POLITECNICO DI TORINO

DOCTORATE SCHOOL
Ph.D. in Metrology: Measuring science and Technique – XXVI doctoral cycle

PhD Thesis

Process Intensification Vs. Reliability

Gabriele Baldissone

Tutor	**PhD course coordinator**
Prof. Micaela Demichela	Prof. Franco Ferraris

February 2014

Acknowledgements

Summary

1 Introduction

Over the centuries the equipment used by the process industry went through little changes: it have been perfected but it have never been substantially changed. Indeed the type of chemical reactor currently used is the stirred tank, that works in the same way of a similar one built in 1800; logically, materials, control systems or safety systems changed, but the basic engineering remained the same. In recent years, a new equipment was proposed: it performs the same functions as the existing one, occupying less space, requiring less power and operating in a safer way.

The changes required in a plant to achieve the above mentioned objectives are called Process Intensification; it can be described as the following (Stankiewicz and Moulijn, 2000):

"Any chemical engineering development that leads to a substantially smaller, cleaner, safer and more energy efficient technology is process intensification".

From the Process Identification point of view, it is possible to mention the development of new equipment, such as the Spinning Disk Reactors and Heat Exchange (HEX) Reactors, characterized by a remarkable technological jump with respect to the existing equipment: designers began to use physical phenomena previously neglected, such as the centrifugal force in the spinning disk reactor, or to combine into one equipment more unit operations, such as Reverse-Flow Reactors, Reactive Distillation ...

These recent developments certainly provide more compact and cleaner plants, but there are more uncertainties about their capability to produce an actual increase of the safety.

The use of more complex equipment, in example with moving parts or with more intense sources of energy, can even bring to safety problems not detected in traditional plants, also modifying the reliability of the system.

Under the definition of Process Intensification it is possible to indicate different kinds of improvements to the plants: in order to analyze the effects of these improvements on safety and reliability, we made an assessment of the reliability in a traditional plant, and in an intensified plant, comparing their results.

The process analyzed is related to a plant for the VOC (Volatile Organic Compound) abatement in a stream of inert gas. The traditional system is based on a fixed bed reactor; the intensified plant uses a Reverse-Flow Reactors.

The selected plants were firstly subjected to a traditional safety analysis, using an operability analysis and then operating the extraction and quantification of the fault trees.

During the analysis, we realized that the traditional methods (HAZOP and FT) worked well if applied to conventional systems, which arrive to a steady-state, but they were less suitable for modern plants, that work in a transitional regime.

After the traditional safety analysis, we proceeded with a Integrated Dynamic Decision Analysis, that allows to evaluate more in detail the behavior for not stationary plants, in case of failure.

From the application of the methodology to the specific case some general conclusions have been drawn.

2 Process intensification

At the end of the Renaissance, the first handbook on the extraction of metals was published: De Re Metallica (Agricola, 1556), with interesting woodcuts which describe the processes. I.e., Figure 1 shows a woodcut that describes the method for the extraction of gold from rocks. The mineral was crushed in a mortar "G", then it was further milled in the mill "F", moved by the wheel "C". The fragmented rock was then mixed with mercury in tanks "O", by agitators "S". The paste of gold and mercury was then filtered, in order to recover the mercury and obtain the gold.

In some parts of the world, gold is still extracted in this way, with all the environmental and safety problem related to the use of mercury.

On closer view, some pieces of the equipment showed in Figure 1 evidence a great similarity with those used today in the chemical industry. In example, it is clear the similarity between the tanks represented in the Figure 2 and modern reactors, or between the agitation systems

Figure 1: Woodcut on gold production (Agricola, 1556)

employed 400 years ago and those on the market today.
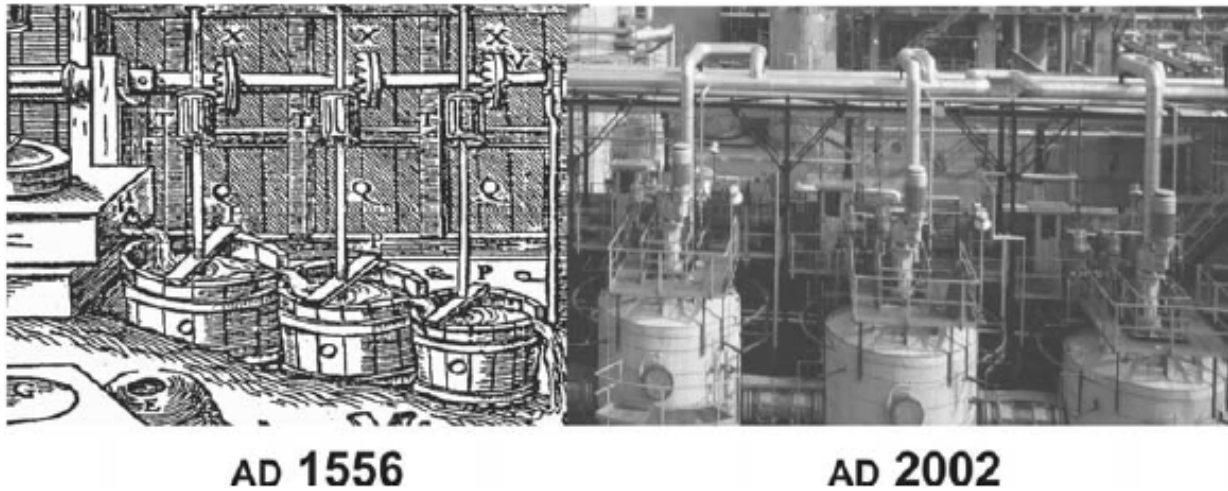
Figure 2: Comparison of the tank represented in De Re Metallica and modern reactors.
(Stankiewicz and Moulijn, 2004)

A real discontinuity in the technology used in chemical industry was reached only in the last century, when designers proposed static mixers (Taber and Hawkinson, 1959; Chemtech, 1997) which can be classified as the first examples of Process Intensification. They were not an improvement of existing models, because they were based on different principles. This example captures the essence of Process Intensification (P.I.): it is a discontinuity in the nature of the equipment, not a continuous evolution of existing ones.
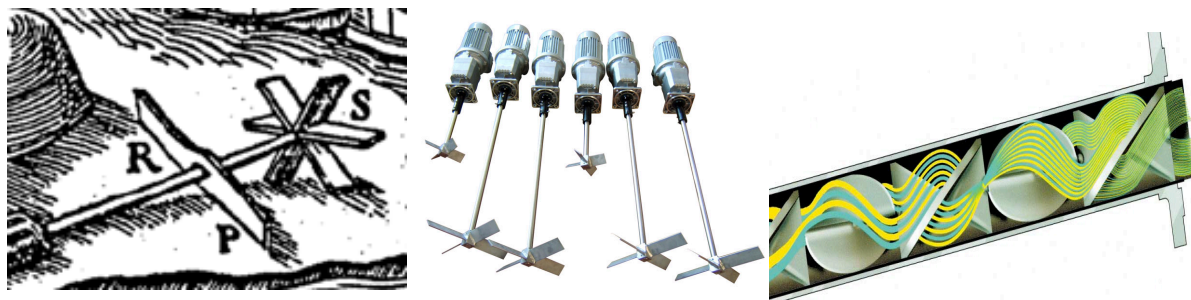
Figure 3: Comparison of agitation systems described in the 16th century, some modern and a static mixer

In the scientific literature, the term Process Intensification appeared in the mid-1960s and early 70s, in East European publications about metallurgical process (Chvatal, 1965; Chervotkin et al., 1969; Grekov, 1970; Kolpakov et al., 1971), then in chemical engineering publications (Leszczynski, 1973; Romankov, 1977; Kleemann and Hartmann, 1978).

The birth of Process Intensification as a chemical engineering discipline occurred several years later in the United Kingdom, with the publication in 1983 of the Colin Ramshaw (1983) paper, where the studies on the application of centrifugal forces in distillation processes were descripted.

Until the early 1990s, Process Intensification was principally a British discipline and it focused primarily on four areas: use of centrifugal forces, compact heat transfer, intensive mixing, and combined technologies.

In 1995, during the first congress on P.I., the first real definition was given: "Strategy for making dramatic reductions in the size of a chemical plant so as to reach a given production objective" (Ramshaw, 1995). At the time, a particular importance was given to the reduction of the size of the equipment, disregarding other possible effects of P.I.

"By that time, however, Process Intensification had already become an international business, for many research centers in different countries had entered the field. In Holland, for instance, Delft University of Technology, together with DSM, carried out research on structured reactors (Stankiewicz et al., 1995). Another group in Delft investigated centrifugal adsorption technology (Bisschops, van der Wielen and Luyben, 1997). In France, Greth CEN institute in Grenoble carried out extensive studies on compact heat exchange equipment (Thonon, 1995). In Germany, research on microtechnology flourished in the Institut für Mikrotechnik Mainz (Ehrfeld, Hessel and Löwe, 2000), while in China a special center at Beijing University was established to carry out R&D activities in the area of high-gravity processing (Zheng et al., 1997). In the United States a number of research institutes started PI-related studies too, e.g., Pacific Northwest National Laboratory in the field of microchannel heat exchangers (Tonkovich et al., 1996) and MIT in the field of microreactors (Quiram et al., 2000; Tonkovich et al., 1996). Also early on, a number of chemical companies got involved in process intensification. This involvement resulted in the first successful commercial-scale applications, such as the methyl acetate process of Eastman Chemical (Siirola, 1995), the hydrogen peroxide distillation system of Sulzer (Meili, 1997), and the hypochlorous acid process of Dow Chemical (Trent and Tirtowidjojo, 2001)." (Stankiewicz and Moulijn, 2004)

At the beginning of the century, a new definition arrived:

"Any chemical engineering development that leads to a substantially smaller, cleaner, safer and more energy efficient technology is Process Intensification" (Stankiewicz and Moulijn, 2000) .

This new definition focused the attention not only on reducing the size, but also on jumping at the next level in the fields of energy saving, environmental and security.

In recent years, the P.I. is still developing in the fields in which it was born, but it is also extending to other sectors such as biotechnology (Chisti and Moo-Young, 1996; Hamilton et al., 1999; Stewart, 2000) and fine chemicals (Laird, 2001).

One of the latest definitions in order of time is contained in the European Roadmap for Process Intensification (SenterNove, 2007): "Process Intensification (PI) presents a set of often radically innovative principles ("paradigm shift") in process and equipment design, which can bring significant benefits in terms of process and chain efficiency, capital and operating expenses, quality, wastes, process safety, and more.". This definition shows that a technology must bring a substantial change with respect to existing plant and should bring great benefits in multiple fields, in order to be defined P.I.

2.1 Possible advantages of P.I.

As mentioned in previous paragraphs, the P.I. is a breaking point with tradition in the chemical industry, in order to obtain great benefits in various fields.
The first advantage is the reduction of the process costs, followed by possible environmental benefits, energy savings and safety.
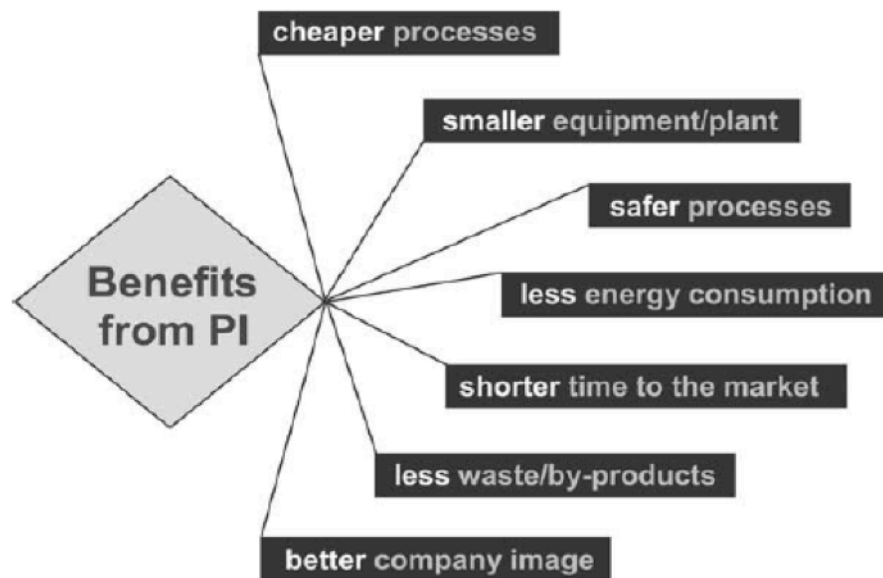
Figure 4: Main benefits from process intensification (Stankiewicz and Moulijn, 2004)

2.1.1 Costs

Process Cost reduction is one of the first targets for the P.I., obtained through the reduction of the spaces occupied.

This objective is particularly important when an increase of the territorial extension of existing installations is impossible or difficult. By replacing existing plants with intensified ones, it is possible to obtain a higher production or to produce more products in the same space.

The P.I. can also bring the reduction of other costs, such as the installation costs (for example the reduction of the pipes) or the use of raw materials of lower quality.
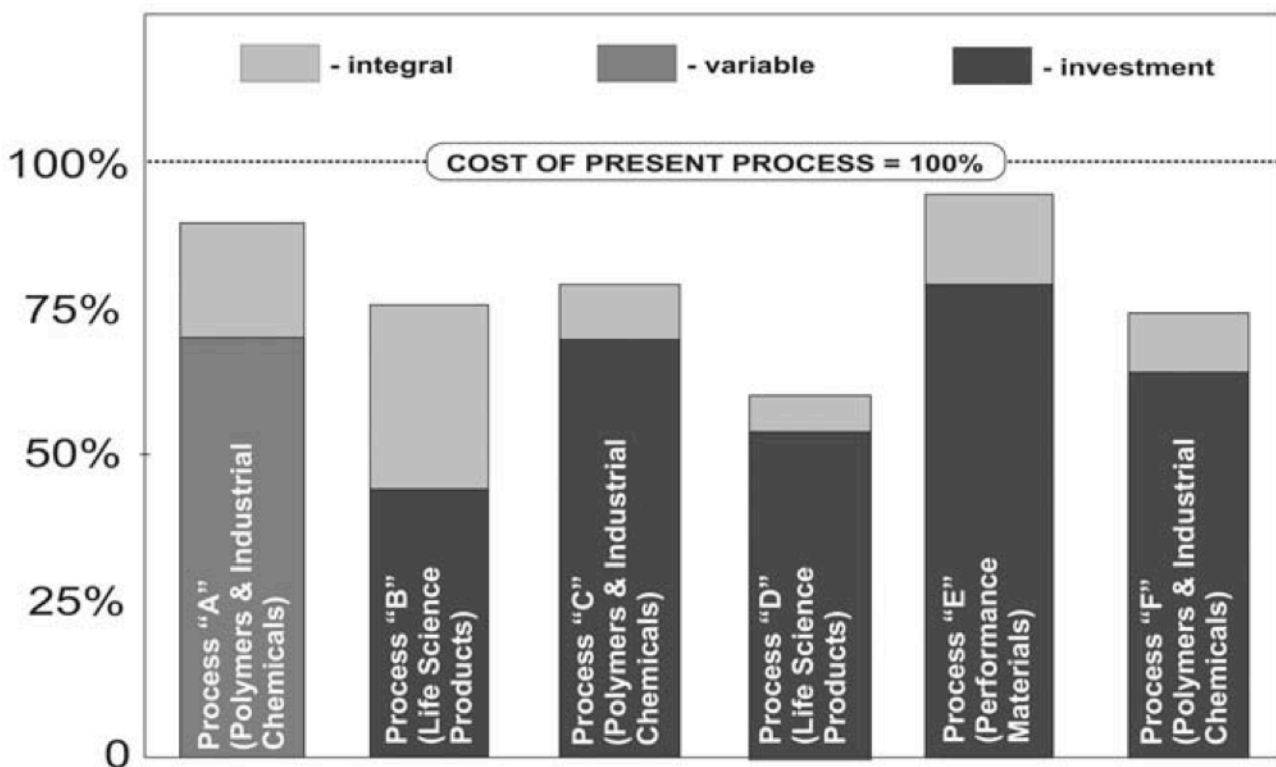
Figure 5: Estimated savings in some DSM technologies, achieved by applying PI principles to process and plant design (grass-roots situation) (Stankiewicz and Moulijn, 2004)

2.1.1.1 Reactive separation

One of the most interesting applications of P.I. is the possibility of combining two of the key moments in chemical industry: the reaction phase and the separation of the products. In this way, it is possible to have several advantages in investment cost savings, in operating costs savings, and in energy savings, obtaining an increased productivity due to the movement of chemical equilibrium. However, to clarify ideas about the reactive separations, it is useful to report what written in (Stankiewicz and Moulijn, 2004):

"Chemical manufacturing companies produce materials based on chemical reactions between selected feed stocks. In many cases the completion of the chemical reactions is limited by the equilibrium between feed and product. The process must then include the separation of this equilibrium mixture and recycling of the reactants. The fundamental process steps of bringing material together, causing them to react, and then separating products from reactants are common to many processes.

Conventionally, each unit operation—whether mixing or absorption, distillation, evaporation, crystallization, in fact, any of the heat-, mass-, and momentum- transfer operations so familiar to chemical engineers—is typically performed in individual items of equipment, which, when arranged together in sequence, make up the complete process plant. As reaction and separation stages are carried out in discrete equipment units, equipment and energy costs are added up from these major steps. However, this historical view of plant design is now being challenged by the combination of two or more unit operations into one plant unit. The potential for capital cost savings is obvious, but there are often many other process advantages that accrue from such combinations (Noble, 2001).

In recent decades, a combination of separation and reaction inside a single unit has become more and more popular. This combination has been recognized by chemical process industries as having favorable economics for carrying out reaction simultaneously with separation for certain classes of reacting systems, and many new processes (called reactive separations) have been invented based on this technology (Doherty and Buzad, 1992; Zarzycki and Chacuk, 1993; Agar, 1999; Kelkar and Ng, 1999; Stankiewicz, 2003; Fricke, Schmidt-Traub and Kawase, 2001; Bart, 2001; Noeres, Kenig and Górak, 2003).

Reactive separation units may also be treated as a kind of multifunctional reactor in which the functionalities of several processes are combined to generate the new reactor concept (Figure 6).
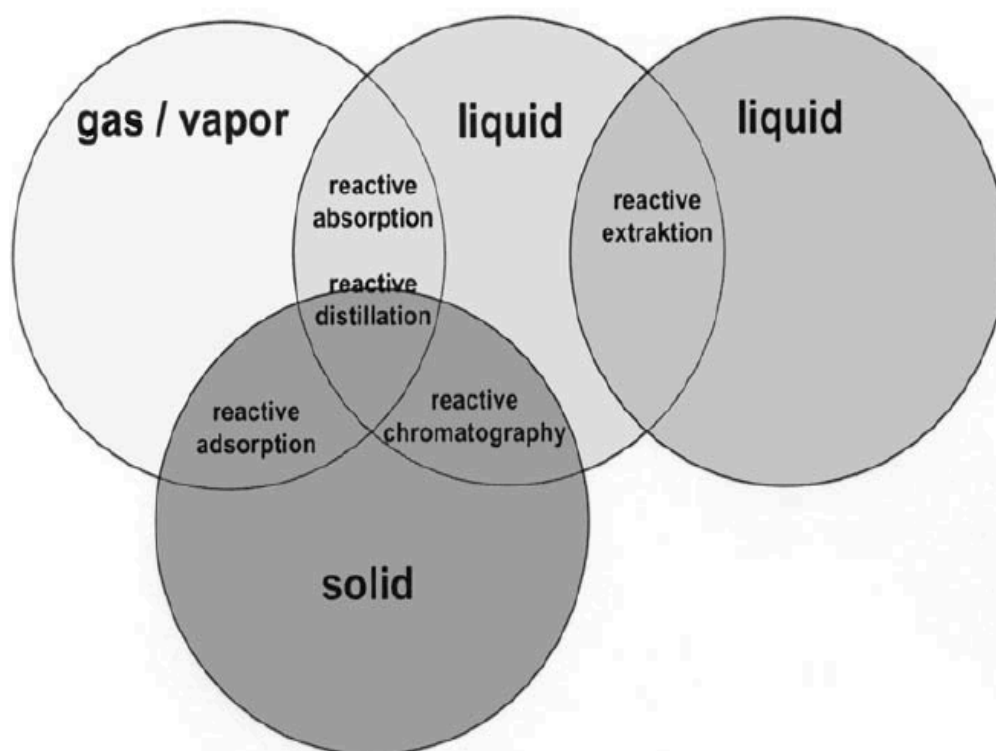
Figure 6: Reactive separation units as multifunctional reactors (Inspired by (Agar, 1999))

The most important examples of reactive separation processes (RSPs) are reactive distillation (RD), reactive absorption (RA), and reactive extraction (RE). In RD, reaction and distillation take place within the same zone of a distillation column. Reactants are converted to products, with simultaneous separation of the products and recycling of unused reactants. The RD process can be efficient in both size and cost of capital equipment and in energy used to achieve a complete conversion of reactants. Since reactor costs are often less than 10% of the capital investment, the combination of a relatively cheap reactor with a distillation column offers great potential for overall savings. Among suitable RD processes are etherifications, nitrations, esterifications, transesterifications, condensations, and alcylations (Doherty and Buzad, 1992).

Similarly, in RA, reactions occur simultaneously with the component transport and absorptive separation, in the same column zone. These processes are used predominantly for the production of basic chemicals, e.g., sulphuric or nitric acids, and for the removal of components from gas and liquid streams. This can be either the clean-up of process gas streams or the removal of toxic or harmful substances in flue gases. Absorbers or scrubbers where RA is performed are often

considered gas–liquid reactors (Hatcher, 1986). If more attention is paid to the mass transport, these apparatuses are instead treated as absorption units.

Reactive absorption, distillation, and extraction have much in common. First of all, they involve at least one liquid phase , and therefore the properties of the liquid state become significant. Second, they occur in moving systems; thus the process hydrodynamics plays an important part. Third, these processes are based on the contact of at least two phases , and therefore the interfacial transport phenomena have to be considered. Further common features are multicomponent interactions of mixture components, a tricky interplay of mass transport and chemical reactions, and complex process chemistry and thermodynamics.

On the other hand, RD, RA, and RE have a number of specific features that should be considered with care and described by different approaches. Before going into detail, it is worthy to note that the operating window of reactive separations may be somewhat limited, since these operations are feasible only if they allow for both separation and reaction within the same range of temperature and pressure and, on the other hand, for the safe operation from the constructional point of view (Figure 7)."
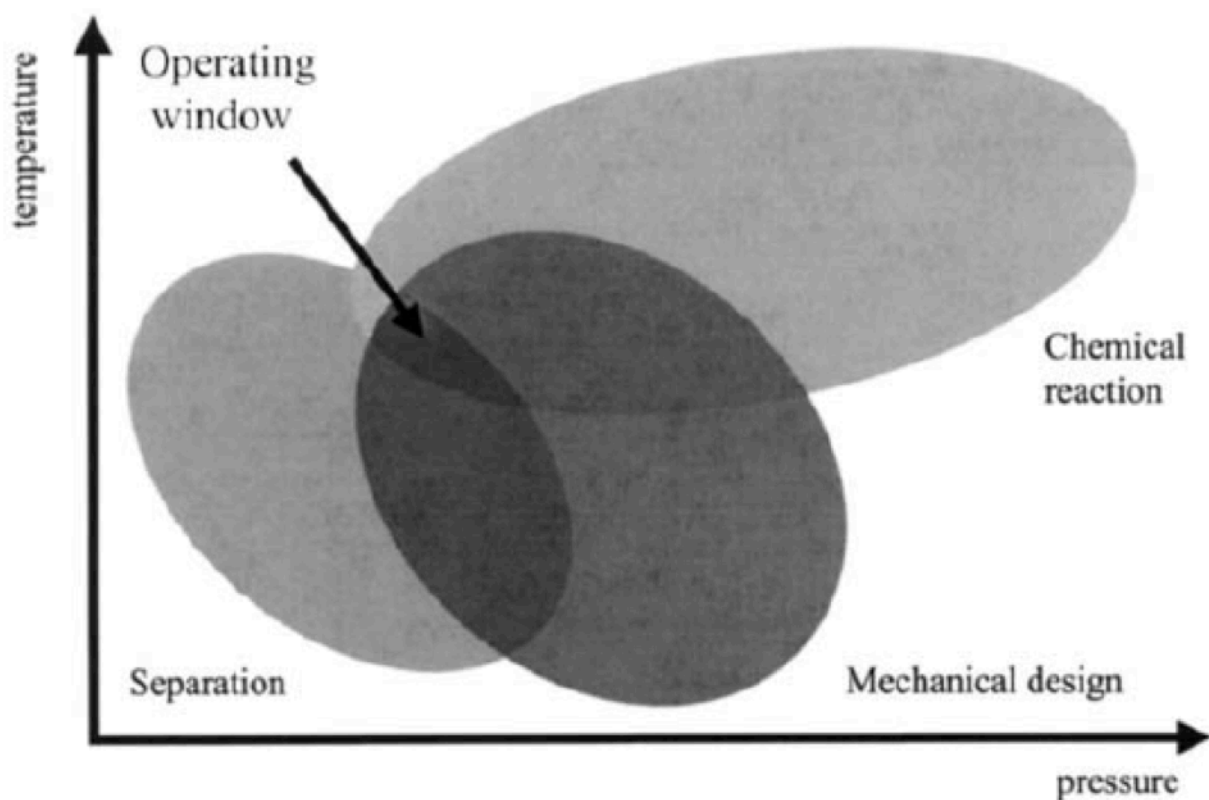
Figure 7: Feasibility of reactive separation, depending on mechanical design, chemical reaction, and separation performance

10

2.1.2 Energy saving

One the major benefits in P.I. is related to energy saving, as well explained in (Reay and Ramshaw, 2008): "The effectiveness of the PI strategy is ultimately dependent upon success in identifying techniques for dramatically increasing the intensity of the fluid dynamic environment, so as to accelerate the transfer of heat, mass and momentum within a process or operation. A high fluid dynamic intensity may be used to minimise the concentration, temperature and velocity differentials involved in transferring mass heat and momentum. When a process is considered from a thermodynamic standpoint these differentials may be regarded as irreversibilities that impair the ideal process energy efficiency. For example, a heat transfer operation performed with very high heat transfer coefficients will generate less entropy and preserve most of the thermodynamic potential of the heat transferred. An analogous situation is provided by an electrochemical operation for which the cell voltage attains the thermodynamic ideal value at very low current densities. However, the delivered voltage can fall substantially when realistic currents are involved. This voltage loss is incurred by mass transfer, conductivity and catalytic factors, which can be alleviated by an intensification approach".

In recent years, many scientists proposed P.I. solutions for energy saving in chemical industry: (De Groot and van Dorst, 2006; Jachuck et al., 1997; Reay, 2008) are just few examples.

In example, Gocate (2008) presented a comparison between the cavitation reactors, classified as P.I., and traditional systems, demonstrating that cavitation reactors required less energy than the traditional ones (Figure 8).

No	Technique	Time (min)	Yield (%)	Yield (Kg/KJ)
1	Acoustic[a]	10	99	8.6×10^{-5}
2	Hydrodynamic[b]	15	98	3.37×10^{-3}
3	Conventional[c]			
	With stirring	180	98	2.27×10^{-5}
	Under reflux	15	98	7.69×10^{-6}

Figure 8: Results obtained from Gocate with various types of reactors (Reay and Ramshaw, 2008)

"Arthur D. Little, in 2005-6 carried out a study with SenterNovem of The Netherlands. The authors of this book were involved in giving information during the study (Anon, 2006). The outcome of the study was the identification of a plan for implementing PI in a number of sectors, using specified P.I. technologies. The effort was costed and potential stakeholders identified, and the work is being followed by a current study as part of the European Roadmap of Process Intensification, principally involving The Netherlands and Germany. With regard to energy use, there were many interesting and encouraging applications data, and these are summarized in Figure 9". (Reay and Ramshaw, 2008).

	Bulk chemicals	Fine chemicals	Food
Multifunctional equipment (advanced distillation)	50–80% energy savings in 15% of processes. 9–18 PJ	Limited to separation processes, i.e. 10% of sector. Increase efficiency by 50%, saving <1 PJ	Drying and crystallisation. 10% total energy saving, worth 3–5 PJ
Micro/milli-reactors	A study by ECN in Holland suggests 20 PJ savings using heat exchanger reactors. Micro-reactors extend this to 25 PJ.	Applications in 20% of processes in the sector saving 20% of energy – 1 PJ. Reduce feedstock and additives by 30% in 10% of processes saving 5–7 PJ	Spill-over from fine chemicals: <1 PJ
Microwaves (electrical enhancement)	*	Reduce feedstock and additives by 20–40% in 5% of processes: 2–3 PJ	20–50% saving in 10% of drying market: 1–1.5 PJ; 10% energy reduction in product processing: 1–1.5 PJ
High gravity fields (e.g., spinning disc reactor, HiGee)	*	Reduce feedstock, solvents, etc., by 50% in 5% of processes: 1–3 PJ	Assuming 20% of electricity in food production goes to emulsification, mixing, etc., 10–20% saving worth 0.5 PJ

Note: Energy Saving is in PJ/annum
* ECN suggested that too little was known of the effects of microwaves and HiGee in the bulk chemicals sector.

Figure 9: Energy saving potential of PI technologies as identified by the ADLSenterNovem study (Reay and Ramshaw, 2008)

2.1.2.1 Spinning disc reactor

As previously mentioned, the birth of P.I. was based on studies for the use of centrifugal forces in rotating equipment for the chemical industry (the spinning disk reactor (SDR)).

As shown in Figure 10, the reagent liquid is poured from the top and slids along the disc set in rotation. The speed of the disc controls the thickness and the type of the liquid layer: in this way it is possible to govern the reaction, changing the transfer of heat and material inside the liquid. With this type of equipment, it is possible to use very thin layers of liquid with high temperatures and short reaction times, reducing the occurrence of secondary reactions.
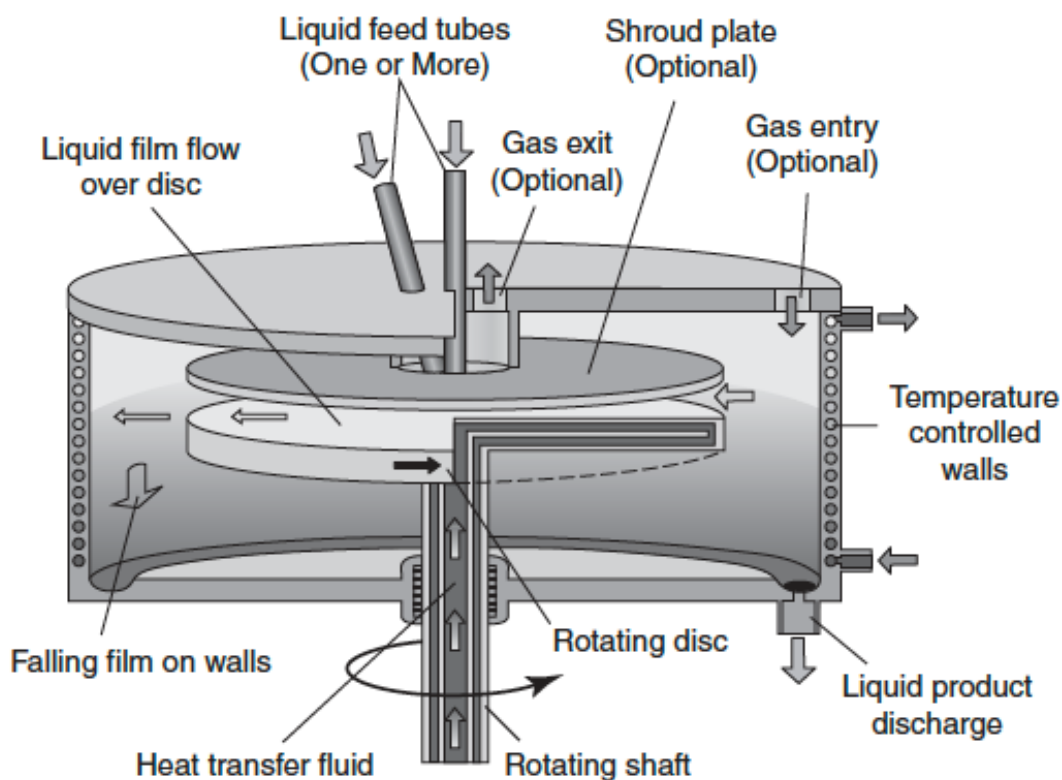
Figure 10: Diagram of a spinning disc reactor

The performances obtained on the transport of heat and mass are reported by Ramshaw (2008): "One of the attractive features of the SDR is that its high fluid dynamic intensity favors the rapid transmission of heat, mass and momentum, thereby making it an ideal vehicle for performing fast endothermic reactions which usually also benefit from an intense mixing environment. It must be noted, however, that heat transfer from the process liquid to any cooling/heating fluid behind the disc involves a second film coefficient which may severely limit the overall heat transfer rate (this is discussed later). Some of the more relevant recent experimental studies of spinning disc performance may now be considered.

13

Koerfer (1886) investigated the desorption of oxygen using a range of perforated, grooved and smooth 600 mm diameter discs at speeds up to 600 rpm. The average mass transfer film coefficient (after accounting for the contribution from the peripheral liquid spray) is shown in Figure 11. As can be seen, the performance of the disc with concentric grooves (10 mm wide, 2 mm deep) was significantly better than that of the smooth disc. The perforated disc had 1.5 mm holes on a triangular pitch which gave 31% open area. This resulted in even higher performance, with mass transfer coefficients up to 70×10^{-6} m/s compared with 5×10^{-6} m/s under equivalent conditions for the smooth disc. Some of this improvement was attributed to the extra surface area created as the film jumped across the holes.

Bell (1975) used the CO_2-diethanolamine system to evaluate area-averaged mass transfer performance of a range of smooth, mesh and perforated discs. Once again the smooth disc gave the lowest mass transfer coefficient, while the perforated and mesh discs were broadly similar. For all the discs a pronounced maximum coefficient was noted at a critical rotational speed. This phenomenon was ascribed to film breakdown in the peripheral regions of the discs as the rotational speed increased. The existence of peripheral dry areas was confirmed photographically.

Aoune and Ramshaw (1999) measured both local and average heat and mass transfer film coefficients on a smooth 0.5 m diameter disc rotating at up to 900 rpm. For pure water at inner radial positions the heat transfer coefficient was relatively high, but it exhibited a minimum at intermediate radii before increasing to the peripheral value. Typical coefficients were in the range 10-20 kw/m^{2}K whereas a 40% water/60% propylene glycol mixture (with a tenfold higher viscosity) only gave 5-10 kw/m^{2}K. Mass transfer with water was

Figure 11: Mass transfer performance of a rotating disc in oxygen desorption

relatively insensitive to radial position, being in the range (3-9) 10^{-4} m/s. The Higbie unsteady state mass transfer model, when based on the film exposure time on the disc, grossly under predicted the mass transfer rates. Bearing in mind the wavy nature of the flow, this suggests that much shorter exposure times are encountered in practice. The unexpectedly high inner heat transfer rates were attributed to the additional shear stress involved in bringing the feed liquid up to the disc rotational speed - which was not taken into account by the Nusselt model.

Another study by Jachuck and Ramshaw (Jachuck and Ramshaw, 1994) explored the influence of surface profile on the heat transfer performance of a spinning disc. Using a smooth disc as a benchmark it was shown that disc surfaces disrupted with metal powder or grooves gave a significantly improved performance - presumably due to better film mixing. The best performance at modest disc speeds was obtained with 'undercut' grooves as shown in Figure 12, which were originally conceived as a means for improving the circumferential distribution of any radial rivulets. At higher disc speeds, the film radial velocity was such that liquid was projected off the disc, thereby compromising the heat transfer process.
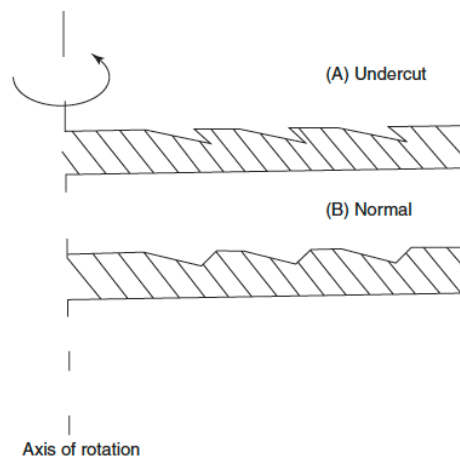
Figure 12: Types of disc grooves tested at
Newcastle University

When exo- and endothermic reactions are to be performed on a spinning disc, some provision is required to supply, or remove, the reaction heat involved as rapidly as possible. It has been shown above that the heat transfer film coefficient associated with the process fluid is high. However, care must be taken to ensure that the thermal resistance associated with the heat transfer fluid and the conductive resistance of the disc material does not significantly restrict the overall heat transfer rate. A stainless steel disc 2mm thick incurs a conductive resistance of around 8 kW/m^{2}K, while an organic heat transfer fluid film coefficient may only be 5 kW/m^{2}K. It is therefore imperative to

match, or exceed, the process fluid heat transfer coefficients if possible by using thin conductive disc material and by optimising the flow conditions for the heat transfer fluid. One SDR design is shown in Figure 10, where it can be seen that the heat transfer fluid flows over, then under, a stationary 'splitter' plate which is held within the rotating assembly. In order to restrict the pressure drop to reasonable levels the inner flow gap may need to be greater than that at the periphery.

An alternative, even more effective, SDR design is shown in Figure 13, which is based on a spiral configuration for the heating fluid channels beneath the disc, whereby the outflow and return channels are comprised of interleaved spirals".

Figure 13: The structure of the spinning disc heat transfer surface. Overall heat transfer coefficient of 10 kW/m^2 K for low viscosity process fluids and water or glycol as heat/cool fluid. A 0.5 m dia disc with delta T 20 K will transfer 39 kW, thanks to patented double spiral disc design, copper construction (with chrome plating for corrosion resistance)
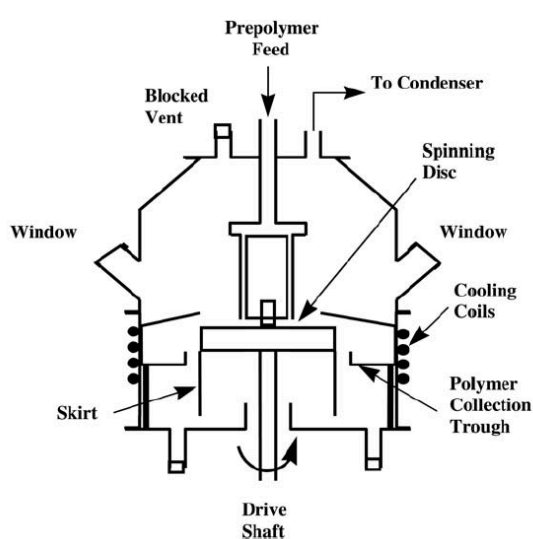
Figure 14: Schematic of an SDR styrene polymerizer

Some examples can be find in Stankiewicz and Moulijn (2004):

"Polymerization

Polystyrene. The manufacture of polystyrene from various grades of prepolymer has been performed (Boodhoo, Jachuck and Ramshaw, 1995; Boodhoo, Jachuck and Ramshaw, 1997) on a 36 cm brass SDR using the arrangement shown in Figure 14. A series of concentric grooves was machined in the disc surface in order to improve liquid mixing within the film. The reaction operates via free radicals, which were initiated in this case using benzoyl peroxide. In

the first instance a series of batch runs was performed in a conventional laboratory-scale stirred vessel in order to produce a calibration curve (Figure 15) of conversion versus time.
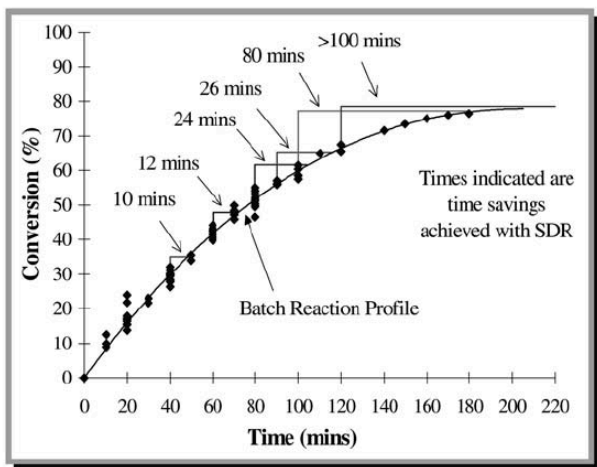
Time saving in SDR operated at 850 rpm

Figure 15:Free-radical polymerization of styrene

This vessel was then used to produce about 200 mL of prepolymer at a range of conversions that was supplied to the inner spinning disc surface over a period of about 30 seconds. The SDR was heated from below by a stationary radiant ring, and the polymer produced was collected in a cooled annular trough surrounding the disc. The styrene was diluted with about 16% $^w/_w$ toluene in order to reduce the viscosity.

Figure 15 also shows the increment in polymer conversion in one pass over the disc as a function of the initial conversion in the preliminary batch.

It can be seen that the equivalent batch time that can be ascribed to one pass on the disc increases (up to 58 minutes) as the initial conversion increases to 63%. This implies that the benefits of the SDR become more marked as the polymer viscosity increases. It is envisaged that the process can be scaled up either by using a larger disc or by mounting several discs on one shaft. The latter approach (i.e., several discs in series) does, however, involve the problem of transferring polymer from the peripheral collection trough to the center of the next disc. An alternative may be to operate discs on one shaft in parallel. For the experiments just described, the feed rate was roughly 5–10 mL/s, which is equivalent to an output of up to 250 tons/year on a continuous basis, though at this early stage this should not be considered the ultimate limitation.

The fundamental reasons for the high performance of the SDR are still a matter for debate. The significance of micromixing and the consequent improved probability of radical interaction has already been mentioned. However, another factor is expected to be the divergent character of the flow on the disc. This may be expected to align the polymer molecules and thereby encourage the juxtaposition of the reactive groups.

Polycondensation.

The reaction between maleic anhydride and ethylene glycol has been studied as an example of polycondensation (Boodhoo, Jachuck and Ramshaw, 1997). Since the reaction proceeds on an equilibrium basis, in order to drive it to completion the water produced must be eliminated from the increasingly viscous polymer melt. The grooved brass 36 cm disc described earlier for the

polystyrene experiments was used at a temperature of 200°C and a disc speed of 1000 rpm. As before, the experimental procedure involved the establishment of a benchmark batch calibration against which the subsequent disc runs could be compared. A typical acid number plot versus batch time is presented in Figure 16. As the acid number decreases, the conversion to polymer increases.
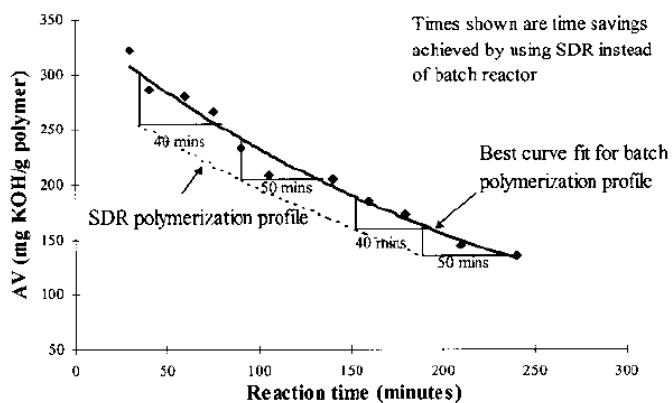
Figure 16: Time savings in the SDR for polyestirification

The water of reaction was removed from the polymer film by maintaining a large nitrogen purge to the vapor space. This technique, rather than the application of a vacuum, was the preferred method for reducing the water vapor partial pressure.

It can be seen that the increment in polymerization following one pass in the SDR corresponds to many minutes of reaction in the small batch reactor used as a reference. This is particularly encouraging because the mass transfer intensity in the laboratory stirred reactor is likely to be much greater than its industrial-scale equivalent, and it therefore provides a demanding benchmark for the spinning disc performance.

Fine Chemical Manufacture

The intense heat and mass transfer environment that can be established within the liquid film flowing over the disc allows high selectivities and conversions to be achieved when fast liquid-phase reactions are performed. Very encouraging results were achieved in an industrial study of a phase-transfer-catalyzed (p-t-c) Darzen's reaction to produce a drug intermediate (Oxley et al., 2000). In comparison with the currently used batch processes, the ptc reaction on the SDR had a 99.9% reduced reaction time, a 99% reduced inventory, and a 93% reduced impurity level. A more recent study has involved a 20 cm diameter SDR with a catalytically activated surface to perform the rearrangement of α-pinene oxide to campholenic aldehyde (Vicevic, Jachuck and Scott, 2001), which is an important intermediate used in the fragrance industry. The comparative performance of the batch reactor and the SDR is shown in Figure 17. For equivalent conversion and selectivity, the unoptimized SDR gave a much higher throughput than the equivalent batch reactor and avoided the need to separate a catalyst slurry from the product".

	Batch process	SDR (continuous)
Process time (s)	300	1
Processed feed	1.2 kg/h	209 kg/h
Conversion (%)	100	100
Selectivity (%)	64	62
Note	Catalyst separated from the product mixture	No loss of catalyst

Figure 17: Comparison of the Best SDR Runs with Batch Results for Conversion of α-Pinene Oxide to Campholenic Aldehyde

2.1.2.2 Regenerative reactor

The definition "regenerative reactor" concerns those systems in which the heat content in the reactor bed is used in order to reduce the request of energy. One of the possible technical solutions is the Reverse Flow Reactor: at regular time intervals, the flow direction of the reagents is reversed, in order to obtain a large energy saving.

A more detailed description is reported in Stankiewicz e Moulijn (2004):

"Regenerative reactors, that is to say, those exploiting heat storage on fixed beds, remain a somewhat neglected option in reaction engineering. Although the principle of heat regeneration had been utilized previously in the chemical industry, for example, in a process for high-temperature thermal for nitrogen fixation (Hendrikson and Daniels, 1953), and is a common feature in related process industries, such as power generation and steel manufacture, its most recent renaissance was brought about the development (Mastros, 1989) and refinement (Nieken, 1993) of the reverse-flow reactor concept (Figure 18), which has now established itself firmly in the niche of oxidative waste-gas treatment. Additionally, regenerative heat transfer is an important feature of conventional reactor operation, for instance, in the occurrence of the transitional "wrong-way" behavior with temperature levels in excess of the adiabatic value that can arise when a fixed-bed reactor is shut down (Pinjala, Chen and Luss, 1988).

Figure 18: Reverse flow reactor concept

Regenerative heat exchange in chemical reactors offers clear benefits, such as simplicity, robustness, low costs, and high efficiencies, against which must be set its inherently unsteady-state operation, the limited potential for an exact regulation of temperature profiles, and the restriction of its use to gaseous reaction media."

Recently, this type of approach was proposed for different purposes: methane steam reforming (Glockler, Kolios and Eigenberger, 2003), removal of methane in discharges (Salomons et al., 2004), removal of SO$_2$ (Zagoruiko and Vanag, 2013) and removal of VOCs (Ramdani, Pontier and Schweich, 2001; Edouard, Hammouri and Zhou, 2005; Baldi, Fissore and Barresi, 2007).

2.1.3 Environment

Another of the possible benefits of P.I. concerns environmental compatibility, an issue of increasingly importance. The P.I. can be a possible way to achieve environmentally sustainable chemical plants.

One of the most serious environmental problems in recent years is global warming. As reported in the previous section, the P.I. can reduce energy requirements for chemical plant, limiting the emission of greenhouse gases.

The P.I. works for the reduction of greenhouse gas emissions also in another way, through the removal of the transportation phase: indeed it allows to switch from a system based on localized production and subsequent distribution to users, to a diffused production in direct contact with users. .

The procedure is explained in Reay and Ramshaw (2008):

"This is similar to the existing practice for tonnage oxygen supply, where the plant is installed within or adjacent to the customer's site, as described below.

Prior to 1970 all commercial scale oxygen and nitrogen demands met by companies such as Air Liquide were met by cryogenic distillation and distribution from a centralized production facility serving many customers. Distribution methods varied, depending upon the demand of specific customers - large users may have a dedicated pipeline. For needs less than 20 tonnes/day, liquid oxygen or nitrogen could be delivered by road or rail tankers, or as a gas in pressurized bottles.

At the beginning of the 1990s a revolution in the sector occurred. This was the introduction of local production of liquid gases, on the users' sites. The reasons for this included close match of the needs of the oxygen user (high purity, reactive capacity and pressure) and cost reduction (in terms of energy use and capital cost)."

Another potential environmental problem, to which P.I. can give some solution, is the photochemical pollution:

"The formation of photochemical oxidants is mainly due to volatile organic compound (VOC) emissions. Seventy to ninety percent of VOC emissions from chemical plants are from leaking flanges, seals, etc. (Schaic, 1991). Process intensification can reduce considerably the number of pieces of equipment and thereby the number of flanges and seals. Moreover, the few remaining flanges could be designed such that fugitive emissions are below the limits for smog formation, and the additional cost can be limited. This means fewer leaks and lower fugitive emissions to air, water, and soil. The introduction of process intensification could therefore make a major contribution to VOC emission reduction." (Stankiewicz and Moulijn, 2004)

Finally, the P.I. can help also for the management of industrial effluents: traditionally, the methodology foresees the treatment and cleaning of the outflows; the P.I. permits to prevent the formation of the pollutants.

"Rather than accept mere 'end of pipe' remediation of pollution problems, we must generate reactor fluid dynamics which allow us to fully exploit the intrinsic chemical process kinetics, however rapid these are. There is then a much better chance of designing reactors which operate intensively and which give high conversion and selectivity with minimal by product formation. This will permit us to approach the green ideal of delivering a high quality product without an extensive downstream purification sequence. This observation leads us neatly into the discussion of the ways in which PI can benefit energy use which, of course, impacts on the environment in a number of ways, in particular in carbon emission mitigation." (Stankiewicz and Moulijn, 2004)

2.1.3.1 *Membrane distillation*

The P.I. can also be applied to the phase separation in the products, in order to obtain a higher quality output with a lower energy demand.

An example of this application is the membrane distillation, which combines two separation processes in order to obtain a better result than the simple sum of the techniques.

Concerning membrane distillation, Stankiewicz e Moulijn reported interesting observations (2004):

"Membrane distillation is considered a promising separation method applicable primarily in environmental technologies. In membrane distillation a microporous and hydrophobic membrane separates aqueous solutions at different temperatures and compositions, as shown in Figure 19. The temperature difference existing across the membrane results in a vapor pressure difference. The molecules are transported through the pores of the membrane from the high-vapor-pressure side to
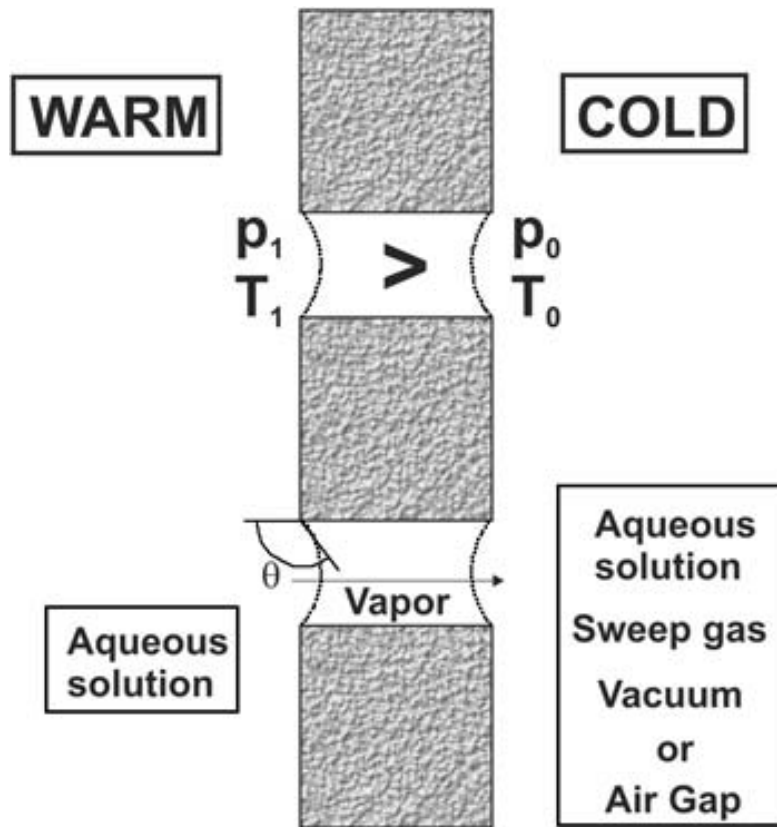
Figure 19: Scheme of a membrane distillation process

the low vapor-pressure side. At least one side of the membrane remains in contact with the liquid phase. Benefits offered by membrane distillation include (Lawson and Lloyd, 1997):

100% (theoretical) rejection of ions, macromolecules, colloids, cells, and other non volatiles

Lower operating temperatures than conventional distillation

Lower operating pressures than conventional pressure-driven membrane separation

Reduced chemical interaction between membrane and process solutions

Less demanding membrane mechanical property requirements

Reduced vapor spaces compared to conventional distillation

Membrane distillation systems may be classified into four different categories (Velazquez and Mengual, 1995):

Direct contact membrane distillation (DCMD), in which the membrane is in direct contact with the liquid phase on both sides

Air-gap membrane distillation (AGMD), in which an air gap is interposed between the membrane and the condensation surface

Vacuum membrane distillation (VMD), in which the vapor phase is evacuated from the liquid through the membrane and the condensation takes place in a separate apparatus

Sweeping-gas membrane distillation (SGMD), in which a stripping gas, instead of vacuum, is used as a carrier

Currently, the most important application area for membrane distillation is water desalination technology. Figure 20 shows one of the water desalination processes developed by a Japanese organization, the Water Re-Use Promotion Center, in cooperation with Takenaka Corporation and Organo Corporation (CADDET Center for Renewable Energy, 2001).
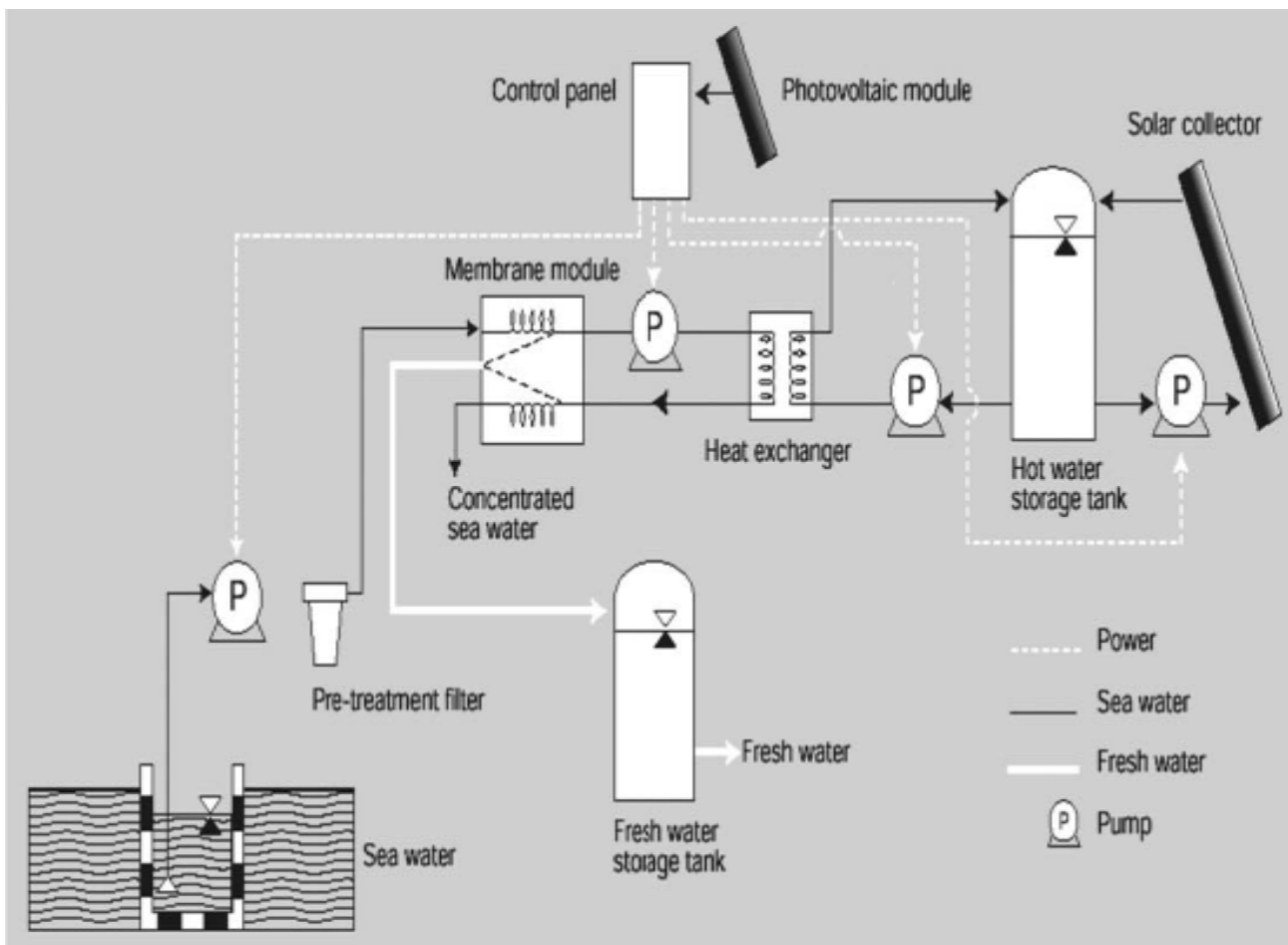
Figure 20: Scheme of the demonstration test plant for water desalination using solar energy and membrane distillation. (Courtesy: CADDET, Center for Renewable Energy, Harwell, UK)

The process uses solar energy and can therefore be installed at locations without an electricity supply. Other application areas for membrane distillation reported in the literature are summarized in Figure 21.

System/process	Selected refs.	Remarks
Concentration of H$_2$SO$_4$, H$_3$PO$_4$, NaOH, HNO$_3$, and HCl solutions	(Kimura and Nakao, 1987; Ubriot, Araque and von Stockar, 1994; Tomaszewska, Gryta and Morawski, 1995)	
Concentration of 2,3-butanediol from fermentation broths	(Qureshi, Meagher and Hutkins, 1994)	VMD process
Wastewater treatment in the textile industry	(Calabrò, Drioli and Matera, 1991)	Integrated reverse osmosis/membrane distillation process
Radioactive wastewater treatment	(Howell and Noworyta, 1995)	Integrated reverse osmosis/membrane distillation process
Removal of benzene traces from water	(Banat and Simandl, 1996)	VMD process
Concentration of protein solutions	(Ortiz De Zárate, Rincón and Mengual, 1998)	
Removal of halogenated VOCs	(Couffin, Cabassud and Lahoussine-Turcaud, 1998)	VMD process
Concentration of oil–water emulsions	(Gryta and Karakulski, 1999)	
Concentration of sugar/sucrose solutions	(Izquierdo-Gil, García-Payo and Fernández-Pineda, 1999; 1999b)	DCMD and AGMD processes
Separation of water and glycols	(Rijncón, Ortiz de Zárate and Mengual, 199)	DCMD process
Ethanol–water separation	(Banat and Simandl, 1999)	AGMD process
Acetone and ethanol removal from aqueous solutions	(Banat, Al-Rub and Shannag, 1999)	AGMD process
Propanone removal from aqueous streams	(Banat and Simandl, 2000)	AGMD process
Acetone–butanol–ethanol (ABE) solvent recovery	(Banat and Al-Shannag, 2000)	AGMD process
Fermentative ethanol production	(Gryta, Morawski and Tomaszewska, 2000; Gryta, 2001)	Integration of MD infermentation resulted in ca. 2x increase of production rate
Concentration and purification of fluosilicic acid	(Tomaszewska, 2000)	
Removal of trichloroethylene	(Duan, Ito and Ohkawa, 2001)	VMD process

Figure 21: Application Areas of Membrane Distillation

In 2002, the TNO Environment, Energy and Process Innovation institute in the Netherlands developed a membrane-based distillation concept that radically improves the economy and ecology of existing desalination technology for seawater and brackish water. This so-called Memstill$^®$ technology (Figure 22a) combines multistage flash and multieffect distillation modes into one membrane module.
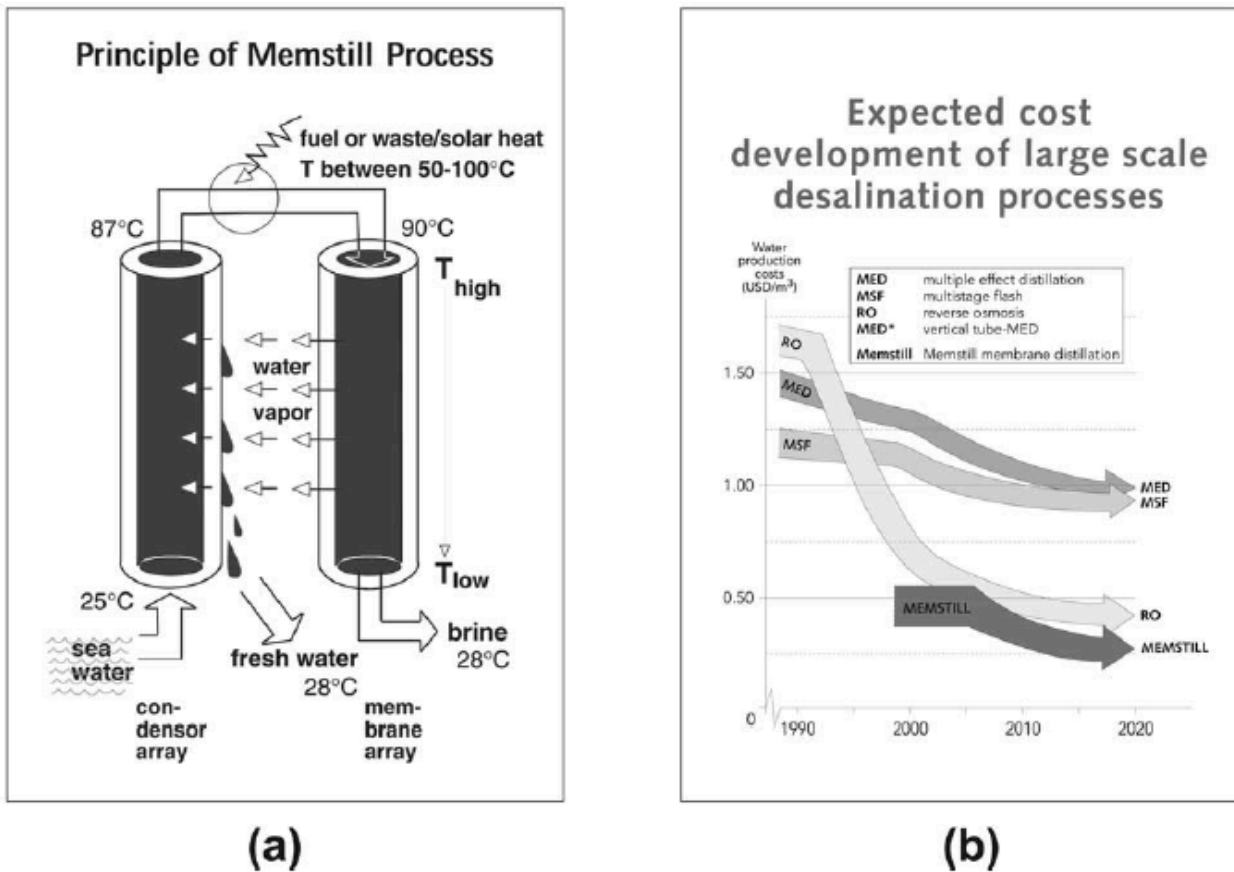
Figure 22: Memstill$^®$ technology of seawater desalination developed at the TNO institute: (a) principle of the process; (b) cost comparison with other desalination techniques. From (TNO Environment, Energy and Process Innovation, 2002)

Since the Memstill$^®$ module houses a continuum of evaporation stages in an almost ideal countercurrent flow configuration, a very high recovery of the evaporation heat is possible. The economic advantage of the Memstill$^®$ technology, compared to the "classical" desalination techniques, is shown in Figure 22b.

An academic-industrial consortium is currently developing and improving the Memstill$^®$ process concept and module design From (TNO Environment, Energy and Process Innovation, 2002). The same TNO Institute has also developed a concept of another membrane-based distillation

technology for fractionation of non-water-based systems (TNO Environment, Energy and Process Innovation, 2002). The technology, called MEMFRAC, offers high energy efficiency in compact equipment. The study carried out for fractionation of benzene from toluene showed that with MEMFRAC technology a HETP between 5 and 10 cm could be obtained. Additional advantages of the MEMFRAC technology include: lack of entrainment, flooding, foaming, or channeling (due to indirect gas–liquid contact), independent gas/liquid control, and the possibility for modular plant design. Such a modular MEMFRAC distillation unit is schematically presented in Figure 23.

On the other hand, a pervaporation membrane can be coupled with a conventional distillation column, resulting in a hybrid membrane/distillation process (Moganti, Noble and Koval, 1994; Stephan, Noble and Koval, 1995)".

Figure 23: Scheme of a modular MEMFRAC distillation unit for fractionation of non-water-based systems, developed at the TNO Institute. From (TNO Environment, Energy and Process Innovation, 2002)

2.1.4 Safety

The P.I. is expected to bring some benefits also in safety field. In general terms, the P.I. tends to reduce the volume of the plant and the amount of hazardous material stored and used. In this way, it could reduce the possible extent of the damage in case of an accident. In addition, since the equipment have reduced volumes, they are easier to be protected.

The safety in P.I. is in line with what was expressed by Trevor Kletz "What you don't have can't leak!" (Kletz, 1978). This approach can be defined Inherent Safety.

Stankiewicz e Moulijn (2004) wrote:

"Approaches to inherently safer process design have been categorized in a number of ways. The Center for Chemical Process Safety (1996) describes four strategies for inherent safety, derived from Kletz's initial proposals (Kletz, 1978; Kletz, 1998):

- Minimize —Use smaller quantities of hazardous substances, including process intensification approaches. Example: Use a small, continuous reaction system for the production of nitroglycerine in place of a large batch reactor.

- Substitute —Replace a material with a less hazardous substance. Example : Aqueous latex paints reduce both flammability and toxicity hazards when compared to solvent-based paints, both during manufacture and for the final consumer.

- Moderate —Use less hazardous conditions or a less hazardous form of a substance. Example: Plastic resins can be produced in pellet or granular form, reducing dust explosion hazards when compared to a powder form of the same material.

- Simplify —Design processes and facilities that eliminate unnecessary complexity and that are tolerant of human error. Example : Design piping to permit gravity flow of hazardous materials in a plant, eliminating the need for pumps, which can leak."

Regarding the P.I., the miniaturizing of the equipment reduces the amount of material or energy involved in an accident, thus reducing the extension and severity of possible damage.

Some examples are given below, taken from (Stankiewicz and Moulijn, 2004):

"Nitration

Nitration reactions are highly exothermic, can generate high pressure in a closed system from noncondensible by-products from undesired side reactions, and often produce unstable reaction products, such as explosives. Many years ago, products such as nitroglycerine were manufactured in large batch reactors. As engineers began to understand the physical and chemical processes involved in nitration chemistry, they recognized that the chemical reaction actually occurs very rapidly once the reactants come into contact with each other. The large reactor size and long reaction times were actually the result of poor mixing, poor removal of the heat of reaction, and poor mass transfer in two-phase reaction mixtures. This knowledge of the physical and chemical processes involved in an industrial-scale nitration process was used to design new types of reactors to efficiently contact the reactants and liquid phases and remove the heat of reaction. Modern nitration plants use very small continuous stirred-tank reactors with intense mixing and large heat transfer area or jet reactors of various designs to provide intense mixing and rapid contacting of reactants (Kletz, 1998).

Polymerization

A number of innovative polymerization reactors using loop reactors, plug-flow and static mixer reactors, and continuous stirred-tank reactors have been reported. For example, Wilkinson and Geddes (Wilkinson and Geddes, 1993) describe a 50 liter reactor that has the same capacity as a 5000 gallon batch reactor. Extruders, thin-film evaporators, and other devices designed to provide intense mixing for viscous or unstable materials have also been used as reactors.

Tubular or Jet Reactors

Continuous reactors, including simple plug-flow pipe reactors, tubular reactors containing static or other mixing devices, and jet reactors of various types, have been used to efficiently produce toxic materials for immediate consumption in downstream processing operations with little or no inventory. Some examples follow.

Methyl isocyanate (MIC), the material that was released at Bhopal, can be produced and immediately converted to final product in a process that contains a total inventory of less than 10 kg of MIC (Kletz, 1998).

Caro's acid, an equilibrium mixture of sulfuric acid, water, and peroxymonosulfuric acid, is used in the metal-extraction industry. It is manufactured by reacting concentrated sulfuric acid with hydrogen peroxide. Caro's acid is a powerful oxidizing agent and decomposes readily. A process was developed to manufacture 1000 kg/day of Caro's acid in a tubular reactor with a volume of 20 ml and a residence time of less than one second, with the product immediately mixed with the solution to be treated (Whiting, 1992).

A continuous tubular reactor was developed to manufacture phosgene for immediate consumption by a group of batch-processing buildings (Osterwalder, 1996). One plant using the new design contains 70 kg of phosgene gas, compared to a total inventory of 25,000 kg of liquid phosgene in the old plant. Because the new plant is small, it is also feasible to provide a secondary containment building for the equipment containing phosgene, providing an additional barrier between a highly toxic material and people and the surrounding environment (Delseth, 1998).

Heat Exchangers

Heat exchange equipment varies widely in efficiency in terms of available heat transfer area per volume of inventory contained in the exchanger. Innovative heat exchanger design can reduce the volume of hazardous material in a heat exchanger by a factor of 10 or more when compared to a standard shell-and-tube exchanger. Some more efficient alternatives include plate, shell-and-finned tube, plate-fin, and rotary exchangers. With some of these devices, it is important to consider the potential for additional leak scenarios, such as gasket leaks in plate exchangers or hazards associated with seals and moving parts in rotary exchangers. The designer must balance the benefits

of reduced inventory against the possibility that leaks may be more likely. Kletz (1998) discusses alternative heat exchanger designs.

Distillation

Innovative design of distillation devices can greatly reduce inventory and can also reduce the residence time in the distillation system, which may be important for safely processing thermally sensitive materials. Wiped film evaporators have been in use for many years, particularly for distillation of reactive materials, such as monomers, and for other heat-sensitive compounds. In more traditional distillation equipment, columns and trays can be designed to minimize the inventory of liquid in the column. Often the largest inventory of hazardous liquid is contained in the bottom of the column and in the reboiler. This is particularly undesirable for a reactive or thermally sensitive material because this is part of the distillation column that is at the highest temperature. It is possible to design the bottom of a column to minimize this inventory. For example, use a conical column bottom or a small-diameter column bottom that still provides sufficient liquid head for bottoms or reboiler recirculation pumps but reduces the total quantity of hot liquid.

Centrifugal distillation equipment such as Higee (Kelleher and Fair, 1996) can be much smaller than conventional distillation equipment.

Extraction

Extraction columns are often very large devices, and they may contain a large quantity of flammable or toxic solvent. The inventory of hazardous material in an extraction system can be greatly reduced by using a centrifugal extractor. In this case, the inherent safety benefits of reduced inventory must be balanced against the new hazards introduced by the centrifugal extractor, including operation at high speed and potential for leakage from seals, to determine the best choice for a particular application.

Combined Unit Operations

Equipment that combines more than one unit operation in a single piece of equipment is another approach to process intensification. Reactive distillation is a good example. In one case, a traditional process for the manufacture of methyl acetate uses a stirred-tank reactor, eight distillation columns, and an extraction column. A new, reactive distillation process uses one reactive distillation column and two additional columns (Center for Chemical Process Safety (CCPS), 1996). The total inventory of combustible material in the process is reduced. In this example, the reactive distillation system also results in a simpler plant—one with fewer major vessels. The process is also simpler because there is much less supporting equipment—condensers, reboilers, pipes, valves, pumps, instruments. Safety is enhanced because every valve seal, flange, pump seal, and instrument connection that is eliminated from the plant is one less place that the

process can leak. This reduces fugitive emissions from this equipment, which contribute to plant emissions and pollution, and also the likelihood of bigger leaks that can cause a fire, personnel exposure or injury, or a significant environmental incident.

Innovative Energy Sources

Energy sources such as laser light, ultraviolet light, microwaves, and ultrasonic energy can be used to apply energy in a controlled fashion to a chemical reaction or physical unit operation to increase efficiency. For example, technology for the distributed, small-scale manufacture of hydrogen cyanide using microwave energy to direct heat to the reactor catalyst is under development (Koch, Kraus and Mehdizadeh, 1997). This would allow hydrogen cyanide to be manufactured in small quantities where it is needed, rather than manufacturing it in a large central facility, storing it, and transporting it to the sites where it is needed".

What previously described for the Inherent safety and the P.I. results generally true, but there are some examples where these principles are not verified: in Klais et al. (2009; 2009b), it is shown that Inherent Safety is not reached in the analyzed reactors.

Summarizing what previously said, the P.I. can bring great benefits for safety, reported in the following list (Etchells, 2005):

- "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 start-up 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 (Etchells, 1997) "

But, at the same time, P.I. can cause possible disadvantages (Etchells, 2005):.

- "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 high-energy sources may introduce new hazards that have to be considered when applied to hazardous substances, e.g., whether or not it is safe to use microwaves on thermally unstable substances or mixtures.

- The processes may be more complex or call for more complex control systems and safety may suffer. An example is given in Hendershot (1995) which cites a chemical reaction where the reaction mass became dangerously unstable if one of the reactants was overcharged—the process was simpler to control safely by charging the reactant into an excess of the other in a semi-batch reactor. However, the author also makes the point that this needs to be balanced against the safety advantages of moving to a smaller inventory in the intensified process.

- As the residence time for many intensified processes will be in 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 becomes more responsive to changes in process conditions. Where it is possible that safety may be compromised as a result, then these issues should be addressed before the process is implemented. In some cases, it may mean that the process is unsuitable, or that new and novel techniques are needed to control them that 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. This could have significant safety implications, unless the reaction has been adequately assessed first, for example, if the enhanced reaction generates a gas rather than a liquid. Whilst time-proven techniques and procedures are available for assessing the likely reaction thermo-chemistry in traditional reactors, this is less evident for some of the new designs of intensified equipment.

- 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.

- Although the instantaneous inventory can be quite low, the throughput may be quite high. It is important to consider the possibility of 'off spec' products being transferred and

accumulating rapidly downstream. Where necessary, suitable analysis and control measures will be required.

- Unlike the case with many large processes, people may be closer to smaller plant, particularly during the development stages."

Therefore, the use of P.I. can be one of the most important tools to increase safety in the chemical industry, but at the same time it can produce new hazards. Consequently, it is important to carry on the evaluation of the effects on safety case by case.

2.1.4.1 Micro-reactor

During the 20th century, there was a race to miniaturization: in example, in electronics a microchip replaced thousands of transistors. Also the chemical industry started to approach miniaturization, with decades of delay in respect to electronics.

An example of this transition concerns the micro-reactors: the description of how the micro-reactors are made and work is reported in Reay e Ramshaw (2008):

"It was often assumed in the past that a high degree of turbulence equated to good mixing and this is indeed generally true, but this is only the case for larger scale mixing phenomena, principally turbulent eddies; there are other phenomena, such as diffusion, that can be used to effect mixing. Micro-reactors, as the name suggests, are reactors with channel sizes of the order of micro-metres, at which diffusion is the dominant mixing mechanism. They typically consist of series of plates with machined or etched channels less than 1 mm in width.

The term 'micro-reactor', however, has come to refer to reactors with small channels varying in size from catalytic plate gas phase reactors involving channel dimensions of 1-2 mm, to liquid phase processors which may contain channels of 200 μm equivalent diameter. In the context of the commodity and fine chemical industry, it is unlikely that the 1 micron channels, currently being investigated at various laboratories, will be a viable process technology in view of their minute production capability, even when several thousand channels operate in parallel (which would have significant attendant many folding problems-see below). The study of 'true' micro-reactors has become a vast field, too large to be covered in this text, hence this section focuses on 'larger' micro-reactors, which extends to cover catalytic plate reactors and heat exchanger (HEX-) reactors.

Chemical engineering interest in this technology centers on the use of such reactors in manufacturing drugs and fine chemicals at scales of up to, for example, 500 tones/year, rather than for bulk chemical production although, as illustrated later, the work of Chart Energy and Chemicals with their plate fin heat exchanger reactor has extended into the bulk application area.

Since the pressure drop in laminar flow for a given mass flow rate varies as (diameter) there is a strong disincentive to use the 1 micron channels currently being considered for the latter application. Hence the interest centers on the use of multi-layer matrices comprising many sets of 100-200 parallel micron channels. The risk of fouling will also increase with decreasing channel width.

The use of falling films, as in the IMM micro-reactor system shown in Figure 24, may seem to be a strategy having some risk, owing to the perceived lack of control of the film (governed by gravity). However, there are many options described elsewhere in this book for lending a helping hand to manage the flow. This particular unit was described in a recent paper (Loewe and Hessel, 2006) in its use for the fluorination of toluene at 15°C, where it replaced a process that normally required operation at -70°C.
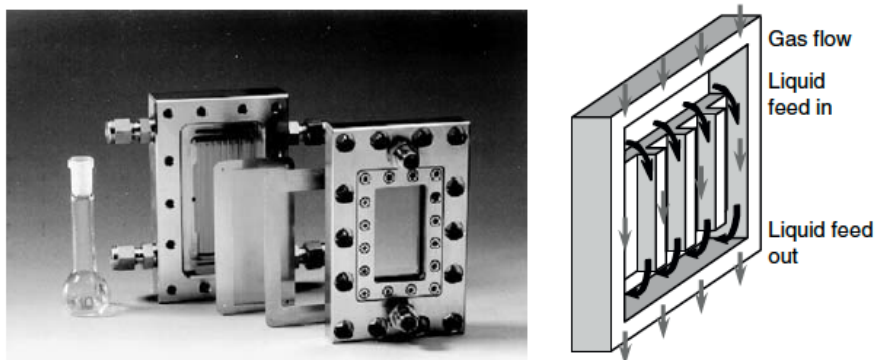

Figure 24: Steel falling film micro-reactor of IMM. Characteristics: 64 channels, each 300 μm wide, 100 μm deep and 65 mm long; surface area 20,000 m^2/m^3 (courtesy of UCL)

Some micro-reactors use narrow channels in polymer or metallic blocks. Burns and Ramshaw (1999) describe a unit where industrially competitive reaction rates can be achieved in a liquid-liquid reactor with modest bore sizes of between 127 μm and 254 μm.

Returning to the subject of manifolding, the general area of microprocessor development for single-phase liquid reactions has been spearheaded by mainland Europe and the US, though the more difficult applications involving multi-phase (liquid-liquid) reactions have been relatively neglected. This is partially due to the difficulties associated with ensuring uniformity of distribution of the reactants when perhaps 10000 parallel streams are involved, with reactants having differing viscosity. Thus manifold design is absolutely critical.

An approach adopted in France, based upon the work in the US of Professor Adrian Bejan (Luo et al., 2007) uses the concept of 'dichotomic branching' (each branch divides into two sub-branches)

and it imposes strong geometric constraints (square outlet zone for example). It is therefore necessary to design different structures, using a similar principle in order to gain geometric freedom and allow them to be adapted to 'real' heat exchangers or micro-reactors.

The unit reported by the authors distributes an inlet flow (such as 300 l/h) into 256 outlet flows evenly distributed over a square cross-section of 6x6 cm^2. The 256 flow paths are all hydraulically equivalent. The distribution of channel diameters is optimized according to Murray's criterion, with a scaling ratio of $2^{1/3}$. The device was manufactured by stereo lithography in the laboratory of one of the partners.

Manifold optimization is a compromise between pressure drop and porous volume, on which the channel diameter has opposite effects. This leads to an optimal channel diameter distribution with scaling laws, while the lengths are determined by the specification of the outlet surface. For distributors with a dichotomic structure, such as that shown, and in conditions of laminar flow, the main theoretical limitations of this treatment are that it neglects inertial effects, and thus applies only at very small Reynolds numbers. In addition to the use of this design method in manifolds for micro-reactors, the research team in France has identified interest in several other areas, including:

- cooling radioactive fluids using compact exchangers that are later treated as waste;
- formulation of multi-component products: continuous mixing of powders and additives, cosmetics, detergents, food;
- controlled-size emulsions, mixing of viscous fluids;
- generation of controlled swarms of bubbles and drops in extraction and washing processes."

2.1.4.2 Static mixer

The P.I. does not only deal with reactors, but also with other unit operations of the chemical industry.

One example can be the mixing equipment; this is a historically important example, because it can be traced back as the first example of P.I. (Taber and Hawkinson, 1959). In addition, in some cases the improvement of mixing can bring to an energy savings of the 10 -20% (Reay and Ramshaw, 2008).

The description of the static mixers is provided by Reay e Ramshaw (2008):

"There are many types of static mixers available commercially, all with similar operating principles. Most units have a number of mixing elements, the 'mix' of element configurations depending upon the mixer type. These are inserted into the pipe work at the point where mixing is needed. Their

main advantage is the lack of moving parts, keeping operating and capital costs relatively low. Cleaning is, of course, required where product or feedstock changes may be involved.

Static mixers are used to achieve good homogeneity between two or more streams, which can help in achieving good conditions upstream of, for example, a catalyst where reactions between the two are taking place. The intensification process using these mixers allows the components of the stream to be highly mixed within a distance of a few pipe diameters, with no external energy input apart from the modest additional pressure drop.

Andrew Green of BHR Group (Green et al., 2001), a leading UK laboratory on mixing and reactor technologies, compared the static mixer, where 100 s of W/kg in mixing energy could be delivered, with a stirred tank, where 1-2 W/kg was more typical. The up to 100-fold higher mass transfer rates in static mixers (compared to stirred tanks) is characterized by uniform energy dissipation, plug flow and good radial mixing.

Static mixers are perhaps the simplest and most versatile of process intensification equipment, with application in reactions where at least one phase is a liquid. They are tube inserts that use the pumping energy/pressure drop to induce mixing and can be roughly divided into three categories:

1. Turbulent flow mixers that rely on the vortices shed from tabs positioned on the walls of the device. They promote mixing in an axial direction and so approximate well to plug flow devices.

2. Laminar flow mixers that physically redistribute, stretch and fold the fluid.

3. Those used for both regimes.

Such mixers are marketed as heat transfer enhancement devices by several companies, including Cal-Gavin, whose product is called HiTran .The in-line static mixer has also proved to be effective in gas-liquid contacting. A1 Taweel et al. (2005) used a specific design of static mixer to generate narrow-sized liquid-liquid dispersions and succeeded in generating contact areas of the order of $2200 m^2/m^3$ in the region close to the woven wire screen mixer elements. The performance of the system with regard to industrially-relevant streams such as those containing surfactants had yet to be characterised.

Hessel and colleagues at IMM Mainz (Hessel et al., 2005) have investigated mixers at the micro-scale. At the top of Figure 25 is a slit type micro-mixer made in glass, with flow rate capabilities in the range 10-1000 ml/h. The lower units are stainless steel mixers for pilot and production scale uses, with capabilities an order of magnitude greater than the micro unit illustrated".
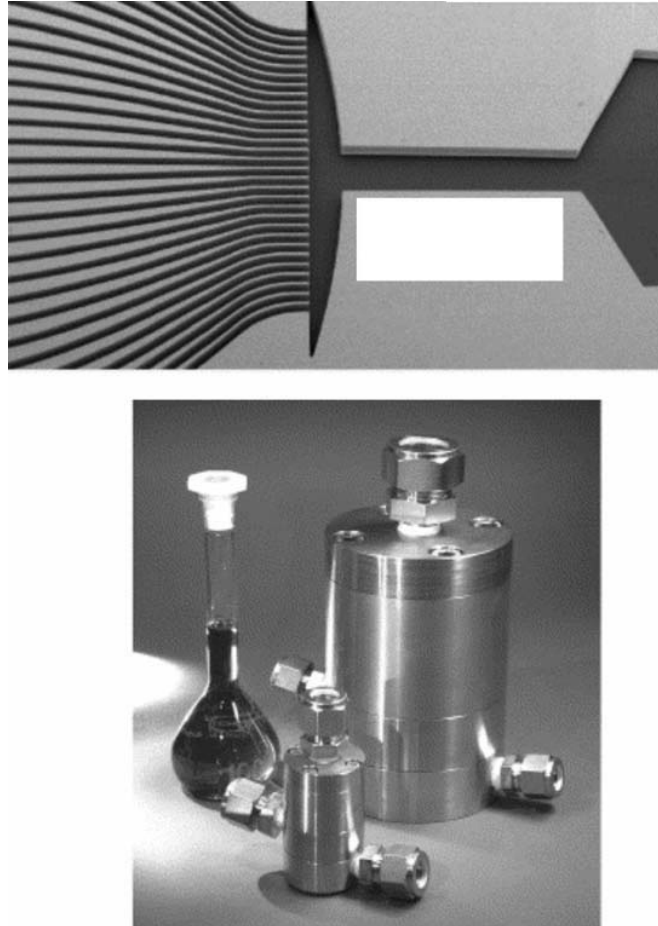
Figure 25: Micro-mixers in glass and stainless steel (Hessel et al., 2005)

2.2 Resistance to the adoption of P.I.

Despite of the possible advantages given by the P.I., the new technologies have a difficult diffusion, due to several reasons.

The first reason is that the P.I. requires to replace equipment and processes with a consolidated tradition: companies tend to be wary towards new equipment, not tested at full industrial scale. They rather prefer to wait for some trailblazers' results, in order to acquire more data on the reliability of the components and the profitability of the new plant.

In addition, so far now there are no codified calculation methodologies for the design and management of the intensified plant, so these two processes still have many uncertainties. Furthermore, the behavior of the system at changing conditions is not always well-known.

However, presumably in the next years, the P.I. will continue to extend, increasing the knowledge, and favoring the development.

2.3   Structure of P.I.

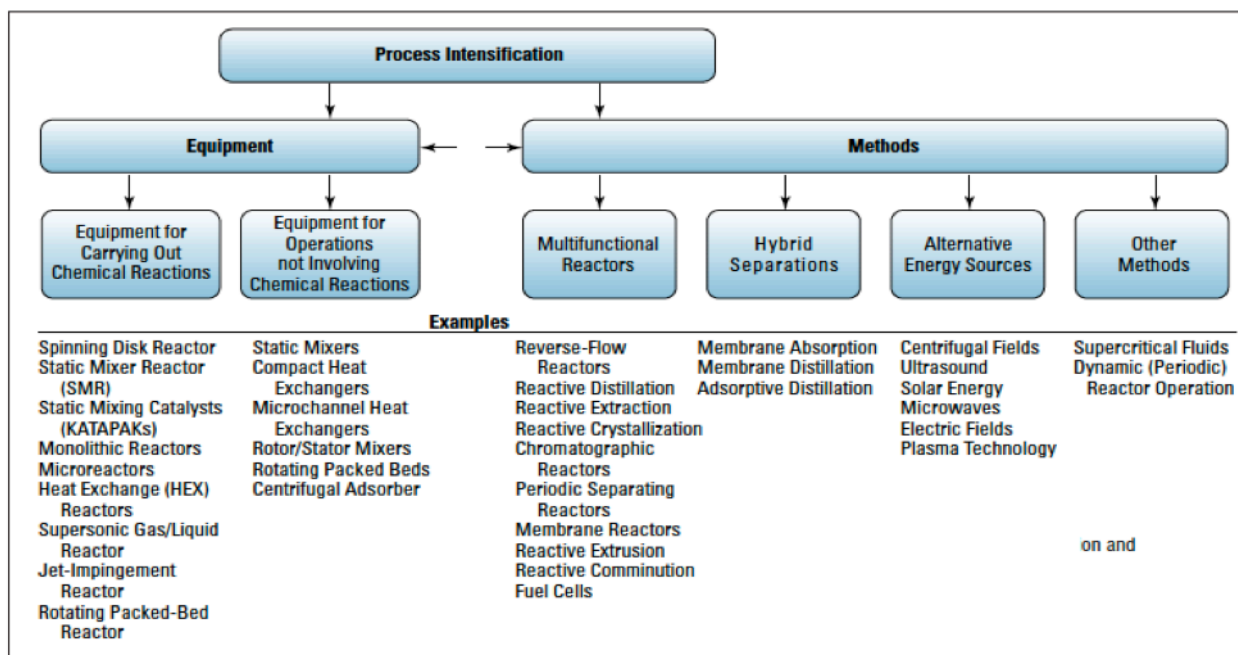Typically the P.I. is schematically described as in Figure 26.

Figure 26: Classification of equipment developed by the P.I. (Stankiewicz and Moulijn, 2000)

"As shown in Figure 26, the whole field generally can be divided into two areas:

• process-intensifying equipment, such as novel reactors, and intensive mixing, heat-transfer and mass-transfer devices; and

• process-intensifying methods , such as new or hybrid separations, integration of reaction and separation, heat exchange, or phase transition (in so-called multifunctional reactors), techniques using alternative energy sources (light, ultrasound, etc.), and new process-control methods (like intentional unsteady-state operation).

Obviously, there can be some overlap. New methods may require novel types of equipment to be developed and vice versa , while novel apparatuses already developed sometimes make use of new, unconventional processing methods." (Stankiewicz and Moulijn, 2000)

2.4   Case study

The case study refers to a plant used for the removal of VOCs from an inert gas stream in a polymerization plant, in order to maintain the correct conditions in the polymerization reactor downstream of the plant.

VOCs (Volatile Organic Compounds) are a set of several chemical components, defined as (European Communities, 1999):

"Volatile organic compound (VOC) shall mean any organic compound having at 293,15 K a vapor pressure of 0,01 kPa or more, or having a corresponding volatility under the particular conditions of use".

The case study refers to the removal of VOCs from an inert stream in a closed recirculation for process purposes, but the same system can be used for the control of the emissions into the atmosphere.

The removal of VOCs occurs for catalytic combustion; if necessary, it is possible an addition of oxygen to support the combustion. After the combustion phase, the reaction products are removed and the gas returns into the production line.

The analyzed plant treats a stream of 5000 Nm^3/h, with an inlet temperature of 230°C, a pressure of 1.17 bar absolute and a composition of nitrogen with 0.2% of VOC. In this case, we will consider the VOCs only represented by ethylene glycol.

The removal takes place according to the following combustion reaction:

$$C_2H_6O_2 + \frac{5}{2}O_2 \rightarrow 2CO_2 + 3H_2O \quad \Delta H = -1.059 * 10^9 \frac{J}{kmol} \text{ (Perry, Green and Maloney, 1999)}$$

2.4.1   Plant with fixed-bed catalytic reactor

The traditional plant uses a fixed bed catalytic reactor, as shown in Figure 27.

The gas to be treated, after the entrance in the plant, passes in the zone of filtration, made of two filters (F01A, F01B), where one is in use and the other in stand by. In this system, there is a differential pressure alarm (PdAH18403) that alerts the operator when the filter in use is blocked. In this case, the operator intervenes and turns the flow of gas on the other filter, then he restores the exhausted filter.

The oxygen required for the reduction of VOC is added to the gas in small excess with respect to the stoichiometric quantity. The flow rate of oxygen is regulated in feedback (AIC18415), on the basis of its concentration in the exhaust gases.
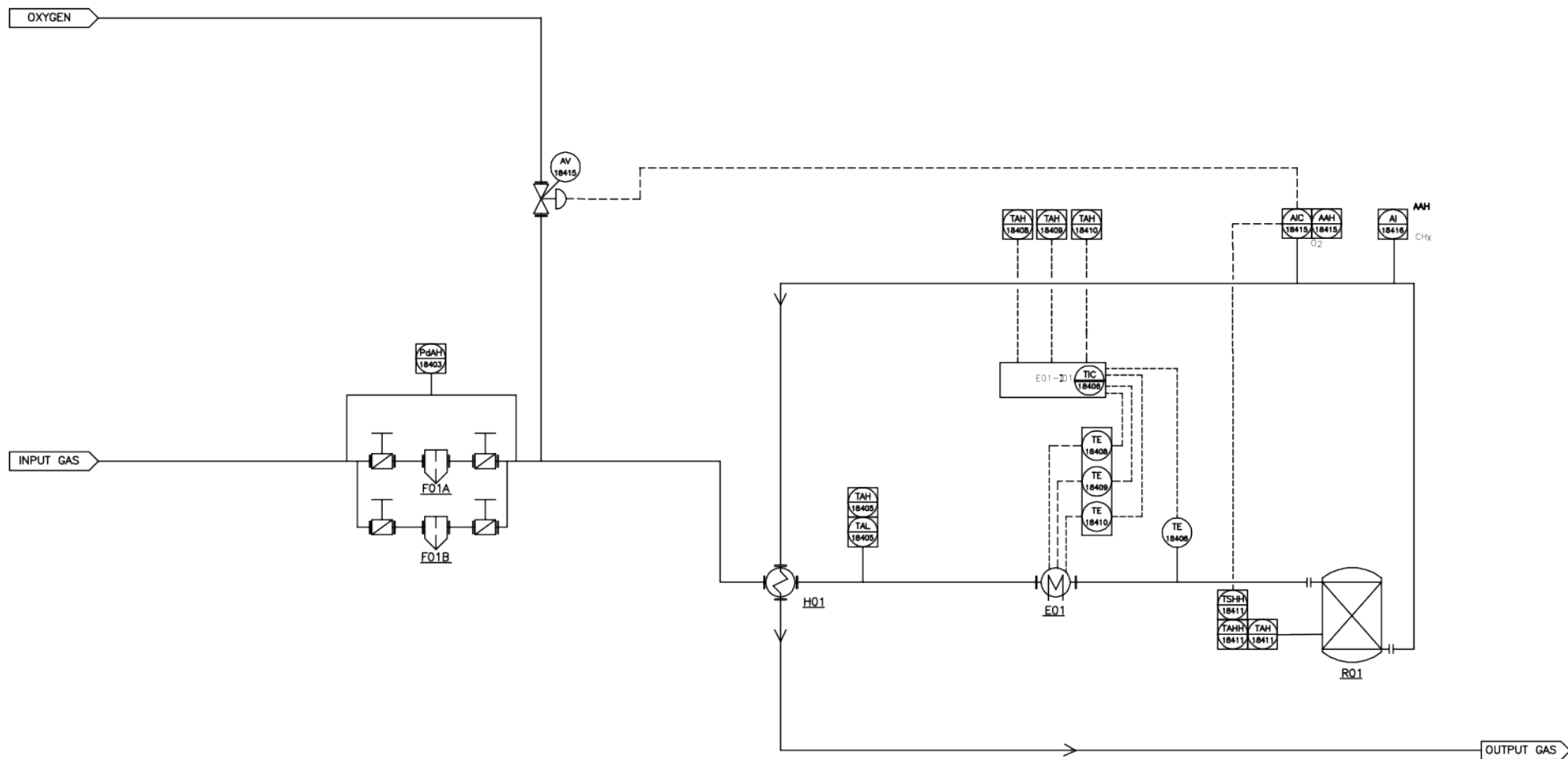
Figure 27: Flow sheet of traditional plant

At this point, the gas passes through a heat recovery unit (H01): in this equipment the treated gas, which has a high temperature, transfers its heat to the fresh gas, operating an energy recovery. In this heat exchanger, the designers tried to obtain the maximum possible heat recovery, and consequently the outlet temperature is not controlled. For this reason, on the outlet line, there are a high temperature alarm (TAH18405) and a low temperature alarm (TAL18405). The purpose of the high temperature alarm is to alert the staff when the exit temperature could damage the next heater and especially the catalyst inside the reactor. The purpose of the low temperature alarm is to evidence a very low temperature, which wouldn't permit to reach the reaction temperature even with the heather working at its maximum power,, producing a shutdown of the re-actor and a lacking removal of VOCs. In case of alarm, the operator monitors the temperature value: if, after a few minutes, the temperature does not return to normal values, he puts the plant in an emergency state, which means that he closes the oxygen, with a consequent interruption of the reaction and shutdown.

The preheated gas passes through an electric heater (E01) (about 100 kW power), which objective is to raise gas temperature until it reaches the heat necessary for the reaction. Therefore, when the gas comes in contact with the catalyst, the reaction occurs.

This equipment is provided with a control system on the outlet temperature (TIC18406), which is measured by a series of sensors operating logic on voting (2:3). A series of alarms in redundancy (TAH18408, TAH18409, TAH18410) are connected to this control: they alert the operator in case the temperature is reaching the level which can cause the thermal degradation of the catalyst.

Following the above-mentioned alarm, the operator focuses his attention on the temperature value and if, after a given time, it does not return below the alarm threshold, he disconnects the power supply to the heater, putting the system in an emergency state and shutting down the reactor.

The next equipment is the fixed bed reactor (R01): its length is around 0.7 m and its diameter is around 1.5 m. In order to reduce energy costs, the reactor works with temperatures relatively low, using a catalyst based on metals such as Platinum and Palladium.

On the reactor there are two alarms (TAH18411, TAHH18411) and an automatic protection system (TSHH18411) for high temperatures. When the temperature rises, there is an initial alarm level, that activate the sound warning for high temperature. If the operator does not intervene and the temperature continues to grow, it reaches a second alarm level, which activates a second alarm and a protection system. The protection system immediately puts the system in emergency mode, closing the input of oxygen and consequently shutting down the reactor. If the temperature continues to rise, it can provoke the sintering of the catalyst, with a consequent shutdown of the reactor.

Even for reactor alarms, the operator focuses his attention on the temperature: if the values do not return to alarm level in time, he puts the system in emergency mode.

After the reactor, the concentrations of oxygen and VOCs in the outlet gas are measured. The value of the oxygen concentration is used to check the flow of oxidant at the entrance. In addition, on this value a warning threshold is applied: beyond a certain level, an alarm goes off (AAH18415); indeed too much oxygen in output can damage the polymer product from the main plant.

The concentration of VOCs at this point is compared to an alarm threshold (AAH18416): in case the level exceeds this value, it means that the removal system is not working, and the main plant may have some problems on the final product.

Also in these cases, at the sound warning, the operator focuses his attention on the element that exceeded the alarm threshold, and if it does not turn back below the alarm threshold, the operator puts the system in emergency mode, closing the intake oxygen.

In the end, the treated gas passes through the heat recovery, where it transfers its heat to the inlet gas.

The advantage of this type of system is that it is based on consolidated technologies, where the dynamic of operations is known in detail, so that the designers can use a smaller number of alarms, placed in key points.

2.4.2 Plant with reverse-flow reactor

The intensified plant is described by (Baldi, Fissore and Barresi, 2007; Fissore et al., 2005). The system uses a reverse-flow catalytic reactor to reduce the energy demands.

The plant analyzed is represented in Figure 28.

On the input line is placed a concentration alarm (AAH01), which indicates if the incoming gas contains too much VOCs; indeed this condition could damage the reactor.

The gas is compressed by a blower (B-01), in order to give it enough pressure to overcome the plant pressure drops. At this point, the control of the gas flow is operated through a bypass of the blower. Immediately after the blower, there is a high temperature alarm (TAH03), which scope is to avoid possible damages to the following filter or to the reactor.

Later, the gases are filtered (F-01) to avoid that solid particles could enter the reactor, and compromise the catalyst. A possible blocking of the filter is indicated by an alarm of differential
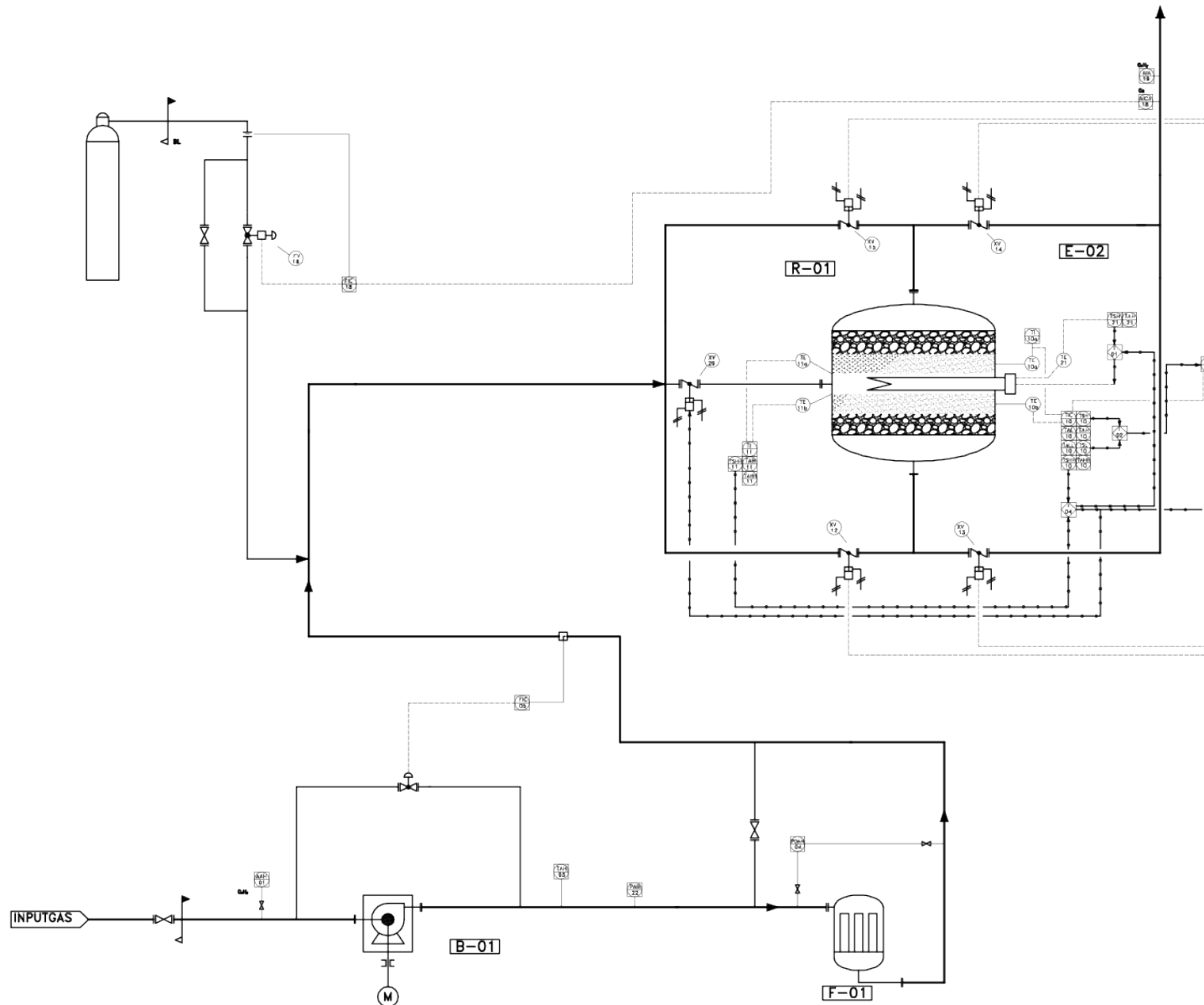
Figure 28: Flow sheet of plant with reactor reverse-flow

pressure (PDAH04). In case of alarm, the operator intervenes by turning the gas stream on the bypass and isolating the filter; after this, the operator proceeds with the operations for the recovery of the filter. In case of lacking recovery, the upstream pressure continues to rise, pointed out by a high pressure alarm (PAH22) which alerts the operator about the presence of a problem in the filter. After the filter, there is the oxygen addition. In the analyzed case study, it is necessary to add oxygen because it is not present in the stream of inert gas This phase isn't necessary for plants which work on exhaust gases, because the oxygen needed for the combustion is already present (air).

In our case, the oxygen concentration is controlled in feedback (FIC18), on the basis of its concentration in the outlet stream of the reactor; oxygen is dosed with a small excess in respect to the stoichiometric conditions.

At this point, the gas enters the reactor (R-01): the device has a length around 0.7 m and its diameter is around 1.5 m. As shown in Figure 29, the reactor consists of a fixed bed, made of five different sections (Figure 29). At the tops, there are two layers of inert solid, whose function is that
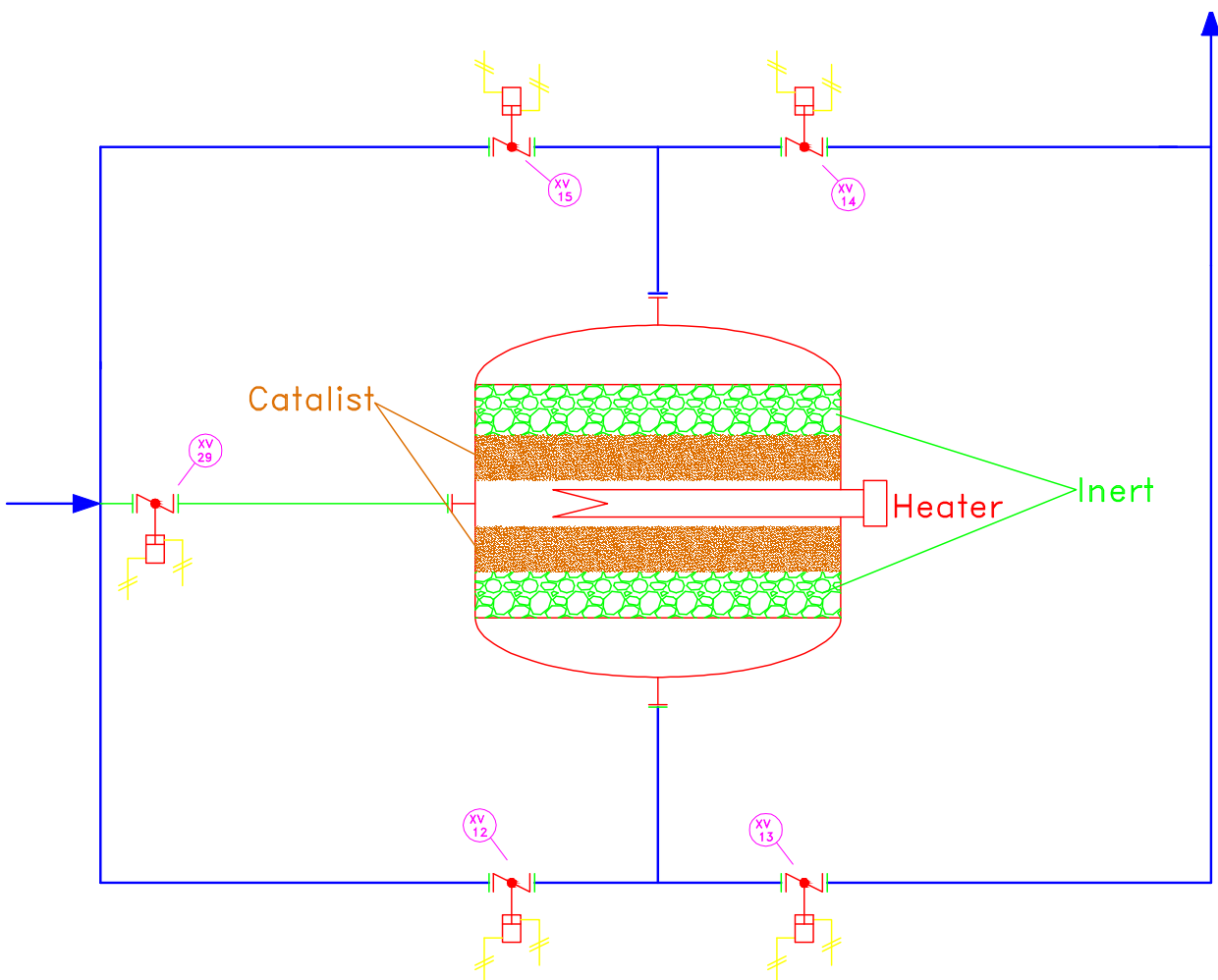

Figure 29: Scheme of the reactor

of thermal flywheel: they accumulate heat from the treated gas, and return it to the inlet gas, to bring it at the reaction temperature level. The inner layer contains the catalyst; and this is the layer where actually the combustion reaction takes place. In the middle of the reactor, there is a small electric heater (E-02), which provides additional heat to the reactor in case of small transient conditions.

In the reactor, the gas circulates alternately from bottom to top and vice versa. In this way, the cold gas runs into the hot solid, that releases its heat, bringing the gas at the reaction temperature level. When the gas temperature reaches the reaction level, with the gas reacts with the catalyst: since the the reaction is exothermic, the temperature of the gas increases further. In the second part of the reactor, the gas runs into a cold solid, to which it transfers its heat. Therefore, in the reactor there are two fronts of temperature that go to the gas: a front of low temperature, where the gas enters, and a front of high temperature on the other side (Figure 30). After a certain time, the gas flow is inverted so that the inlet gas finds the hot solid.
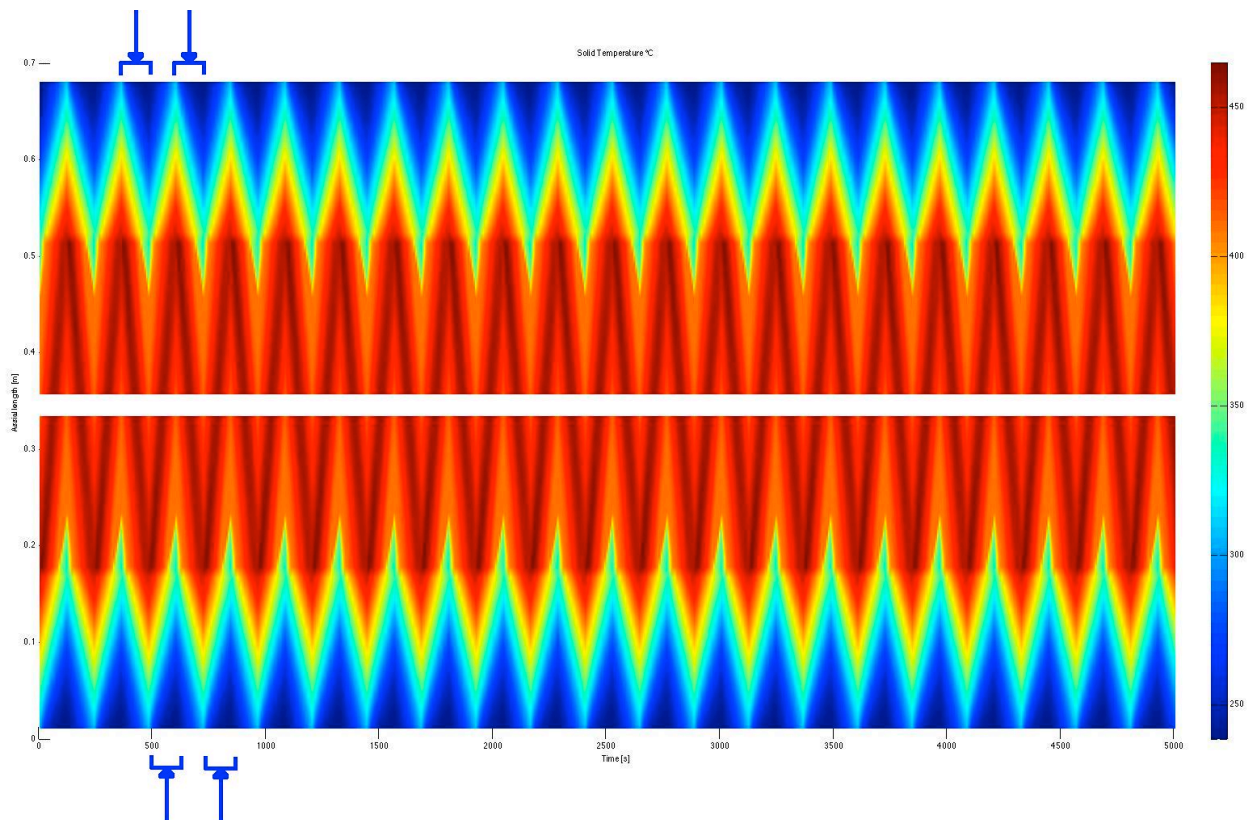

Figure 30: Temperature trends inside the solid, indicating the direction of the gas flow

In this type of reactor the key factor that determines the temperature in the reactor is the time of inversion: an increase of the time corresponds to a decrease of the temperature of the reactor .

44

The control system of the reactor works in a discontinuous way. Starting from the set point temperature, if the temperature level decreases beyond a certain threshold, the control system requires an increased heat to the heater. If the temperature continues to decrease, the protection system (TSL10) intervenes, putting the heater to its maximum power and reducing the time of inversion, in order to reinstate an adequate temperature of the reactor. At the same time, a first alarm level (TAL10) is activated.

If the temperature continues to decrease and overtakes a second low temperature threshold, a second level alarm (TALL10) is activated: it points out that the temperature in the reactor is below the level necessary for the reaction, and the reactor risks to shut down.

If the temperature, on the contrary, starts to rise, the control system switches off the internal heater. If the temperature overtakes a first threshold level, the protection system (TSH10 and TSH21) intervenes, turning off the heater and extending reversal time. It continues to extend the time as long as the temperature continues to grow. This intervention should decrease the temperature of the reactor. At this level, it is also activated the first level of the high temperature alarm (TAH10, TAH11 and TAH21).

In case the temperature continues to rise and overtakes a second high temperature threshold, another protection system (TSHH10 and TSHH11) is activated, that puts the plant in an emergency state, in order to protect the catalyst from a possible thermal degradation. Putting into emergency the reactor means opening the valve (XV29) that introduces the gas in the center of the reactor, and the outlet valves (XV13 and XV15). In this way, the gas immediately cools the catalyst and the reactor shuts down. At the same temperature threshold, a second level alarm (TAHH10 and TAHH11) is activated.

If the temperature continues to grow, the catalyst can undergo thermal destruction, followed by the shutdown of the reactor because of the loss of heat in the chemical reaction.

Given that the thermal demands are relatively small and the reactor can operate at higher temperatures compared to a conventional reactor, it is possible to use a catalyst based on oxides of copper and manganese: it can work at higher temperatures compared to those of the catalysts based on metals such as Platinum and Palladium, and also it has a lower investment cost.

The treated gas , after the exit from the reactor, is subjected to the last control points and related alarm systems, related to high concentration of VOCs (AAH19) and high oxygen concentration (AAH18). The first is used to check the VOCs elimination, the second is used to avoid, in the line of production of the polymer, an excess of oxygen, which could create a potentially explosive atmosphere downstream, and cause the degradation of the polymer product.

In case of alarm, the operator puts the variable under observation and if after a short period of time it has not stabilized or it is not returned in the values of the project, the operator shuts down the reactor.

The intensified plant presents a higher quantity of alarms (13) and protection systems (5), in particular concerning the monitoring of the temperature in the reactor, in respect to the traditional plant.

The biggest advantage of this type of system is the strong reduction of energy consumption. The consumption at design conditions is about 16.5 kW for pumping and 2 kW for heating the reactor, compared to the about 80 kW for heating in traditional plant.

In addition, it is possible to operate at higher temperatures and to use a catalyst less active but not based on expensive metals, with a strong reduction of the cost for charging the catalyst.

2.4.3   Analysis

Different analysis were applied to the two plants above described, in order to investigate the effects of P.I. on the safety and reliability of the plants.

Initially, a traditional analysis methodology was applied an operability analysis followed by a Fault Tree for quantification, in order to estimate the probability of the events described by the trees.

Then an Integrated Dynamic Decision Analysis was applied, in order to obtain both the probability of the selected events and the value of the risk.

In order to compare the plants, the probability of occurrence of selected events and the value of technological risk of these events were used as parameters. The technological risk is the product of the probability of occurrence and the possible consequences. In this case, the consequences are measured through the operating costs of the plant, a value that changes on the basis of the operation conditions and of the failures of the system.