Course Handout

Process Intensification

Master II: Chemical Engineering

Master II: Environmental Process Engineering

Dr. GUELLA Soufiane-Associate Professor A
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Summary

Preface

The chemical industry, although one of the most advanced industrial sectors, is often perceived in a negative light by the general public, despite its crucial role in satisfying our everyday needs in fields as varied as food, pharmaceuticals, energy and textiles.

In response to the risks associated with this sector and the growing pressure of globalization on business competitiveness, increasingly stringent safety and environmental standards are being introduced. It is against this backdrop that the concept of process intensification has emerged, aimed at developing cleaner, safer and more economical facilities.

One of the key approaches to process intensification is to reduce the size of units in relation to their production capacity and energy consumption. This strategy can be applied to all stages of production, from reaction to shaping to separation.

The handout is aimed at Process Engineering students at the end of their Environmental Process and Chemical Engineering specialization. The program for the Process Intensification module of the MASTER ACADEMIQUE HARMONISE (2022) national program, in French, is :

Chapitre 1.Bases de l'intensification des procédés

Définitions. Principes et applications de l'IP. Mise en œuvre de l'intensification des procédés : approche basée sur les équipements ou les méthodes.

Chapitre 2. Les équipements pour l'Intensification des procédés

Microréacteurs : Réacteurs à baffles oscillantes, Réacteurs à disque tournant

- Absorbeur centrifuge
- Colonnes garnies rotatives
- Exemples d'application de ces équipements dans différents procédés

Chapitre 3. Les méthodes de l'Intensification des procédés

Réacteurs multifonctionnels (Distillation réactive, Réacteurs à membrane). Séparations hybrides (Membrane- absorption , Membrane- distillation). Exemples d'applications de ces différentes méthodes.

Chapitre 4.Sources d'énergies alternatives

Energie solaire. Ultrasons. Micro ondes.

Chapitre 5. Autres méthodes d'intensification des procédés :

Nouveaux solvants (Fluides supercritiques, Liquides ioniques). Exemples d'application de ces solvants.

Chapter I. Basics of process intensification

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I.1 INTRODUCTION

Process intensification, as defined by Stankiewicz and Moulin, aims to improve various aspects of industrial operations while meeting environmental and economic imperatives. Objectives include reducing costs, improving safety, increasing productivity, reducing energy consumption and preserving the environment by limiting the formation of undesirable by-products.

This approach can be divided into two main categories: specific equipment and methods dedicated to process intensification.

Specific equipment includes new devices designed to meet these objectives, such as micro-reactors, rotating disk reactors, compact heat exchangers and static mixers. These devices are designed to optimize chemical reactions and processes in such a way as to reduce the size of the equipment required compared with that traditionally used, while minimizing energy consumption and the production of by-products.

In addition, the methods adopted for process intensification make different use of existing equipment. This can include the use of multifunctional reactors to combine several reaction or separation steps, the adoption of hybrid separation techniques such as extractive distillation, the exploration of alternative energy sources such as ultrasound, or the use of methods such as supercritical fluids to improve existing processes.

In short, process intensification offers a wide range of applications designed to improve the efficiency, sustainability and profitability of industrial operations, while reducing their environmental impact.

The aim of process intensification is to reduce production costs and design cost-effective processes. This can be achieved by making improvements to existing technologies, but an essential aspect of process intensification is also the development of new technologies. The design philosophy in process intensification is to design a process that has chemical kinetics alone. This means that all other process limitations such as mass transfer, heat transfer and hydrodynamics are eliminated.
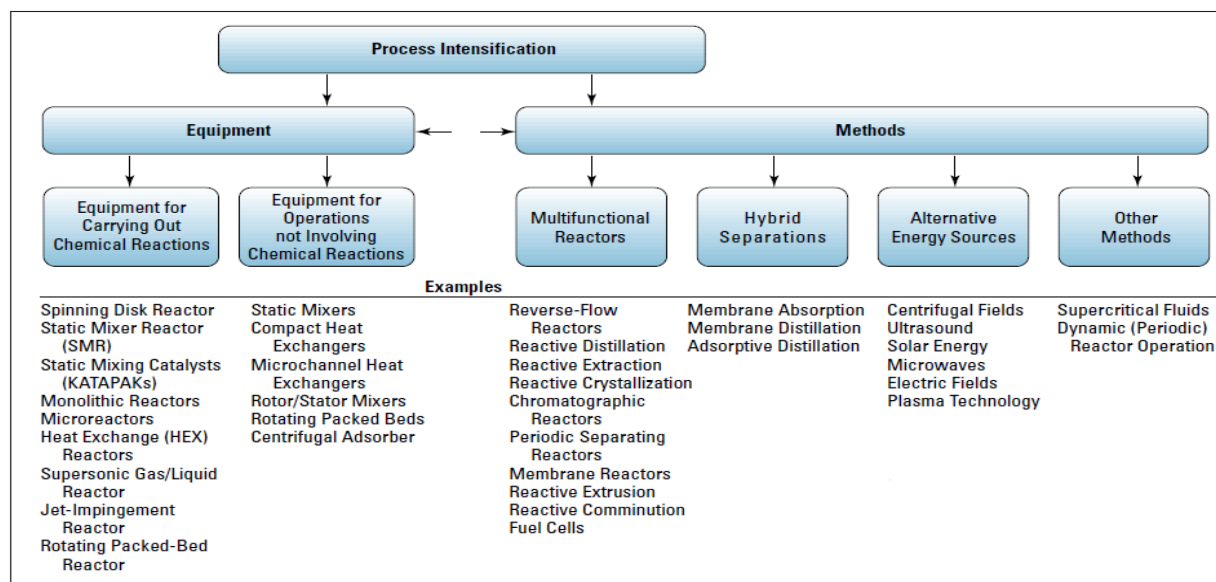
Figure I.1. Illustrative diagram of process intensification classification according by Stankiewicz and Moulin (2002)

I.2 Principles and applications of P.I

Process intensification aims to create new equipment that is more environmentally friendly, safer and more efficient, while reducing the size of plants in relation to their production capacity, their consumption of resources (energy, water, fuels) and their production costs. This is an absolute necessity if we are to revolutionize the chemical industry, requiring a genuine transformation of plants and a thorough overhaul of processes.

There are two main thrusts to this intensification. On the one hand, intensification methods involve, for example, the coupling of several unit operations to create multifunctional processes, or the re-appropriation of equipment for functions different from their initial uses. On the other hand, intensification technologies, such as micro-technologies, accentuate transfer and mixing phenomena, or use innovative materials to improve processes.

I.3 The different approaches of PI

I.3.1 The micro-structuring aspect

In 1995, at the opening of the first International Conference on Process Intensification in the Chemical Industry, Ramshaw, one of the pioneers in this field, defined process intensification as a strategy aimed at achieving dramatic reductions in the size of a chemical plant in order to meet a given production target. These reductions can be achieved both by reducing the size of individual pieces of equipment and by reducing the number of unit operations or devices involved. Ramshaw stipulates that the degree of reduction must be significant, evoking a volume reduction of the order of 100 or more, which is particularly difficult. However, in our

opinion, a reduction by a factor of two already constitutes a drastic change and should therefore be considered as process intensification. Ramshaw's definition is rather restrictive, focusing solely on the reduction in plant or equipment size, whereas this is in fact one of several possible effects. Indeed, a significant increase in production capacity within a given volume of equipment, a gradual reduction in energy consumption per tonne of product, or even a marked reduction in the formation of waste or by-products are also considered forms of process intensification. It is therefore logical that process intensification, driven by the need for revolutionary changes in operations, should focus primarily on new methods and equipment, while also incorporating established technologies and materials.

I.3.2 Reduced surface/volume (S/V) ratio

The fundamental principle involved in miniaturizing devices is to increase their surface/volume ratio, while preserving their production capacity. The main consequences of this approach include improved heat transfer, thanks to increased surface area, and improved material transfer, thanks to reduced molecular diffusion characteristic lengths.

Improving heat transfer in compact reactors and exchangers:

The improvement of thermal phenomena is a vital factor in the treatment of exothermic reactions. As with the intensification of material transfer, channel design with its high surface-to-volume ratio is the key to improved heat transfer in compact reactors and exchangers.

The use of highly conductive materials, such as silicon carbide or aluminum, also facilitates heat exchange between the reaction fluid and the wall.

Characterizing heat transfer involves studying the overall heat exchange coefficient U. It is often preferable to look at the intensification coefficient UA/V rather than the U coefficient alone, in order to take reactor compactness into account. In this expression, A represents the exchange area and V the volume of process fluid in contact with the reactor wall.

Chapter II. Equipment for process intensification.

II.1 Introduction

Technological progress and research in the field of process intensification are leading to the development of new equipment adapted to various functions, in particular the implementation of chemical reactions. This equipment must meet a number of requirements, such as :

- Rapid heat exchange.
- Mix reagents and/or products quickly and efficiently.
- Withstand high temperature and pressure conditions.
- Continuous operation at high flow rates to compensate for loss of reaction volume.
- Improve operator safety.
- Occupy less space thanks to compact design (miniaturization).

For the design of these intensified technologies, particularly for reactors, four essential parameters need to be taken into account:

- Reactor heat transfer performance.
- The nature of the flow inside the reactor (piston, mixture, etc.).
- Reactor dynamics.
- Reactor residence time.

II.2 Continuous reactors

II.2.1 Compact heat exchanger reactors

We present the final and potentially most significant category of intensified technologies: compact reactor-exchangers.

This equipment is based on the concept of plate heat exchangers, where heat exchange between two fluids takes place through the plate wall. The idea was to divert the usual functions of these exchangers by designing plates specially adapted to support chemical reactions.
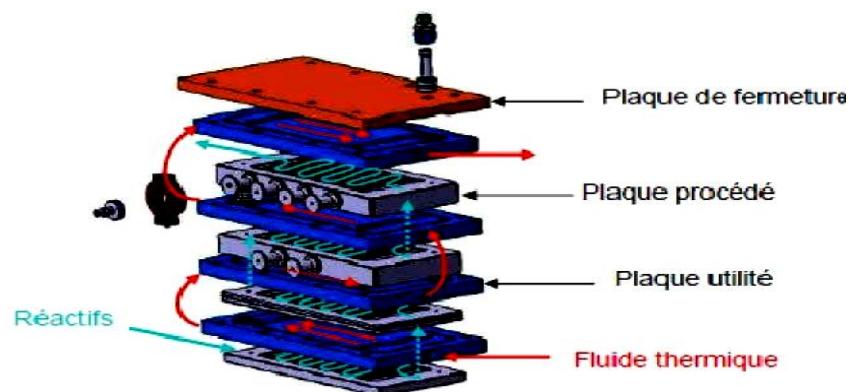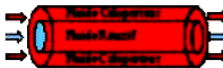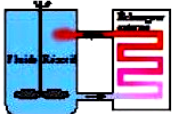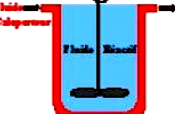
Figure II.1. Compact heat exchanger reactors

If we compare the thermal performance of the various conventional reactor types (Table II.1), we can see that the batch reactor does not offer many possibilities in terms of heat exchange, and that the compact exchanger-reactor can perform considerably better than the batch reactor in terms of the intensification coefficient defined by : $I = U. S/V$. With U, the overall heat exchange coefficient in W/m²°C., S, the exchange surface area in m^2 and V, the reaction volume in m³.

The exchange surface is also much greater in a compact exchanger-reactor than in a batch reactor with a double envelope or an external exchanger.

Table II.1. Thermal performance of different reactors

Procédé	Echangeur- réacteur compact continu[a]	Echangeur-réacteur tubulaire continu[b]	Echangeur-réacteur discontinu avec échangeur externe[b]	Echangeur-réacteur discontinu avec double enveloppe[b]
Schéma de principe				
S/V (m²·m⁻³)	800	400	10	2.5
h (W·m⁻²·K⁻¹)	5000	500	1000	400
ts (maximum)	Quelques minutes	Quelques minutes	Quelques heures	Quelques heures
hS/V (kW·m⁻³·K⁻¹)	4000	200	10	1

II.2.2 Presentation of the LokiR exchanger-reactor

The proposed reactor is a plate exchanger made up of 5-plate elementary modules (Figure II.2). Simply connect a number of elementary modules in series to build a reactor, and then connect the reactors in parallel to produce the desired quantity of hydrogen.
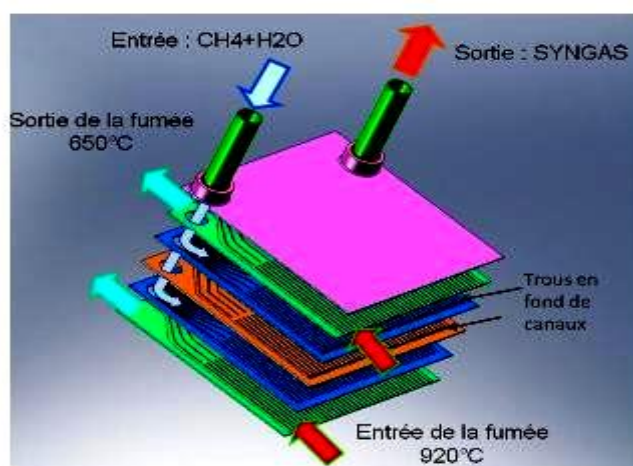
Figure II.2. Schematic of an elementary module of the heat exchanger-reactor

An elementary module consists of two flue gas heat exchanger plates (green plates), surrounding two reaction plates (blue plates), which in turn surround a heat exchanger plate through which the syngas, or SYNGAS, produced flows (orange plate). The heat transfer required for the reforming reaction relies on convective and conductive heat transfers.

The heat exchange plate through which the synthesis gas flows (orange plate) and the upper reaction plate (blue plate) are perforated at the bottom of the channels to allow the synthesis gas to pass in counter-current, enabling heat to be recovered on site.

The reaction plates (blue) consist of two distinct zones. In the first zone, called the distribution zone, the mixture of natural gas and steam receives heat from both the smoke plates (green) and the syngas cooling exchange plate (orange), until it reaches a temperature sufficient to initiate reforming. In the second zone, known as the reaction zone, the mixture, in contact with the catalyst, reacts on the surface of the microchannels to produce SYNGAS. A simplified diagram of the operation of an elementary module is shown in figure II.3.
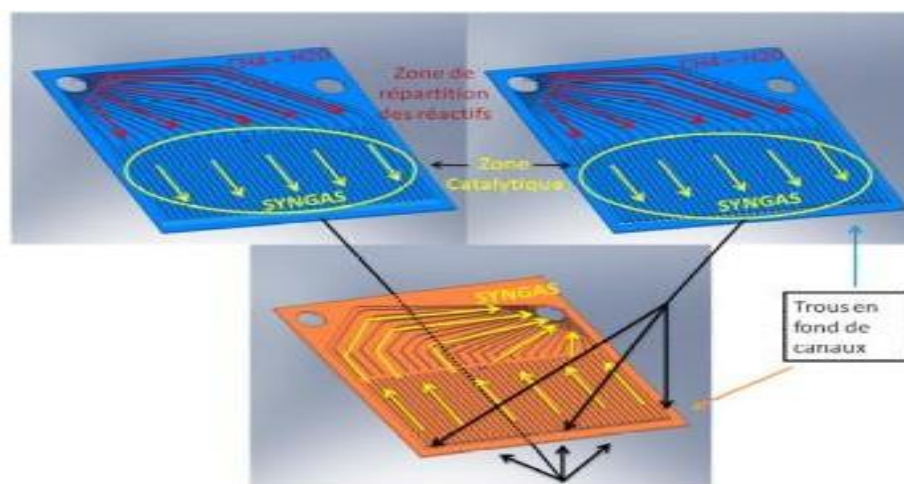
Figure II.3. Path followed by gas.

The potential energy savings result from optimized heat exchange. In a conventional tubular reactor, the heat stored by the syngas during the sudden cooling from 850°C to 350°C at the outlet of the main reformer is lost. In the case of the exchanger-reactor, the syngas flows back against the current. There is therefore a heat transfer between the syngas and the natural gas/water vapor mixture arriving at a lower temperature.

II.3 Microreactors

Heat transfer coefficients in microreactors often exceed those of conventional heat exchangers. These reactions can be carried out in microreactors, where values of up to 20,000 W/m^{2}K have been observed. Microreactors are very small chemical devices, generally structured in sandwich form, consisting of several layers with microchannels of the order of

10 to 100 micrometers. Each layer performs different functions, from simple mixing to catalysis, heat exchange or separation. Integrating these different functions in a single unit is one of the main advantages of microreactors.

The extremely high heat transfer rates achievable in microreactors enable isothermal operation of highly exothermic processes, which is of particular importance in kinetic studies. Because of their very low reagent volume/surface area ratio, microreactors are potentially attractive for processes involving toxic or explosive reagents. Moreover, the use of arrays of several microreactors is becoming economically and technically feasible on a significant scale.

The geometric configuration of microchannel heat exchangers, with stacked cross-sectional structures, bears similarities to that of cross-flow monoliths, although the materials and manufacturing methods used differ.

II.3.1 Spinning disk reactor (SDR)

The Spinning Disc Reactor (SDR) consists of a rotating plate housed in a closed chamber. This horizontal plate, with a diameter ranging from 0.06 to 1 meter, is rotated by a motor at speeds ranging from 100 to 6,000 rpm. The plate is cooled or heated by a fluid circulating inside it, as illustrated in Figures II.4 and II.5. This technology exploits centrifugal force to produce thin films on the surface of the disc (100 to 200 micrometers), thus intensifying the transfers favored by the undulations generated within the fluid by centrifugal force. The liquid film formed on the surface of the disc also has a very high surface-to-volume ratio, a crucial parameter in terms of intensification.

The reagents are introduced into the center of the disk and spread radially over its rotating surface. They rapidly pass through this zone, forming a thin film in which the reaction takes place, before the products are collected in collectors located on the sides of the device. This makes it possible to achieve very high heat transfer coefficients, 5 to 10 times higher than those of conventional coolers and heaters, as well as excellent mass transfer coefficients for reactions in homogeneous liquid, heterogeneous gas/liquid or liquid/solid phases.

The temperature inside the SDR is carefully regulated, ensuring process safety and enabling operation at high temperatures to compensate for short residence times. The flow is similar to a piston movement, and it is possible to coat the disc with catalyst. SDR technology can be used for a wide range of reactions, such as rapid organic synthesis followed by precipitation, polymerization, and nano and microparticle production. Production rates are comparable to those required in the fields of fine chemicals and pharmaceuticals.

However, the SDR principle is based on a rotating disc, whose diameter increases with the required dwell time. However, due to safety concerns, manufacturers are still reluctant to use rotating equipment.

Despite this, the characteristics of the SDR reactor make it a good candidate for highly exothermic reactions and those limited by material transfer. The discs contain very small quantities of reagents, with residence times of the order of a second, thus eliminating any risk of thermal runaway. What's more, the products can be cooled as they flow down the walls of the chamber where the discs are sealed.

The main SDR operating variables are residence time, feed rate, rotation speed and film thickness, which plays an important role in process design. Table II.2 lists some orders of magnitude of these variables.

Table II. 2. Examples of residence times and film thickness in an SDR for different operating conditions.

Volumetric flow rate (mL.s^{-1})	Viscosity (Pa.s)	Rotation speed (rpm)	Average residence time (s)	Film thickness (μm)
1	0.001	200	1.5	60
10	0.001	200	3.1	125
1	0.001	7000	0.14	5
10	0.001	7000	0.02	10
1	1	200	14	590
10	1	200	3	1275
1	1	7000	1.4	55
10	1	7000	0.3	120

Examples of some reactions carried out with an SDR

- Polymerization reactions: polymerization of n-butyl acrylate by photoinitiation;

- Reactions in gas-liquid systems: sulfonation of olefins, alkyl benzenes or primary alcohols with SO_3 ;

- Reaction in gas-liquid systems: synthesis of 1-oxaspiro (2,5)-carbonitrile (Darzen reaction);

- De-pollution reaction: ozonolysis, photo-catalytic degradation;

- Fine chemistry reaction: catalytic rearrangement of pine oxide;

- Precipitation of barium sulfate;

- Mesylate salt crystallization.
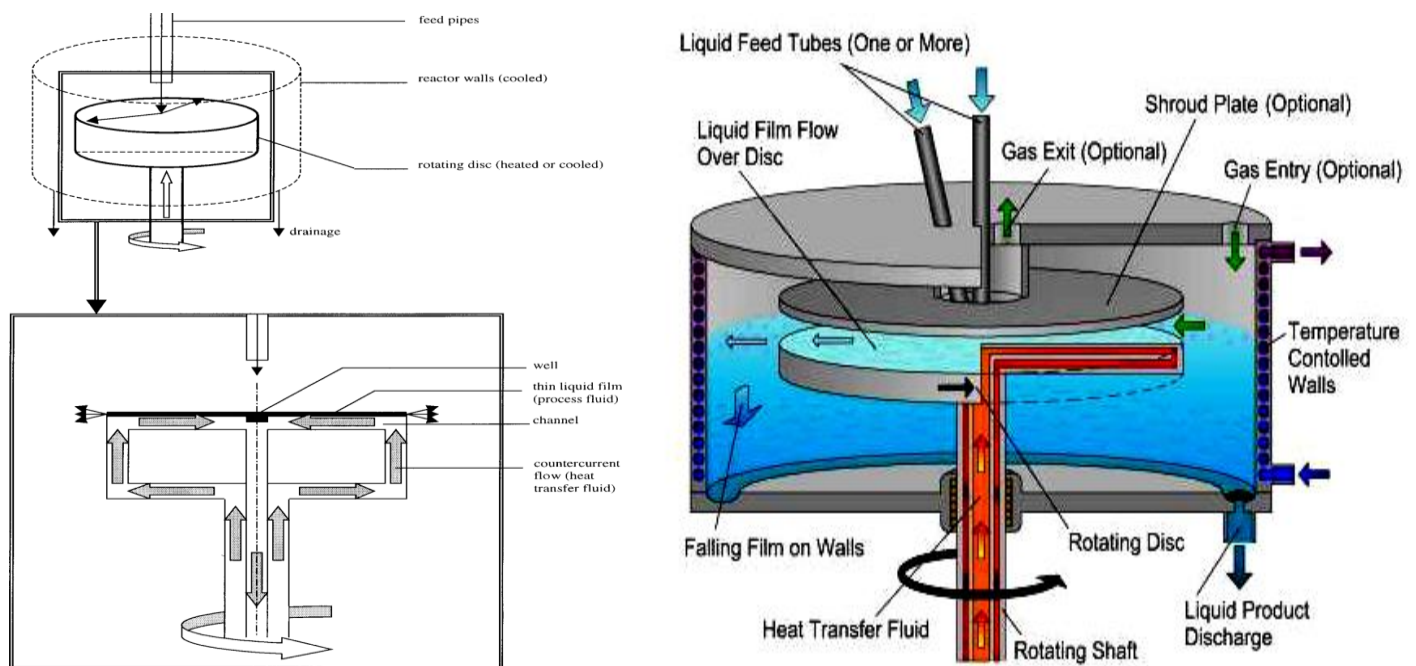
Figure II.4. Schematic of rotating disk reactor principle

Figure II.5. Example of an SDR reactor

II.3.2 Oscillating Baffle Reactor (OBR)

The Oscillatory Baffled Reactor (OBR), illustrated in figure II.6, consists of a column or tube with regularly spaced baffles, arranged transversely to the main flow in order to disrupt the boundary layer along the tube wall. Oscillatory motion is applied to the flow, creating oscillations in the reaction medium that enhance mixing by forming vortices. As a result, the reactor functions as several well-mixed tanks in series. Mixing in the OBR differs considerably from that generated in a conventional stirred reactor. Pulsed mixing is considerably more homogeneous, and the intensity of radial mixing is comparable to that of axial mixing, regulated by the opening and spacing of the baffles. This is how the OBR achieves plug flow.

The OBR offers the possibility of replacing batch manufacturing in the existing batch process with continuous manufacturing, while maintaining a similar level of production. It eliminates downtime and enables a more compact reactor to be used, thus reducing energy consumption and space requirements, improving process safety and reducing environmental impact.

Table II.3. Comparative example of OBR and batch process characteristics.

	Batch production	**Production with OBR**
Reactor volume (l)	1600	270
Surface area used (m^2)	1200	60
Efficiency (%)	83	83
Product purity (%)	99,5	99,5
Production kg/day	180	150

To evaluate the efficiency of the OBR reactor-exchanger, several reactions were tested:

- acid-base reaction (Prat et al., 2004),
- oxidation reaction (Prat et al., 2004, Elgue et al., 2007),
- esterification reaction (Elgue et al., 2007; Benaissa, 2006),
- nitration reaction (Elgue et al., 2007).

The study of this reactor shows that it has a piston-like behavior with good mixing of reactants at the nominal operating point. The heat transfer coefficient varies between 2000 and 2500 W.m^{-2}.K^{-1}. It is an exchanger reactor capable of supporting highly exothermic reactions.
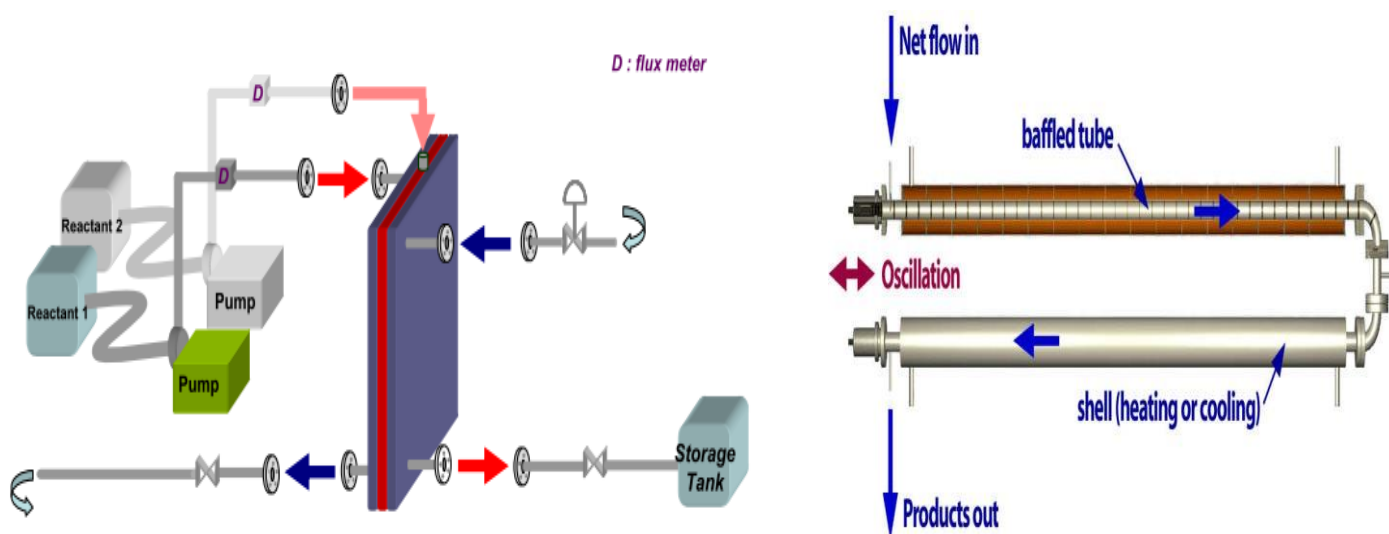

Figure II.6. Oscillating Baffle Reactor (OBR)

Advantages

- Piston flow

- Efficient two-phase liquid mixing: Improved heat transfer and improved mass transfer

- Mixing uniformity, low shear

- Reduced energy consumption: lower operating costs

 - Small reactor: lower investment costs.

II.3.3 Rotary Packing Bed (RPB) reactor

Centrifugal reactors, also known as rotating packed bed (RPB) reactors or intensive contactors, amplify mass transfer by exploiting the effects of a high gravity field (figure II.7). The liquid is sprayed inside the packed bed by a set of well-distributed nozzles. The centrifugal force generated by rotor rotation propels the liquid radially outwards, forming a very thin film on the surface of the packed bed.

The gas enters the fixed housing and passes through the rotor from the outside in, while a dynamic seal at the top of the rotor ensures that the gas passes through the packed bed. The extremely short retention time resulting from the high gravity field promotes a very high conversion rate, virtually free of by-products. This enables intensive spontaneous contact between gas and liquid. What's more, the space required for installation, especially the installation height, is only a fraction of that needed for a traditional tower. The use of special materials significantly minimizes the capital costs of the equipment.

The rotating packed bed (RPB) was initially used in biocatalytic hydrolysis reactions, dramatically improving micro-mixing of substrate and lipase thanks to the centrifugal force of the RPB. The high gravity factor (β), crucial for mass transfer in the RPB, was studied in the hydrolysis reaction of soya oil. Three other oil species were also tested in the RPB hydrolysis system, adjusting the β value for each application. Hydrolysis yields of these oils in the RPB exceeded those obtained in a conventional continuous stirred tank reactor (CSTR) by 15% to 25%, with a reduction in reaction time of 30% to 50%. This demonstrates the superiority of the RPB reactor for oil hydrolysis over the CSTR system.
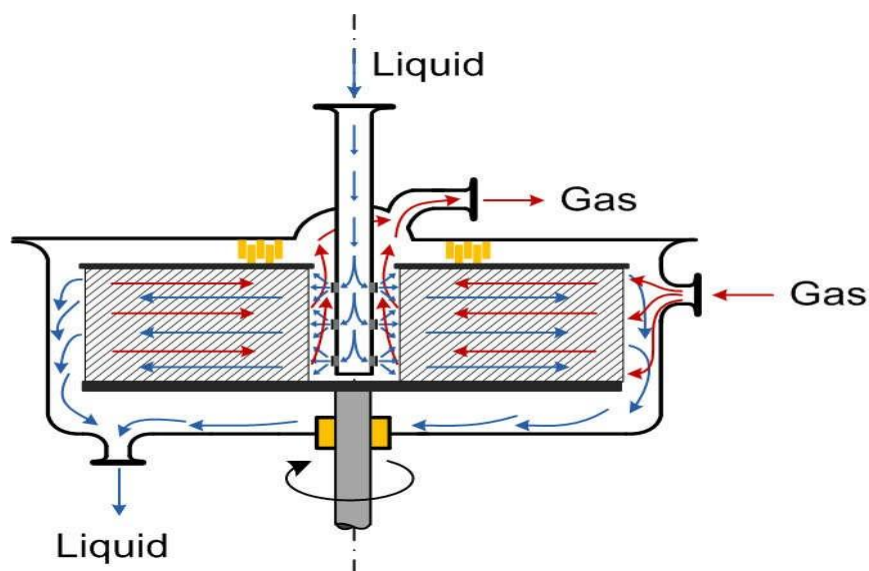
Figure II.7. Rotary packing bed reactor (RPB)

II.3.4 Compact heat exchanger reactor (HEX reactor)

Unlike previous reactors, HEX reactors (figure II.8) are above all heat exchangers in which reactions have been carried out. As a consequence, their design is largely based on compact heat exchangers geometries. To improve reaction conditions (mixing, residence time, etc.), metallic foams, fins, etc. can be inserted. Then, different HEX Reactors have been designed and built.

Plate heat exchangers offer many benefits compared to shell and-tube heat exchangers. Heat transfer coefficients are higher and as a consequence the surface area required for a given heat duty is one-half to one-third that of a shell-and-tube heat exchanger. Thus, costs, overall volume and maintenance are reduced. Moreover, the high turbulence due to plates reduces fouling to 10–25% compared with shell-and-tube heat exchangers and residence time distribution is narrow. Indeed, with the appropriate corrugation angle and in a range of values for the Reynolds number, a quasi plug flow behaviour can be obtained which could be suitable to carry out reactions. Plate heat exchangers consist of a number of thin, rectangular corrugated plates that are pressed together. To ensure tightness, three technologies are available: gaskets, welding or brazing. Gas-keted plate heat exchangers are the most common in industry. Indeed, they can be easily dismantled for inspection, cleaning or maintenance and expanded or adapted by adding or replacing plates when the conditions change. Temperature up to 200∘C and pressure up to 25 bars can be achieved. However for some applications, gaskets are undesirable: high pressure and temperature or very corrosive fluids. In these cases, welded or brazed heat exchangers are available. The drawbacks of these technologies are that the apparatuses cannot be opened (and thus cleaned, etc.) and fouling will limit the range of

applications.
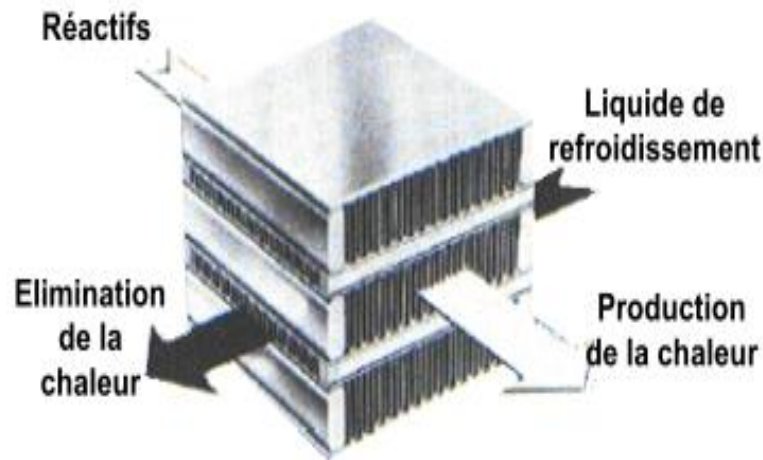
Figure II.8. Heat exchanger reactor (HEX reactor)

II.4 Static mixers

A static mixer consists of a series of immobile elements arranged in series in a tube. Each element has a specific rigid geometric structure that splits and then recomposes the flow (see figure II.9). These elements are designed to ensure optimum mixing. In general, contact between the fluids is favored by the radial movement generated inside the static mixer. The fluids are circulated by a pump, the characteristics of which depend on the pressure drop in the static mixer and the desired flow rates. These mixers are commonly used to intensify physical and chemical processes in liquids, including the dissolution of gases and solids.

Static mixers come in a variety of geometric shapes (see figure II.9). They consist of a series of elements fixed around an axis and harness the energy of the flow to create a homogeneous mixture between two or more fluids, thus avoiding any separation. The main aim of these devices is to ensure optimum mixing with minimum pressure drop, whatever the conditions: low or high viscosity, presence of fibrous or non-fibrous materials, need for instantaneous mixing. The advantages of these equipment include:

- low retention volume ;

- low energy consumption (low head losses);

- homogeneous residence time (limiting dead zones and back-mixing).

Figure II. 9. Some examples of helical static mixers in transparent tubes.

II.4.1 Static mixer reactor (SMR)

In the last 25 years, agitation technology has intensified remarkably, particularly in liquid/liquid and gas/liquid systems. This progress has been achieved mainly through the growing adoption of static mixers, to the detriment of traditional mechanical mixers. The latter, as examples of process intensification, offer a more efficient and economical method of mixing and contacting fluids, while expanding their fields of application.

The Static Mixing Reactor (SMR), for example, is used in processes requiring simultaneous mixing and intensive heat transfer, such as nitration or neutralization reactions. Static mixers are made up of structural elements immobilized in series inside a tubular body, which can be installed in pipes, columns or reactors, and supplied with fluids by a pump system. Their special geometry ensures excellent mixing, thanks to a principle that divides and redistributes fluids perpendicular to their flow, without the need for external energy.

Compared with conventional mixers, static mixers consume less energy and require less maintenance, as the elements are immobilized inside the tube. Moreover, they enable internal heat exchange, since the static elements are traversed from the inside by a heat transfer fluid, while the process fluid circulates outside these elements. This concept is the basis of SMR static mixers (figure II.10), making them ideal for fast, highly exothermic reactions, as well as for those whose viscosity increases as they progress.
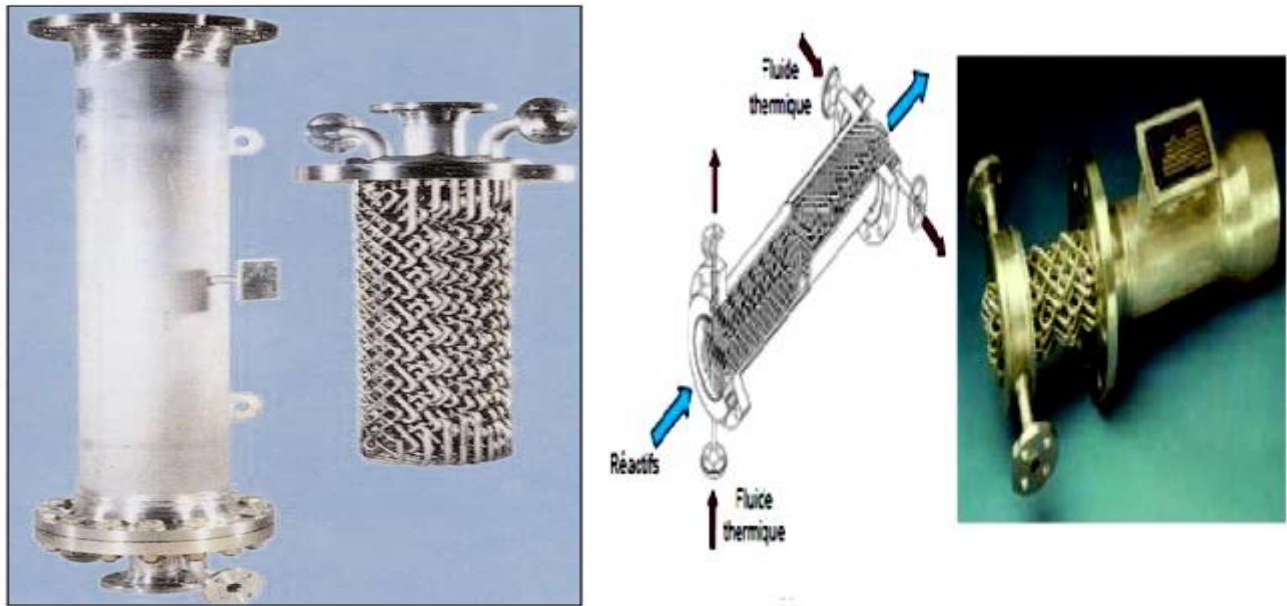
Figure II.10. Static mixer reactor (SMR)

II.4.2 Mixer/Heat-Exchanger

The Fluitec mixer / heat exchanger (figure II.11) is a combination of a static mixer and a multitube heat exchanger. It can be used for mixing, heat and mass transfer or – thanks to its optimal residence time distribution – as a plug flow reactor.

The design of the mixer / heat exchanger equates to a combination of a static mixer and a multitube heat exchanger in which a highly viscous product on the shell side flows through the static mixer. The advantages of these two distinct systems are aggregated for use at laminar flow.

CSE-XR series production   CSE-XR DN 200
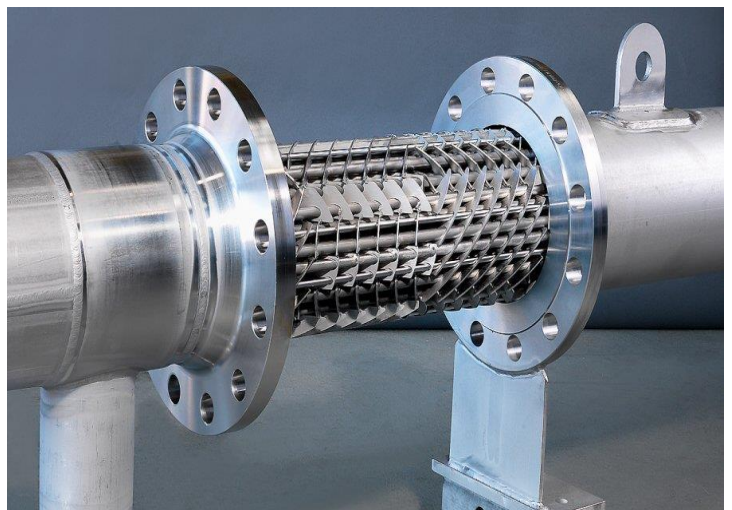
Figure II.11. Fluitec mixer / heat exchanger

Since the design is consistently based on the geometry of the CSE-X – the most efficient mixer type of all – excellent homogeneity, a narrow residence time distribution and a uniform shear field over the cross-sectional area are guaranteed along the entire length of the apparatus. The very high radial mixing efficiency constantly ensures an intensive flow against the internal heat transferring tubes integrated in the mixing element. Far more heat is transferred than with heat exchanger arrangements with no internal elements (e.g. monotube heat exchangers, where the tubes have a double shell). From a fluid dynamics viewpoint, the heat transferring tubes are ideally positioned in the mixing element; this is very important since it facilitates the exceptionally compact design.

APPLICATIONS:

Static mixers and dosing systems from Fluitec have proved their worth particularly in the evaporation of ammonia water and in the mixing of ammonia in flue gas. They are used in the following branches of industry

 - Municipal waste incineration plants

- Chemical industry

- Cement production units

- Burner boilers

- Sludge and special waste incinerators

- Exhaust gas purification for large engines

II.5 Centrifugal extractor

A centrifugal extractor (Figure II.12), also known as a centrifugal contactor or annular centrifugal contactor, exploits rotor rotation to mix two immiscible liquids outside the rotor and separate the liquids inside the rotor under the influence of gravity. This device ensures continuous extraction of one liquid phase into another.

Two immiscible liquids of different densities are rapidly introduced and mixed in the annular space between the rotating rotor and the fixed space. The mixed phases are directed towards the center of the rotor by radial vanes at the base of the housing. When liquids enter the rotor's central opening, they are accelerated towards the wall. The mixed phases are then accelerated at rotor speed, and separation begins as the liquids are moved upwards. A system of weirs at the top of the rotor allows each phase to leave the rotor and reach an annular collector for discharge. Flow between stages is by gravity, eliminating the need for pumps. In this way, centrifugal contactors act as mixers, centrifuges and pumps simultaneously.
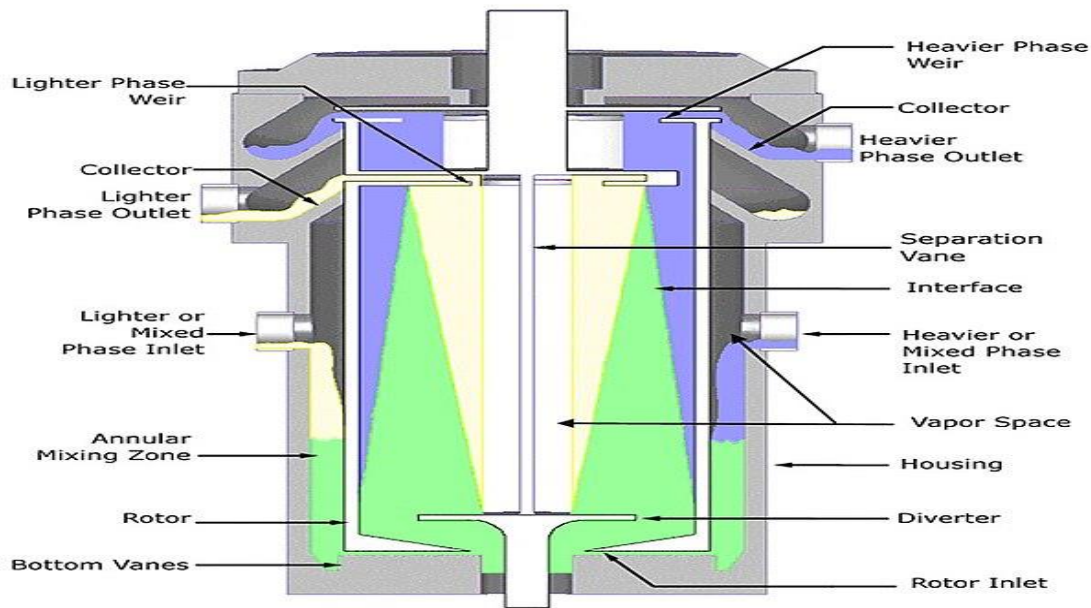
Figure II.12. Centrifugal extractor.

II.6 Monolithic catalysts

Monolithic substrates used in contemporary catalytic applications come in metallic or non-metallic form, offering a multitude of narrow, straight channels of uniform cross-section. To ensure adequate porosity and enhance the catalytically active surface, the inner walls of these monoliths are usually coated with a thin layer of washcoat, serving as a support for the catalytically active species. Here are the most important characteristics of monoliths:

- They present a very low pressure drop in single-phase and two-phase flow, one to two orders of magnitude lower than that of conventional packed-bed systems.

- They offer high geometric zones per reactor volume, typically 1.5 to 4 times greater than those of reactors using particulate catalysts.

- Their catalytic efficiency is exceptionally high, reaching almost 100%, thanks to very short diffusion paths in the thin washcoat layer.

- Their performance is particularly remarkable in processes where selectivity is limited by mass transfer resistances.

Monolithic catalysts can also be installed in-line, in a similar way to static mixing elements, using the latter as gas/liquid dispersion devices. In-line units offer additional advantages:

- Reduced investment costs, as monolithic in-line reactors are ready-to-use modules installed in a single section of pipeline.

- Compact installation layout; in-line monolithic reactors can even be placed underground, for example in cement ducts.

- The ability to meet more stringent safety and environmental standards than conventional reactors; for example, by placing the reactor unit below ground level.

- Quick and easy replacement, e.g. in the event of catalyst deactivation, simply by exchanging a pipeline segment, rather than unloading and loading the new catalyst.

- The ability to distribute several feed points along the reactor.

Figure II.13. Monolithic catalysts.
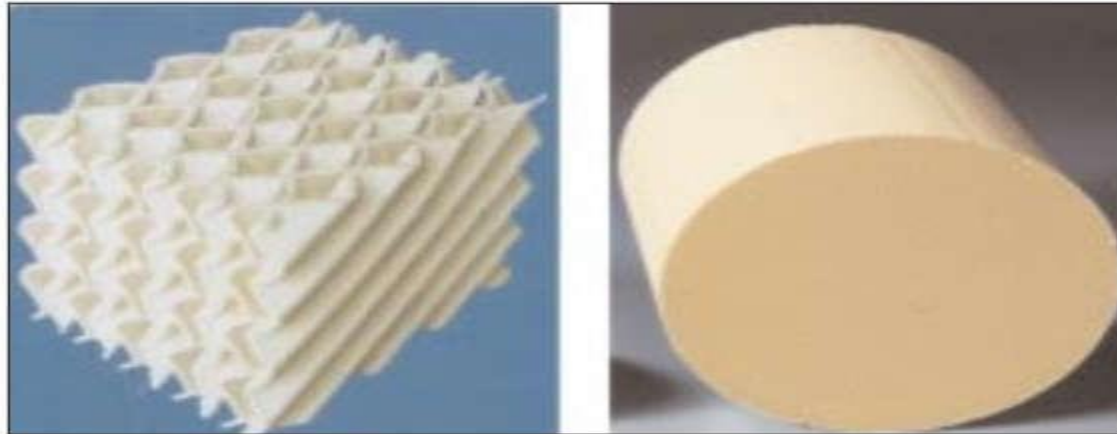
Chapter III. Process intensification methods

III.1 Multifunctionality concept

The concept of multifunctionality is based on the idea of using a multifunctional reactor in which at least one additional operation is integrated compared with conventional reactors. This additional operation may concern the transfer of matter, heat, momentum, phase changes or separation. In this type of reactor, the additional functions can be as follows:

- Coupling unitary separation operations with chemical reactions, such as membrane reactors, reactive distillation, reactive extraction, etc.

- Integrate multiple functions, such as mixing and conversion, as in reactors with static mixers.

- Amplify a particular mechanism, be it transfers or reactions, as in reactors activated by ultrasound or microwaves.

- Favor continuous operation, enabling miniaturization of equipment.

III.2 Reactive separation

The basic principle of reactive separation is based on the use of a multifunctional reactor, which can be defined as a device in which, in addition to separation, a chemical reaction takes place in parallel.
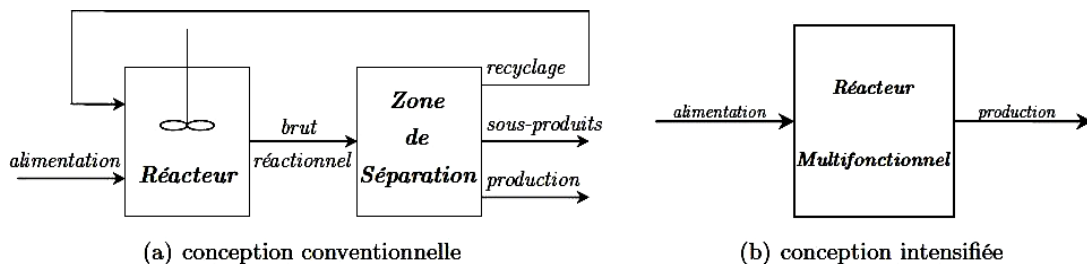
Figure III. 1. Diagram of conventional process design approach

Although we always speak of reactive separation, one of the two reaction or separation phenomena is often considered to take precedence over the other, and two different operating modes can be distinguished:

- **Separation can be used to support the reaction:** in this case, the separation is carried out in the reaction medium to promote the reaction. An emblematic example is reactive distillation.

- **Reaction can be used to support separation**: in this case, separation of the components of a mixture is difficult, if not impossible, using conventional methods. For example, we may encounter mixtures that are virtually indistinguishable in a conventional plant, but which can be isolated by adding a selective reagent that acts only on one of the constituents. The component that has

not reacted is recovered after this first operation, while the second component and the reactive agent are regenerated by carrying out the reverse reaction in a second step. In this way, the reaction is used to improve separation.

III.3 Reactive distillation

In the vast field of process intensification, one particularly attractive application is reactive distillation. Although known for over a century, it has only gained in importance over the last twenty years in academic and industrial research, thanks to technological advances in catalysis, instrumentation, advanced models and simulations, and control.

III.3.1 Principles and benefits of reactive distillation

Reactive distillation (figure III.2) can be defined as the simultaneous combination, in the same apparatus, of chemical reactions and the distillation operation. Its fundamental principle is based on the theory of chemical equilibrium enunciated by Le Châtelier as early as 1884: when external modifications are made to a physico-chemical system in equilibrium, it evolves towards a new state of equilibrium by opposing the perturbations and attenuating their effects. For example, an endothermic reaction is favored by an increase in temperature, as this shifts the reaction equilibrium in the direction of the direct reaction; similarly, the elimination of a reaction product favors the formation of this product.

It is precisely the latter case that forms the core of reactive distillation: as the reaction progresses, a constituent is separated by distillation (due to differences in volatility) from the rest of the mixture, so that starting from a stoichiometric mixture, the reactants are completely converted into products (total reaction).
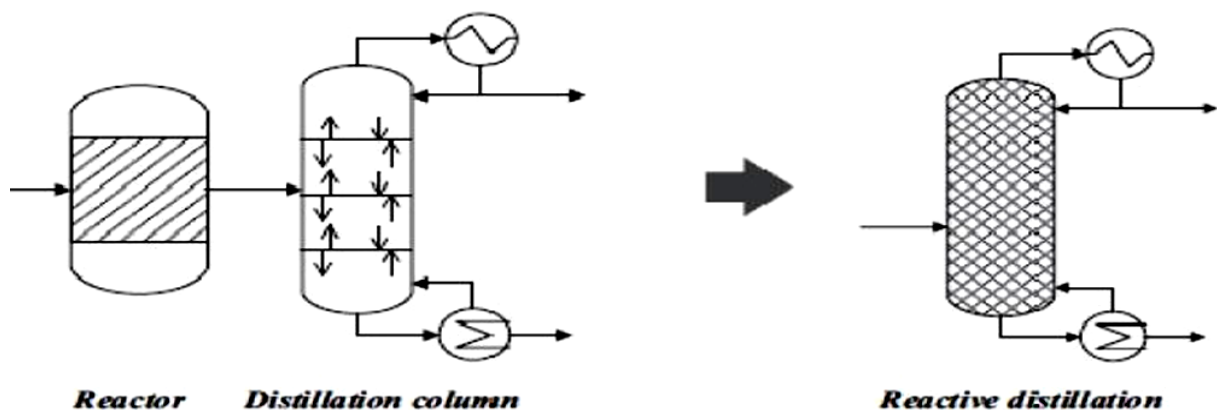

Figure III.2. Reactive distillation

III.3.2 Advantages of reactive distillation

In addition to increasing conversion, reactive distillation offers several other advantages:

- Increased selectivity: the rapid removal of reaction products from the reactive zone increases the selectivity of the reaction, thus avoiding the formation of by-products resulting from secondary reactions.

- Energy integration: if the reaction is exothermic, the heat released helps to separate the mixture, contributing to greater energy efficiency.

- Ease of separation: although defined as a reactive separation technique, reactive distillation sees the separation of certain mixtures facilitated by the presence of reactions, thus simplifying the overall process.

- Enhanced production quality: products are heated only once, reducing the risk of thermal degradation and ensuring higher quality end products.

- Economy of scale: process equipment such as pumps, valves and sensors, which can represent a significant proportion of costs, is reduced thanks to the consolidation of reaction and separation operations.

- Catalyst protection: the temperature at any point in the column is limited to the bubble temperature of the mixture, eliminating the risk of catalyst degradation and the formation of hot points.

III.3.3 Reactive distillation and the environment

In parallel with the notion of intensified processes, the concepts of green chemistry and clean processes have recently emerged. Based on the 12 principles of process design, reactive distillation meets most of the principles of clean process design in many respects. However, these principles still need to be expressed quantitatively in order to optimize the design of reactive distillation with these objectives in mind.

III.3.4 Constraints on applications

In exploring the concept of process intensification or the major industrial successes of reactive distillation, one might be tempted to extend the concept of reactive separation to all conventional processes. However, combining reaction and separation is not always economically advantageous, or even technically feasible in some cases. A number of favorable conditions must be met for reactive distillation to be applied successfully:

- By its very nature, reactive distillation is particularly suitable for balanced and/or competitive reactions.

- The operating temperature ranges for reaction and separation must be compatible with each other, and with that of the catalyst.
- A high concentration of reactants must be maintained in the reactive zone while removing reaction products.
- The reaction must be fast enough to limit the retention volume and therefore the column size.
- If the catalyst is solid, its lifetime must be adequate to ensure the economic viability of the process.

III.3.5 Technology elements

Homogeneous catalysis

In practice, the simplest method for making a distillation column reactive is to place a supply of liquid catalyst (usually a strong acid) at the top of the column. This technique has been used since 1920 in the Estman process for the production of methyl acetate. In order to promote the reaction as much as possible (and thus approach equilibrium), a sufficiently high retention rate (depending on the reaction involved) is required. The most efficient technology is to use tray columns and to operate in the foaming regime. The use of packed columns (bulk or structured) is also possible if the reaction speed is such that retention (trickling film) is sufficient. However, the use of homogeneous catalysis has a number of major drawbacks:

- The use of a homogeneous catalyst increases the unit's operating costs;
- The presence of a homogeneous catalyst can give rise to corrosion problems if the materials chosen for the process are unsuitable: stainless steel, for example, is strongly oxidized by a strong acid in aqueous media;
- The risk of secondary reactions between the catalyst and one of the species can be excluded.

III.3.6 Reactive distillation applications

Methyl acetate production

Reactive distillation offers a number of advantages compared with a conventional reaction process. In this section, the advantages are illustrated using the example of the methyl acetate production process.

Methyl acetate (CH_3OOCH_3, MeOAc) can be produced by the esterification reaction of acetic acid ($CH3COOH$, AcOH) with methanol (CH_3OH, MeOH), catalyzed by H_2SO_4 or an acid resin.

$$MeOH + AcOH \overset{H_2SO_4}{\rightleftharpoons} H_2O + MeOAC$$
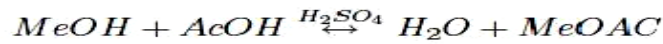
The conventional process uses one or more liquid-phase reactors with a large excess of a reagent to achieve a relatively high conversion. The flowsheet for the conventional process is shown in figure III.3. The reactor is followed by eight distillation columns, a liquid-liquid extraction unit and a decanter. This process requires a large investment in equipment, a very high energy cost and a large quantity of solvents.

Intensified process for methyl acetate production (invented by Eastman Chemical Company in the 1920's) production is carried out entirely in a single column, as shown in Figure III.4. In this column, high purity methyl acetate is obtained without additional purification steps and without recycling unreacted reagents. By distilling methyl acetate from the reaction mixture, conversion is increased without employing an excess of any of the reagents. As the reaction is limited by chemical equilibrium, the continuous removal of products by distillation continuously shifts the direction of the reaction in the direction of product formation. The column contains three different sections. The reagent zone is located below the catalyst feed (gray zone in Figure III.4). The lightest reagent, MeOH, is fed to the lower section, while the heavier acetic acid is fed to the upper section. The lower section serves to strip the MeOH from the water. The steam leaving the reactive section contains MeOAc- MeOH azeotrope, which is broken by feeding acetic acid continuously into the upper section. As in this example the reaction is catalyzed by a homogeneous catalyst (H_2SO_4), an additional separation step is required to recover the catalyst or to purify the catalyst products. Although a solid catalyst can be used this avoids this additional step. With this new technique, energy consumption and investment costs are cut by a factor of five compared with the conventional process.
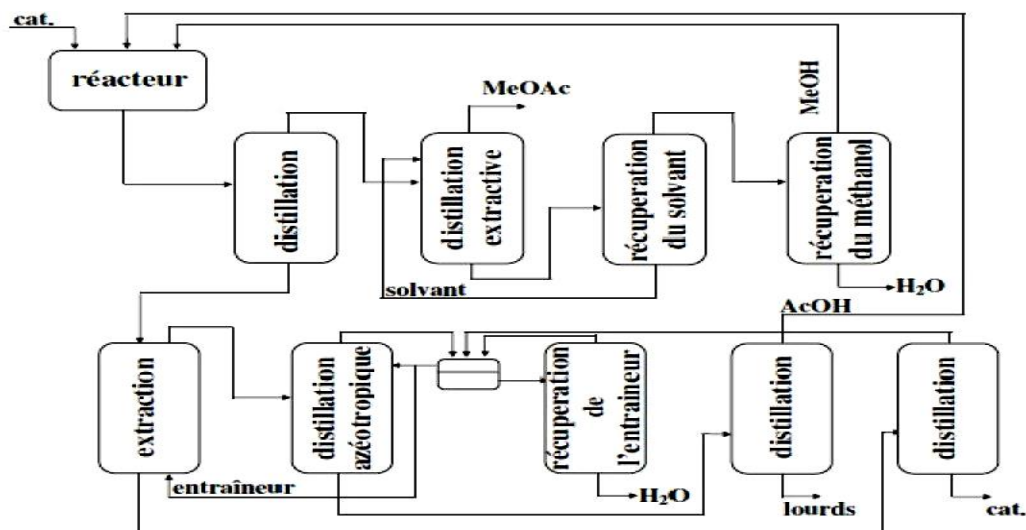
Figure III.3. Conventional methyl acetate production process
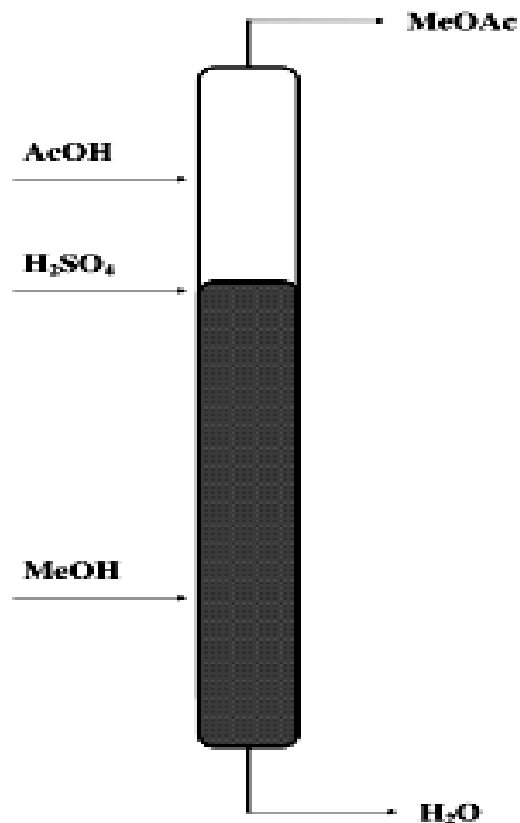
Figure III.4. Intensified methyl acetate production process

III.3.6.1 Advantages

In the previous example, the main advantage lies in the total reduction in plant volume. By consolidating several separate operations into a single unit, lower investment and operating costs are achieved. Another major advantage of reactive distillation is the significant increase in conversion rate. By allowing a balanced reaction to progress towards the products, while performing continuous separation, reactive distillation improves productivity. What's more, by combining separation and reaction simultaneously, by-product formation can be limited as contact time between reactants is reduced, inhibiting secondary reactions. The risk of product and catalyst degradation is also reduced, as the mixture is heated only once, and the temperature is limited by the boiling point of the mixture. In the case of exothermic reactions, the heat generated by the reaction can be used for separation, reducing the amount of heat required at the boiler (this is known as energy integration).

III.3.6.2 Application constraints

Combining reaction and separation is not always advantageous, and in some cases may even be impossible. The temperature and pressure required for reaction and separation must be

compatible to make the process feasible. It is crucial that the operating temperature does not degrade the catalyst or affect its efficiency or service life. To achieve reaction equilibrium, a sufficiently long residence time is required, which implies high retention in the reactive section. However, high retention can reduce separation efficiency by reducing the available interface surfaces. Since the reaction requires a certain residence time, a higher volume retention is necessary, which limits the column geometry. In addition, the catalyst structure used in the reactive distillation column can result in external limitations to mass transfer, potentially affecting reaction rate and product selectivity.

III.4 Membrane distillation

Membrane distillation is an emerging technology still in the experimental stage. As opposed to reverse osmosis, for example, this hybrid method combines distillation with a membrane process. In this process, the membrane does not play the same separation role. The driving force behind the transfer is the difference in water vapor partial pressures between the two sides of the membrane, rather than the total pressure.

The operating principle is as follows: a vapour pressure gradient is created by heating the salt water on the feed side, thereby increasing its vapour pressure and promoting evaporation near the membrane. Only water vapour can pass through the membrane due to its hydrophobic nature, while liquid cannot penetrate the pores. Thus, the membrane acts solely as a support at the liquid-gas interface. The water vapour that passes through the membrane is then condensed by various possible processes before being collected in liquid phase.

Advantages and disadvantages

- This process has many advantages over other separation processes: it is possible to work at temperatures below the boiling point of the water to be desalinated;
- clogging is reduced.
- the process is highly selective (theoretical salt rejection rate of 100%).
- the technology requires little space.
- the process is less sensitive to feed concentration than, for example, reverse osmosis. Water containing up to 300 g/L of salts can be treated with a variant of membrane distillation: vacuum membrane distillation.
- this process can be coupled with renewable energy.

However, it has a number of disadvantages which mean that, for the time being, this technology remains at pilot scale:
- neither membranes nor modules have been designed specifically for this hybrid process

- productivity is low compared with reverse osmosis.

- the process is energy-intensive.
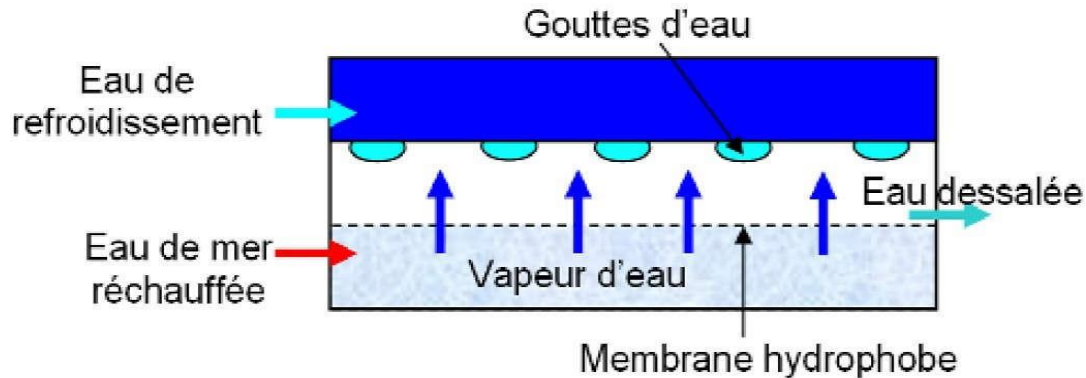
Figure III.5. Principle of membrane distillation

III.5 Membrane reactors

A membrane reactor is a system in which both chemical conversion and membrane separation processes take place. The integration of reaction and separation in a single unit is financially attractive, both in terms of capital and operating costs. By modifying the distribution of reactants and/or reaction products, this combination can lead to increases in conversion rates and/or the production of high-purity products.

Membrane reactors promote the reaction process in several ways: by selectively removing at least one of the products from the reaction zone across the membrane, thereby shifting the equilibrium towards the desired output, and by supplying only a particular reactant to the reaction zone across the membrane. As a result, yield can be increased (typically above the equilibrium level) and/or selectivity can be improved by avoiding further undesirable side reactions.

- For reactions with thermodynamic limits, the selective addition or removal of constituents makes it possible to overcome the thermodynamic limitations of one or more reactions, or to increase the recovery rate of intermediate compounds in the case of consecutive reactions. The membrane reactors used in these applications are often referred to as extractors.

- In the case of competitive reactions, the controlled addition of a reagent can favor the fastest reaction by adjusting the stoichiometry. These are known as membrane distributor reactors.
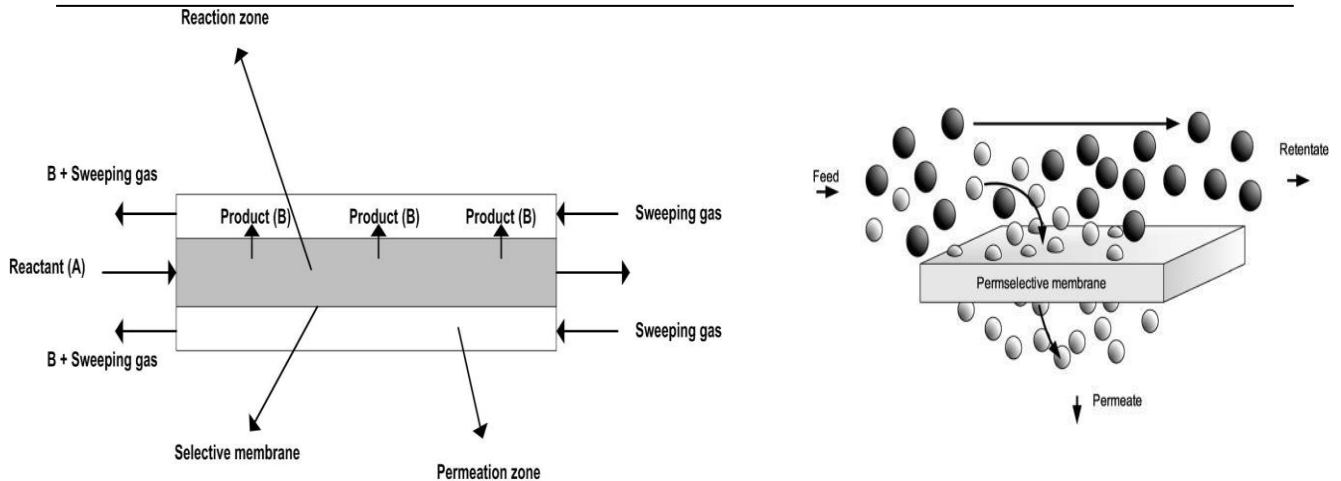
Figure III.6. Principle of a chemical reaction in a membrane reactor

III.5.1 Membrane reactor performance

The performance of a membrane reactor depends essentially on the following points :

– membrane properties: pore size, porosity, membrane thickness.

– physico-chemical properties of fluids: viscosity, conductivity, heat capacity.

– operating pressures.

III.5.2 Classification of reactors by membrane type

a. Inert membrane reactors: in these reactors, the membrane plays no active role in the chemical reaction. Instead, it acts as a barrier for the reactants and some of the reaction products. An example of this type of reactor is the fixed-bed membrane reactor.

b. Catalytic membrane reactors: in these reactors, the membrane either consists of a catalytic layer, or the entire membrane is considered a catalyst. In both cases, the membrane actively participates in the chemical reaction. Some reaction products pass through the membrane to leave the reactor.

III.6 Steam-forming process intensification application

III.6.1 Hydrogen synthesis processes

Hydrogen can be synthesized from fossil resources (natural gas, coal), renewable resources (biomass) or water electrolysis.

Hydrogen synthesis by SMR (Steam Methane Reforming)

Steam reforming of methane is a highly endothermic reaction, making the process very energy-intensive. To accelerate reaction kinetics at lower temperatures, nickel (Ni)-based catalysts are widely used. The reaction can take place at temperatures of 600°C and above, under a pressure of 25 to 30 atm, with significant efficiencies.

$$CH_4 + H_2O \rightarrow CO + 3H_2$$
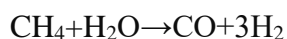
The process flow diagram (Figure III.7) shows all stages, from reactant input to product output.

Natural gas is a raw material containing impurities such as sulfur-containing elements, methane (CH_4) and other gaseous hydrocarbons (ethane, butane, propane) in small quantities. Since sulfur is poisonous to catalysts, natural gas is first sent to a desulfurization unit. The catalysts used in this process are mainly composed of zinc oxide (ZnO). The sulfur is then captured by reaction with the zinc oxide to form zinc sulfide (ZnS).
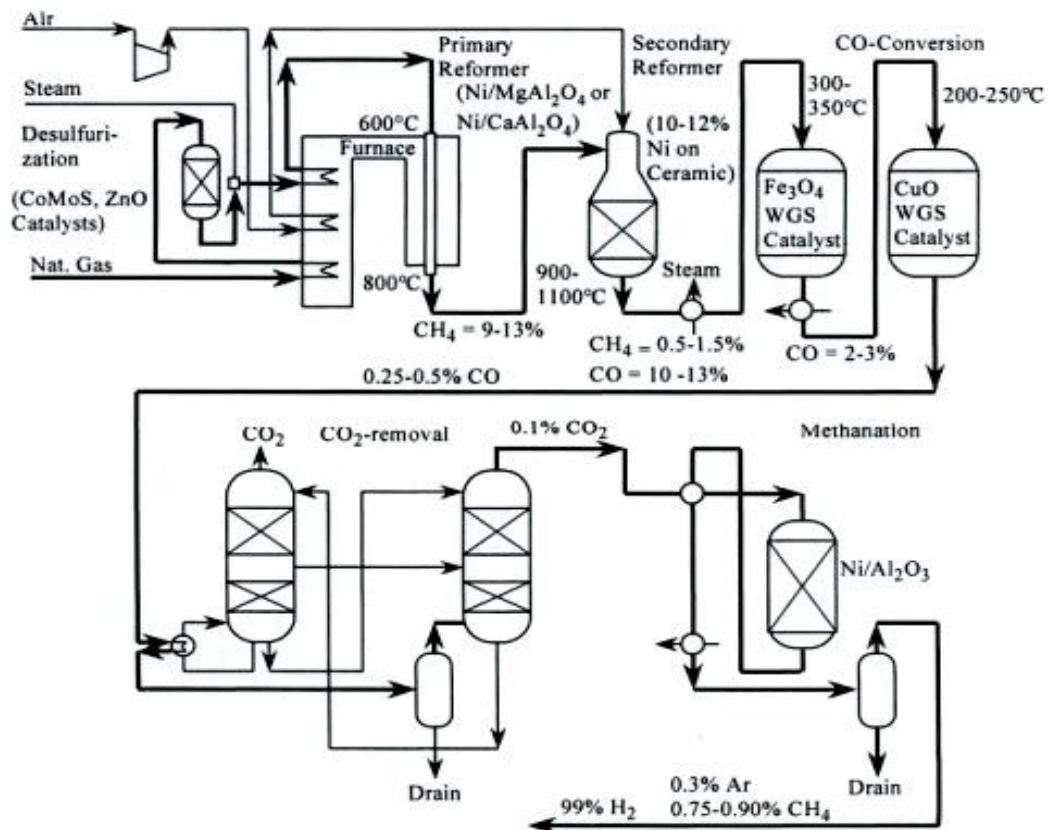
Figure III.7. Steam Methane Reforming unit

Before entering the main reformer, natural gas purified of sulfur is mixed with steam and generally passed through a pre-reformer. The purpose of this pre-reformer is to initiate the steam reforming reaction by converting hydrocarbons containing more than two carbon atoms. It also acts as a buffer reactor, containing a sacrificial catalyst charge, deliberately loaded with nickel to trap any sulfur residue escaping from the desulfurization unit.

The reactive gas mixture, with a ratio of 2.5 to 4 moles of water per mole of methane, is preheated to a temperature of 450°C to 650°C before entering the main reformer, where a large proportion of the hydrocarbons are converted to hydrogen.

The reactors take the form of refractory alloy metal tubes, with an average height of around 10 metres and a diameter of around 10 cm. Heat exchangers are used to recover heat from the gas leaving the reactors, which is partially used to produce steam and preheat the reactive gas mixture.

As the reaction is endothermic, the temperature of the catalytic bed at the reactor head drops to 600°C. Thus, the length of the tubular reactor is determined primarily by heat exchange.

Although it is possible to reduce plant size by increasing the inlet temperature of the reactant mixture, this entails the risk of thermally cracking the hydrocarbon reactants and producing coke in the preheater.

At the outlet of the secondary reformer, the gas mixture from the various tubular reactors is collected in a refractory concrete header. It is then rapidly cooled to around 350°C, as the H/CO mixture is highly corrosive to metals. The reaction product, called syngas, contains mainly hydrogen (85%), methane (0.5-1.5%), and a mixture of carbon monoxide (10-13%) and carbon dioxide (5%).

The performance of the industrial steam reforming process is limited by design aspects (pressure drop, heat transfer) and catalytic aspects (deactivation). Understanding these limitations led to the development of a microstructured exchanger-reactor. At present, the efficiency of the SMR process is restricted by the design of the units, which requires long contact times (of the order of a second) to enable the reaction to take place.

III.6.2. The benefits of micro structured heat exchangers- reactors

The creation of an exchanger-reactor is part of a process intensification strategy, defined as the development of new devices or techniques offering significant improvements over reference processes.

Over the past decade, studies on reactor-exchangers have increased considerably. In the context of methane steam reforming, the replacement of existing tubular reactors by microstructured plate reactor exchangers offers a number of potential advantages: increased surface/volume ratio, optimized heat and mass transfer, reduced pressure drop, and potentially lower plant size and operating costs.

Currently, in steam methane reforming (SMR) production units, the contact time between reactants and catalysts is around one second. By improving heat transfer, microreactors offer

the possibility of reducing the contact time required for the reaction. As a result, thermodynamic equilibrium in terms of methane conversion can be achieved for contact times in the millisecond range.

Tests carried out over a period of 100 hours demonstrated the stability of the methane steam reforming reaction for contact times of 27 milliseconds at 900°C. In a typical microreactor, the catalyst becomes the performance-limiting factor.

The development of a reactor exchanger must therefore be accompanied by the development of suitable catalysts, as conventional commercial catalysts are not designed to achieve such high performance (in this case, 27 ms). The key lies in maximizing the metal surface available for the reaction. This means dispersing active particles as small as possible on ceramic supports with high specific surface area and stability at high temperatures (900°C).

III.6.3.1 Catalysts: principle and current limits for application in a heat exchanger-reactor

The intensification of the methane steam reforming process must be accompanied by the development of a catalyst adapted to the performance requirements imposed by the 3D architecture of the exchanger-reactor. Reducing the time required for the reaction (from seconds to hundreds of milliseconds) is only relevant if the intrinsic performance of the catalyst makes it possible to achieve this level of performance.

III.6.3.2 Catalysts for the steam-reforming reaction of methane

For steam reforming reactions, the most commonly used catalysts are nickel particles dispersed on a refractory support based on alumina doped with calcium ($CaAl_4O_7$, $CaAl_{12}O_{19}$) or magnesium ($MgAl_2O$).

Hydrocarbon molecules are adsorbed and dissociated on the metal sites, while water is adsorbed on the metal oxide sites. The adsorbed water can then migrate to the active metal sites to react with the dissociated hydrocarbons.

III.6.3.3 Development perspectives

Our knowledge of the problems faced in industrial steam-reforming methane reactors means that we need to develop catalysts with enhanced performance, in parallel with the exchanger-reactor.

The first area for improvement is the use of rhodium instead of nickel.

Rhodium's catalytic activity is superior to that of nickel and, above all, it is more refractory than the latter (Table III.1). The use of rhodium is inextricably linked to consideration of its cost.

Tableau III.1. Caractère plus réfractaire du rhodium par rapport au nickel

	T $_{Hüttig}$ (°C)	T $_{Tammann}$ (°C)	T$_{FUSION}$ (°C)
Nickel	436 °C	727	1455
Rhodium	589	982	1964

Chapter IV. Alternative energy sources

IV.1 Intensified extraction processes

The extraction of molecular compounds from plant or wood materials using conventional methods is often laborious and time-consuming, requiring extensive use of solvents. This approach generally leads to alterations in the treated materials, particularly under the effect of heat, and reduces extraction yields. Currently, there is a growing demand for innovative extraction techniques designed to reduce operating time, solvent consumption and effluent production. Modern methods such as microwave- or ultrasound-assisted extraction, supercritical fluid extraction and accelerated solvent extraction are fast and efficient for extracting chemical compounds from solid plant matrices. These techniques can be performed at high temperature and/or high pressure, which considerably improves extraction kinetics.

IV.2 Extraction by conventional method (Soxhlet)

On a laboratory basis, the Soxhlet device is used for extraction. The material to be extracted is placed in an extraction compartment inside filter paper. The solvent is poured into a flask and heated to boiling point. The solvent vapour rises through a vapour tube into the extraction compartment, then rises to the cooler. Cold water circulating through the walls of the cooler condenses the solvent vapour. The condensed liquid then flows into the extraction compartment, where it passes through the plant material, performing a brief maceration. Once the siphon in the compartment is full, the extract flows into the flask. This process is repeated continuously until the substrate is depleted of extractable compounds. A schematic diagram of the process is shown in Figure IV .1.
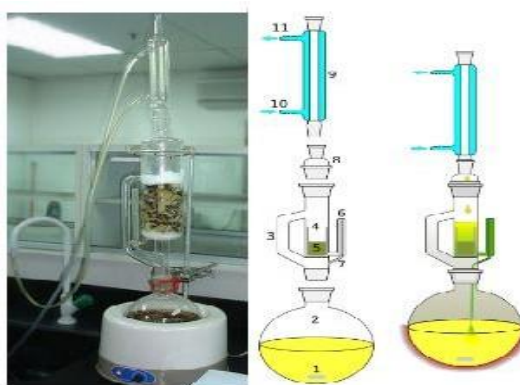

Figure IV.1. Soxhlet extraction system.

IV.3 Ultrasound-assisted extraction

IV.3.1 The principle

The propagation of high-intensity sound waves in ultrasound-treated liquids leads to high-pressure (compression) and low-pressure (rarefaction) cycles, the speeds of which depend on the frequency used. During the low-pressure cycle, high-intensity ultrasonic waves form small

vacuum bubbles in the liquid. When these bubbles reach a certain volume where they can no longer absorb energy, they burst violently during the high-pressure cycle, a phenomenon known as "cavitation". During implosion, extremely high temperatures (around 5000 K) and very high pressures (around 2000 atm) are reached locally. It is important to note that the level of temperature and pressure reached depends on the ultrasound frequency applied. The implosion of cavitation bubbles also generates liquid jets reaching speeds of up to 280 m/s. The resulting shear forces mechanically destroy the cell envelope, enhancing mass transfer from the cell to the solvent. In addition, the reduction in particle size caused by ultrasonic cavitation increases the contact surface between the material to be extracted and the solvent. The extraction set-up is illustrated in figure IV.2.

Figure IV.2. Ultrasonic extraction on a laboratory

IV.3.2 Comparison with conventional methods

Several studies have compared the effectiveness of ultrasound-assisted extraction techniques with conventional techniques such as Soxhlet or maceration for extracting active compounds from various plant materials. The use of ultrasound enables modifications to be made to operating conditions, such as lowering temperature or pressure, unlike some conventional techniques. One study revealed that the optimum temperature for ultrasonic extraction is between 40 and 60°C. Compared to the high temperatures required for Soxhlet extraction, this technique avoids the degradation of certain thermolabile compounds. It is important to note, however, that ultrasound generates heat, which must be controlled by precise monitoring of the bath temperature; similarly, extraction time must be carefully optimized, as excessive time can alter extract quality. Several studies have also shown that the time required with this method is considerably less than that needed to obtain an equivalent yield by solvent maceration or Soxhlet extraction. A recent study by Khan et al (2010) demonstrated that ultrasonic extraction of flavanone-type phenolic compounds from orange peel (Citrus sinensis L.) achieves maximum yield in just 15 minutes, compared with 60 minutes by maceration with the same parameters (solvent, temperature, etc.).

IV.3.3 Advantages and disadvantages

IV.3.3.1 Advantages

- Low-cost technique.

- Simple, effective alternative to conventional methods.

- High extraction yield.

-Increased extraction kinetics.

-Reduced operating time.

-Allows extraction of thermolabile compounds without degrading them.

-Compared with other new methods such as microwave-assisted extraction, ultrasonic extraction is less expensive and easier to implement.

-Can be used with a variety of solvents, as with conventional methods.

IV.3.3.1 disadvantages

-The effect of ultrasound on extraction yield and speed may be linked to the nature of the plant material matrix.

-The presence of a dispersed phase contributes to the attenuation of ultrasonic waves in the medium, and the active part of the ultrasound inside the extractor is restricted to a localized area around the ultrasound emission source. These two factors must be taken into account when designing ultrasonic extractors.

IV.3.4 Ultrasonic extraction on an industrial scale

Ultrasonic extraction is a technique currently recognized and applicable on an industrial scale in the phyto-pharmaceutical, nutraceutical or cosmetic sectors for the extraction of bioactive compounds from a wide range of plants. At present, the largest ultrasonic extraction cell has a power rating of 16kW and can be configured in series or in parallel modules.
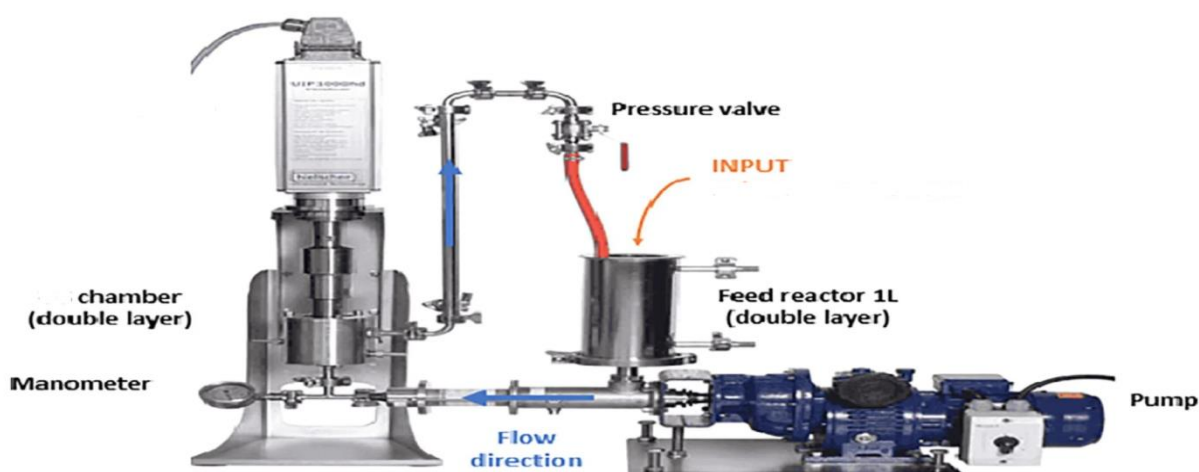

Figure IV.3. Ultrasonic extraction on an industrial.

IV.4 Microwave assisted extraction

Microwaves are electromagnetic waves with frequencies between 0.3 and 300 GHz. Domestic and industrial microwave appliances generally operate at 2.45 GHz, and sometimes at 0.915 GHz in the USA and 0.896 GHz in Europe. One characteristic of microwaves is their ability to penetrate biological materials and interact with polar molecules such as water present in these materials, thus generating heat. In this way, microwaves can raise the temperature of an entire material by penetrating deep into its structure.

Microwave-assisted extraction (MAE) offers rapid energy distribution across the entire volume of the solvent and the solid matrix of suspended tissues. This homogeneous heat distribution results in an efficient and uniform temperature rise of both the solvent and the solid to be extracted. The energy released by the microwaves is absorbed by the water present in the tissue, resulting in a significant increase in temperature at this point and promoting the desorption of chemical compounds from the matrix into the solvent. In addition, the migration of dissolved ions increases the solvent's ability to penetrate the matrix, facilitating the release of chemical compounds. These microwave-induced phenomena thus improve extraction efficiencies. However, the effect of microwave energy is highly dependent on the dielectric properties of the solvent and the plant matrix.

This new technique has seen its greatest development in the extraction of plant products, but its application is not limited to this field. It has been extended to the analytical field for the extraction of organic products. Advances in microwave extraction have given rise to three main methods:

- Microwave-assisted solvent extraction;

- Microwave distillation;

- Microwave hydrodiffusion/gravity.

IV.4.1 Microwave-assisted solvent extraction (MAE)

The MAE (Microwave Assisted Extraction) technique was patented in 1990 by Paré and Bélanger (figure IV.4) . With this technique, the solid matrix is immersed in a solvent heated by microwaves.

Figure IV.4. Microwave extractor

IV.4.2 Extrapolation problems in chemical synthesis

In the literature to the present day, there seem to be no general methodologies for dimensioning stirred microwave reactors on an industrial scale. To extrapolate a reaction in closed mode, the commonly used method is multi-tank parallel synthesis in multimode mode. The main advantage of conventional heating lies in the well-developed and widely accepted industrial-scale technology for chemical synthesis processes. Although microwave technology is well developed for laboratory reactors, its large-scale application is not yet generalized.

Although progress has been achieved in activating chemical reactions using microwaves, there are still many obstacles to large-scale use in industry. Although recent years have seen advances from the gram scale to that of hundreds of grams or even kilograms, this still falls short of industry expectations. The main obstacles include :

- The loss of interesting effects observed at small scale, such as rapid temperature rise, when moving to large scale.

- The inability to maintain extreme operating conditions on a large scale (e.g. 300°C/30 bar) to achieve the necessary microwave heating effect.

- Rapid cooling on a small scale, which becomes difficult to achieve for large volumes.

- The depth of penetration of the waves in the medium, which limits their effectiveness on a large scale.

- The uneven distribution of the electromagnetic field on a large scale, compared with the small size of the cavity.

- Adaptation of the technology to the characteristics of the reaction to be carried out (phase present, viscosity, temperature, reaction time, etc.) for the extrapolation of chemical synthesis from the laboratory to industry.

However, the authors agree that for microwave synthesis to become a widely accepted technology in industry, it is essential to develop techniques capable of daily production of a few kilograms or more.

Microwave synthesis reactors are often developed according to industrial needs by equipment specialized in microwave technology.

IV.4.3 Example of an industrial synthesis

IV.4.3.1 Laurydone synthesis (lauric ester of L-PCA)

The production of Laurydone marks a significant milestone in the industrial application of microwave fine chemistry on a large scale (1m³). Laurydone, a lauric ester of L-pyrrolidone carboxylic acid, is a common ingredient in many cosmetic products due to its hydrating properties.

Traditionally, the esterification reaction to produce Laurydone takes place at 110°C in the presence of toluene as solvent and is catalyzed by p-toluenesulfonic acid and sulfuric acid. Under microwave irradiation, this reaction can be carried out solvent-free at a temperature of 150°C and requires no catalyst, thus simplifying the purification step.

This transition to microwave reaction reduced process time by 80% and energy consumption by 40%, mainly due to the simplification of the steps. It should be noted that, in this case, no effect on reaction acceleration was observed. A number of L-PCA derivatives for cosmetic applications are produced on the same principle.

IV.4.3.2 Production of fatty acid ester

Fatty acid esters are widely used in the manufacture of cosmetic products. For example, stearyl stearate is an emollient and moisturizing agent for the skin, distinguished by its ability to spread easily and be absorbed quickly by the skin. Its synthesis involves an esterification reaction with fatty acids, catalyzed by montmorillonite. This reaction can be carried out dry to minimize environmental impact. However, maintaining the temperature at 170°C to avoid the formation of undesirable products represents a major challenge.

To adapt this process to a larger production scale, a semi-industrial continuous microwave reactor has been developed by ATO-DLO (Wageningen, Netherlands). This reactor can process quantities ranging from 10 to 100 kg per hour. The technical solution adopted consists in carrying out the reaction on a conveyor belt inside an adapted microwave enclosure, with a power of 6 kW and a length of 150 cm. This configuration makes it possible to achieve yields

of up to 95% for the production of fatty esters, with a reaction speed 20 to 30 times faster than in a conventional reactor. What's more, the system's energy consumption is comparable to that of industrial reactors, as revealed by the measurement of power consumption.

IV.4.4 Coupling microwave and ultrasonic technology

Microwave heating generates energy that is not sufficient for molecular activation (of the order of 10^{-6} eV). One solution for activating chemical reactions is to combine this technique with ultrasound, thus achieving energy levels close to those of chemical bonds, i.e. of the order of a few eV.
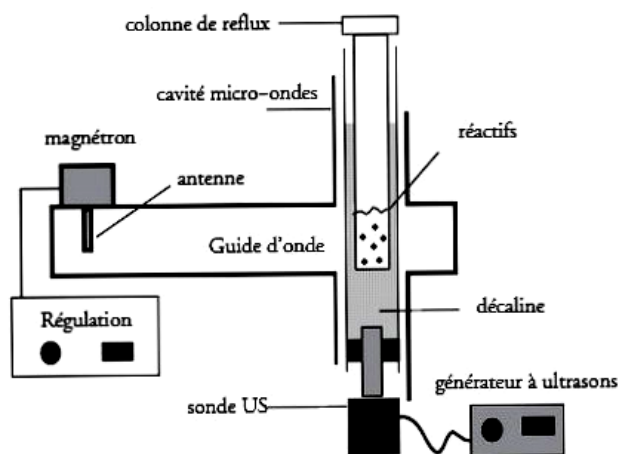
Figure IV.5. Reactor combining microwave and ultrasonic

Chapter V. Other process intensification methods.

New solvents (supercritical fluids, ionic liquids).

V.1 Extraction with supercritical fluid

V.1.1 Principle

Supercritical fluid extraction (SFE) is an alternative method for reducing the use of organic solvents while increasing extraction yields.

The critical point of a pure substance is the highest point of temperature and pressure at which the substance exists in equilibrium between the liquid and gaseous states. Above this point, the substance is in a supercritical state, with the characteristics of both a gas and a liquid. Supercritical fluid is capable of dissolving a wide variety of organic compounds, and its solvent power can be adjusted around its critical point by slightly modifying temperature or pressure. Thanks to its low viscosity, low surface tension and high diffusion coefficient, supercritical fluid has superior mass transfer properties. It can thus penetrate the micropores of materials, facilitating extraction of the desired compounds.

V. 1.2 The nature of the solvent

Supercritical carbon dioxide (CO_2) has remarkable properties that make it the solvent of choice for many applications of this technique. Non-toxic, non-flammable, non-corrosive and inert, supercritical CO_2 benefits from a relatively low critical temperature (304˚K) and moderate critical pressure (73 atm). What's more, it's abundant, inexpensive and environmentally friendly, meeting stringent environmental standards.

However, supercritical CO_2 is only effective for the extraction of apolar molecules such as hydrocarbons or certain terpenoids. To extract polar compounds, polar supercritical fluids such as Freon-22, nitrous oxide and hexane have been considered. However, their use remains limited due to their adverse effects on the environment and the safety issues they raise.

Although supercritical and superheated water can effectively extract polar compounds, they are not suitable for extracting thermolabile bioactive compounds. Research has therefore been undertaken to overcome the low solubility of polar substances in supercritical CO_2.

V. 1.3 The process

The schematic of a supercritical fluid extraction system is shown in figure V.1. During the extraction process, the solid material is introduced into an extraction reactor equipped with inlet and outlet temperature and pressure control valves to maintain the desired extraction conditions. The extraction reactor is pressurized with fluid using a pump. The fluid and dissolved compounds are then transported to separators where the solvent power of the fluid is reduced by lowering the pressure. The extracted product is then collected via a valve located in the lower part of the separators. Finally, the fluid is regenerated for recycling.
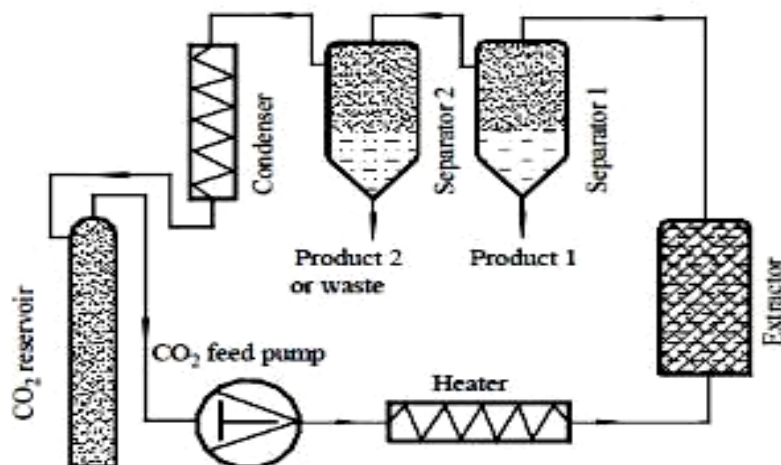
Figure V.1. Supercritical fluid extraction process

V.2 The ionic liquids

V. 2.1 Definition

Ionic liquids are compounds formed entirely of ions. With a theoretical number of possible cation-anion combinations of the order of 1018, this class of compounds is one of the most extensive in chemical science. Currently, over 350 ionic liquids are commercially available.

These liquids have melting temperatures close to or below room temperature, and remain in the liquid state over a wide temperature range. In general, cations are organic and large in size, while anions can be organic or inorganic and smaller.

An essential property of ionic liquids is their virtually zero vapor pressure, making them suitable for applications at very high temperatures or very low pressures. They are also non-flammable and easily recyclable. Depending on the nature of the anion, they can be hydrophilic or hydrophobic. They have wide electrochemical windows, high conductivities and high heat capacities. Their miscibility with water or with organic or inorganic solutes can be adjusted.

The nature and dimensions of ions influence physicochemical properties such as density, viscosity, etc., as well as their ability to dissolve organic, inorganic or gaseous compounds. By modulating these properties through a judicious choice of ion combinations, ionic liquids are considered Designer Solvents.

Technologies that use or plan to use ionic liquids can help to make chemical processes more environmentally friendly "green".

V.2. 2 Examples of ionic liquids

The most commonly used cations are derived from imidazolium, pyrrolidinium, pyridinium, phosphonium, ammonium and sulfonium. Anions are equally diverse, ranging from halides such as chlorides, bromides and iodides, inorganic anions such as tetrafluoroborate ($[BF4]-$),

hexafluorophosphate ([PF6]-), tris[pentafluoroethyl]trifluorophosphate or [eFAP]-([PF3(C2F5)3]-), bis[trifluoromethylsulfonyl]amide ([NTf2]-), as well as organic anions such as acetate ([OAC]-) and lactate ([Lac]-). Representative examples of cations and anions are shown in figure V.2.
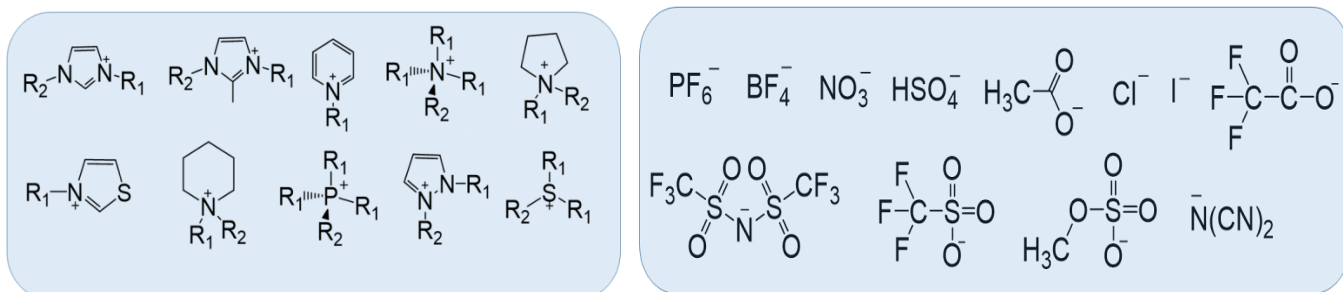

Figure V.2. Cations and anions currently used in the preparation of ionic liquids.

V.2. 3 Applications of ionic liquids

Due to the remarkable, adjustable properties of ionic liquids, their use in various fields of technology has grown considerably in recent years. They are now used in a multitude of applications, including separation techniques, analytical chemistry, heterogeneous and homogeneous catalysis, as media for biological and enzymatic reactions, and electrochemistry. In addition, they are used as reference fluids in thermometers, are involved in the synthesis of materials used in the manufacture of semiconductors, contribute to the design of lunar telescopes, are used as pistons for gas compression and storage, act as additives in lubricants, and even find applications in cosmetics and pharmaceuticals, among others.

V.2. 4 Solubility of gases in ionic liquids

Research on gas solubility began in the 2000s, notably in connection with the use of ionic liquids in reaction environments such as hydrogenation, oxidation and hydroformylation reactions. Subsequently, the study of gas solubility was extended to assess the potential of ionic liquids in gas storage and separation. In the context of gas separation and carbon dioxide capture applications, it is crucial to understand the solubility, selectivity and transport properties of gases in ionic liquids. For example, ionic liquids have been considered for the removal of carbon dioxide from post-combustion flue gases and in natural gas treatment.

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