developed a very compact intensified reactor (RAPTOR[®]) [AET 10] of less than 1 liter, whose production capacity is that of a several cubic m³ stirred tank, but for a reduced investment cost.

This proves that the cost of an intensified equipment can, in some cases, be significantly lower than that of a conventional equipment, but there is no general rule. As a whole, the market of intensified equipment is currently not fully mature, and it is estimated that many prototypes are made at high costs that should decrease. However, we have to keep in mind that in general, in a complex process, the reactor accounts for only about 10% to a maximum of 20% of the total cost; even for a significant reduction by a factor 2 in the reactor cost, the overall gain in investment is only 5–10%. The significant reduction in the CAPEX (*Capital Expenditure*) is mostly due to the impact of intensification on the entire production line, as shown in some examples of fine chemicals using tested technologies (IMM, Corning). One of the arguments often identified with the reduction in investment costs is the reduction in the number of stages (reaction or separation) in comparison with a conventional process [MAC 11, PIS 10, SCH 10, ROB 05, ROB 08]. Depending on the cases, intensified processes allow a CAPEX gain of about 15–25% in comparison with a conventional unit.

This notable difference between the investment gains, estimated on the reactor itself and the process as a whole, illustrates the difference in strategic choices between the application of intensified equipments to improve an existing process or to create a completely new unit. Let us consider in the case of an extremely simple process consisting of a reactor followed by a separator enabling us to recycle part of the reactants at the reactor inlet (Figure 12.10). The overall efficiency of the transformation process of a reactant A into a product P , depends on both the conversion X in the reactor and the efficiency η of the separator, and is given by the equation $C_p/C_{A0} = X / [1 - \eta(1 - X)]$ illustrated in Figure 12.10.

Let us consider the two different scenarios of the improvement of an existing unit and of a new unit.

Improvement of an existing process: the process uses a low efficient conventional reactor (conversion rate $X = 70\%$), followed by a 90% effective separator, to achieve a total efficiency of nearly 96%. By replacing the reactor with a more efficient intensified technology ($X = 90\%$), the overall efficiency of the process increases to almost 99% (the same separator is retained).

The choice of the technological change estimated by calculating the ROI time is conditioned by the operating gains brought about by the reactor intensification (productivity and separation energy). The separator being already available, its investment cost is not involved in the calculation of profitability.

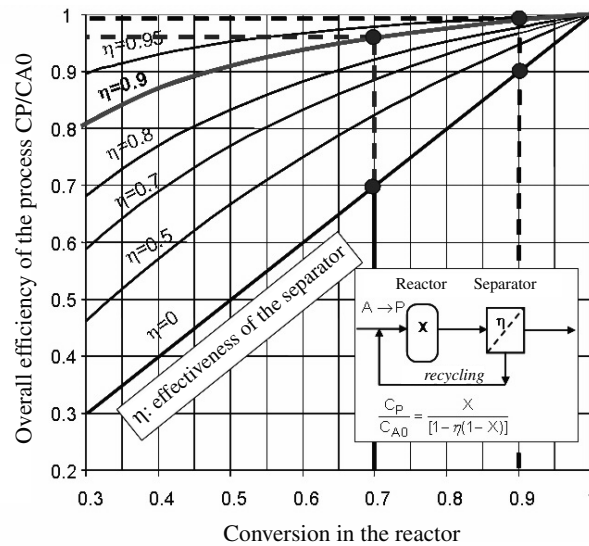


Figure 12.10. Comparison of the overall efficiencies of a conventional process and of an intensified process

Setting up a new unit: we must choose the technology corresponding to the economic optimum of investment and operating costs. Let us assume that the desired overall efficiency is 96%. On the one hand, if a low efficiency reactor (conversion rate $X = 70\%$) is chosen, it is necessary to invest in a separator with high effectiveness ($\eta = 90\%$), whose energy consumption can be quite substantial. On the other hand, by choosing an intensified reactor with a high conversion rate ($X = 93\%$), a separator with a lesser effectiveness ($\eta = 50\%$) is sufficient, which is much less expensive in terms of investment and operating costs, to achieve the overall efficiency of 96%. In this case, it is necessary to take the separation into account; an element that depends largely on the proportion of the cost of energy in the final cost of the manufactured product.

This example shows the complexity of the choice of the layout of intensified technologies in the processes according to the industrial sector considered. This explains the difficulty to draw up general application rules.

12.5.3. Technico-economic advantages of the modular plant

The concept of process units or modular chemical plants, which have drawn more attention in the last few years, results from the compactness of the intensified equipment associated with the possibility of extrapolation by duplication.

This increased attention is motivated by a combination of factors such as the difficulties of very strong international competitiveness, the reduction of product lifecycle (between launch and decline) and a high volatility of markets, coupled with an excessive rise in energy costs, which lead to particularly poor economic forecasts. In this difficult context, the plant of the future must become more flexible to adapt itself better to the market demand.

However, it seems that the economic models set up after World War II, based on the increase in mass consumption, are becoming less and less suitable. The economies of scale associated with high production capacities require very high investments, which, in a fluctuating market, lead to increased risks and a reduced net present value. According to S. Shah [SHA 07], the investment costs of a process unit or a plant, which represent about 4–5 times the equipment cost (Lang's index), and which are too high, are due to a too specific design of each manufacturing unit, even for an identical manufactured product.

There are many reasons, such as the age of installations that can be different and some units may have benefited from technical improvements or local constraints (supply of raw materials, specificities of the product market, and regulatory market). Shah foresees that a modular plant, based on identical, reusable, standardized, and mass-produced modules, would considerably reduce the investment costs and make these modular plants fully competitive in comparison with the large units benefiting from economies of scale.

Figure 12.11 illustrates the economies of stages in the design and implementation of the modular plant. This design is based on the reusable mass-produced modules that can be easily interfaced and connected to other modules (decrease of the connection costs). The modules are not specific but are considered to be functional and versatile elementary parts that can be used in different types of processes. For a maximum reduction of the costs, each module meets a standard (size, connector technology, throughput, etc.) in order to facilitate assembly and interconnection procedures.

In the case of an alkylamine synthesis unit, Shah believes that a 36 ktons/year modular plant helps to achieve overall production costs 10% lower than those of a conventional plant with a five time higher production capacity.

There is also another significant advantage to modular plants related to their ability to adapt to market demand. Lier and Grünewald [LIE 11] have thus shown, based on studies of various scenarios, that the modular plant has a higher net present value for the first 10–15 years in comparison with a conventional plant.

In fact, in the investment or the construction phase, the smaller and more effective modular plant in comparison to the conventional plant can be developed more quickly. It therefore helps to generate income and to take market share more quickly.

This is a notable advantage for a company that makes new products with a relatively short lifecycle requiring considerable efforts in research and development. Moreover, the staggering over time of capital expenditures is a substantial advantage in comparison with a high capacity conventional plant, whose entire efficiencies allowing real economies of scale, will be achieved several years later.

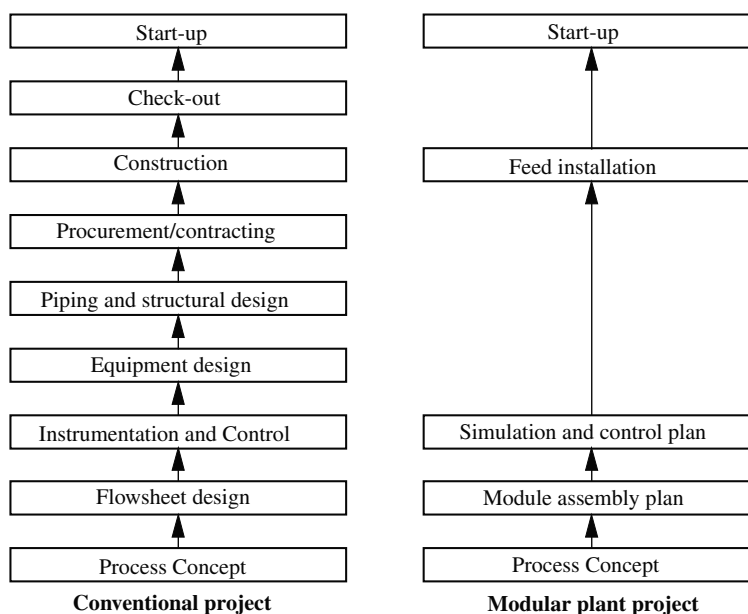


Figure 12.11. Comparison of design and construction approaches of the modular plant compared with the conventional plant (according to Shah [SHA 07])

The flexibility of the modular plant has other advantages, whose non-exhaustive list is given in Table 12.1.

The first concepts of modular plants for the chemical and pharmaceutical industries emerged in 2000 and are now implemented.

Figure 12.12 shows an artistic rendering of a miniplant mounted on a truck, proposed by [BHR 10], which enables onsite production and production on demand for some production campaigns. The AET Group proposes small capacity continuous units (4–40 kg/h) for the onsite and demand production of phosgene [AET 10], which is immediately consumed in a downstream continuous reactor, by reaction with a second reactant (e.g. with an alcohol to form chloroformates or carbonates, or with an amine to make carbamoyl chloride, isocyanate or urea) for on demand synthesis applications.

Advantages	Disadvantages
Development, investment, and construction phase	
Fewer extrapolation steps Shorter development times Shorter time for entering the market → decrease in terms of time for incomes and market shares. Separation of the manufacture and operation stages of the modules. → growth of production capacities adapted to demand; no excessive capacity. Production of modules in series. → gain of experience and learning effect in favor of reduced costs for the following modules. Investments spread over time. → increase of liquid assets.	Material surplus Space necessary to set up modules → loss of efficiency
Operational phase	
Flexibility of the production capacities: unit start-up and shutdown. → adaptation to demand. Each unit operates in optimum conditions of efficiency and energy. → material and energy gains. Ease of maintenance.	Each unit operates independently. → additional need for workforce → more complex measurement and control systems and procedures.

Table 12.1. *Advantages and disadvantages of the modular plant [LIE 11]*

In the field of pharmaceuticals, there are currently many important developments on the transformation of batch process units into continuous, intensified, and modular process units [FLE 10, HUW 10, NIC 10, SMI 04].

These real benefits of the modular plant require however flexible and interchangeable modules, whose dimensions and connector technologies must be standardized in order to facilitate assembly or interconnection procedures. The main objective of the European project F3Factory [F3F 10] is to design and develop such modules based on intensified and automated pieces of equipment that are assembled on a backbone facility delivering utilities from a dedicated platform. The advantage of a multipartner platform is to share the investment and operating costs.



(a) Concept of self-supporting skid-mounted miniplant (artistic rendering, [BHR 10]),



(b) Continuous and on-demand phosgene generation module [AET 10]

Figure 12.12. Examples of skid-mounted modular systems

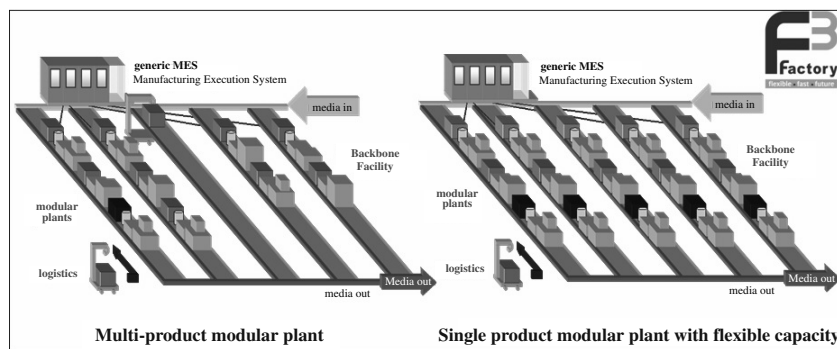


Figure 12.13. Concept of intensified modular plants developed as part of the European project F3Factory (FP7) (<http://www.f3factory.com/scripts/pages/en/home.php>)

12.6. Conclusion

In this chapter, we have provided some examples that show the different possible applications of intensification. These few examples do not constitute an exhaustive list of all the possibilities. Readers can refer to the specialized scientific literature.

If intensification is a concept which has been created with a very specific purpose, which was original at that time, of equipment miniaturization, then nowadays, we can see that intensification covers a much broader field of “modern” process engineering that aims at developing processes for the sustainable chemical plant. It becomes an integral part of process engineering so that everyone “makes prose without knowing it.”

Intensification involves however two very important concepts:

- transition (very often) from batch to continuous production equipment (which does disclude the concept of batches, as we can produce by campaign);
- equipment miniaturization, which necessitates extrapolation by paralleling the channels and/or equipment, if we wants to process high capacities.

This mode of extrapolation by duplication is a major revision of methods for the design and improvement of devices, since in principle, it is enough to optimize the operating conditions on a basic part in laboratories or in piloting, in order to define the operating conditions of the industrial equipment.

However, it would be unrealistic to state that, by means of intensification, all future plants will be small, clean, safe, and confined units. The basic products with large tonnage will continue to be produced in large plants. Moreover, in many processes, solid products are handled (catalysts, dissolution of solids, formation of precipitated or crystallized products): thus remains a challenge for some intensified processes implementing small equipment volumes. In addition, the intensification potential is not the same for every process; some processes may benefit from significant technological breakthroughs, whereas others might not. Finally, depending on the total amount of investments to be made, it might be better to retain more conventional installations that have been improved, modernized, and debottlenecked, rather than to build completely new units. Finally, there are some processes that have been hardly addressed by intensification, such as bioprocesses whose reaction kinetics are slow and microorganisms, highly sensitive to all “intensified” operating conditions, are thus more stressful. Yet, the stakes for processes of treatment and transformation of biomass are essential for the plant of the future.

Despite the difficulties outlined, intensification brings about innovation concepts that can redefine the conventional production modes and renew the economic models of enterprises.

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