EUROPEAN ROADMAP OF PROCESS INTENSIFICATION

- TECHNOLOGY REPORT -

TECHNOLOGY:

HEX REACTORS

TECHNOLOGY CODE: 2.2.1

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1. Technology

1.1 Description of technology / working principle

(Feel free to modify/extend the short technology description below)

Process Intensification is particularly suited to processes which have underlying reaction timescales of minutes, seconds or less. Many of these rapid reactions are either highly exothermic or endothermic. Combined chemical reactor-heat exchangers (HEX Reactors, Figure 1) have been under development for a number of years. The underlying principle of combined chemical reactor-heat exchangers (HEX Reactors) is to match mixing, heat transfer and residence time of the reactor to the kinetic rate, heat production and reaction time of a rapid, highly exothermic process. As a result the reaction can proceed at its natural rate, unlimited by the performance of the reactor, leading to processes which are 'safer, cleaner, smaller and slicker.'

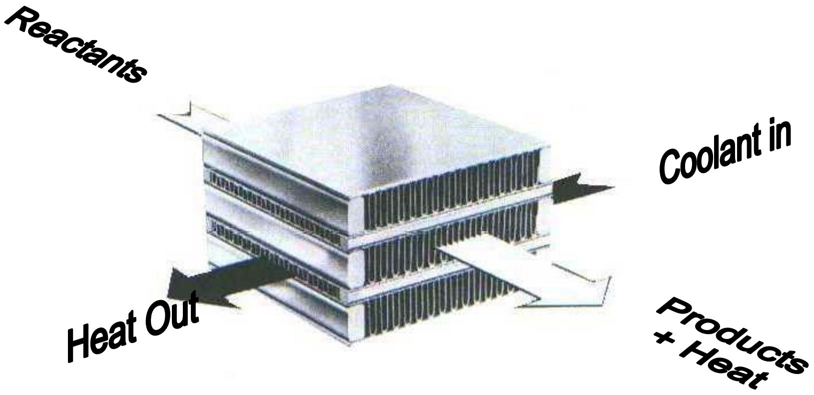

Figure 1 HEX Reactors: Principle of Operation

A variety of HEX Reactors has been under development since the mid-1990s. Generally these are based on compact heat exchangers (modified to improve mixing performance), intensive mixers (modified to add heat transfer capability) or are bespoke designs aiming to optimise both mixing and heat transfer.

There is an overlap between 'HEX Reactors' and 'Microreactors'. There are a number of examples described as the latter, which might more accurately fall into the HEX Reactor category. Any boundary between the two will be arbitrary, but for the purposes of this Report, HEX Reactors are considered to be reactors with characteristic channel dimensions of ~ 500 μm or greater, which rely primarily on turbulent or chaotic mixing, rather than diffusion.

1.2 Types and "versions"

(Describe the most important forms/versions of technology under consideration, including their characteristic features, differences and similarities)

HEX Reactors tend to fall within two divisions: *non-catalytic* and *catalytic* HEX Reactors.

Non-catalytic reactors tend to be used for liquid phase reactions, such as those found in the fine and speciality chemicals industries. These reactors fall into three basic types.

(i) **Jacketed Static Mixer Reactors**. Static mixers provide a highly effective and efficient mixing environment for rapid reactions. Heat transfer capacity can be provided by utilising either single mixers in jackets or multiple mixers in a shell and tube geometry.

(ii) **Compact Heat Exchangers.** Various designs of commercially-available heat exchangers (enhanced shell and tube, plate and frame, plate fin and diffusion-bonded (Heatric)) have been tested and/or utilised as reactors (Edge et al, 1997). Such devices provide extremely effective heat transfer, but are not optimised as reactors, compromising their efficiency.

(iii) **Bespoke HEX Reactors.** One example is the Marbond Reactor, supplied by Chart Industries (Phillips, 1997, Figure 2). This has been designed specifically as a heat exchanger-reactor, combining high heat transfer with effective mixing. Passageways are constructed using chemical etching to make thin 'shims', which are then diffusion bonded together. Typical passage widths are ~ 1mm.

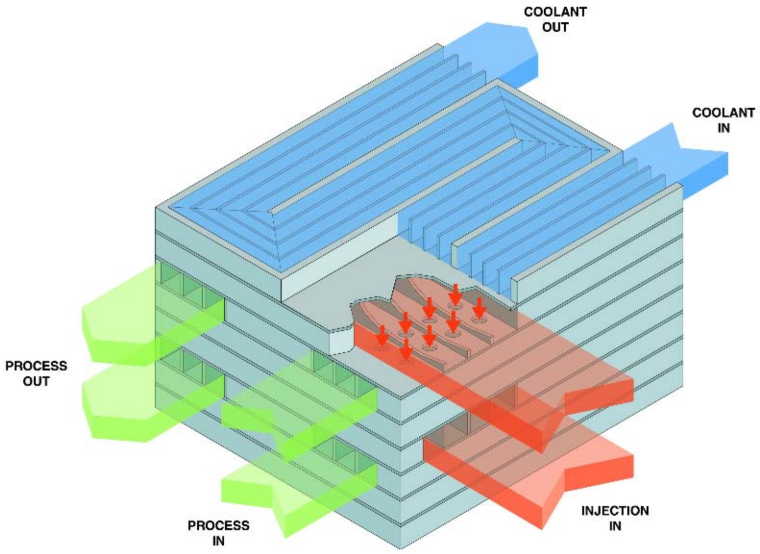

Figure 2 **Marbond Reactor**

Other non-catalytic reactors developed in recent years include the following.

- *FlexReactor* (BHR Group, Jackson & Green, 2004, www.bhrgroup.co.uk/pi). This design is based on static mixer technology, packaged to achieve good heat transfer and a high degree of flexibility. The static mixers ensure excellent mixing and good plug flow behaviour, but the relatively large passage sizes (several mm and above) mean that the area available for heat transfer is limited.
- *Open Plate Reactor* (Alfa Laval Vicarb, Prat et al, 2005). Designed around a 'plate and frame' concept, reactor 'blocks' can be built up in a flexible manner to provide appropriate mixing and heat transfer functionality. The blocks incorporate flow-directing inserts to achieve effective mixing.
- *SMR* (Sulzer, www.sulzerchemtech.com). Perhaps the 'original' HEX Reactor, the SMR is a pipe reactor with static mixer inserts which in fact comprise pipes carrying cooling fluid. Such reactors are used for polymerisation processes (eg polystyrene), but tend to operate at very low flow velocities and long residence times.
- *Helix Reactor* (TNO, Xu, 2001, www.tno.nl). This simple design comprises twin open pipes (one for process, one for cooling), tightly wound together in a spiral. The spiral flow path induces secondary flows in the pipes, which enhances mixing and heat transfer.

- *Corning Microreactor* (Corning, www.corning.com). Although described as a microreactor, under the definition above, this classes as a HEX Reactor, with passage sizes typically of 100's or 1000's µm. The unit appears to be unique in HEX reactor design, in that it is constructed from glass. This makes it particularly suited to reactions with high corrosivity: Corning is targeting the pharmaceutical and fine chemical markets.

Catalytic HEX reactors are generally used for gas phase applications, and comprise narrow passageways, sometimes with internal structures, coated with, or containing, catalyst. A range of such designs are currently being developed, with a particular emphasis on fuels processing and energy (eg gas to liquid, Fischer-Tropsch, fuel cells). Developments include the coupling of exo-and endothermic processes within a reactor. Examples include:

- *Heatric PCR* (Printed Circuit Reactor, Johnston et al, 2001, www.heatric.com). Heatric pioneered compact heat exchanger design, with its Printed Circuit Heat Exchanger technology. In recent years, this has been developed as, particularly, a catalyst-coated reactor.
- *Chart Shimtec* (http://www.chart-ind.com/app_ec_reactortech.cfm). This comprises a range of reactor designs which can be coated or packed with catalyst.
- *Velocys Reactors* (www.velocys.com). These are again similar to the Chart and Heatric designs, with multiple small passageways typically of size 0.1 – 1mm.

1.3 Potency for Process Intensification: possible benefits

(In Table 1 describe the most important documented and expected benefits offered by the technology under consideration, focusing primarily on energy; CO_2 emission and costs, providing quantitative data, wherever possible. Add other benefits, if needed).

Table 1: Documented and expected benefits resulting from technology application

Benefit	**Magnitude**	**Remarks**
Energy reduction	70% in a typical application	Achieved mainly through reduced stirring and recovery of heat.
Capital Cost	Variable, but figures of up to 60% reported	Achieved mainly through reduction in infrastructure costs from reduction in plant size, rather than main plant items
Safety	99% plus reduction in reacting inventory	Hex reactors are particularly well-suited to processes where safety hazards may prevent use of conventional technologies.
Reduced Byproduct	Very application-specific	99% plus reduction in byproduct reported in one application. Optimisation of mixing and removal of heat can drive a process towards the desired, rather than byproduct-forming, reaction.

1.4 Stage of development

As indicated above, a range of fully-developed reactors is already available, in some cases with manufacturing technology capable of relatively large-scale units. Scale up issues are understood well (usually involving 'scale out'). Fully-engineered miniplant (production capacity ~ 100 tonnes per annum) incorporating HEX reactors have been built by BHR Group (UK) and Zeton (NL).

2. Applications

2.1 Existing technology (currently used)

(Describe technology (-ies) that are conventionally used to perform the same or similar operations as the PI-technology under consideration)

Conventional processing technology generally involves batch processing in stirred tanks for the ‘non-catalytic’ HEX reactors. Because of large reacting inventories and high heat production, processes are usually operated semi-batch, with feed rate limited by the cooling capacity of the reactor rather than the inherent kinetics. Catalytic HEX Reactors potentially replace conventional packed bed or packed tube catalytic reactors.

2.2 Known commercial applications

(Is the technology broadly applied on commercial scale? In which process industry sectors is the technology most often applied: large volume chemicals – specialty chemicals & pharma – consumer products – ingredients based on agro feedstocks? What is the estimated number of existing applications? In Table 2 provide the most prominent examples of realized applications and provide their short characteristics)

Table 2. Industrial-scale applications of the Technology (existing and under realization)

Sector	Company - Process/Product name/type	Short characteristic of application	Production capacity/ Plant size	Year of application	Reported effects
Polymers	Linpac – Polystyrene	Sulzer SMR	4000 kg/hr (32000 tpa)	1995	HEX technology enabled 50% increase in capacity
Speciality Chems	Dow Corning – Hydrosilylation reaction	Marbond HEX reactor	100 tpa (equivalent)	1999	Byproduct reduced by 99%
Pharma	Various	Corning Microreactor	50 tpa equivalent	2007	Flexible miniplant, built by Zeton
Biofuels	BHR Biofuels	FlexReactor	500 tonnes per day	2007	Reaction time reduced from ~ 1 hour to < 1 min

2.3 Known demonstration projects

(Are there any demonstration projects known related to the technology under consideration? In which process industry sectors are those projects carried out: large volume chemicals – specialty chemicals & pharma – consumer products – ingredients based on agro feedstocks? In Table 3 provide the short characteristics of those projects.)

Table 3. Demonstration projects related to the technology (existing and under realization)

Sector	Who is carrying out the project	Short characteristic of application investigated, including product name/type	Aimed year of application	Reported effects
Speciality /Fine Chems	BHR Group	OSPRI (on site process intensification), to demonstrate HEX Reactors on 4 processes	Design study in 2001; plant not yet realised	52 – 75% reduction in energy 72 – 96% reduction in plant footprint 98.6 – 99.6% reduction in reacting inventory
Fine Chems	EPSRC Projecct Reference GR/S15327/01. Cardiff University, Johnson Matthey plc	Parallel Processing for the Scale Out of Fine Chemical Catalysis		Results are awaiting publication.
Fuels	"Hydrofueler" University of Warwick Manufacturing Group *et al*	Reforming natural gas to hydrogen in a compact reformer		Full report awaiting publication. 10-fold higher performance than anticipated. 5000m^3/day of H_2 can be produced in a reactor less than 1m^3

2.4 Potential applications discussed in literature

(Provide a short review, including, wherever possible, the types/examples of products that can be manufactured with this technology)

The relatively high flow rates required to operate even the smallest practical HEX Reactor means that, whilst there are many papers discussing potential applications and presenting results with test reactions, there are few documented results from actual appplications. Some examples do exist, though:

Non-catalytic HEX Reactors

- Hydrosilylation and peroxide oxidation (Green et al, 2001)
- Grignard hydrolysis
- Oxidation & reduction reactions
- Hydroformylation

Catalytic HEX Reactors

- Steam Methane Reforming (hydrogen production)
- Ethylene
- Fisher Tropsch (Gas-to-Liquid)

Further potential applications are discussed in Section 5.2.

3. What are the development and application issues?

3.1 Technology development issues

(In Table 4 list and characterize the essential development issues, both technical and non-technical, of the technology under consideration. Pay also attention to "boundary" issues, such as instrumentation and control equipment, models, etc.) Also, provide your opinion on how and by whom these issues should be addressed)

Table 4. Technology development issues

Issue	**Description**	**How and by whom should be addressed?**
Materials of Construction	HEX Reactors are suited to highly energetic reactions, which often involve highly corrosive materials. This places limitations on the applications that some HEX reactor technologies can be used in.	Manufacturers need to develop technologies for making their reactors in corrosion-resistant materials (eg Hastelloy)
Scale up/down	Continuous flow reactor technologies such as HEX reactors require a minimum scale (and flow rate) to achieve turbulent flow and hence rapid mixing. This means that, generally, several litres of reactant are required for a test, which may be prohibitive for high value products such as pharmaceuticals. For liquid-phase systems, a 'dead zone' exists for passageways between a few 10's of micron and ~ 1mm where rapid mixing cannot be achieved, because diffusion timescales are long, but the Reynolds number of the flow is too low to achieve good turbulent mixing.	Improved protocols for relating small-scale, intense batch and continuous (eg microreactor) systems to HEX operation; requires collaboration between HEX and microreactor manufacturers, academia and research institutes.
System integration	Whilst a number of HEX Reactor designs are available, equivalent technology for up- and downstream processing is not.	Universities to focus on concepts for intensive separation, crystallization, solids incorporation etc. Collaborative projects to investigate system integration.

3.2 Challenges in developing processes based on the technology

(In Table 5 list and characterize the essential challenges, both technical and non-technical, in developing commercial processes based on the technology under consideration. Also, provide your opinion on how and by whom these challenges should be addressed)

Table 5. Challenges in developing processes based on the technology

Challenge	**Description**	**How and by whom should the challenge be addressed?**
Proving the concept	Carrying out 'proof of concept' testing requires expensive equipment and significant amounts of material.	EU and industry to fund demonstration projects and open-access 'proof of concept' facilities.
Case histories	Lack of publicly-available case histories demonstrating the case for HEX Reactors.	Establish demonstration project(s).
Lack of process knowledge	Lack of data on kinetics/thermodynamics of candidate reactions.	Develop laboratory equipment/protocols to deduce sufficient

		information of kinetics etc without recourse to full kinetic analysis.
Scale up/down	See Section 3.1	
Catalysis	Development of heterogeneous catalysts (liquid or gas phase reactors) in a form suitable for coating surfaces of HEX Reactors, with sufficiently high levels of activity to exploit their short residence time/high heat transfer.	Catalyst manufacturers, HEX reactor developers and universities to collaborate toegether to develop catalysts and coating techniques

4. Where can information be found?

4.1 Key publications

(Provide the list of key publications in Table 6)

Table 6. Key publications on the technology

Publication	**Publication type (research paper/review/ book/report)**	**Remarks**
Stankiewicz, A & Moulijn, J (eds), "Re-engineering the Chemical Processing Plant", Marcel Dekker, 2004, New York	Book	Good general PI reference, with information on HEX Reactors in Chapters 4, 7 & 10
Caze, P "Engineered Reactors for Chemicals Industrial Production", presented at PIN Meeting, April 2007 (www.pinetwork.org)	Presentation	Description of Corning 'Microreactor'
Edge, A M, Pearce, I and Phillips C H "Compact heat exchangers as chemical reactors for process intensification (PI)", 2nd International Conference on Process Intensification for the Chemical Industry, Antwerp, 1997	Research Paper	Paper describing early work on HEX Reactors
Enache, Thiam, Dumas, Ellwood, Hutchings, Taylor, Stitt. "Intensification of the solvent-free catalytic hydroformylation of cyclododecatriene: Comparison of a stirred batch reactor and a heat-exchange reactor." Catalysis Today 128 (2007) 18-25	Research Paper	10-fold increase in reaction rate, no mass transfer limitation and improved selectivity compared to a stirred batch reactor
Green, A et al "Combined Chemical Reactor/Heat Exchangers: Validation and Application in Industrial Processes". 4th International Conference on Process Intensification for the Chemical Industry, Brugge, 10-12 September 2001.	Research Paper	Two industrial reactions operated. 97% and 99.9% reduction in reaction time, with a 99% reduction in impurity levels for second reaction.
Hugill, J A, "HEX Reactor Applications in the Netherlands", ECN Report ECN-C-03-015, 2003	Report (available from ECN website)	Non-confidential summary of a study of potential HEX Reactor applications
Jackson, R & Green A "A Small, Flexible, Continuous Pilot Rig - The FlexPlant", Paper presented at Batch to Continuous Conference, London, November 2004	Research Paper	Describes operation of FlexReactor on 3 processes
Johnston et al, "Application of Printed Circuit	Research Paper	Summary of the potential

Heat Exchanger Technology within Heterogeneous Catalytic Reactors", presented at AIChE Annual Meeting, November 2001		for diffusion-bonded heat exchangers as catalytic HEX reactors
Moreau, J "Energy Saving Heat Exchanger Reactor at DSM", NPT Procestechnologie, 3, May – June 2003	Research Paper	Qualitative description of the application of a simple static mixer-based HEX reactor to two processes (un-named) at DSM
Phillips, C H et al "Intensification of Batch Chemical Processes by using Integrated Chemical Reactor-Heat Exchangers" Applied Thermal Engineering, Vol 17 Nos 8 – 10, pp 809 – 824, 1997	Research Paper	Summary of the results of an EU-supported project on HEX Reactors
Prat, L et al "Performance evaluation of a new concept 'Open Plate Reactor' in non-conventional experimental domain" 6th International Conference on Process Intensification for the Chemical Industry, Delft, September 2005	Research Paper	Paper describing performance characteristics of Alfa Laval OPR and performance with test reactions
Xu, Z "Converting Batch Production into Continuous Processes; Development of the Helix Reactor," 4th International Conference on Process Intensification for the Chemical Industry, Brugge, 10-12 September 2001.	Research Paper	Description of the Helix Reactor, with case study of the synthesis of glycidyl ether.

4.2 Relevant patents and patent holders

(Provide the list of relevant patents in Table 7. Under "remarks" provide, where applicable, the names/types of products targeted by the given patent.)

Table 7. Relevant patents-

Patent	**Patent holder**	**Remarks, including names/types of products targeted by the patent**
"Spiral Heat Exchanger", International patent WO9207226	TNO	Patent for spiral heat exchanger, subsequently used as a HEX Reactor
"Method and Apparatus for Continuous Production of Polymers, European Patent EP0752268	BASF	Novel polymerization reactor, comprising two heat-exchange bundles connected by static mixers – particularly suited to co-polymerization
"Maximum Reaction Rate Converter System for Exothermic Reactions" USA Patent US2006099131	Kellogg Brown & Root	Catalytic HEX Reactor for Ammonia production, with different temperature zones to optimize conversion
"Reactor and Process for Carrying out Exothermic or Endothermic Reactions", World Patent WO2006045457	Haldor Topsoe	'Reversed' Shell and Tube catalytic heat exchanger reactor, with the shell packed with catalyst and heat exchange fluid passing through the tubes, including part-tubes at the shell outer wall.
"Apparatus with a Heat Exchanger Coated with Catalyst", European Patent EP1825887	SABIC	Catalyst-coated heat exchanger, specifically for conversion of alkylene oxide to alkylene glycol. Includes Sulzer SMR as an example.

“Heat Exchanger and Chemical Reactor”, World Patent WO0242704	Chart Industries	Patent covering the Marbond Reactor
“Flow Directing Insert for a Reactor Chamber and a Reactor”, US Patent US2006159600	Alfa Laval	Patent describing the form of the Alfa Laval Open Plate Reactor
“Reactor Apparatus and Mixing Inlet and Methods”, World Patent WO02072254	BHR Group	Patent covering the FlexReactor
151 Patents listed	Velocys	Patents on equipment and processes
“Method and Microfluidic Reactor for Photocatalysis”, European Patent EP1415707	Corning	Use of glass reactor for photocatalysis – no general patents found for the Corning Microreactor
“Multiple Reactor Chemical Production System”, World Patent WO2007096699	Heatric	Multiple stream catalytic HEX reactor, particularly aimed at equilibrium reactions (eg methanol synthesis)

4.3 Institutes/companies working on the technology

(Provide the list of most important research centers and companies in Table 8)

Table 8. Institutes and companies working on the technology

Institute/Company	**Country**	**Remarks**
Alfa Laval	Sweden	Has developed the Open Plate Reactor (OPR) Concept and is working with a number of organisations to exploit the technology
BHR Group Limited	United Kingdom	Has carried out characterisation work on a range of HEX Reactors and has developed its own technology (FlexReactor)
Chart Industries	UK & USA	Has developed a range of catalytic and non-catalytic HEX Reactors (‘Shimtec’ & ‘Fintec’)
Corning	France	Has developed glass ‘microreactors’ with passage sizes up to a few mm.
ECN (Energy Research Centre of the Netherlands)	Netherlands	Has undertaken research into potential applications of HEX Reactors in the Dutch Chemical Industry
Heatric	UK	Has developed catalytic HEX reactors based on its diffusion-bonded compact heat exchanger technology
Laboratoire de Génie Chimique, Toulouse	France	Has worked with Alfa Laval in characterising the OPR.
TNO	Netherlands	Has developed the Helix reactor
Velocys	USA	Has developed a range of ‘microreactors’, many with passage sizes up to a few mm. Main focus is on gas-phase

		applications

5. Stakeholders

5.1 Suppliers and developers

(Provide the list of key suppliers/developers in Table 9)

Table 9. Supplier and developers

Institute/Company	Country	Remarks
As per Table 8		

5.2 End users

(Describe the existing and potential end-users, other than those already listed in Table 2)

Beyond those listed in Table 2, the author is not aware of other end-users currently using the technology. Potential End Users and applications fall into the following categories.

Non-catalytic HEX Reactors

Potential reactions (features):

- Single (liquid) phase, immiscible liquids or gas-liquid
- Rapid reactions (inherent reaction times less than a few minutes, and ideally seconds or less)
- Highly exothermic (or endothermic) reactions
- Competitive reactions
- No catalyst, homogeneous catalyst or slurry catalyst (for some designs)
- Examples: oxidation, nitration, halogenation, polymerisation

Potential End Users:

- Active Pharmaceutical Ingredient (API) manufacture – particularly for (relatively) large scale products (> 10 tpa)
- Fine Chemical Manufacturers
- Specialty Chemicals

Catalytic HEX Reactors

Potential reactions (features)

- Gas phase reactions
- Highly exothermic, endothermic or combinations of both
- Examples: Steam reforming, catalytic combustion, Fischer Tropsch, gas-phase oxidations

Potential End Users

- Petrochemicals
- Bulk Chemicals
- Hydrogen manufacturers

6. Expert's brief final judgment on the technology

(maximum 5 sentences)

HEX Reactors provide a valuable weapon in the PI armoury, particularly for rapid, highly exothermic reactions. A range of different technologies already exist, and are scalable from tonnes per annum of product up to 10,000's tonnes per annum or more. The major barrier against more widespread implementation is the lack of publicly available, convincing case histories. Improved collaboration between HEX Reactor and Microreactor manufacturers to develop improved understanding of how to select the appropriate solution and scale between the two technologies would enhance take-up of both.