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## Heat exchanger/reactors (HEX reactors) : Concepts, technologies: State-of-the-art — Source link

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# Heat exchanger/reactors (HEX reactors): Concepts, technologies: State-of-the-art

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## A B S T R A C T

Process intensification is a chemical engineering field which has truly emerged in the past few years and is currently rapidly growing. It consists in looking for safer operating conditions, lower waste in terms of costs and energy and higher productivity; and a way to reach such objectives is to develop multifunctional devices such as heat exchanger/reactors for instance.

This review is focused on the latter and makes a point on heat exchanger/reactors.

After a brief presentation of requirements due to transposition from batch to continuous apparatuses, heat exchangers/reactors at industrial or pilot scales and their applications are described.

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### Keywords:

Process intensification  
Heat exchanger reactor  
State-of-the-art  
Technology  
Continuous reactor

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## 1. Introduction

Process intensification [1] is an approach that has been around for quite some time but has truly emerged only in the past few years (1980s) as a special and interesting discipline of chemical engineering. Stankiewicz suggests the following definition:

Process intensification consists of the development of novel apparatuses and techniques that, compared to those commonly used today, are expected to bring dramatic improvements in manufacturing and processing, substantially decreasing the equipment-size/production-capacity ratio, energy consumption, or waste production, and ultimately resulting in cheaper, sustainable technologies.

Or in other words: any chemical engineering development that leads to a substantially smaller, safer, cleaner, and more energy-efficient technology is process intensification.

The opportunities that process intensification offers to a chemical company lie primarily in three areas [2,3]:

- **Costs:** process intensification should lead to substantially cheaper processes, particularly in terms of land costs (much higher production capacity and/or number of products per unit of manufacturing area), investment costs (smaller equipment, reduced piping, etc.), costs of raw materials (higher yields/selectivities), costs of utilities (energy in particular), and costs of waste-stream processing (less waste in general).
- **Safety:** Process intensification may drastically increase the safety of chemical processes. It is obvious that smaller is safer. For instance, material inventories will be lower which is safer in case of hazardous substances. Moreover, keeping processes under control will be easier thanks to an efficient heat removal from exothermic reactions for instance.
- **Improved chemistry:** Process intensification leads to a better control of the reaction environment (temperature, etc.). Thus chemical yields, conversions and product purity are improved. Such improvements may reduce raw material losses, energy consumption, purification requirements and waste disposal costs as seen before.

Yet, in spite of these benefits linked to process intensification, there are still important barriers [3] which stop deeper changes in the chemical industry.

In the pharmaceutical and fine chemical fields, most of the production is operated in batch or semi-batch reactors. Indeed, stirred tank reactors are reliable and flexible [4], operating modes are well-known and residence time is as long as required. However, they have many technological barriers and particularly as regards safety. Indeed, the poor heat removal of stirred tank reactors and the low ratio between the heat exchange area and the reactor volume are limiting parameters [5].

As a consequence removing heat from the reactor during an exothermic reaction is an important characteristic to improve. The solution lies in the intensification of heat transfer between utility and process streams in continuous apparatuses. The development of continuous multifunctional reactors [6–8] and specially heat exchanger-reactors follows this line since they combine a reactor

and a heat exchanger in only one unit. The many benefits of using such apparatuses are similar to those of process intensification [5]:

- Diminution of waste of energy and raw materials;
- High selectivity and yields due to enhanced heat and mass transfer;
- Minimised risk of runaway reaction due to enhanced heat transfer;
- Smaller and cheaper plant.

Moreover, the transposition from batch processes to continuous ones will reinforce the industries' reactivity against fluctuating market demand and will improve process safety by avoiding the storage of dangerous chemical intermediaries. It is also expected to operate at higher temperatures and higher throughputs, contributing to a reduction of energy costs and to increased productivity.

This paper makes a point on intensified heat exchanger/reactors. First of all, requirements due to transposition from batch to continuous apparatuses are listed. Four main parameters are important to transpose a reaction from batch reactor to heat-exchanger/reactor: thermal and flow behaviours, reactor dynamics and residence time. Then a difference is made between existing apparatuses (reactors, mixers, etc.) with intensified heat exchange and compact heat exchanger/reactor (HEX Reactor), in which both functions are coupled: the former are devices whose thermal performances have been boosted and which are exclusively developed to perform chemical reactions whereas the latter are compact heat exchangers (or apparatuses whose geometry is largely based on heat exchangers' one) in which chemical syntheses are performed. Finally, devices at industrial or pilot scales and their applications are described.

## 2. Transposition from batch to continuous heat-exchanger/reactor

### 2.1. Thermal intensification

Chemical reactions in the process industry are temperature dependent. As a consequence, removing heat generated by an exothermic reaction is necessary to control the reaction temperature and to avoid thermal runaway reactions or to suppress endothermic by-product reactions for instance [9].

Therefore, many traditional designs such as stirred tank reactors incorporate heat transfer in the process (double jacket, external or internal coil, etc.). However, in these devices there is a significant distance between the heat transfer site and the site of the chemical reaction where heat is released. As a consequence semi-batch mode is implemented instead of batch mode and/or systems are diluted.

The aim of thermal intensification is to reduce this distance by supplying or removing the heat almost as rapidly as it is absorbed or generated by the reaction [10], i.e. combining the reaction and heat transfer into a single piece of equipment: using for instance a heat exchanger as a chemical reactor, the so-called HEX reactor. As a result this technology may offer better safety (through better thermal control of the reaction), improved selectivity (through more isothermal operation) and by-products reduction.






Process	Compact Multifunctional Heat Exchanger		Tubular exchanger reactor	Batch reactor with outer heat exchanger	Batch reactor with a double jacket
	Metallic foams [10] Re=1000	Offset Strip Fins [9] Re=2000			
Schematic diagram					
Specific Area, S/V (m <sup>2</sup> .m <sup>-3</sup> )	400	800	400	10	2.5
Global heat transfer coeff., U (W.m <sup>-2</sup> .K <sup>-1</sup> )	3500	5000	500	1000	400
US/V (kW.m <sup>-3</sup> .K <sup>-1</sup> )	1400	4000	200	10	1

Fig. 1. Heat exchange capability for different reactors [10].

The comparison between different kinds of reactors presented in Fig. 1 shows the major advantages of HEX reactors in terms of thermal performances [11].

Finally, heat transfer in a compact multifunctional heat exchanger is much better than traditional designs. Thermal intensification in such apparatuses appears to be very interesting.

## 2.2. Flow intensification

Flow intensification is made thanks to apparatuses in which flow behaves like a perfect plug flow; reactor internals have to be made accordingly. Indeed, dead zones, i.e. reactant accumulation, must be avoided in order to have better selectivity and yields but also no hot spots formation which would generate safety problems.

Moreover flow geometries should be defined in order to enhance mixing between reactants. Indeed, mixing and in particular micromixing has an important influence [9,11] on product quality in industrial reactions such as polymerization or precipitation especially if the characteristic reaction time is close to the micromixing time (instantaneous or fast reactions). As a consequence, by investigating the combined influences of heat transfer and mixing in the same apparatus, it appears that a small change in the mixing intensity in a heat exchanger-reactor has a substantially greater effect than an equivalent change in an adiabatic reactor such as a simple static mixer [12,13].

## 2.3. Reactor dynamics

The volume of heat exchanger/reactor is low; therefore quantity of products is small. It is obviously an advantage from a security point of view. But it is also interesting if characteristic times are considered. Indeed they will be short and as a consequence, the heat exchanger/reactor will be relatively flexible and easier to manipulate in start-up and shutdown procedures [2].

## 2.4. Residence time

The main restriction of heat exchanger/reactors is the short residence time, typically from few seconds to few minutes. As a consequence, the challenge is to optimise heat and mass trans-

fers in laminar regime which is often necessary to keep a sufficient residence time.

Nevertheless, as shown in previous paragraphs, properties of heat exchanger/reactor change the traditional kinetics and finally

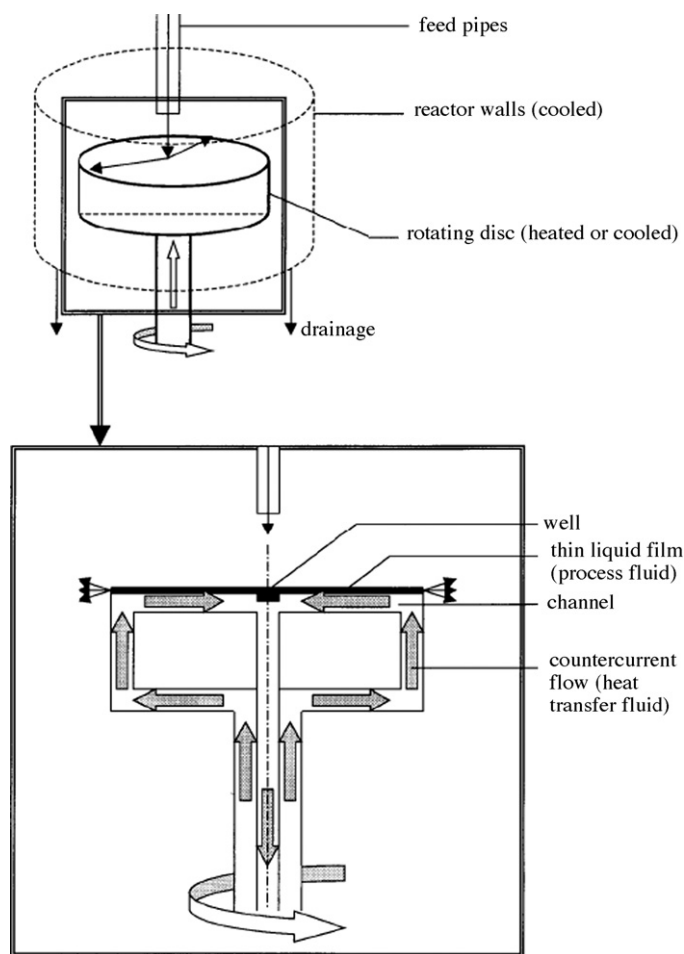


Fig. 2. SDR operating principle [15].

operating mode will be performed in few minutes whereas many hours were necessary in batch or semi-batch mode.

### 3. Reactors with intensified heat exchange

#### 3.1. Spinning disk reactor (SDR)

SDR [14–16] is an horizontally circular plate that is rotated thanks to a motor from 100 to about 6000 rpm and that can be cooled or heated with a fluid which flows inside the plate. The technology is based on centrifugal forces which produce thin films on the surface of rotating disks. The working principle is detailed on Fig. 2. Reactants are introduced in the centre of the disk, travel rapidly across the surface forming the thin film (the chemical reaction occurs during this step) and are collected on the edge of the disk.

The thin film (typically 100  $\mu\text{m}$ ) promotes very high heat-transfer rates between the film and the disk ( $14 \text{ kW m}^{-2} \text{ K}^{-1}$ ) and high mass transfer between the liquid streams or between the film and the gas in the surrounding atmosphere. As a consequence, the SDR provides intense mixing in the thin liquid film and thus can maintain uniform concentration profiles within a rapidly reacting fluid. Moreover, residence time is short and as a consequence may allow the use of higher processing temperature. Finally SDR presents plug flow characteristics and safer operating conditions thanks to the small reactor hold-up and the excellent fluid temperature control. The apparatus is moreover easy to clean and presents a low fouling. However, the spinning disk reactor remains a rotating device with a large circular plate to increase residence time. Unfortunately, for safety considerations, industrialists may be frightened by these rotating equipments.

The SDR has been successfully used to perform fast organic reactions and precipitations [15], polymerizations [3,14,17] or production of nano- and micron-size particles [3,15].

#### 3.2. Microchannel reactors

Literature on microchannel reactors is widespread and many reactions have already been carried out in these apparatuses to characterize their performances [18–21]. Microchannel reactors, considered as a reactor with intensified heat transfer, are the subject of this paragraph. Indeed, microchannel reactors are characterized by small length scales for transfer and particularly, a high surface area to volume ratio. As a consequence, heat is transferred or removed very easily and efficiently. This improved control of transfer processes and heat management may lead to smaller and safer apparatuses and therefore increase the process selectivity and product purity. Moreover, chemical reactions under aggressive conditions of pressure and temperature can be performed. As a consequence the entire chemical path would have to be rethought [22,23]. Indeed, reactions which were performed during many hours in a batch reactor will last only few minutes in a microchannel one.

Applications are various and industrial units already exist [24]. Merck, Germany, was the first chemical company to install a production plant [25,26] (Fig. 3) based on micro-units (here micromixers) for the synthesis of metallo-organics. The yield of this reaction was 23% better than in the batch process.

Similarly, Siemens Axiva (today Siemens Solution Process Industries) developed a process for radical acrylate polymerization and designed a plant with a capacity of 2000 tons/year [27].

At lab scale many organic syntheses [28] (pharmaceutical industry), liquid-phase reactions (catalytic or non-catalytic), gas-liquid reactions (halogenations, nitrations, etc.) and gas-phase reactions (oxidations, hydrogenations, etc.) [29] have been successfully

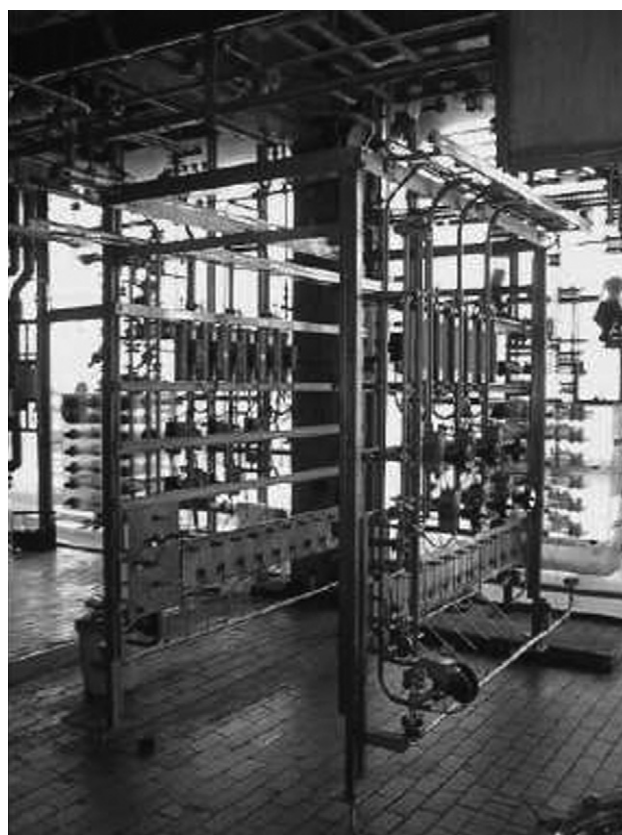


Fig. 3. Production plant (Merck, Germany) [24].

performed and future works aim at scaling up these lab scale experimentations to pilot or even plant scale. However, even if numbering up is attractive it is not as easy as it seems and that is the reason why many processes are not yet industrial [22,24].

Finally, technology of microstructured reactors can be applied to heat exchanger reactors. It will combine benefits of microstructured devices and efficient heat transfer of heat exchangers [14,30]. Equipment size will be sharply reduced and operating conditions for strongly exothermic reactions for instance will be safer. FZK (Forschungszentrum Karlsruhe), Germany, developed micro heat exchanger [31] with a high surface to volume ratio ( $15,000 \text{ m}^2 \text{ m}^{-3}$ ) and high heat transfer coefficient up to  $25 \text{ kW m}^{-2} \text{ K}^{-1}$  at flow rate of  $1000 \text{ L h}^{-1}$ .

#### 3.3. Static mixers

Static mixing consists in mixing without any mechanical stirring elements. It is made up of identical motionless elements placed in a pipe or a channel. Geometries of these elements are various and sometimes patented. Fig. 4 shows a kind of static mixer.

Products are mixed by flow energy alone. Thus it does not require external power except the pumping power required to flow the fluids through the mixer. The elements of the static mixer divert the flow radially towards the pipe walls regardless of the velocity. As a consequence the products are continuously intermixed to eliminate radial gradients of temperature, velocity and composition.

These static mixers have many properties and functions [32,33]. The first of them is of course the mixing of miscible components regardless of the volume, density, viscosity and properties of the fluids. It is also interesting to use them as contactor of liquids with gases. It creates high mass transfer and high rates of absorption, reaction, vaporization and condensation.



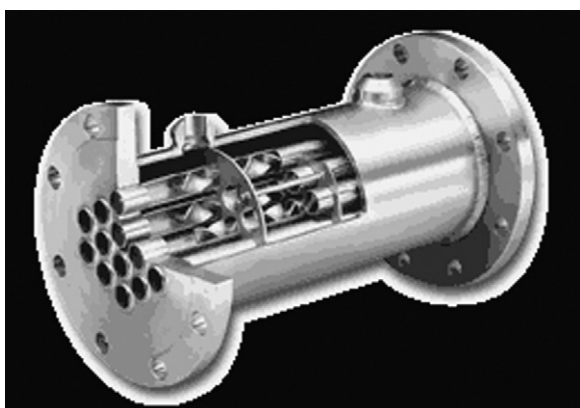


Fig. 4. Kenics® heat exchangers (courtesy of Chemineer).

But static mixers can also be used in shell and tube heat exchangers [32]. The mixing elements are generally inserted in the tubes (see Fig. 4). Heat is efficiently supplied or removed (3–10 times greater transfer rates than empty tubes [34]) which could be interesting for temperature dependent reactions: polymerizations, exothermic reactions, etc. (Sulzer SMXL, SMX, SMR Mixers [33]).

Indeed, static mixers can also be inserted in reactors. Such reactors behave like plug flow reactors even at low Reynolds number with high residence times without the traditionally required increase of the reactor volume or decrease of flow velocity. A characterization [35] of this kind of reactor revealed good heat transfer characteristics which allow the implementation of an exothermic chemical synthesis. Results showed high conversion, high product yields and very low impurity levels (Sulzer SMV Mixers). However, at high flow rate, conversion is lower than in batch reactors. So, increasing residence time, through enhancing reactor length, would be expected while paying attention to pressure drops.

### 3.4. Oscillatory flow reactor

The oscillatory flow reactor is a good example of an equipment with intensified heat transfer [36]. Indeed, it combines a reduction of the reactor volume and a better control of the reaction with enhanced safety and better selectivity and yield. It consists in baffled reactor tubes (Fig. 5) which are fitted to an oscillator unit. It provides variable intensity oscillation, superimposed on a mean flow rate. By applying the right oscillation intensity to the flow rate ratio, it is possible to control the residence time with the flow rate whereas mixing is controlled only by oscillation intensity. This is the special feature of these reactors.

Literature on the subject is rich and highlights the advantages of oscillatory flow reactors: effective droplet break-up and controlled droplet size in liquid–liquid dispersion [37], reduced dispersion [38] in baffled tubular reactors which leads to a plug flow behaviour by controlling the ratio of the oscillation intensity to the flow rate and last but not least, enhanced heat transfer [39]. Mackley et al. studied the effects of both steady and oscillatory flow conditions on the heat transfer enhancement for a single phase fluid in a shell and tube heat exchanger containing periodic baffles. They showed that the heat transfer rate was dependent on the product of the frequency with the amplitude of oscillation. Thus by choosing a particular frequency and amplitude, it becomes possible to control the heat transfer rate. Thus, an advantage of an oscillatory flow reactor is that mixing effects and heat transfer rates are decoupled from flow velocity [40].

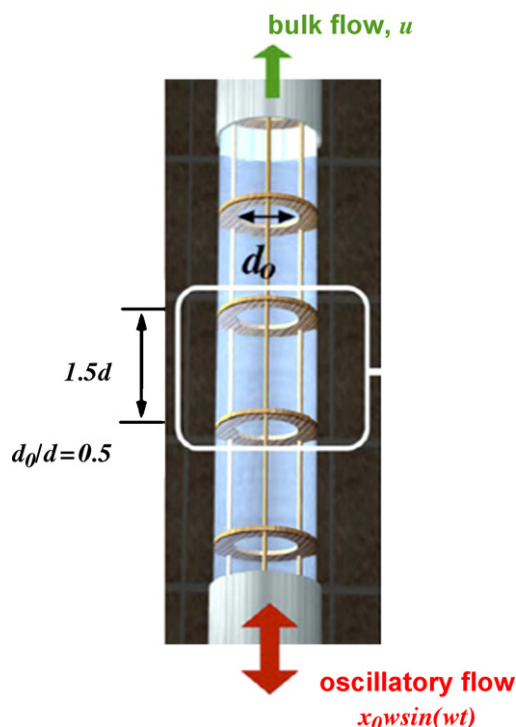


Fig. 5. Tube of oscillatory flow reactor [36].

Thanks to these interesting properties about mixing and heat transfer, a feasibility study has been led to replace a batch reactor with a continuous oscillatory flow reactor operating as close as possible to a plug flow reactor. The works are about an ester hydrolysis reaction currently performed only in a batch process [40]. It was shown that the oscillatory flow reactor could be run for long periods of time at steady state, with a constant production rate and conversion. Moreover, the residence time in the batch reactor was eight times superior to the one in oscillatory flow reactor: mixing limitations have been overcome in oscillatory flow reactor. Finally, a 10 times reduction in reactor volume has been reached which is a clear example of the managed intensification.

## 4. Compact heat exchanger reactor (HEX reactor)

Unlike previous reactors, HEX reactors are above all heat exchangers in which reactions have been carried out. As a consequence, their design is largely based on compact heat exchanger 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. They are presented in the last part of this report.

### 4.1. Compact heat exchangers

#### 4.1.1. Plate-type heat exchangers

Plate heat exchangers offer many benefits compared to shell-and-tube heat exchangers [13]. 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-

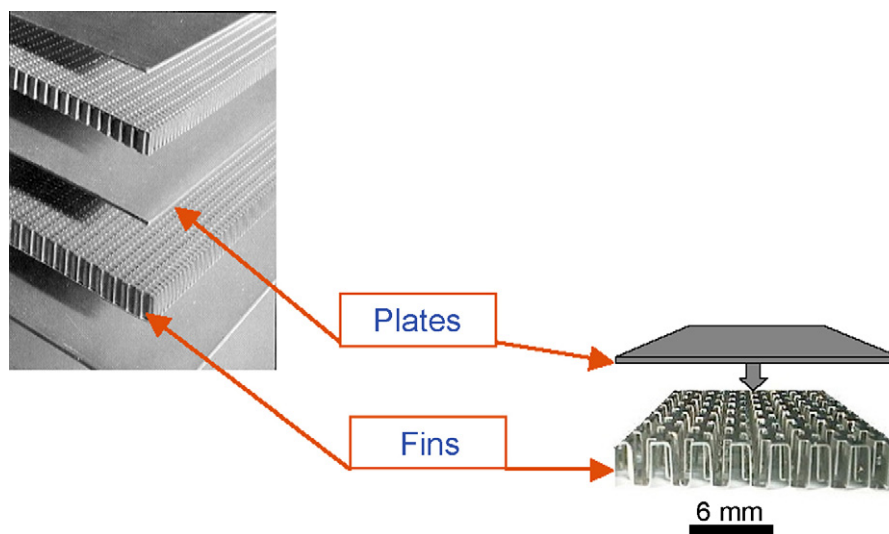


Fig. 6. Basic components of a plate-fin heat exchanger.

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. Gasketed 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.

#### 4.1.2. Extended surface heat exchangers

To enhance heat transfer and/or mixing and thus compactness of the heat exchanger, fins can be added on the primary surface on one or both fluid sides. Many geometrical configurations of fins are available depending on the applications and the efficiency required. Plate-fin and tube-fin heat geometries are the most common types of extended surface heat exchangers.

Plate-fin heat exchangers [41] are made up of fins sandwiched between parallel plates as shown in Fig. 6. The plates separate the two fluids and the fins form the individual flow passages. Fins can be inserted in process fluid side and/or cooling fluid side. The former offers the possibility of carrying out reactions for the purpose of mixing two reactants for instance.

In general, plates and fins are assembled by brazing. As a consequence, it forms a single block which can cause problem in case of fouling.

Plate fins are categorized as plain and straight fins; plain but wavy fins, and interrupted fins. Straight fins and straight perforated fins act like parallel tubes with a rectangular or triangular cross-section. As a consequence, the flow structure is almost identical to pipe flows and convective heat transfer occurs due to the friction of the fluid with the channel walls. The channels of interrupted fins are discontinuous and thus turbulence is more important. Indeed, there is a high degree of mixing and the flow becomes turbulent even at low Reynolds numbers. For air flows, louvred fins are used whereas for process applications offset strip fins are more widespread.

#### 4.2. Influence of inserts

The previous compact heat exchangers offer many opportunities in terms of heat transfer. However, to be used as reactors in the chemical processing industry, they also must be characterized in terms of mixing intensity and residence time distribution. Indeed, mixing has an important influence on product quality in industrial reactions such as polymerization or precipitation and it may be a limiting parameter for instantaneous reactions.

A way to enhance mixing and at the same time heat transfer is to work with turbulent flow. Nevertheless, this approach involves a significant increase of pressure drops and a reduced residence time. As a consequence, the challenge of adding inserts in compact heat exchangers is to enhance both heat and mass transfer while being in a laminar regime. In the literature, different geometries have been tested and are described below.

##### 4.2.1. Offset strip fins

Offset strip fins consist in a fin surface which is broken into a number of small sections as shown in Fig. 7. For each section, a leading edge is encountered, and thus a new boundary layer starts

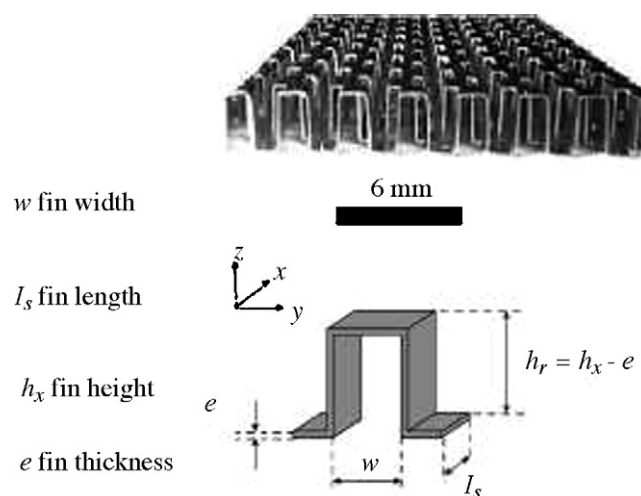


Fig. 7. Geometrical parameters of the OSF insert ( $x$ : offset length;  $b$ : fin height;  $s$ : fin pitch;  $t$ : fin thickness).

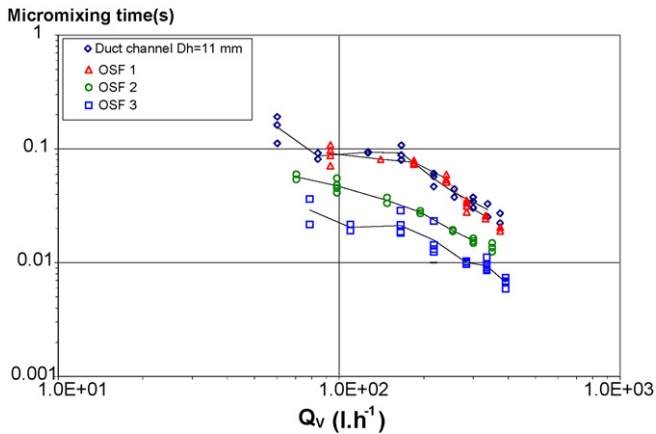


Fig. 8. Micromixing time vs. flow rate for three different offset strip fins and a duct channel [11].

to develop and is then disrupted at the end of the fin offset length. The objective is to prevent the thickening of the boundary layer and hence provide high heat transfer coefficients.

Many experiments [11] have been carried out in order to quantify the mixing level of an apparatus filled with offset strip fins, to characterize it and to compare its properties with an empty duct channel so as to implement, then, chemical reactions.

First of all, to evaluate and then compare the mixing level of offset strip fins with an empty duct channel, Ferrouillat et al. [11] used a chemical method developed by Villermaux and co-workers [42]. Three geometries of offset strip fins, inserted into the same duct channel, were tested and compared with an empty duct channel.

They showed that turbulence, micromixing and pressure drops depend on the geometry, the size and the number of fins. For instance, whatever the geometry, the micromixing time decreases with the flow rate. Moreover, for a given flow rate, the empty duct channel is the worst in micromixing performance, as shown in Fig. 8, but generates the smallest pressure drop. As a consequence, for applications as a heat exchanger reactor, a compromise between pressure drop and micromixing level should be made.

In other works, Ferrouillat et al. [10] studied the influence of offset strip fins in the case of two exothermic chemical reactions. The reactor is composed of three independent and superimposed

channels with rectangular cross-sections. Reactants flow in the central channel and coolant fluid in both side channels as shown in Fig. 9. Offset strip fins have only been inserted in the central channel without any welding or brazing.

Two exothermic chemical reactions have been carried out: an instantaneous one and a fast one. They showed that the offset strip fins insertion leads to an increase of the global heat transfer coefficient compared with an empty duct channel. However, for the instantaneous reaction, which presents a very local exothermicity, the enhanced micromixing due to offset strip fins has not increased the reaction kinetics but has provided a faster heat removal from the reaction. Finally, the conversion rate of the second reaction, which is limited by the reactant mixing, is enhanced thanks to the offset strip fins insertion.

Actually, the insertion of offset strip fins increases the chemical reaction conversion rate and yield thanks to better heat and mass transfer.

#### 4.2.2. Metallic foams

Many works about metallic foams have been carried out to test their thermal performances in conventional heat exchangers [11,43–45]. Pavel et al. [45] studied the influence of metal foams in an empty channel, without brazing, on heat transfer performances and pressure drops. Different geometries and porosities of foams were tested. They showed that heat transfer enhancement can be achieved by increasing the diameter of the porous material or by decreasing its porosity. However, a compromise should be found because these two parameters have a negative impact on pressure drops. Boomsma et al. [44] obtained the same results as shown in Fig. 10.

Moreover, they studied the thermal performances of metallic foams inserted in an industrial heat exchanger and showed that for the same pumping power, metallic foams lead to less thermal resistance than in the traditional heat exchanger (see Fig. 11).

Finally, metallic foams were compared to other kind of inserts; offset strip fins [11] and louvered fins [43].

Metallic foams with different pore and ligament diameters were tested. The authors studied the influence of the flow rate and the geometry on the micromixing, heat transfer and pressure drop. Ferrouillat et al. [11] showed that metallic foams are the geometry which generates the best micromixing level for a given residence time. However, pressure drop is the main drawback since it remains

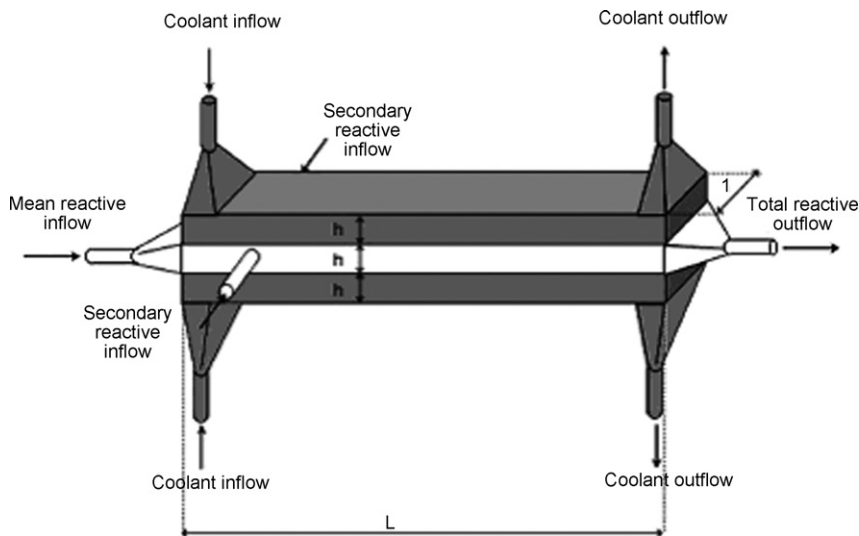


Fig. 9. Schematic view of the reactor [10].



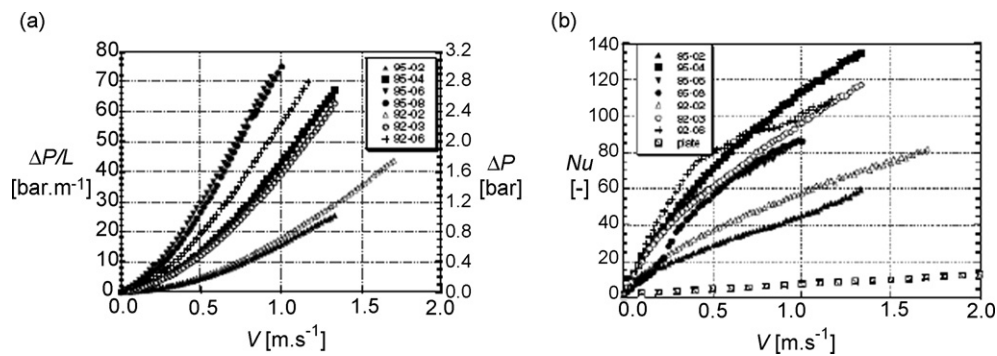


Fig. 10. Pressure drop curves (a) and Nusselt number (quantifying heat convection) curves (b) for different compression factors and porosities of the metal foams in the heat exchanger [44].

higher than offset strip fins one, which is itself higher than the pressure drop in an empty duct channel. Similar results concerning pressure drops have been observed in works of Kim et al. [43]. Indeed, for given heat transfer performances, metallic foams generate higher pressure drops than louvered fins but lead to more compact units.

Thus, it is necessary to take into account in the process design the pumping power needed by the system, the process compactness and the required micromixing level.

In addition, metallic foams have other interesting properties to implement chemical syntheses. They have a large specific area and they create homogeneous flow thanks to their isotropic geometry. The former is interesting in using metallic foams as a catalyst support and the latter allows a quasi-plug flow behaviour.

This property was studied by Ismagilov et al. [46]. They manufactured a heat exchanger tubular reactor and placed metallic foam on both internal and external surfaces of the stainless steel metal tube as shown in Fig. 12.

The use of foams aims at providing an efficient heat transfer between the outside of the reactor wall where an exothermic reaction takes place and the inside where an endothermic one takes place. The reaction concerns catalytic combustion of methane and steam reforming of methane. The authors showed that the heat transfer was efficient enough to supply the endothermic steam reforming process. However to optimize the combustion, the thickness of the catalyst layer is important and must not be thinner than 2.5 mm. Finally, thanks to the use of catalytic metallic foams and by adjusting the composition of

combustion gas, the methane conversion in combustion section increases to 65% which is an interesting application of metallic foams.

#### 4.2.3. Vortex generators

Vortex generators have been studied in order to combine heat and mass transfer in a compact heat exchanger so as to use it as a mixer or a chemical reactor. This perspective may offer the well-known advantages of a better reaction control, improved selectivity, byproduct reduction and enhanced safety.

Usually, to increase heat transfer, two different approaches are considered. The first one consists of increasing the heat transfer area per unit volume. The second approach consists in working in turbulent regime which may lead to an increase of pressure drops and a decrease of residence time.

A way to reach high heat transfer coefficients with reasonable pressure drops is to use vortex generators. Indeed, these elements create longitudinal vertical structures which allow the heat removal from the core of the flow to the wall by means of large-scale turbulence. As a consequence the transition between laminar and turbulence flow occurs at a lower Reynolds number.

In their works [47], Ferrouillat et al. studied two forms of vortex generators: rectangular winglet pairs and delta winglet pairs as shown in Fig. 13.

Thermal and hydraulic properties of these kinds of vortex generators have already been studied [48]. It has been shown that delta forms are slightly more efficient than rectangular ones in terms of heat transfer enhancement and that for given heat transfer coefficients, pressure drops are lower than in compact plate-fin heat exchangers. Moreover heat transfer does not increase for angles of attack ( $\beta$ ) larger than  $65^\circ$ . Ferrouillat et al. [47] pursued these works in order to characterize the mixing

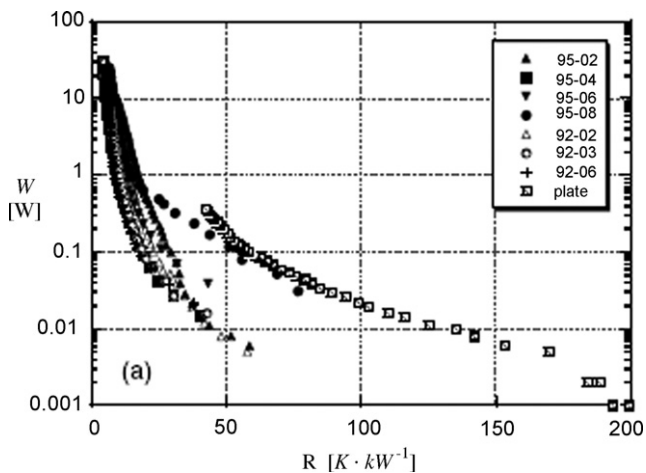


Fig. 11. Plot of the required pumping power against the corresponding thermal resistances for different metal foams and for the plate heat exchanger [44].

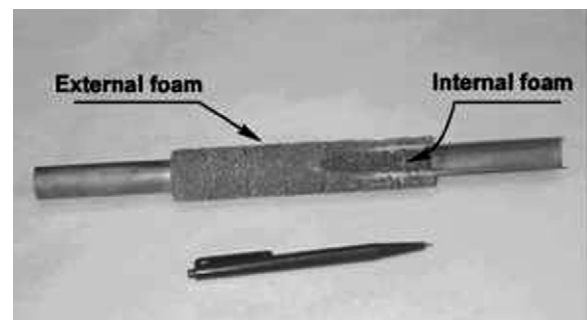


Fig. 12. Heat exchanger tubular reactor [46].

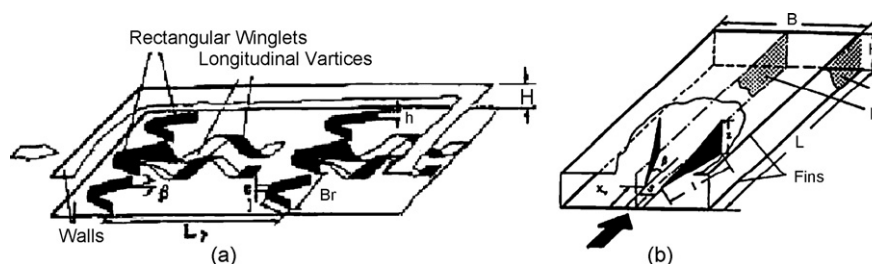


Fig. 13. (a) Rectangular vortex generator geometry; (b) triangular (delta) vortex generator geometry [47].

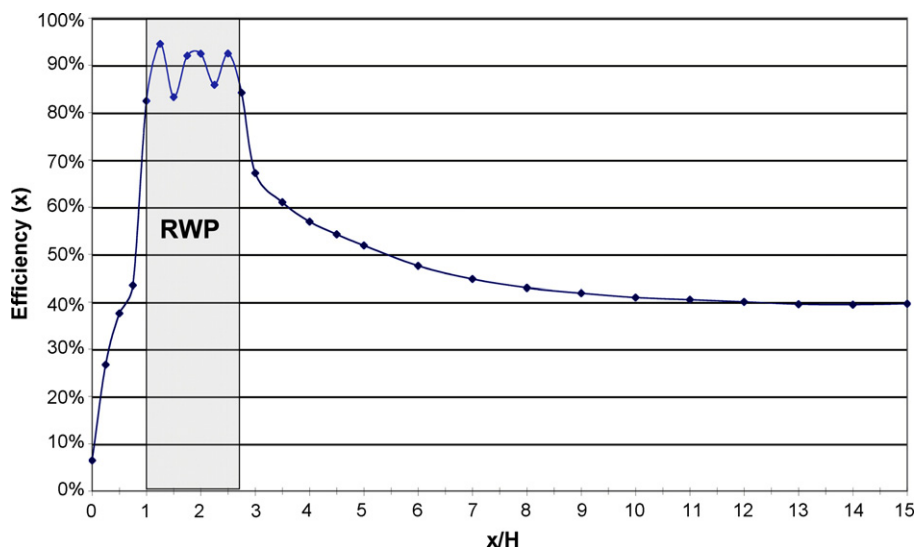


Fig. 14. Mixing efficiency vs. downstream coordinate [47].

properties of vortex generators. This was made thanks to numerical simulations and they showed that the rectangular winglet pair significantly increases the mixing efficiency as shown in Fig. 14.

Moreover, based on a compactness factor developed by Tiggelbeck et al. [48], it has been shown that delta winglet pairs increase the compactness of the heat exchanger reactor compared with rectangular winglet pairs. Indeed, at a Reynolds number of 8000, the compactness factor of delta winglet pair is 25% higher than the one of rectangular winglet pairs.

#### 4.2.4. Patented fins

In general, shell-and-tube heat exchangers are not commonly used as heat exchanger/reactor. However, a shell-and-tube apparatus with specific inserts has been patented [49]. Each tube is filled with a specific structure which can be coated with catalyst as shown in Fig. 15. Thus, the heat transfer is increased without too much of a pressure drop. This structure consists of thin layers filled with fins which promote turbulence. Each layer is metallic (stainless steel, nickel, etc.) or ceramic 50  $\mu\text{m}$  thick.

#### 4.3. Applications

Finally, the heat transfer performances of the previous compact heat exchangers are of prime importance to carry out chemical reactions. Moreover, an analysis of flow and the characterization of mixing and residence time distribution are necessary. Indeed, residence time must be sufficient to ensure a complete reaction in the heat exchanger, reactants must be mixed enough if they are not premixed, pressure drops must be acceptable and of course the fluid temperature must be controlled. That is the reason why stud-

ies have been made on inserting elements in these compact heat exchangers.

Finally, once compact heat exchangers have been so characterized, they can play the role of chemical reactors in many applications that are subsequently described.

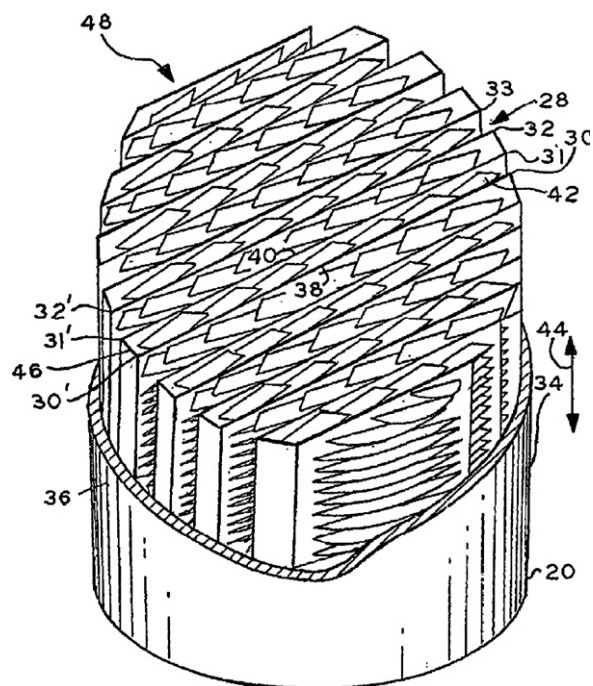


Fig. 15. Schematic view of a tube filled with the inserts [49].

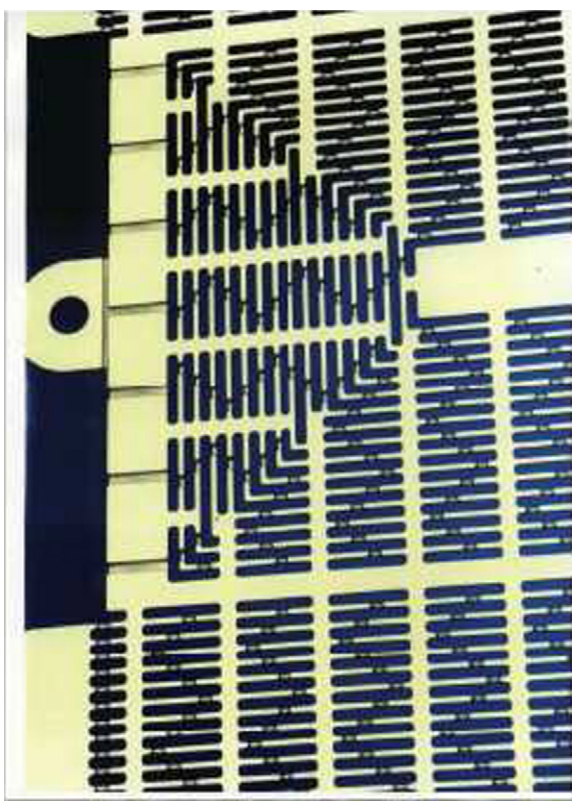


Fig. 16. Photochemically etched plate [51].

#### 4.3.1. Marbond™

The Marbond™ heat exchanger reactor has been designed and built by the Chart Company. It is described in detail in a patent they own [50]. The apparatus [51] consists in a stack of plates that are etched to form a series of slots as shown in Fig. 16.

Plates are stacked without perfect alignment of the slots so as to form discrete flow path as shown in Fig. 17. Adjacent flow paths are separated by means of solid plates. Thus, two or more separate flow paths can be formed enabling fluid streams (reactants, cooling medium, etc.) to flow parallel to each other in adjacent layers according to many configurations: multi-pass, counter-current, co-current, etc.

Plates are assembled by diffusion bonding which has the following advantages: high integrity joints which minimise the risks of leakage; and high working pressure. An inside view of the heat exchanger reactor is shown in Fig. 18.



Fig. 17. Layers of slotted plates forming flow paths [51].

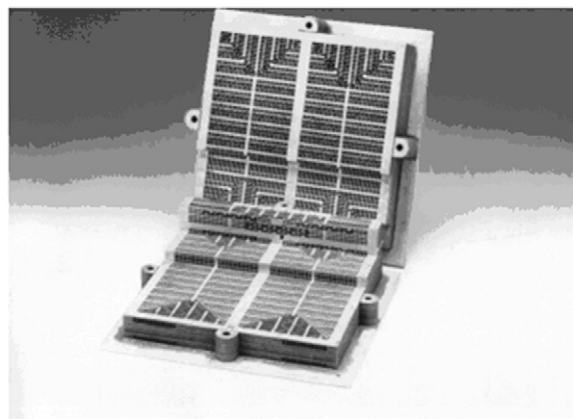


Fig. 18. Inside view of Marbond™ [51].

To characterize the Marbond™ and to compare its performance with the ones of a commercialized plate-fin heat exchanger (also developed by the Chart Company), chemical syntheses have been carried out [51]. The first one is the reaction of 1- and 2-naphtol with diazotised sulfanilic acid which leads to four dye products. The products are formed at different rates which allow the estimation of mixing intensity. Indeed, the higher the amount of byproduct, the lower the mixing intensity. Results show that the Marbond™ has a markedly higher mixing efficiency compared with the plate-fin heat exchanger. Indeed, under comparable conditions, there is 30% less byproduct in the Marbond™.

The second studied synthesis is an hydrolysis reaction: Walker scheme that characterizes both mixing and heat transfer. It comprises two steps. Step 1 is a very fast and slightly exothermic reaction; one of the reactants of step 1 is the catalyst of step 2 which is considered as an undesirable reaction. As a consequence, the more step 2 products are formed, the lower the rates of mixing and heat transfer. The performances of the Marbond™ under adiabatic and isothermal conditions were compared. The results (Fig. 19) show that the removal of the heat generated by the reaction allows a reduction of the amount of byproduct formed by step 2.

In this case, the reduction in the amount of byproduct is relatively small. This is due to the low exothermicity of step 1 ( $-55.8$  kJ/mol), but for more exothermic processes such as polymerization or nitration ( $-500$  kJ/mol), the high heat removal and mixing intensity are expected to provide significant decreases in byproduct formation.

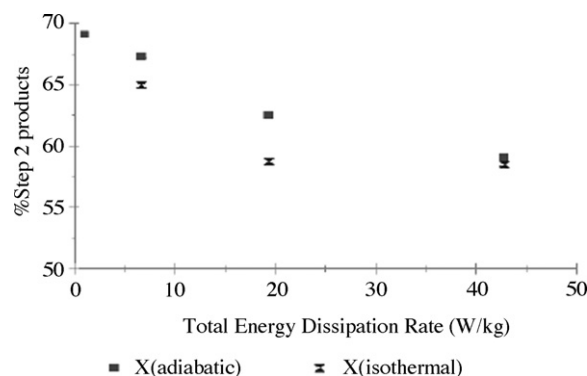


Fig. 19. Walker scheme applied to the Marbond™ for adiabatic and isothermal modes of reactor operation [51].



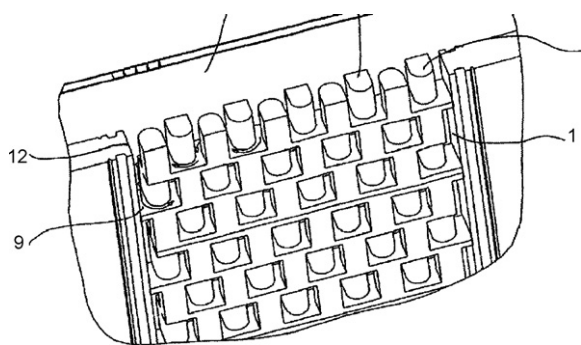


Fig. 20. Drawing of the flow inserts from Chopard [54].

Based on the previous results, Phillips et al. [51,52] developed and validated a mathematical model to simulate the Marbond™ performances for industrial processes. Results have been obtained for an ICI Acrylics' process. Currently, the amount of byproduct in plant is near 2%. By using the Marbond™, simulation shows that the byproduct amount could be reduced down to 0.5%.

However, it is important to note that the Marbond™ develops higher values of pressure drop than the plate-fin heat exchanger. Pressure drop can increase up to 50% against the plate heat exchanger at high mixing intensities [52].

#### 4.3.2. Plate heat exchanger reactors

4.3.2.1. *Open plate reactor.* The open plate reactor, designed by Alfa Laval, is based on the concept of the plate heat exchanger. It is made of reaction plates, inside which reactants mix and reactions occur, and cooling plates which are inserted between the reaction plates.

Reaction plates are filled with specific inserts which force the reactants to flow in changing directions. These inserts (Fig. 20) were specially designed to enhance heat transfer and micromixing; and patented by Chopard [53,54].

The configuration of the apparatus allows great flexibility: the type and number of inserts can be adjusted depending on the required residence time and the chosen reactions. Secondary reactant can be injected in many points and temperature, pressure or conductivity sensors can be added all along the reactor. Moreover, cooling plates can be laid out so as to have cross-flow or co-current heat exchange pattern and can be cooled to different temperatures depending on the reaction advancement in order to increase the final conversion.

The open plate reactor has been characterized in terms of residence time distribution, thermal performances, reaction behaviour and intrinsically safety [55–57]. Residence time distribution experiments showed that the flow behaviour in the apparatus can be assumed as plug flow behaviour. This interesting property to carry out reactions may be the result of the mixing elements in the reaction plate which offer a good mixing performance [58].

Thermal experiments allowed the characterization of the heat exchanger reactor in terms of global heat transfer coefficient ( $U$ ). Authors [55] showed that, in the open plate reactor,  $U$  varies from 1850 to 2500  $W m^{-2} K^{-1}$ . These values are intermediary between plate heat exchangers (from 4000 to 6500  $W m^{-2} K^{-1}$  for water) and tubular reactors (500  $W m^{-2} K^{-1}$ ). This efficient heat transfer combined with the good mixing performances is necessary to carry out exothermic (or endothermic) reactions in the open plate reactor.

As a consequence, two different chemical syntheses have been performed for the reaction characterization. The first one is the oxidation reaction of sodium thiosulfate by hydrogen peroxide which is irreversible, fast and highly exothermic ( $-586 kJ mol^{-1}$ ). A conversion rate of 100% is reached for adequate utility flow rates and high reactant concentrations. With such conditions, the oxidation

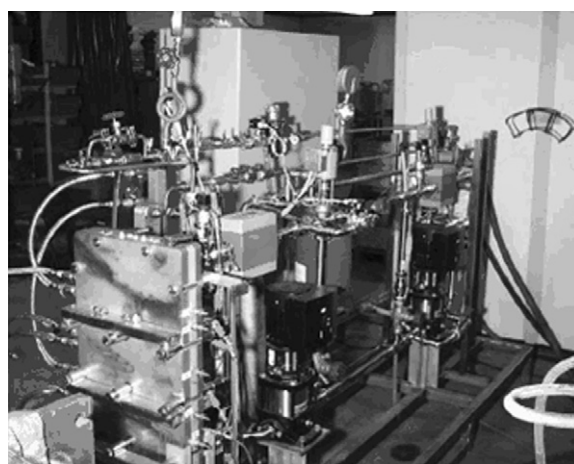


Fig. 21. The experimental system setup at Alfa Laval laboratory [59].

could not have been performed in a batch reactor because of the adiabatic temperature rise. The only way to perform it would have been to dilute or to feed slowly the reactants.

The second studied reaction is an acid-base neutralization which is instantaneous and exothermic ( $-92 kJ mol^{-1}$ ). Unlike the previous reaction, the neutralization occurs at the very beginning of the reactor and so is the heat generated.

Moreover, a specificity of the open plate reactor is that the process fluid circulates in one continuous channel with 0.5  $cm^2$  cross-section; which is different from microstructured reactor heat exchanger or Marbond™ reactor. On the one hand this design leads to a lower ratio between heat exchange surface/reaction volume compared with plate exchanger or static mixer but on the other hand it will allow the use of viscous media or in certain conditions of solid-liquid or liquid-liquid media.

Also, work [59] has been carried out to perfect a process control system and a patent has been published [60]. The objective was to have complete conversion of the reactants to the desired product. Thus the main focus was to maximize the outlet concentration of desired product with a limitation: the available inlet temperature of the cooling water which comes from a nearby river. To design the control system concerning the utility, an experimental system (Fig. 21) was setup.

The control system was tested and validated with the oxidation reaction of sodium thiosulfate by hydrogen peroxide; and the simulations show that very good conversion can be achieved while maintaining temperature under safe constraints. Moreover, the process control system allows operation closer to the constraints, thus increasing the conversion and increases the safety of operations by reducing the impact of external disturbances.

Finally, the thermal, reaction and mixing characteristics of the open plate reactor make it very interesting to perform highly fast and exothermic reactions in safe, clean and efficient conditions by working in unusual temperature, pressure and concentration fields (see Fig. 22). The opportunity to work with high concentrations and thus with high kinetics compensate the low residence time in the reactor.

4.3.2.2. *Corrugated plates.* To characterize heat exchanger reactors with corrugated plates as shown in Fig. 23, Edge et al. [12] worked in two steps. First they developed a micromixing numerical model which studies the influence of mixing intensity and heat transfer on conversion. It also allows the prediction of reactants and products concentrations and thus the conversion. To test this model, authors used the reaction scheme of Walker which is described in Section

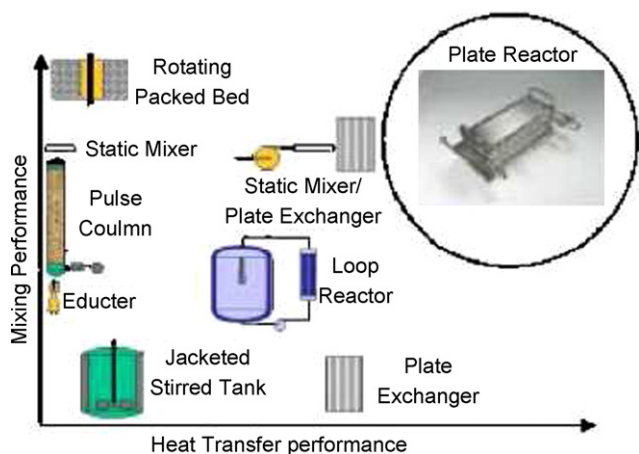


Fig. 22. Heat transfer and mixing performances for the open plate reactor and other kinds of chemical reactors, courtesy of P. Sharrat (UMIST).

4.3.1. Step 1 characterizes the mixing intensity since it is limited by the mixing and step 2 plays the role of an undesired reaction and is sensitive to the rates of both mixing and heat transfer. Results of the simulation show that, as expected, byproduct formation is sensitive to the mixing intensity and the heat transfer. The rate at which the heat is removed can markedly improve the selectivity. Moreover a change in the micromixing intensity will have more positive effects than the same change in a traditional reactor.

Then, an experimental system was setup to perform the previously simulated reaction. The aim of this step is to validate the numerical model. Similar trends were observed; it allows therefore the validation of the numerical model.

Finally, simulations of this plate heat exchanger-reactor to an industrial process have been realised. It allows the comparison of performances with traditional reactors. It has been shown that using such a reactor has significant effects on byproduct formation. Indeed, under normal operating conditions, a reduction in the byproduct formation of 50% has been obtained.

These results on the plate reactor performances have also been confirmed by other authors who studied the same reaction Walker scheme in the same apparatus [61].

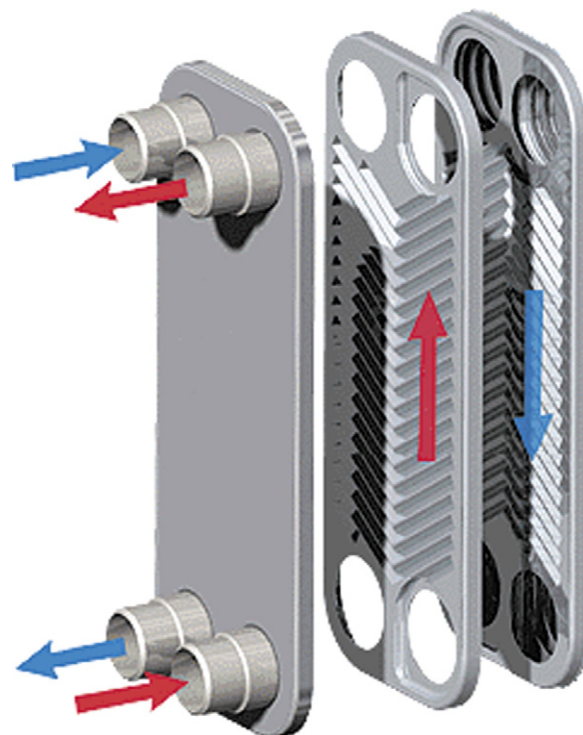


Fig. 23. Schematic view of the characterized plate heat exchanger-reactor.

The numerical model developed by Edge et al. can be used as an interesting design tool for other industrial processes since it seems to correctly predict the reaction behaviour in this apparatus; and thus, it may enhance the development of plate heat exchangers used as chemical reactors. However, to be more polyvalent, the model should be extended to two-phase reactions, viscosity changing reactions and meso or macromixing.

An example of a plate heat exchanger has been patented by Reinke [62]. It is shown in Fig. 24. It consists of stacked plates. On each plate, process and utility fluids flow with a counter-current

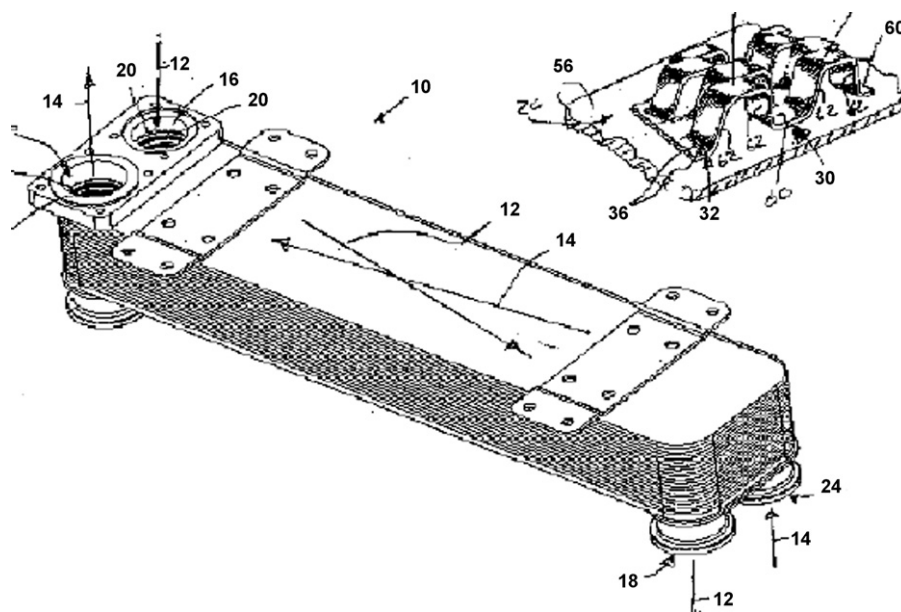


Fig. 24. Schematic view of the heat exchanger/reactor and the inserts [62].



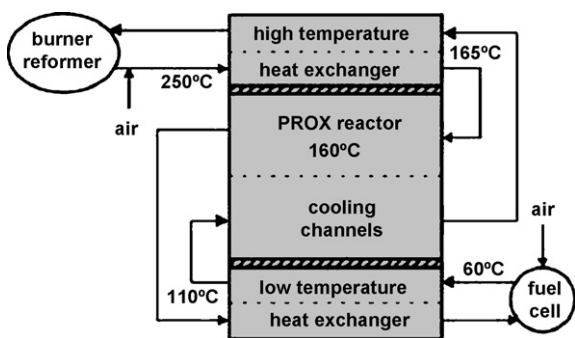


Fig. 25. Process diagram of the ProxHeatex device [63].

mode. Their respective channels are interlaced. Reaction channels are filled with inserts (Fig. 24) which can be catalyst-coated. These inserts are brazed on the plates. Others type of inserts can be used. This apparatus can be used for fuel treatment like hydrogen production, selective oxidations and catalytic reactions in general.

#### 4.3.3. ProxHeatex

ProxHeatex is a microstructured device designed to perform the preferential oxidation of carbon monoxide in a hydrogen-rich atmosphere [63]. It consists of two heat exchangers and a cooled reactor in series as shown in Fig. 25.

The geometry is based on that of plate heat exchangers. Indeed, each part of the apparatus is made of microstructured plates which are stacked together. Two flanges with eight screws at the top and the bottom of the device compress the gaskets between each plate which ensure the whole tightness. The reaction part is made of 19 process plates and 10 cooling plates whereas each heat exchanger is made of 2 process plates and 4 cooling plates. Insulating plates are inserted between the reaction plates and the heat exchangers to thermally separate these parts.

In order to avoid the undesired reaction which is the oxidation of hydrogen, reaction plates have been coated with a specific catalyst that promote the oxidation of carbon monoxide. The schematic view of ProxHeatex is shown in Fig. 26.

The performances of the ProxHeatex device have been evaluated in terms of oxidation selectivity, start-up behaviour and heat transfer efficiency.

Authors showed that the ProxHeatex device allows a reduction in the concentration of carbon monoxide to 7 ppm. However, this interesting result is only observed during the first half an hour of experimentation because of the deactivation of the catalyst. Indeed, after a period of 4 h, the concentration of carbon monoxide rises to 300 ppm. So the ProxHeatex device allows significant improvements in terms of conversion but it is necessary to improve the stability of the catalyst.

In addition, the study of the start-up behaviour showed that it takes over 1 h for the ProxHeatex device to reach the reactor operating temperature. This slow transient period is due to the ratio (heat capacity of all solid material/heat transport capacity of the fluid flows) which is not favourable for the gas-phase microdevice. As a consequence, to improve the start-up behaviour, it would be interesting to reduce the solid fraction by replacing the gaskets technology by a welded or brazed one. In the case of the ProxHeatex device, this operation would lead to a reduction of 70% of the total mass of the device.

Finally, authors studied the heat transfer efficiency of the apparatus. They worked on the influence of the type of insulation plates on the heat transfer performance of the device. Three different sets of insulation plates were tested. The temperature profiles obtained are shown in Fig. 27. It should be noticed that Klingersil® is a com-

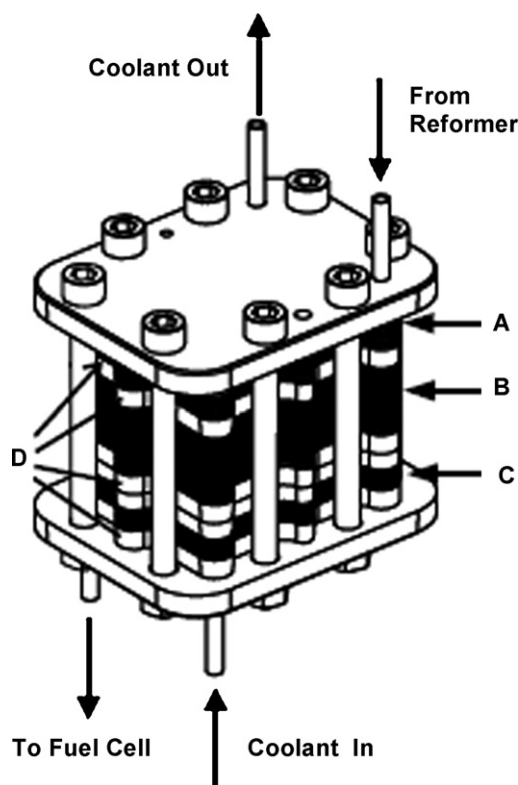


Fig. 26. Schematic view of the ProxHeatex device; (A) high temperature heat exchanger; (B) cooled reactor; (C) low temperature heat exchanger; (D) insulation plates. The outer dimensions are: 66 mm × 53 mm × 50 mm [63].

pressed fibre jointing material with a low thermal conductivity.

Fig. 27 shows that the thermal performances of the ProxHeatex device increase when the thermal resistance between the units is increased. Indeed, the fraction of heat, of the total amount of heat available in the reformate gas and generated by the oxidation reaction, that is exchanged with the coolant gas, increases from 68% with the steel insulation plates to 78% with the multiple Klingersil sheets.

Furthermore, a two-dimensional model is developed. It describes the temperature fields in a plane, parallel to the microstructured plates in a single micro heat exchanger. Predic-

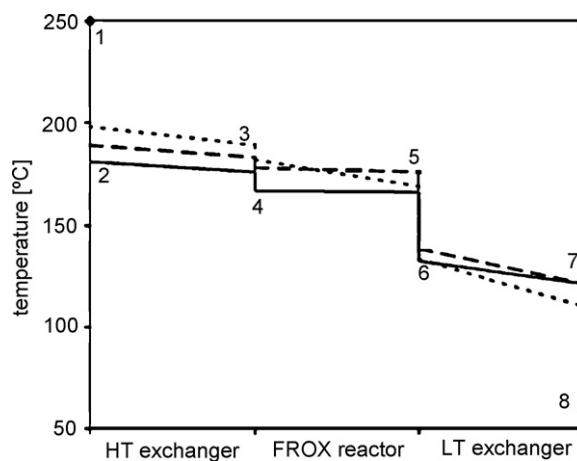


Fig. 27. Measured temperatures profiles in the ProxHeatex device assembled with: steel plates with air chambers (solid line); single Klingersil® sheets (dashed line); and multiple Klingersil® sheets (dotted line) [63].

tions showed that most of the heat exchange occurs in the flow distribution chambers. Consequently, the behaviour of the micro heat exchanger looks more like a co-current or cross-flow apparatus than a counter-current one, leading to a low-heat exchange effectiveness.

So based on the results of this study, a new ProxHeatex device will be built with changed dimensions to increase heat exchange efficiency, welded technology to reduce the mass of the unit and another catalyst to improve the oxidation reaction selectivity.

#### 4.3.4. Microstructured heat exchanger/reactors.

This paragraph details microstructured heat exchanger/reactors which often involve catalysts. The aim of this work is not to draw up an exhaustive inventory of catalytic reactors. Only some heat exchanger/reactors which have been the object of patents or publications are quoted. Of course, other microstructured heat exchanger/reactors, which have been designed by many equipment manufacturers, exist.

4.3.4.1. Oxidation reactions. Many studies have been led on microstructured heat exchanger/reactors and chemical reactions have already been performed. Most of them are oxidation reactions of ammonia or hydrogen. They are presented below.

The oxidation reaction of ammonia is studied because of its high exothermicity. Thus, the selectivity depends on the temperature, which allows the study of the heat transfer effectiveness in the apparatus.

Rebrov et al. studied this reaction in four microstructured equipments with different sizes and geometries [64]. The following paragraph is a short description of these microstructured reactors whose design is based on plate heat exchanger geometry.

(A) Parallel plate reactor: this microreactor consists of a stack of 20 removable plates. The plates are made of aluminium with an alumina layer on the both sides. The reaction microchan-

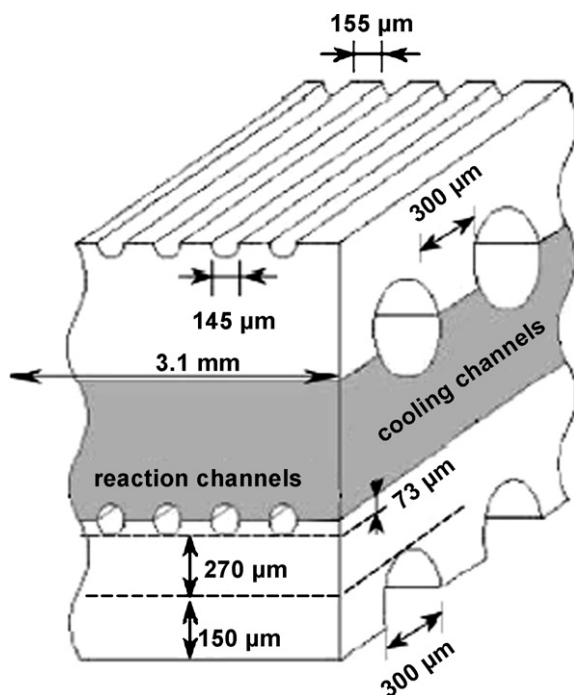


Fig. 28. Schematic view of the aluminium microstructured reactor/heat exchanger [64].

nels are coated with a Pt catalyst. Three different plate parallel microreactors were made corresponding to three different Pt loadings.

- (B) Pt-monolith reactor: this microreactor contains 7 plates with 7 microchannels made in a metallic Pt cube.
- (C) Assembled Pt/Al<sub>2</sub>O<sub>3</sub>/Al reactor: this aluminium microreactor was made in order to verify the feasibility of improving the heat transfer properties of the previous apparatuses. It consists of 14 individual plates with 49 parallel channels.
- (D) Microstructured reactor/heat exchanger: this device is shown in Fig. 28. By stacking two plates, a set of reaction channels is produced; then by adding a third plate a set of cooling channels is produced. A set of reaction channels in one plate is separated from a set of cooling channels with an aluminium layer 270 μm thick. It was designed from experimental results of reactors A, B and C. Thus a cross-flow configuration was adopted.

Authors showed that in terms of conversion of NH<sub>3</sub>, reactor C is the most efficient. Indeed, in this reactor, a conversion of 100% is reached at 325 °C whereas others reactors (A and B) are only partially active at this temperature. Moreover, results on reactor B which is a Pt monolith reactor show that there is a lower nitrous oxide selectivity. This is probably due to the poor thermal behaviour of this reactor. Indeed, because of the relatively low thermal conductivity of Pt ( $\lambda = 72 \text{ W/mK}$ ) compared with the one of aluminium, the heat generated by the reaction is not released fast enough to the cooler. Thus, hot spots appear in the microreactor and lead to poor selectivity control whereas in the case of reactors A and C, the high thermal conductivity of aluminium ( $\lambda = 240 \text{ W/mK}$ ) leads to very small thermal resistances in these apparatuses. As a consequence, even if the geometry of these devices is suitable to provide high heat transfer rates, attention must be turned to the material which may create considerable heat transfer resistance.

Finally, reactor C offers the best properties in terms of selectivity and heat transfer. Thus a kinetic study was realised and showed that decreasing the residence time has positive influence on the selectivity as well as increasing the oxygen concentration in the feed gas.

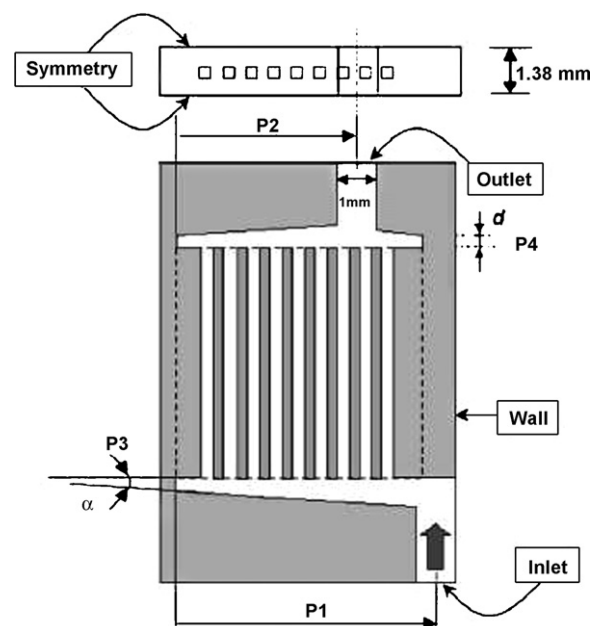


Fig. 29. Schematic view of the flow distribution system [65].

These optimized parameters (material, Pt loading, geometry, composition of the reactants mixture and residence time) were applied to the microstructured heat exchanger/reactor. Then, a numerical model showed some differences of temperatures in the reaction channels which give sometimes a difference in the ammonia conversion of up to 20%. By introducing a non-uniform coolant distribution in the cooling channels, this phenomenon can be minimized as described in subsequent works of Rebrov et al. [65].

Authors studied the influence of the coolant flow distribution and the aluminium thickness on the temperature field. Simulations were first made with Fluent® software; then the optimized device was designed and experiments have been carried out to confirm the simulations. The studied device is the same than in the previous study, as shown in Fig. 28. Each element of the apparatus consists of an aluminium plate containing twenty reaction channels and nine cooling channels machined in a perpendicular direction.

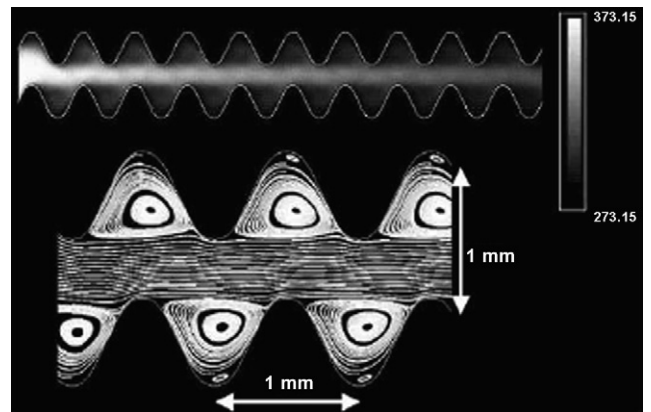


Fig. 32. Temperature distribution and streamlines in the sinewave geometry [67].

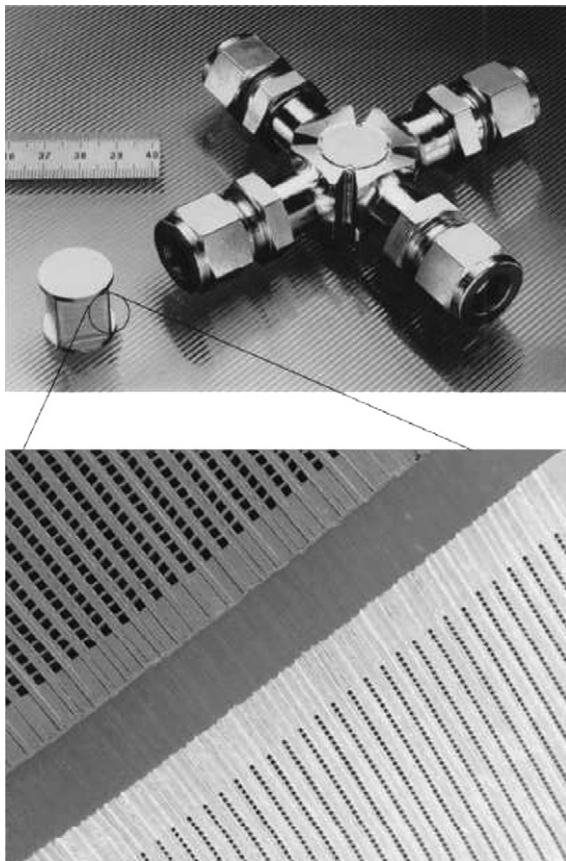


Fig. 30. Photographs of the microstructured reactor/heat exchanger developed and constructed by the Karlsruhe Research Centre. Above is shown the reactor with and without the attached pipe fittings. The bottom picture is a SEM micrograph showing a corner view of the reactor [66].

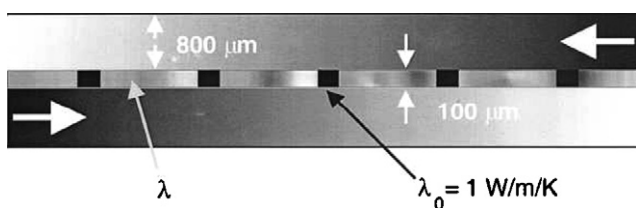


Fig. 31. Schematic view of the counter-current geometry with thermal resistors [67].

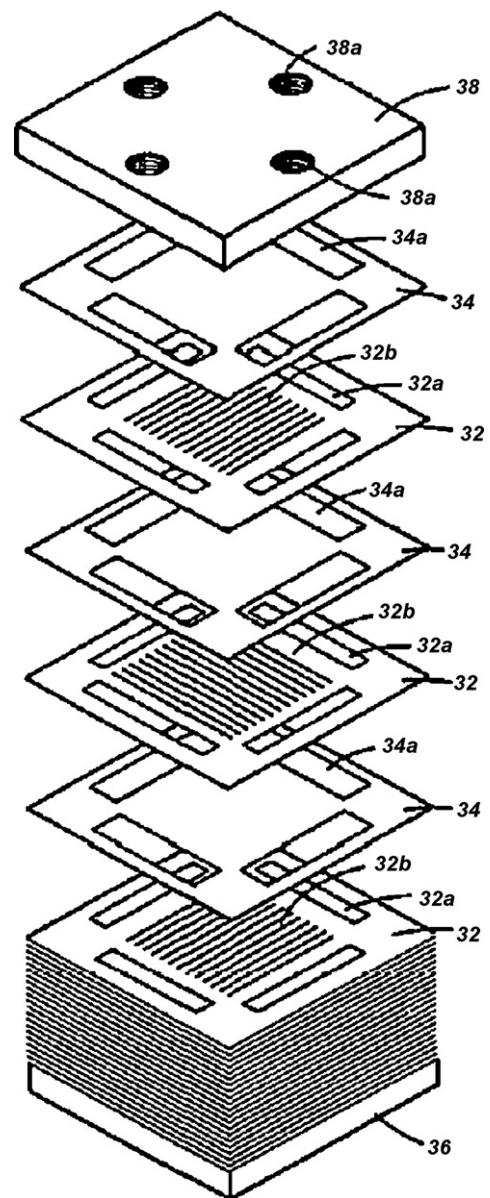


Fig. 33. Schematic view of the microchannel heat exchanger [68].



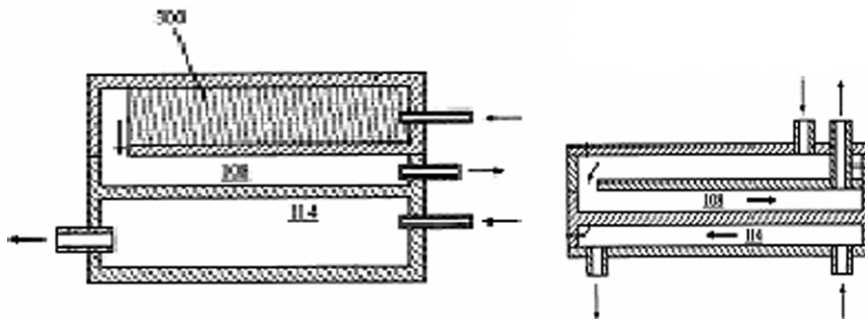


Fig. 34. Schematic view of the microstructured heat exchanger/reactor [69].

It was shown that a non-uniform coolant distribution (see Fig. 29) improves the ammonia conversion and that an optimal aluminium thickness exists. However, from the practical point of view, this distance must be as short as possible to increase the production rate per unit of volume.

Finally, using these optimized parameters, the microstructured heat exchanger/reactor was constructed with eight aluminium plates of  $6.5 \text{ mm} \times 6.5 \text{ mm}$  and tested. Results showed that the catalytic oxidation reaction could be performed at near-isothermal conditions in the optimized reactor. As a consequence, the selectivity is considerably improved. Moreover experiments were in good agreement with the CFD simulations. Thus, such simulations will be able to predict the behaviour of the reactor in many applications.

Another oxidation reaction has been performed in a microstructured heat exchanger/reactor: the catalyzed oxidation reaction of hydrogen from an explosive mixture of gases [66]. This oxidation reaction is very hazardous and requires an explosive reactant mixture. Therefore, experiments in the microstructured reactor/heat exchanger were performed to test the safety of the apparatus and to determine if the heat released by the  $\text{H}_2/\text{O}_2$  reaction could be controlled.

The microstructured heat exchanger/reactor used for this work is shown in Fig. 30. It consists of stainless steel plates with micromachined channels which are stacked together by diffusion bonding. Plates are perpendicular each other which offers a cross-flow configuration. Channels have two different sizes: the set of larger channels ( $140 \mu\text{m} \times 200 \mu\text{m}$ ), coated with  $\text{Al}_2\text{O}_3$  and impregnated with Pt, are used for the oxidation reaction while the smaller channels ( $70 \mu\text{m} \times 100 \mu\text{m}$ ) are used for the cooling fluid.

Three series of experiments were realised. The first one aimed at optimizing in a test reactor the quality and thickness of the  $\text{Al}_2\text{O}_3$

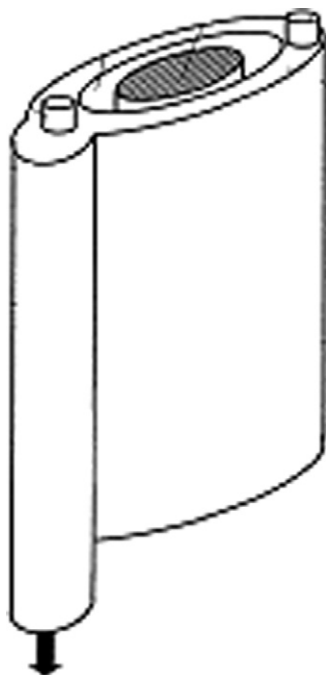


Fig. 35. Concentric microstructured heat exchanger/reactor [70].

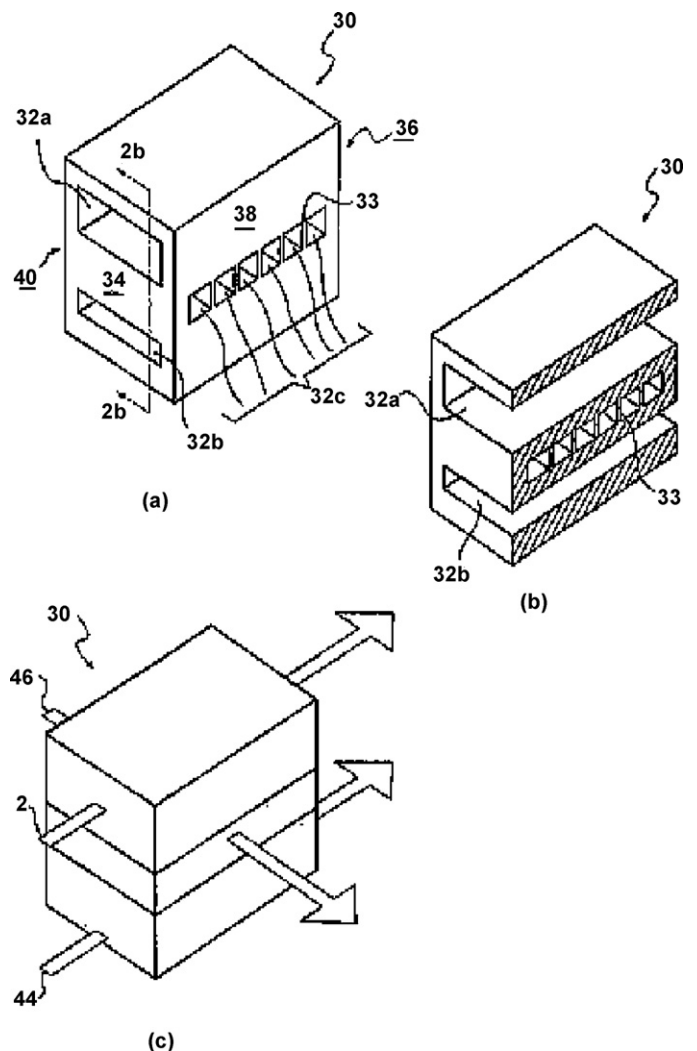


Fig. 36. Multi-stream microchannel device [71].

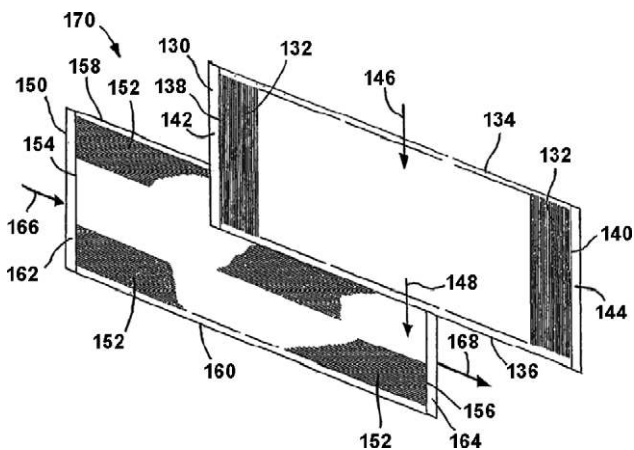


Fig. 37. Microstructured heat exchanger/reactor for Fischer-Tropsch synthesis [72].

coating and at quantifying the increase in surface area that could be expected. The results have then been applied in the microstructured heat exchanger/reactor and the second series of experiments was performed to study the temperature response of the apparatus for a low loading of platinum. Results showed that the heating rate can be controlled by the concentration of the reacting gases. Moreover, the reaction initiates without exploding, and the exiting gases are outside the explosion regime of  $H_2$ , so the microreactor seems to operate safely. And finally, 100% of the  $H_2$  had been converted into water. The reactor has also been successfully performed without diluent gas confirming the inherent safety of the apparatus and demonstrating its ability to manage dangerous mixtures of gases.

Then the third series of experiments was performed to study the temperature response with a high loading of platinum. The conversion of  $H_2$  to  $H_2O$  was still 100% and unlike previous experiments, with a high loading of platinum, the reaction starts at room temperature, eliminating the need for external heaters (in the previous experiments, reactants were preheated up to  $80^\circ C$ ).

Finally, the use of microstructured heat exchanger/reactor in case of mixtures of explosive gases allows a safe and reliable process control. Indeed, reactions have been performed with a complete conversion of hydrogen at controlled temperature. More-

over, explosion experiments have been made to test the ability of the apparatus to act as a flame resistor; an explosion was ignited on one side of the reactor and it could not pass through the microchannel, thus demonstrating the effectiveness of the apparatus to stop the propagation of explosions. So, thanks to its geometry, the microstructured heat exchanger/reactor is safe. Indeed, the small volume minimizes the quantity of explosive mixtures and the dimensions of the microchannels are smaller than the quenching distance for hydrogen.

4.3.4.2. *Geometry.* The two previous studies [64,66] concerning microstructured heat exchanger/reactors were focused on oxidation reactions. The apparatuses have been designed according to a plate heat exchanger geometry and oxidation reactions have been successfully performed. The following paragraph is more focused on the study of the thermal characteristics of the microstructured heat exchanger/reactor and reaction is only simulated in a second step by means of CFD simulation [67].

In a traditional countercurrent heat exchanger, axial conduction in the walls decreases the thermal performance of the system. The first geometry is based on this observation. As a consequence, a periodic arrangement of structures of low thermal conductivity has been inserted in the walls, as shown in Fig. 31; these thermal resistors modify the heat conduction only inside the solid material which does not increase pressure drops and hydrodynamic losses in the reaction channels.

Simulation results show that in usual operating conditions no improvements due to thermal resistors are expected compared with unstructured walls. Consequently, a second geometry has been tested; it consists in folding the channel walls to increase the specific surface area. Simulations were made with a sinewave shape. Results show that the heat exchange was higher than in a parallel plate heat exchanger for high Reynolds numbers ( $Re > 800$ ). However, with such Reynolds numbers, simulations show that the flow does not follow the meanders and large vortices are formed close to the convex sections of the channel walls as shown in Fig. 32. Even if, heat transfer is enhanced, this phenomenon is a handicap to carry out reactions since the residence time distribution will not be satisfactory and pressure drops will increase.

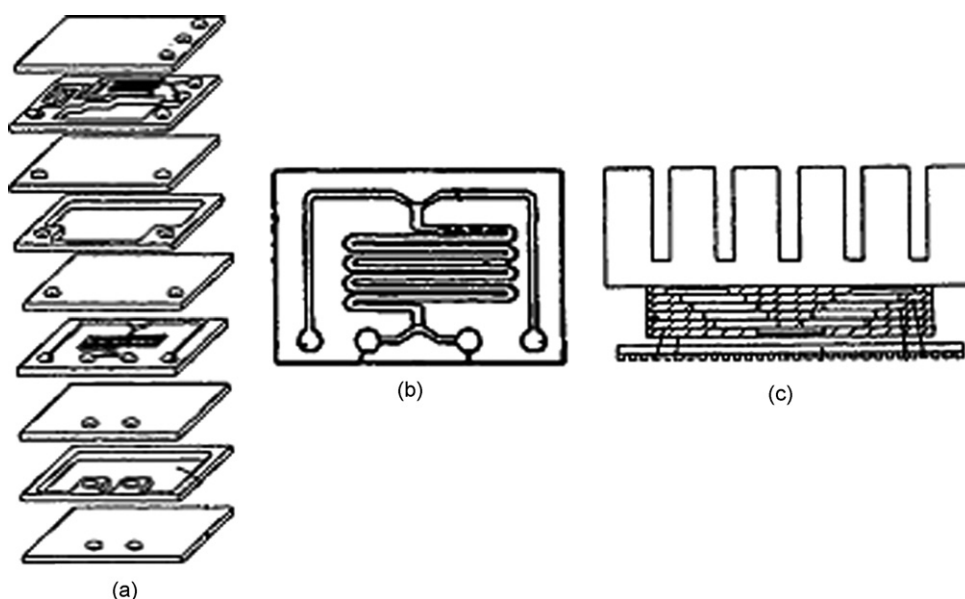


Fig. 38. Microstructured heat exchanger/reactor: (a) microreactor; (b) reaction plates; (c) micro heat exchanger [73].



Finally, the third approach was to consider a straight channel with microfins. Results show that the microfin arrangement provides a better heat transfer. Indeed, the Nusselt number of microfin is six times higher than in a parallel-plate heat exchanger and four times higher than in the sinewave geometry. This result is due to both enhanced heat transfer coefficients and increased surface area. However, at high Reynolds numbers, pressure drops in microfin arrangement are seven times higher than in the sinewave configuration and 80 times higher than in the unstructured configuration. As a consequence, a compromise between pressure drops and heat transfer should be made.

Finally, authors decided to simulate a heterogeneous catalyzed gas-phase reaction in such a microstructured heat exchanger/reactor. The system consists of alternative layers of heating and reaction gas. The two gases are fed into the reactor in countercurrent mode, where the heating gas provides energy for the endothermic reaction. The plates are separated from each other with thermally conductive walls; on the gas side, the walls are coated with the catalyst. The comparison between structured (microfins) and unstructured microchannels was made with numerical simulations. Results show that higher product concentrations are achieved with the former and the specific molar flux can be increased by at least a factor of 2. Thus, the volume of the system and the quantity of catalyst required can be decreased or the conversion can be increased which make the microfin geometry very interesting to carry out reactions.

Finally, this microstructured heat exchanger/reactor was compared with a traditional fixed-bed reactor and authors showed that for a same target conversion, the catalyst mass needed in the former was lower than in a fixed-bed reactor involving a reduction of the reactor volume. For further applications, the results may be now generalized to a broad class of heat transfer limited processes with fast reaction kinetics.

**4.3.4.3. Patents.** Many microstructured heat exchanger/reactors have been patented. The following paragraph is a short description of them in a chronological order.

The first of them was patented in 1985 [68]; it is a microstructured heat exchanger which consists of stacked metallic plates as shown in Fig. 33. Each microstructured plate is sandwiched between two solid plates in order to form microchannels. The fluids flow in a cross-flow mode.

Plates are made in stainless steel and are assembled by brazing. They are from 50 to 200  $\mu\text{m}$  thick. Application was first aim at heat exchange with liquid phase for a stirling motor.

The second one was patented in 2001 [69]. This microstructured heat exchanger/reactor is made of 3 chambers: a reaction chamber (300), a chamber to recover heat by convection (108) and a heat exchange by conduction chamber (114) as shown in Fig. 34. Each chamber is made of microchannels, a porous material can be inserted in the reaction chamber (catalyst, foams, etc.).

The structure of the device is metallic and the porous insert can be in ceramic or in metal. Size of microchannels is 430  $\mu\text{m}$   $\times$  2000  $\mu\text{m}$ . Applications are mainly in fuel cell (evaporator, steam generator, etc.) The oxidation of  $\text{H}_2$  has been performed in 3 different conditions:  $\text{H}_2$  + air to heat water;  $\text{H}_2$  + air to vaporize water and  $\text{H}_2$  +  $\text{O}_2$  to vaporize methanol.

The next patent was published in 2003 [70]. This device is a concentric heat exchanger/reactor as shown in Fig. 35.

The microreactor is surrounded with the heat exchanger which consists of annular plates. When plates are assembled, microchannels in which process and cooling fluids flow in a co- or counter-current mode are formed. Plates are assembled by compression, soldering or welding. This small size device was designed for the car industry.

The next microstructured heat exchanger was patented in 2004 [71]. It can be inserted into a microreactor. Each unit (Fig. 36) can be repeated to form a global unit with industrial capacities.

Fluids flow in a counter-current or co-current mode and process channel can be filled with catalyst. The cross-section of microchannels can be of different shapes (rectangular, circular, etc.). The structure is metallic. Applications are reforming, combustion, etc.

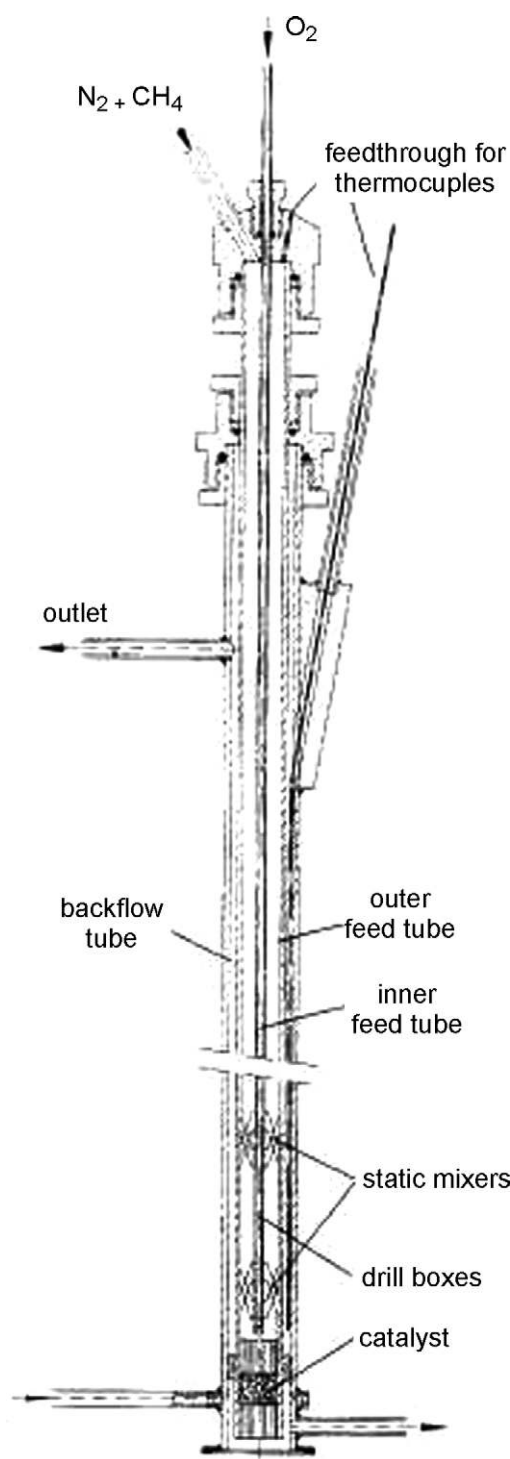


Fig. 39. Schematic view of the counter-current heat exchange reactor [74].

The next patent was published in 2005 [72]. This is a microstructured catalytic heat exchanger/reactor (Fig. 37). Reactants flow in process channels filled with Fischer–Tropsch catalyst. Heat is released by cooling channels. Process and cooling plates are adjacent to each other and work in cross-flow, counter-current or co-current modes.

Plates are assembled by brazing, laser welding or bonding. The apparatus can be built in steel, aluminium, titanium, glass, etc. Applications are Fischer–Tropsch syntheses to produce aliphatic hydrocarbons from a  $H_2$ –CO mixture with catalyst.

Finally, the last one was patented in 2006 [73]. This microstructured heat exchanger/reactor consists of a stack of different plates as shown in Fig. 38.

The microreactor is made of alternating reaction plates, insulating plates and cooling or warming plates. Insulating plates prevent heat exchange between reaction plates. Depending on the nature of the gas stocked in the heat exchanger plates, plates can be thermally isolated from each other or heat can be generated, released or stocked.

The micro heat exchanger is made of perforated plates through which the heating fluid flows from bottom to top storage tank. This device can be added to the microreactor for more efficiency.

#### 4.3.5. Counter-current heat exchange reactor (CHXR)

The counter-current heat exchange reactor was developed for catalytic high temperature partial oxidation of hydrocarbons [74]. These reactions are very hazardous because of the flammable gas mixtures. Therefore special care has been taken to minimize the danger linked to the process. The reactor was designed to fulfil the requirements of a safe, selective and energy efficiency process. Its geometry is based on a shell-and-tube heat exchanger one. It consists of three concentric steel tubes built to withstand very high temperatures. The two inner tubes are the reaction tubes whereas the outermost one is used to flow back the hot, reacted gas in order to preheat the inlet gases in a counter-current configuration. A schematic view of the heat exchanger/reactor is shown in Fig. 39. The catalyst used is an alumina foam monolith coated with Pt or Rh. The contact times between this one and reactants will vary from 10 to 50 ms.

Authors studied the influence of temperature on the conversions and selectivity. Then their results were compared with the ones of a traditional fixed-bed reactor without heat exchange.

Temperature profiles show that reactor entrance and exit are kept at temperatures below  $100^\circ C$  while at the same time gases

are preheated to temperatures around  $800^\circ C$ . This efficient heat exchange between hot, reacted gases and inlet reactants avoid using a preheater which is necessary in the case of a traditional fixed-bed reactor.

Experiments showed that increasing the residence time leads to a decrease of the operating temperature (more heat losses) which leads to a decrease in both CO and  $H_2$  selectivity as well as in  $CH_4$  conversion.

Finally,  $H_2$  and CO selectivity and  $CH_4$  conversion in the counter-current heat exchanger reactor are nearly the same as in a fixed-bed reactor. However, no preheater is required in the case of the counter-current heat exchanger reactor.

#### 4.3.6. Printed circuit heat exchanger

Printed circuit heat exchangers have been developed by Heatric [75]. They are made of chemically etched plates, alternating process plates and cooling plates as shown in Fig. 40. Plates are stacked together and diffusion bonded to form a single block. If necessary, these blocks can be welded together to form larger units.

These heat exchangers offer many opportunities in terms of operating conditions and size. Indeed, for equivalent conditions, they are 85% smaller than a shell-and-tube heat exchanger due to higher surface area density, higher heat transfer coefficients and counter-flow configuration. Moreover they are designed to operate at pressure over 500 bars and temperature up to  $800^\circ C$ . These characteristics allow the use of printed circuit heat exchangers as mixer/heat exchanger/reactors, and more particularly for heterogeneous catalytic reactions which are highly exo- or endo-thermic.

As a consequence the partial oxidation reaction of ortho-xylene with air was studied [75]. This is a strongly exothermic reaction ( $\Delta H = -1285 \text{ kJ/mol}$ ) which operates between  $335$  and  $415^\circ C$  on a catalyst support. It is traditionally performed in a multi-tubular reactor. The reaction was transposed in a printed circuit heat exchanger reactor designed according to two modes: the multiple adiabatic beds mode and the “in passage” one. The former consists in alternating catalyst beds where the reaction occurs, and printed circuit heat exchanger panels, which maintain the required temperature as shown in Fig. 41. The cooling medium can be a utility fluid or another reaction within a separate sequence of catalyst beds.

The second concept, “in passage mode” consists in coating the heat transfer surface with catalyst as shown in Fig. 42. The major difficulty for this concept is to have a suitable catalyst whose life and resistance to poisoning or deterioration are of prime importance since layers of a few microns are considered. Moreover, “in passage” catalysts are not as easy as the multiple adiabatic beds to replace.

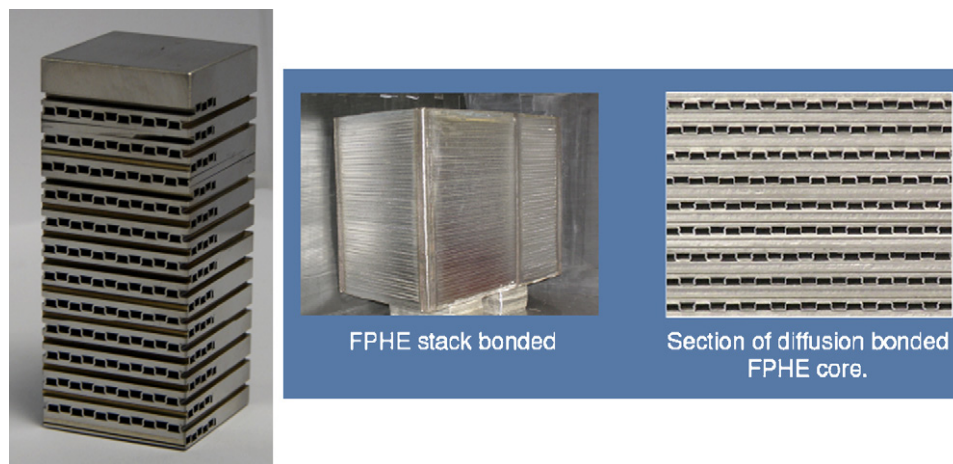


Fig. 40. Printed circuit heat exchanger (courtesy of Heatric) [75].

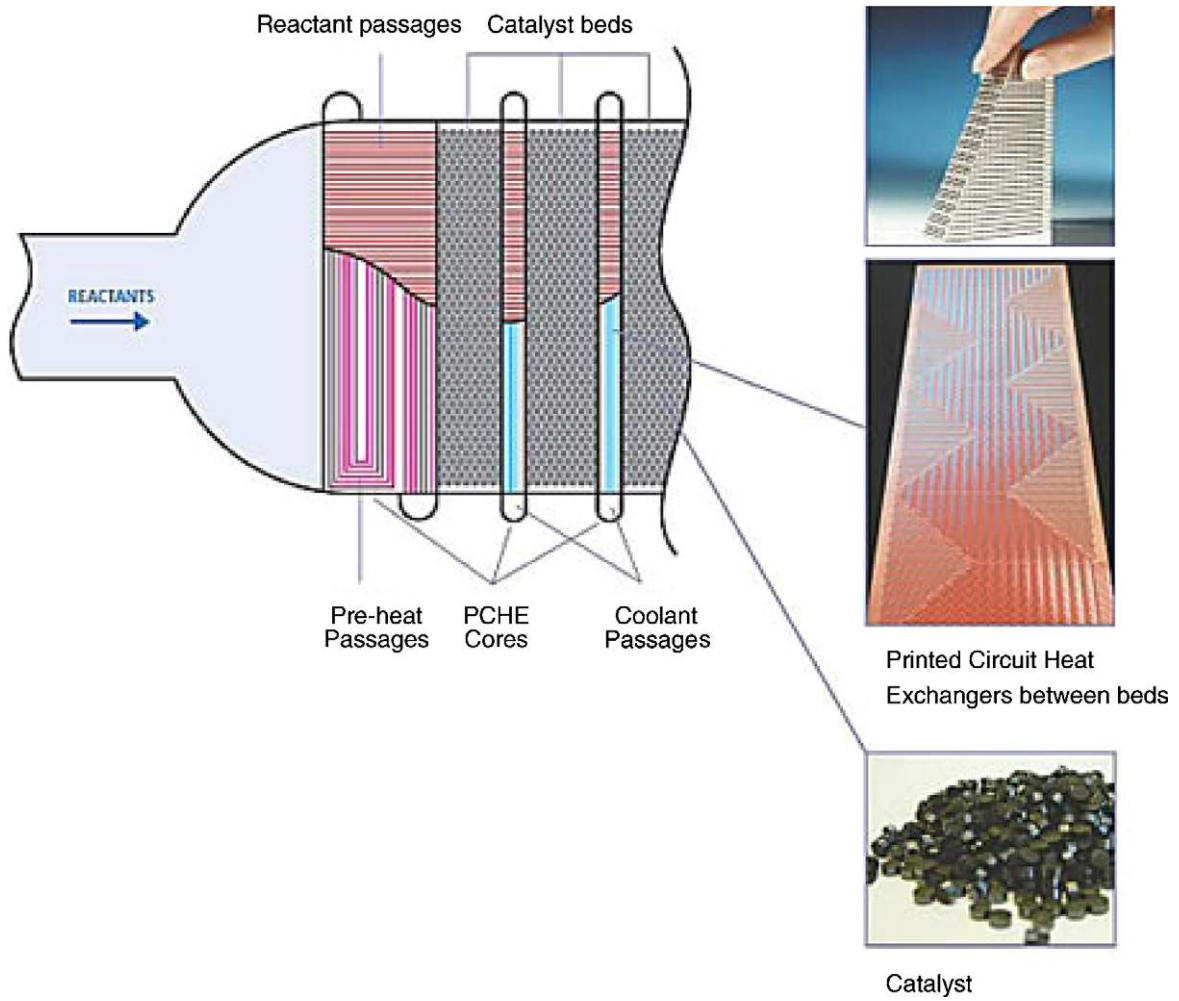


Fig. 41. Multiple adiabatic beds concept (courtesy of Heatric).

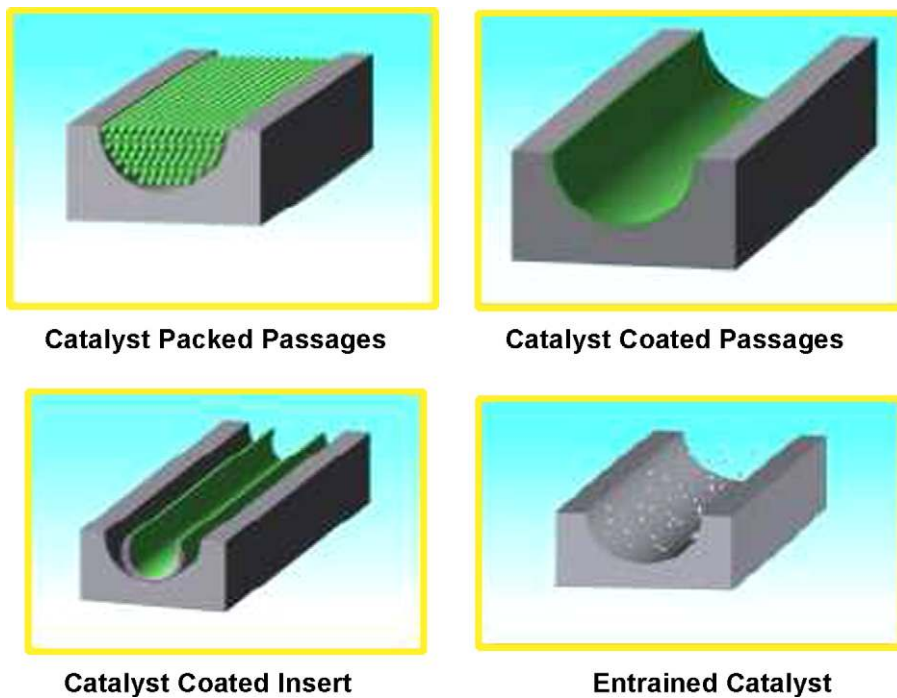


Fig. 42. In-passage catalyst mode.



Authors compared the performances of these two concepts applied in a printed circuit heat exchanger with a traditional multi-tubular reactor. First, concerning multiple adiabatic beds, the process appears to be more compact and cheaper than a traditional one in the same conditions of selectivity and conversion. Indeed, a decrease in the size of 95% has been achieved (from 280 m<sup>3</sup> for a traditional reactor to 14 m<sup>3</sup> for printed circuit heat exchanger reactor) and costs have been reduced by 20%. Moreover other benefits were observed: size of the catalysts and size of the heat exchanger are small enough to quench combustion or explosion, loading and unloading of catalyst is straightforward and finally the catalyst temperature profile is completely controlled by the cooling medium.

In spite of the poor capacity of the "in passage" configuration to replace easily the catalyst, it presents many other benefits. First it can be applied consistently throughout the structure, and then the temperature is closely control as there is no large thermal resistance between the catalyst, the gas and the wall; it leads to quasi isothermal conditions. Moreover, dimensions of the device suppress any explosive tendency, the process volume is still less, attaining 8 m<sup>3</sup> approximately and decrease in costs is around 40% compared with traditional reactor.

Finally, both concepts are interesting in terms of improved temperature control, reduced costs and decreased volumes to carry out highly exothermic reactions but future work is necessary to improve the reaction selectivity which is at present around 80%.

Elsewhere, another application is a pilot plant for steam reforming of methane including printed circuit heat exchangers [76]. The intensified system offers high compactness, safety, high efficiency and excellent scalability.

## 5. Conclusion

According to the required applications and the industrial needs, a wide range of intensified heat exchanger/reactors has been designed, experimented and built. All of them have the following common characteristics: safer operating conditions, more compactness, better control of the reaction(s), higher yields and selectivities, energy savings, fewer unit operations and thus cheaper processes.

However, even if some devices have been implemented in an industrial context, most of the cited apparatuses are developed at lab-scale and scalability is still an important parameter to study (in particular for microstructured heat exchanger/reactors). Indeed, only a few technologies have already been applied to industrial syntheses. The most promising are plate heat exchangers that have been transposed to chemical reactors like the Open Plate Reactor, the Chart Marbond<sup>TM</sup> or the Printed Circuit Heat Exchanger of Heatric.

Moreover, some progress is still required concerning catalysts coating devices and two-phase reactions. The former have been largely studied but further works will certainly lead to improving their fouling resistance, the maintenance and cleaning operations which are at present a problem in such devices. Furthermore, all of the cited apparatuses have been characterized with homogeneous reactions, and an interesting area to study would be the development of solid-liquid or liquid-liquid reactions, which lead to viscous fluids for instance, like polymers. These kind of reactions have still not been studied, except in spinning disk reactors, because of the fouling problem of brazed or microstructured apparatuses but it could be a promising field. Gas/liquid reactions are also neglected reactions, because of the poor heat transfer coefficient of the gas phase, which generates transfer difficulties in heat exchanger reactors, except maybe in metallic foams and microstructured reactors.

Furthermore, studies on inserts are promising since good results on heat transfer, mixing and reactions have been obtained. However, in most cases, works have only studied the insertion of elements (foams, fins, monoliths, etc.) in a single channel, and such studies in a global heat exchanger reactor could be interesting.

Finally, heat exchanger reactors are at the heart of very active research efforts which justify the mobilization of a part of the scientific community, particularly on points to be addressed that are presented in the following table. This table sums up the main advantages that are expected in multifunctional heat exchangers according to three pertinent criteria and points that still require research work.

	Expected advantages	Points to be addressed
Technical criteria	Better control of transport phenomena and better reproducibility, close to chemistry Improvement of yield and products quality Scale-up procedure made easier Compactness and multifunctionality	Design linked to chemistry → low polyvalence? Handling with solid phase and viscous fluids? Fouling, corrosion → choice of suitable material
Economical criteria	Fast to market Productivity thanks to continuous process On-site production	Investment costs? Fight against batch («rush-to-be-second»)
Environment/safety	Better operation of reactions Low waste/energy savings	Process control (problems of deviation detection) Reactor environment: reaction propagation out of the reactor
	Smaller hold-up	

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