



Appendix 1

PI TECHNOLOGIES DESCRIPTION AND REVIEW

INTRODUCTION

The state-of-the-art of PI worldwide has been identified through questionnaires to 70 experts, identifying patents (approximately 1,000), and a complete search for scientific publications including translation of Chinese and Japanese work. 72 PI technologies have been identified, of which 46 technologies have been described by globally-acknowledged experts in full “technology reports”. A description of these 72 technologies, and a review of the 46 reports by three Dutch experts can be found in this Appendix 1. Details are kept in a dedicated database which can be accessed through TU Delft and ECN.

The 72 PI technologies are briefly described and illustrated here. For the 46 technologies for which a full “technology report” is available, a review has been prepared by the Review Panel, consisting of 3 Dutch process technology experts, Jacob Moulijn, Fons Meijs and Ben Stouthamer. The technologies that have not been reviewed by no means have a lower potential than those reviewed. Due to lack of resources and time constraints, it was not possible to finalize technology reports for all 72 technologies.

The review panel has considered the potential benefits (energy efficiency, CO₂ emission, etc.) of each technology only within the boundary of the process step in which it can be potentially implemented; benefits elsewhere in the process chain lie outside the scope of consideration. It should also be stressed that for specific (niche) applications, the evaluation can be different.

List of PI technologies included

Class		Code	Technology/Subtechnology
Structured devices	Non-reactive	1.1.1	Advanced plate-type heat exchangers
		1.1.2	Advanced shell-and-tube heat exchangers
		1.1.3	Structured internals for mass transfer operations
		1.1.4	Static mixers
	Reactive	1.2.1	Structured catalyst-based reactors
		1.2.1.1	Catalytic foam reactors
		1.2.1.2	Monolith reactors
		1.2.1.3	Millisecond (gauze) reactors
		1.2.1.4	Other catalytic structures (e.g. KATAPAK)
		1.2.2	Microreactors (including Micromixers)
		1.2.3.	Membrane reactors (non-selective)
		1.2.4	Static mixers-reactors

Class		Code	Technology/Subtechnology	
Hybrid	Non-reactive	2.1.1	Adsorptive distillation	
		2.1.2	Extractive crystallization	
		2.1.3	Extractive distillation	
		2.1.4	Heat-integrated distillation	
		2.1.5	Membrane hybrid systems	
		2.1.5.1.	Membrane absorption/stripping	
		2.1.5.2.	Membrane adsorption	
		2.1.5.3	Membrane crystallization	
		2.1.5.4	Membrane distillation	
		2.1.5.5	Distillation - pervaporation systems	
		2.1.5.6	Membrane extraction	
		Reactive	2.2.1	HEX Reactors
			2.2.2	Membrane reactors (selective, catalytic)
			2.2.3	Reactive adsorption
	2.2.3.1		Simulated moving bed reactors	
	2.2.3.2		Rotating annulus chromatographic reactor	
	2.2.3.3		Gas-solid-solid trickle flow reactor	
	2.2.4		Reactive condensation	
	2.2.5		Reactive extraction	
	2.2.6		Reactive absorption	
	2.2.7		Reactive crystallization/precipitation	
	2.2.8.		Reactive distillation	
	2.2.8.1		Reactive distillation	
	2.2.8.2		Pervaporation-assisted reactive distillation	
	2.2.9		Other reactive	
	2.2.9.1		Reactive comminution	
	2.2.9.2	Reactive extrusion		

Class		Code	Technology/Subtechnology		
Energy transfer	Rotating	3.1.1	Centrifugal adsorption technology		
		3.1.2	Centrifugal Liquid-Liquid Contactors		
		3.1.3	Rotating Packed Beds (incl. Rotating Foam Reactor)		
		3.1.4	Rotor-stator mixers		
		3.1.5	Spinning Disc Reactor		
		3.1.6	Viscous heating devices		
	Impulse	3.2.1	Ejector (Venturi) -based reactors		
		3.2.2	Hydrodynamic cavitation reactors		
		3.2.3	Impinging streams reactor		
		3.2.4	Pulsed compression reactor		
		3.2.5	Sonochemical reactors		
		3.2.6	Ultrasound-enhanced crystallization		
		3.2.7	Ultrasound-enhanced phase dispersion / mass transfer		
		3.2.8	Supersonic shockwave for phase dispersion		
		3.2.8.1	Supersonic gas-liquid reactors		
		3.2.8.2	Supersonic gas-solid reactors		
	Electromagnetic	3.3.1	Electric field-enhanced operations		
		3.3.1.1	Extraction & dispersion		
		3.3.1.2	Heat transfer		
		3.3.1.3	Mixing		
		3.3.1.4	Other		
		3.3.2	Induction/ohmic heating		
		3.3.3	Microwave-enhanced operations		
		3.3.3.1	Drying		
		3.3.3.2	(Pre)heating		
		3.3.3.3	Separations		
		3.3.3.4.1	Reactions: Non-catalytic or homogeneously catalyzed		
		3.3.3.4.2	Reactions: Heterogeneous catalytic		
		3.3.3.4.3	Reactions: Polymerization and polymer processing		
		3.3.4	Photochemical reactors		
		3.3.5	Plasma (GlidArc) reactors		
		Dynamic	Dynamic	4.1.1	Oscillatory Baffled Reactors
				4.1.2	Reverse flow reactor operation
4.1.3	Pulsing operation of multiphase reactors				
4.1.4	Pulse combustion drying				
Other	Supercritical	5.1.1	Supercritical reactions		
		5.1.2	Supercritical separations		
		5.1.3	Cryogenic separations		

CODE 1.1.1

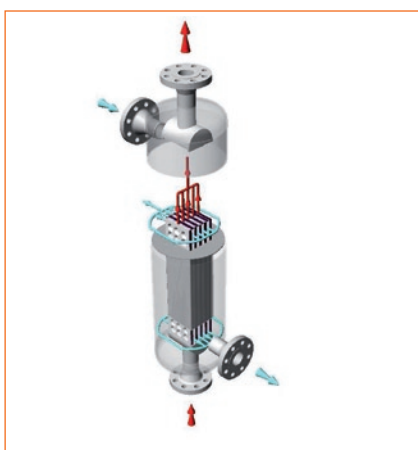
TECHNOLOGY ADVANCED PLATE-TYPE HEAT EXCHANGERS

Sub-Technologies covered

- plate
- plate-fin
- plate-and-shell
- flat tube-and-fin
- spiral
- microchannel
- multistream heat exchangers



Plate heat exchanger
(Courtesy of Alfa Laval)



Platular® heat exchanger
(Courtesy of Barriquand Technologies Termiques)

Description/Basic Features

Plate heat exchanger consists of a pack of corrugated metal plates with portholes for the passage of two fluids between which heat transfer will take place. The plates are fitted with gaskets, which seals the channels and directs the fluids into alternate channels. Basic advantages of the plate heat exchangers are compactness, large heat transfer areas and high heat transfer coefficients.

Plate-fin exchanger consists of stacked corrugated sheets (fins) separated by flat plates with openings for the inlet and outlet of fluids. Flow direction of each of the fluids relative to one another may be counter-current, co-current or cross-flow.

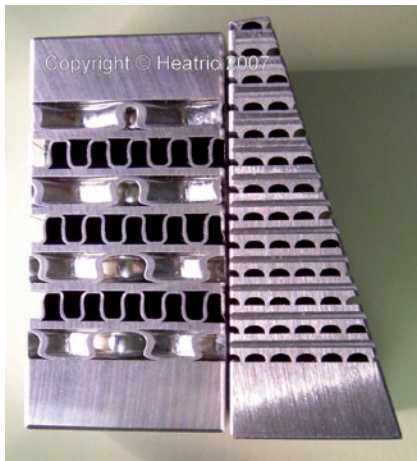
In *plate-and-shell heat exchangers* bundle of plates are inserted in a shell. On the plate side, the fluid flows inside corrugated or embossed channels; on the shell side, the flow is similar to shell and tube heat exchangers and baffles can be inserted.

Flat tube-and-plate heat exchangers have been developed in the automobile industry for engine cooling and air conditioning. Generally on the air side the surface is finned and on the other side the fluid flows in small diameter channels.



Spiral heat exchanger
(Courtesy of Alfa Laval)

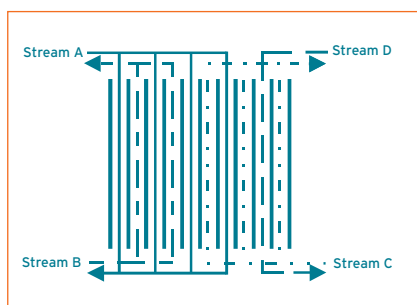
In a *spiral heat exchanger* the hot fluid enters at the centre of the unit and flows from the inside outward. The cold fluid enters at the periphery and flows towards the centre. Passages can be either smooth or corrugated general flow configuration can be cross flow (single or multipass) or counter flow, depending on the configuration of the inlet and outlet distribution boxes.



Microchannel heat exchanger
(Courtesy of Heatric)

The channels in the *micro heat exchanger* plates have sizes around or lower than 1 mm and are fabricated via silicon micromachining, deep x-ray lithography or non-lithographic micromachining. The plates are stacked forming 'sandwich' structures, as in the "large" plate exchangers. All flow configurations (co-, counter-current and cross flow) are possible.

Matrix heat exchanger consists of a stack of perforated plates made of high thermal conductivity material such as copper or aluminium, alternating with spacers of low thermal conductivity such as plastic or stainless steel. They are used for cryogenic and low temperature applications and for fuels cells, and are suitable for a large range of operating conditions.



Scheme of a multistream heat exchanger

In *multi-stream heat exchangers* three or more streams are thermally processed in a single unit. These exchangers have been used in cryogenic plants and in dairy industry. In chemical industries they have been rarely applied so far. The multi-stream configuration can easily be achieved in the conventional plate heat exchangers, simply by installation of an intermediate plate on which the ports have not been cut out.

Evaluation	
Potential for energy savings	Medium
Potential for eco impact CO ₂	Medium
Potential to improve cost competitiveness	High
Ripeness of application in X years	<5
Ripeness of related technology fields	High
Likelihood of overcoming barriers	High
Potential for innovative high quality products	Low
Character of required R&D	Applied

Review (Plate Heat Exchangers)

Plate type heat exchangers are well established in industry. Mechanical refinements continue to be made, aimed at further performance improvement. The advantage of such plate heat exchangers over shell and tube heat exchangers are high heat transfer and hence compact unit size. The cost savings claimed by the author of 1000% needs further

clarification. Unfortunately, limitations for the application of (advanced) plate heat exchangers are not discussed. The equipment is readily available from equipment suppliers.

CODE **1.1.2**TECHNOLOGY **ADVANCED SHELL-AND-TUBE HEAT EXCHANGERS****Sub-technologies covered**

- HELIXCHANGER®
- Rod Baffle
- EM Baffle
- Low-fin tube
- Twisted tube
- Tube insert
- Static mixers-heat exchangers

Description/Basic Features

In Advanced Shell-and-Tube Heat Exchangers the intensification effects are achieved by:

- replacing the conventional baffles by quadrant shaped baffles (HELIXCHANGER®), rods (Rod Baffle) or slit sheets of expanded metal (EM Baffle)
- modifying the tube form by finning or twisting
- placing elements inside the tube to increase flow turbulency or to decrease fouling



Kenics® static mixer heat exchanger
(Courtesy of Chemineer)

Static mixers-heat exchangers (SMHE) belong to the last category. Here, the mixing elements are used to increase the radial dispersion resulting in higher heat transfer coefficients. The flow in pipes of SMHE has the plug-flow character. Due to presence of the static mixers a finely dispersed, two-phase gas-liquid or liquid-liquid flow can be realised. Therefore, SMHEs can be easily used for two-phase applications. The disadvantage of SMHEs is their sensitivity to fouling and to clogging by solids present in the processed stream.

Evaluation	
Potential for energy savings	Medium
Potential for eco impact CO ₂	Medium
Potential to improve cost competitiveness	Medium
Ripeness of application in X years	<5
Ripeness of related technology fields	High
Likelihood of overcoming barriers	High
Potential for innovative high quality products	Low
Character of required R&D	Applied

Review

Shell and tube heat exchangers are commonplace in industry. Depending on the application the performance of such heat exchangers can be improved by modifications on the shell or on the tube side of the exchangers, resulting in improved heat transfer, less fouling, lower pressure drop, less vibration, etc. Energy and capital savings can be

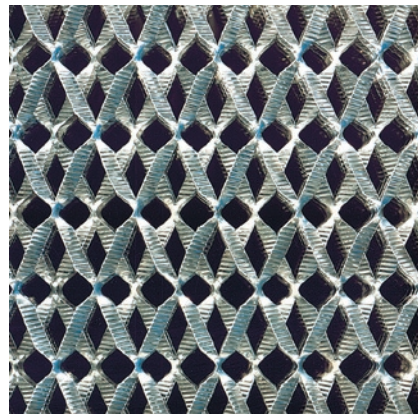
substantial. However, some of the savings claimed by the author (e.g., 200% cost saving and 100% energy saving) need further clarification. The development of such systems is undertaken by both the process industry and by equipment suppliers. The penetration of advanced exchangers is speeding up, the main hurdle being customer confidence.

CODE **1.1.3**TECHNOLOGY **STRUCTURED INTERNALS FOR MASS TRANSFER****Description/Basic Features**

Structured internals are used in various mass-transfer operations, including distillation, absorption and extraction. They provide high interfacial mass transfer areas and good phase dispersion resulting in high NTUs, at low pressure loss. Many various designs of the structured packing are known and applied in the mass transfer operations. Most of them are vertical sheets of corrugated thin gauze / metal / ceramic / glass/ plastic with the angle of the corrugations reversed in adjacent sheets to form a very open honeycomb structure with inclined flow channels and a relatively high surface area. Those internals are applicable for liquid/liquid mixing, generally in co current flow and for liquid/gas mass transfer in counter current film flow. If liquid and vapour phases are involved, the liquid descends in the form of films distributed over the packing surface, and the vapours rise through the spaces between the packing particles.



Mellapak™ structured packing
(Courtesy of Sulzer Chemtech)



Close-up view of Rombopak® structured packing
(Courtesy of Kühni AG)

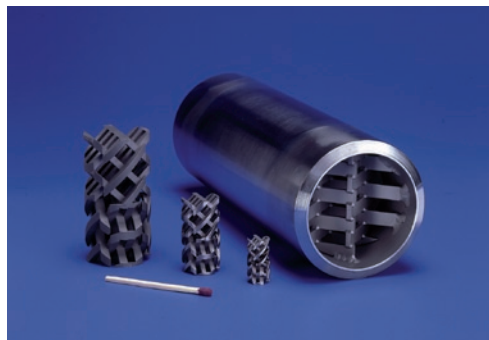
CODE 1.1.4

TECHNOLOGY **STATIC MIXERS****Description/Basic Features**

Static (motionless) mixers are pipe inserts which generate radial mixing (i.e. across the pipe) and (for multiphase systems) interfacial surface area (e.g. to produce fine bubbles or droplets). The energy for mixing is extracted from the mean flow and as such an extra pumping duty is incurred. The number of elements required for any application is dependent on the difficulty of the mixing duty, more elements being necessary for difficult tasks. Static mixers are particularly useful for the continuous processing of chemicals but are also incorporated as part of a batch system in pump around loops. Their main limitation is sensitivity to clogging by e.g. slurry particles.



Kenics® static mixer
(Courtesy of Chemineer)



SMX™ melt homogenizer
(Courtesy of Sulzer Chemtech)

Evaluation	
Potential for energy savings	Medium
Potential for eco impact CO ₂	Medium
Potential to improve cost competitiveness	Medium
Ripeness of application in X years	<5
Ripeness of related technology fields	Medium
Likelihood of overcoming barriers	Medium
Potential for innovative high quality products	Low
Character of required R&D	Applied

Review

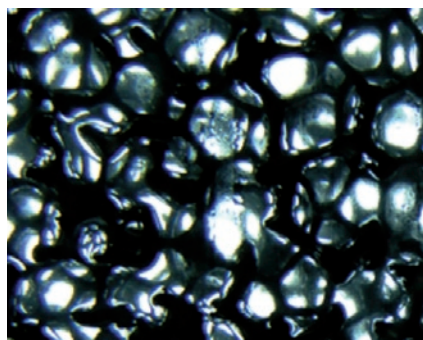
(See also 1.2.1.4 and 1.2.4)

Static mixers are by now well established in the processing industry for liquid/liquid and gas/liquid mixing. Compared to alternative mixing systems they have a very high-energy dissipation rate, resulting in very compact, energy efficient units. The paper draws attention to the fact that the

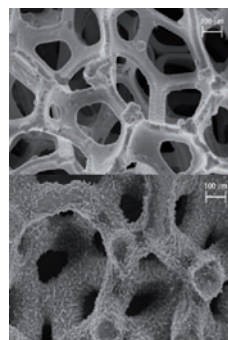
area of solid/solid mixing over static mixers is still under-explored and may offer attractive opportunities, provided the problem of mixer clogging is resolved. No definition of the advantages over alternatives, let alone proof of principle for solid/solid static mixers have been provided.

CODE **1.2.1**TECHNOLOGY **STRUCTURED CATALYST-BASED REACTORS**SUBCODE **1.2.1.1**SUB-TECHNOLOGY **CATALYTIC FOAM REACTORS****Description/Basic Features**

Solid foam catalytic reactors use a solid foam structure (e.g. sponge, but not flexible) as the support for depositing catalyst for the purpose of reacting gas and / or liquid phase reactants. The solid foams may be seen as the inverse of a packed bed of non-porous particles. These materials combine high voidage suitable for low pressure drop application and high geometric surface area (for generation of mass transfer area) and high BET surface area (for depositing the catalyst).



Water-air flow over catalytic foam (Courtesy of Eindhoven University of Technology)



Catalytic foam (Courtesy of University of Twente)

Evaluation	
Potential for energy savings	Medium
Potential for eco impact CO ₂	Medium
Potential to improve cost competitiveness	Medium
Ripeness of application in X years	5-10
Ripeness of related technology fields	High
Likelihood of overcoming barriers	High
Potential for innovative high quality products	Medium
Character of required R&D	Fundamental

Review

Heterogeneously catalysed multiphase reactions as carried out in fixed bed operations require a solid support to enhance mass transfer and a high surface area for deposition of the catalytic material. In the majority of applications, the reactor is filled with high surface area catalyst particles. An alternative approach is to use solid foam

structures as catalyst support and as a means for enhanced mass transfer. The advantage of this approach is the potentially lower pressure drop (and hence energy consumption) over such reactors. In case metallic foams are used, also the heat conductivity is enhanced leading to more equal temperature profile. The disadvantage however is the inherently higher costs of the foam-based catalyst and the relatively low surface area for deposition of the catalytic material. The technology is still in an early stage of development, receiving increased attention mainly in academia. Advantages of this technology over established alternatives are not obvious and needs demonstration; niche applications however may well be possible.

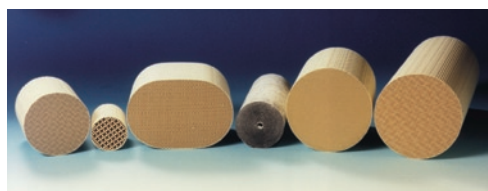
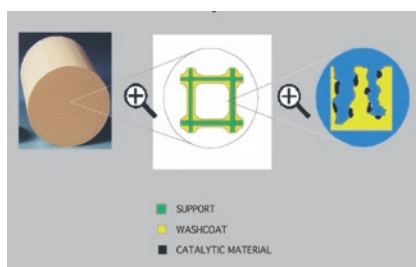
CODE 1.2.1

TECHNOLOGY **STRUCTURED CATALYST-BASED REACTORS**

SUBCODE 1.2.1.2

SUB-TECHNOLOGY **MONOLITHIC REACTORS****Description/Basic Features**

Monolithic catalysts are made of ceramic materials or corrugated metal sheets and consist of a multitude of narrow parallel channels. The walls of the channels are usually covered with the so-called “washcoat” in which nanoparticles of catalyst are deposited (see Figure below). Monoliths are characterized by high specific geometric areas, low mass transfer resistances (due to the thin washcoat) and very low pressure loss (1-2 orders of magnitude lower than in the trickle-bed). Limitation in monoliths is poor radial heat transfer, thus poor heat removal, due to the absence of the radial mixing. Monolithic catalysts are mostly used for gas-phase catalytic processes in environmental applications (e.g. afterburners in cars, de-NO_x-ing plants). First commercial-scale applications in gas-liquid chemical processes have also been realized.



Various types of monolithic catalysts (Courtesy of Delft University of Technology)

Evaluation	
Potential for energy savings	Medium
Potential for eco impact CO ₂	Medium
Potential to improve cost competitiveness	Medium
Ripeness of application in X years	5-10
Ripeness of related technology fields	High
Likelihood of overcoming barriers	High
Potential for innovative high quality products	High
Character of required R&D	Applied

Review

Heterogeneously catalysed reactions are often carried out in fixed bed reactors filled with catalyst particles. An alternative approach is to deposit the catalytic material on a monolithic carrier. The advantage being: lower pressure drop (hence potentially lower energy consumption), narrower residence time distribution (potentially better

selectivity) and high mass-transfer (hence potentially smaller reactor volume). The technology is widely used in gas-phase cleaning of off-gas over catalytic reactors, including car exhaust cleaning. Its wider application requires cost reduction of the monolithic material and particularly the development of monolithic material which allows for a high catalyst loading.

CODE **1.2.1**TECHNOLOGY **STRUCTURED CATALYST-BASED REACTORS**SUBCODE **1.2.1.3**SUB-TECHNOLOGY **MILLISECOND (GAUZE) REACTORS****Description/Basic Features**

Gauze catalysts are well known from the manufacturing of nitric acid, where metal Pt or Rh/Pt are used in the ammonia oxidation reactors. More recently, gauze catalysts have been proposed to carry out some catalytic reactions in very high temperatures with extremely short contacting times.

Evaluation	
Potential for energy savings	Low
Potential for eco impact CO ₂	Low
Potential to improve cost competitiveness	Medium
Ripeness of application in X years	5-10
Ripeness of related technology fields	Medium
Likelihood of overcoming barriers	Medium
Potential for innovative high quality products	Low
Character of required R&D	Combination

Review

The application of millisecond catalytic reactors requires very high reaction rates; an obvious way of achieving this is highly exothermic reactions and that is the industrial area where such reactors are applied (HCN production, NO from NH₃ and methanol to formaldehyde). Recently, short contact time reactors based on partial oxidation of the

feedstock are, both in Industry and in Academia, being investigated for the manufacture of e.g. syn gas, H₂ and olefins.

Whilst the advantages for such applications are clear (high reaction rate and hence small reactors and potentially small-scale use for dispersed application), substantial hurdles still need to be taken (e.g. catalyst stability, product selectivity and overall heat integration). The potential for overall energy saving seems to be limited.

CODE **1.2.1**TECHNOLOGY **STRUCTURED CATALYST-BASED REACTORS**SUBCODE **1.2.1.4**SUB-TECHNOLOGY **STRUCTURES IN ARRAYS AND ARRANGED BEDS OF
CONVENTIONAL CATALYST PARTICLES****Description/Basic Features**

The Arrays of Structured Elements allow and/or force the twisty flow of reactants with a significant component that is perpendicular to the dominant direction of flow of reactants through the reaction zone. The elements are covered with a catalytic species directly or in a layer that is deposited on the element surface. The Arranged Beds of Conventional Catalyst are located in a reaction zone in an ordered way. Particles are placed between elements and the gas contacts particles via diffusion or flow through. Sandwich structures dominate in this category of structured reactors. Parallel-passage reactors (PPR), lateral-flow reactors (LFR), and bead-string reactors (B-SR) belong also to this class of reactors.

Evaluation	
Potential for energy savings	Medium
Potential for eco impact CO ₂	Medium
Potential to improve cost competitiveness	Medium
Ripeness of application in X years	5-10
Ripeness of related technology fields	Medium
Likelihood of overcoming barriers	Medium
Potential for innovative high quality products	Low
Character of required R&D	Applied

Review

Conventional catalytic fixed bed reactors are filled with catalyst particles. An inherent feature of such reactors are a rather broad residence time distribution (potentially leading to lower product selectivity) and pressure drop (leading to energy consumption). In structured reactors, the catalyst is contained structured packets (made of metal,

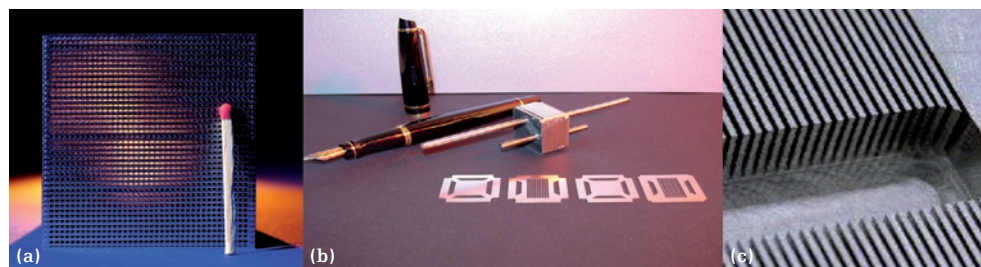
ceramic or fibre). With the right structural configuration narrow residence time distribution and low pressure drop can be achieved. Commercial use of structural reactors is well established in e.g. industrial off-gas clean up and in catalytic reactive distillation). (Multi) tubular reactors loaded with structured catalyst or a sequence of structured catalyst packets and static mixers offer the potential of effective heat removal in highly exothermic reactors, which combined with the low residence time distribution may well result in higher product selectivity. Whilst the technology is entirely feasible, the cost of structural catalyst elements, fast reactor loading and in-situ catalyst regeneration still require attention.

CODE 1.2.2

TECHNOLOGY MICROCHANNEL REACTORS
(INCLUDING MICROMIXERS)**Description/Basic Features**

Microreactors are chemical reactors of extremely small dimensions and usually a sandwich-like structure, consisting of a number of slices (layers) with micromachined channels. Microreactors enable very high heat transfer rates, not achievable in other equipment. This is especially important for isothermal operation of highly exothermic processes or for carrying out kinetic studies. Very low reaction-volume-to-surface-area ratios make microreactors potentially attractive for carrying out reactions involving poisonous or explosive reactants.

Micromixers are devices used for mixing or dispersing two or more components/ phases, usually in conjunction with microreactors. Many various designs and operating principles of micromixers have been developed so far. Usually, the channel diameter in those devices varies between 20-500 μm .



Various types of microchannel reactors (a) – Courtesy of Institut für Mikrotechnik Mainz (b) – Courtesy of Microinnova Engineering GmbH (c) – Courtesy of Velocys Inc.

Evaluation	
Potential for energy savings	Medium
Potential for eco impact CO ₂	Medium
Potential to improve cost competitiveness	High
Ripeness of application in X years	>15
Ripeness of related technology fields	Medium
Likelihood of overcoming barriers	Medium
Potential for innovative high quality products	High
Character of required R&D	Fundamental

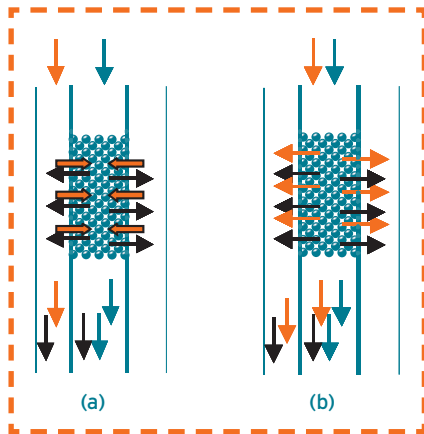
Review

Compared to traditional reactors, in HEX reactors (see 2.2.1) heat dissipation is very much increased by conducting the reaction in a heat exchanger with a large heated or cooled metal wall, compared to the reactor volume. In micro reactors this principle is taken one step further by e.g. passing the reaction fluid through sub-millimetre channels, machined in high

thermally conductive metal blocks which in turn are heated or cooled. The advantage of such systems is excellent reaction temperature control. The disadvantages however are also obvious: high pressure drop, clogging tendency and high unit cost. Applicability of the system may well be restricted to niche applications, in particular in fine chemistry and pharma, and laboratory studies. Unfortunately, the author does not describe why micro reactors should be considered outside these niche applications.

CODE 1.2.3

TECHNOLOGY MEMBRANE REACTORS (NON-SELECTIVE)



Controlled feed (a) and product removal (b) in a non-selective membrane reactor

Description/Basic Features

In a membrane reactors based on non-selective membranes, the membrane is used to provide a structure for the reaction. The reaction can take place either inside the pores of the membrane or on the outside, different flow types can be found, the catalyst can be coated on the membrane itself, but the membrane reactor can also be a packed bed or fluidized bed reactor.

A very large distinction between membrane reactors with selective and non-selective membranes is that it is simple to produce the non-selective

membranes. Although optimizing the micro-structure can be an issue, the challenge in non-selective membrane reactors lies in reactor design and process development.

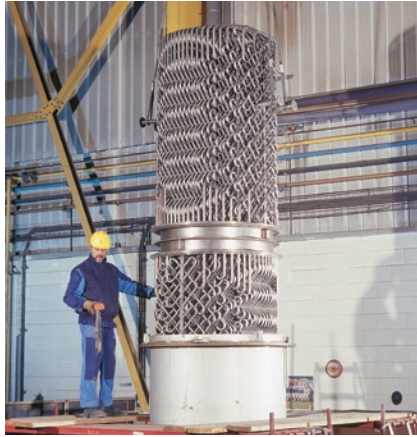
Evaluation	
Potential for energy savings	Medium
Potential for eco impact CO ₂	Low
Potential to improve cost competitiveness	Low
Ripeness of application in X years	>15
Ripeness of related technology fields	Low
Likelihood of overcoming barriers	Low
Potential for innovative high quality products	Medium
Character of required R&D	Fundamental

Review

Two potentially attractive principles for non-selective membrane reactor applications are described:

- controlled dosing of one reactant (e.g. O₂) along the length of the reactor, thus avoiding high local concentrations (risk of explosion, reduction of higher order side-reaction, etc)
- where the membrane provides the support for the catalyst a very effective contact between reactants and catalyst can be achieved, effectively resulting in a short contact time catalytic reactor.

Whilst the principle appears attractive and is the focus of attention in many institutes, the principle is in a very early stage of definition. Challenges that need to be resolved are in the area of membrane system costs and membrane stability; the main issue however is that as yet it lacks definition and demonstration of key technical and economic advantages.

CODE **1.2.4**TECHNOLOGY **TECHNOLOGY: STATIC MIXER REACTORS**

Large-scale SMR™ static mixer reactor
(Courtesy of Sulzer Chemtech)

Evaluation	
Potential for energy savings	High
Potential for eco impact CO ₂	Low
Potential to improve cost competitiveness	Medium
Ripeness of application in X years	5-10
Ripeness of related technology fields	High
Likelihood of overcoming barriers	High
Potential for innovative high quality products	Medium
Character of required R&D	Applied

Description/Basic Features

Static mixer reactors provide a combination of intensive mixing, heat and mass transfer. The mixing and mass transfer is provided by the insertion of mixer elements in the reactor tubes while the heat transfer is realized via the shells or jackets. In the SMR™ reactor shown in the figure, the mixing elements are made of heat transfer coils.

Review

(See also 1.2.1.4 and 1.1.4)

Industry has used static mixers as mixing devices for many years. Increasingly the use of static mixers as reactors gets attention. The first large scale application was polymerisation of styrene; however, they have a much wider potential for application, in particular where relatively

fast reaction rates /short residence times are required. The potential advantages of such systems are:

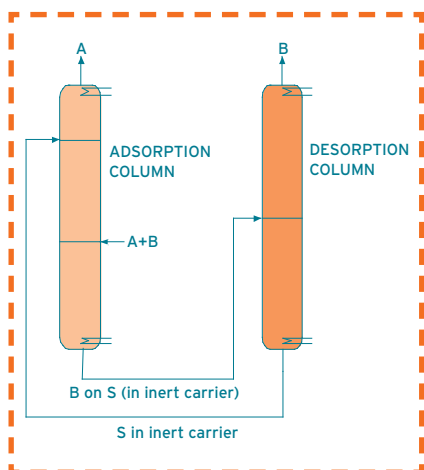
- compactness of unit
- high selectivity due to narrow residence time distribution
- high thermal efficiency

A consequence of the high reaction rate/short residence time and the minimal size of such a static mixer is the required high throughput in experimental facilities which may put them outside the reach of many universities.

The development of non-catalytic static reactors would seem to be rather straightforward; catalytic static reactors still face a major challenge regarding the deposition of the catalytic material and the regeneration of the catalyst.

CODE 2.1.1

TECHNOLOGY ADSORPTIVE DISTILLATION



Simple separation of azeotrope-forming components A and B via adsorptive distillation

Description/Basic Features

Adsorptive distillation is a three-phase mass transfer operation. Here, adsorbent, a fine powder (usually ca. 10 μm), is fluidized and circulated by an inert carrier. Process is carried in two columns: an adsorptive distillation column for increasing separation ability and a distillative desorption column for enhancing the regeneration of the adsorbent. AD increases separation ability and may present an attractive option in the separation of azeotropes or close-boiling components. It can be used for instance for the removal of trace impurities in the manufacturing of fine chemicals (it may allow for switching some fine chemical processes from batch wise to continuous operation).

Evaluation	
Potential for energy savings	Medium
Potential for eco impact CO ₂	Medium
Potential to improve cost competitiveness	Low
Ripeness of application in X years	10-15
Ripeness of related technology fields	Low
Likelihood of overcoming barriers	Low
Potential for innovative high quality products	Medium
Character of required R&D	Fundamental

Review

It is proposed to use a solid adsorptive material (e.g. ion exchange resin, molecular sieve etc) to increase the relative volatility of components to be separated via distillation. In the proposed suspension adsorptive distillation, the setup very much resembles that of extractive distillation with the solid adsorptive material as extractant.

Whilst the principle of this approach seems quite feasible, it must be realised that this technology is still in a very early stage of definition with no demonstration of technical feasibility or of advantage over existing alternatives.

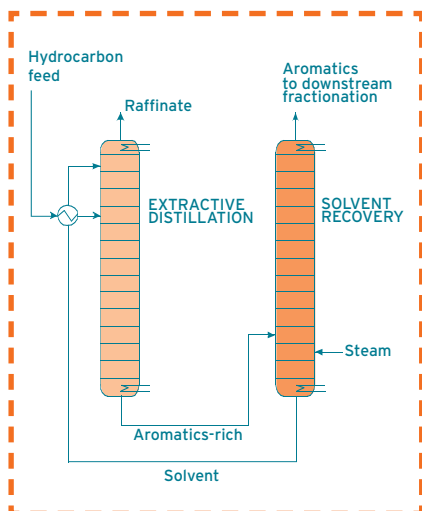
Technical hurdles still to be resolved are e.g. the stable circulation of the solid adsorbent. The attention is still very much in academia. Fixed bed adsorptive distillation seems to be thermodynamically questionable.

CODE **2.1.2**TECHNOLOGY **EXTRACTIVE CRYSTALLIZATION****Description/Basic Features**

In extractive crystallization (non-adductive) the driving force for the separation process is created by altering the solid – liquid phase relationships via the addition of a third component (usually liquid solvent) to the system. The solvent is chosen in such a way that it binds strongly at crystallization temperature but separates easily at another temperature, where it is usually regenerated via distillation. Examples of such defined extractive distillation include separation of m- and p-cresols using acetic acid as the solvent, separation of o- and p-nitrochlorobenzenes using p-dichlorobenzene, separation of lithium sulphate and lithium formate using n-butanol or 2-propanol and separation of p-xylene from m-xylene using pentene. Somewhat similar are the so-called adductive crystallization processes, often (wrongly) called extractive crystallization, where reactions of complex/adduct formation are used to separate compounds that are otherwise difficult to separate.

CODE 2.1.3

TECHNOLOGY EXTRACTIVE DISTILLATION



Example of extractive distillation: BTX process of GTC Technology Corp.

Description/Basic Features

Extractive distillation can be particularly useful in close-boiling-point problems or in systems in which components form azeotropes. In the method, an extra component (solvent) is added to the system, which does not form azeotropes with feed components. The solvent alters the relative volatility of original feed components, allowing distilling overhead. The solvent leaves the column with the bottom products and is separated in a binary column. Energy savings present the most important advantage of extractive distillation over the conventional (non-hybrid) separation methods.

Evaluation	
Potential for energy savings	Medium
Potential for eco impact CO ₂	Low
Potential to improve cost competitiveness	Low
Ripeness of application in X years	5-10
Ripeness of related technology fields	Medium
Likelihood of overcoming barriers	Medium
Potential for innovative high quality products	Medium
Character of required R&D	Fundamental

Review

Extractive distillation is widely used in Industry. In its application, a solvent is used to change the relative volatility of the components to be separated. It is proposed to expand the application of extractive distillation by the use of specifically developed products like e.g. hyper-branched polymers or ionic liquids. Key challenges to be resolved are:

- to identify the relationship between molecular structure and separation performance
- to develop economically attractive manufacturing routes for such *designer solvents*

The attention for this expanded technology is still very much in academia.

CODE 2.1.4

TECHNOLOGY HEAT-INTEGRATED DISTILLATION

Sub-technologies covered

- Dividing-Wall Columns
- Heat-Integrated Distillation Columns (HIDiC)

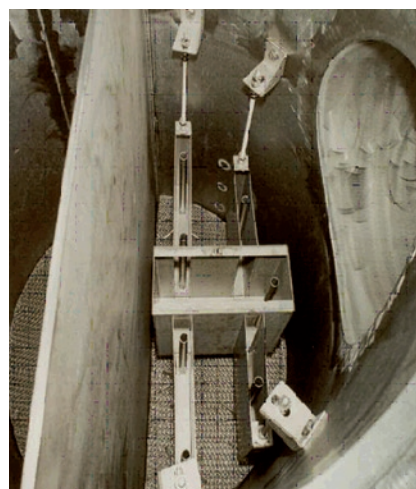
Description/Basic Features

Dividing wall columns represent an improved type of distillation column. They are equipped with one or more vertical partitions inside the column shell. In contrast to conventional distillation columns they are able to deliver pure side fractions. This feature reduces the number of necessary distillation columns in a separation sequence.

In Heat-Integrated Distillation Columns (HIDiCs) the integration is done by combining the rectifying and stripping columns in an annular (or similar suitable) arrangement so that they exchange heat along their lengths, and elevating pressure in the rectifying section.



Heat transfer panels in a pilot HIDiC column
(Courtesy of Delft University of Technology)



Inside view of a dividing wall distillation column
(Courtesy of BASF)

Evaluation	
Potential for energy savings	High
Potential for eco impact CO ₂	High
Potential to improve cost competitiveness	High
Ripeness of application in X years	<5
Ripeness of related technology fields	High
Likelihood of overcoming barriers	High
Potential for innovative high quality products	Low
Character of required R&D	Applied

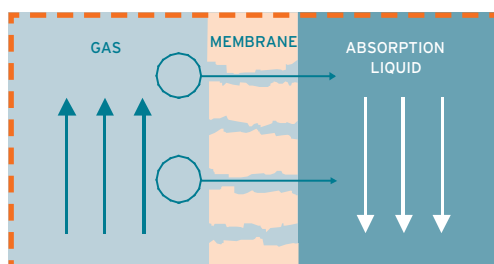
Review (dividing wall columns)

A prime example of heat-integrated distillation is the use of dividing wall columns. They are distillation columns equipped with one or more vertical partitions inside the column shell. In contrast to conventional distillation columns, they are able to deliver pure side-fractions. This feature reduces the number of necessary distillation columns in a given separation sequence.

The technology of dividing wall columns has been successfully introduced in the chemical industry and is on its way to become a standard technology. The economic advantage in terms of energy and investment costs can be as high as 30%.

CODE **2.1.5**TECHNOLOGY **MEMBRANE HYBRID SYSTEMS**SUBCODE **2.1.5.1**SUB-TECHNOLOGY **MEMBRANE ABSORPTION/STRIPPING****Description/Basic Features**

Membrane absorption is one of the processes that Mother Nature had invented a long time before the engineers did. In the simplest case a gaseous component is selectively transported via a membrane and dissolved in the absorbing liquid, as it is shown in Figure below. It is also possible to carry out a membrane-based absorption-desorption process, with two liquids on both sides of the membrane, or a membrane stripping process, in which selected components are removed from the liquid phase through the membrane by a stripping gas. An important characteristic feature of the membrane absorption is that it proceeds without creating a real gas-liquid interface in form of bubbles. Such a bubble-free gas-liquid mass transfer can be of advantage in certain processes, for instance in shear-sensitive biological systems. One of the most important application areas of the membrane absorption is the capture of CO₂ from flue gas.



CODE 2.1.5

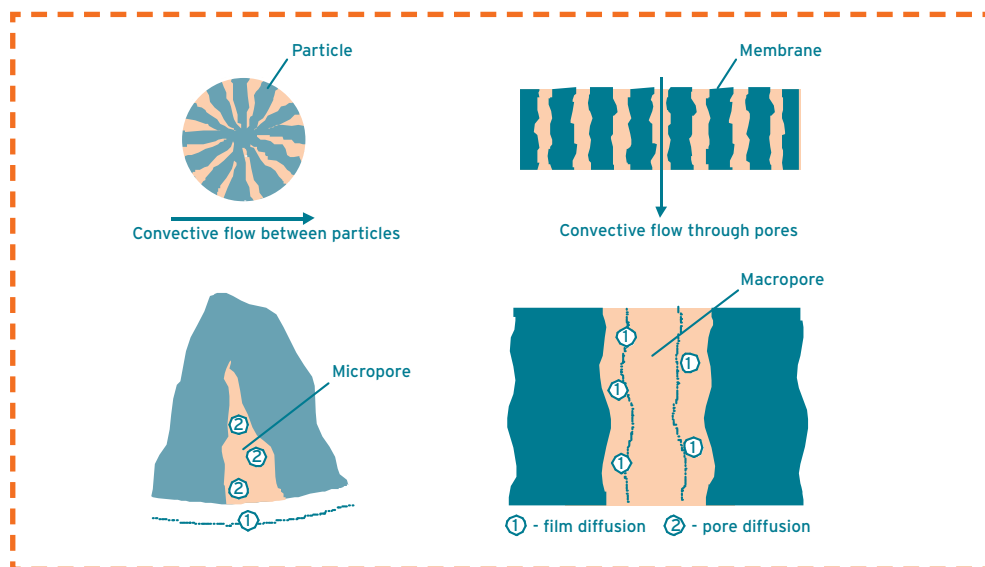
TECHNOLOGY MEMBRANE HYBRID SYSTEMS

SUBCODE 2.1.5.2

SUB-TECHNOLOGY MEMBRANE ADSORPTION

Description/Basic Features

Membrane adsorption (chromatography) is a separation technique, so far used almost exclusively in the downstream processing of proteins. The main feature and advantage of this technique, compared to the conventional ones, is the absence of the pore diffusion, which is the main transport resistance in traditional chromatography (see Figure). Dissolved molecules are carried directly to the adsorptive sites in the membranes by the convective flow, which increases the throughput of the process.



Membrane adsorption (right) compared to traditional chromatography (left)

CODE **2.1.5**TECHNOLOGY **MEMBRANE HYBRID SYSTEMS**SUBCODE **2.1.5.3**SUB-TECHNOLOGY **MEMBRANE CRYSTALLIZATION****Description/Basic Features**

Membrane crystallization is a newly developed crystallization technique that has proven to be superior in producing good crystal forms under operating conditions that are not appropriate to perform the crystallization process by other traditional techniques. It combines membrane distillation and crystallization operations. The solvent evaporates at the membrane interface, migrates through the pores of the membrane and condenses on the opposite side of the membrane. Membrane crystallization has been proposed in the last few years as a new technique for growing protein crystals with enhanced crystallization kinetics starting at lower levels of super-saturation. Polymeric membranes are used as physical support and as active surface promoter of heterogeneous crystallization.

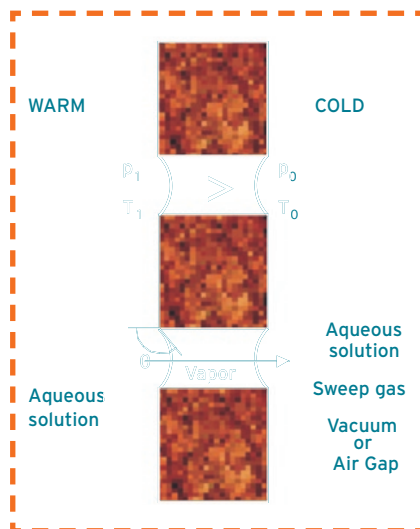
Evaluation	
Potential for energy savings	Medium
Potential for eco impact CO ₂	Medium
Potential to improve cost competitiveness	Medium
Ripeness of application in X years	10-15
Ripeness of related technology fields	Low
Likelihood of overcoming barriers	Low
Potential for innovative high quality products	High
Character of required R&D	Fundamental

Review

Crystallisation is a well-established technology in which solvent is evaporated (by e.g. steam/vacuum) and the concentrate cooled to affect super-concentration followed by crystallisation. Since in the end all solvent must be evaporated, the process can be rather energy-intensive.

Membranes can be used to concentrate a solution by e.g. membrane-distillation to remove solvent. Membrane-distillation can operate at a low temperature-differential compared to the established technology, potentially resulting in energy savings. Moreover, due to the lower temperature differentials the crystallisation process can be carried out at milder conditions and in a highly controlled manner, which could be of particular interest in the pharma-industry.

The technology however is still in the very early concept-stage and no feasible application has been demonstrated as yet. No doubt of potential interest, but the development of stable and low-cost membranes is a major hurdle.

CODE **2.1.5**TECHNOLOGY **MEMBRANE HYBRID SYSTEMS**SUBCODE **2.1.5.4**SUB-TECHNOLOGY **MEMBRANE DISTILLATION**

Working principle
of membrane distillation

Evaluation	
Potential for energy savings	Medium
Potential for eco impact CO ₂	Medium
Potential to improve cost competitiveness	Medium
Ripeness of application in X years	5-10
Ripeness of related technology fields	Medium
Likelihood of overcoming barriers	Medium
Potential for innovative high quality products	Medium
Character of required R&D	Combination

Description/Basic Features

Membrane distillation is widely considered as an alternative to reverse osmosis and evaporation technologies. Membrane distillation basically consists in bringing a volatile component of a liquid feed stream, as a vapour, through a porous membrane and condense it on the other side onto a permeate liquid. Temperature difference is the driving force of the process.

Review

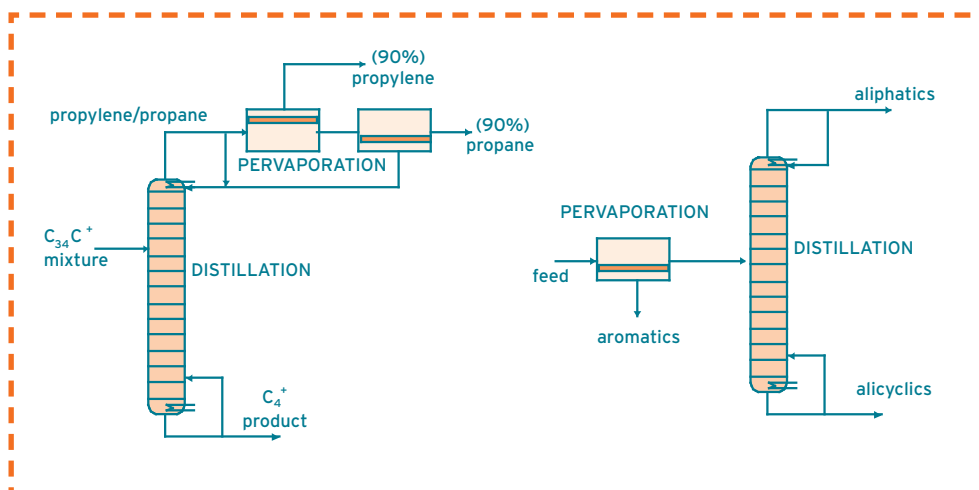
In membrane distillation a liquid feed is evaporated and the vapour is contacted with a (hydrophobic) membrane. The non polar components can pass the membrane and are condensed at the other side, giving the driving force for transport. The technology offers the potential of membrane technology for efficient separation and, in principle, broad

applicability, but as in distillation, energy is needed for vaporization. Advantages are also the absence of concentration polarization.

The main challenge for niche applications is the development of large scale efficient and robust membranes. Benefits are energy savings. Modelling is not seen as a major barrier.

CODE **2.1.5**TECHNOLOGY **MEMBRANE HYBRID SYSTEMS**SUBCODE **2.1.5.5**SUB-TECHNOLOGY **DISTILLATION - PERVAPORATION****Description/Basic Features**

A pervaporation membrane can be coupled with a conventional distillation column, resulting in a hybrid membrane/distillation process. In distillation-pervaporation systems the membrane units can be installed on the overhead vapour of the distillation column, as it is shown in Figure A for the case of propylene/propane splitting, or they can be installed on the feed to the distillation column, as it is shown in Figure B for the case of aromatic/aliphatic hydrocarbons separation.



Evaluation	
Potential for energy savings	Medium
Potential for eco impact CO ₂	Medium
Potential to improve cost competitiveness	Medium
Ripeness of application in X years	<5
Ripeness of related technology fields	High
Likelihood of overcoming barriers	Medium
Potential for innovative high quality products	Medium
Character of required R&D	Combination

Review

In Pervaporation a liquid feed is contacted with the membrane and evaporation is the driving force. In principle it can replace distillation but because of the unfavourable scale-up it is usually better to combine it with distillation. Examples for potential application are breaking the azeotrope (without adding a solvent), increasing the

capacity of a distillation column and improving quality of the bottom and overhead products. The potential of the technology has been widely demonstrated, e.g., dehydration alcohols and separation isomeric hydrocarbons. As is the case in all membrane based processes the development of robust and efficient membranes is a challenge. Benefits are energy savings and higher-quality products.

CODE 2.1.5

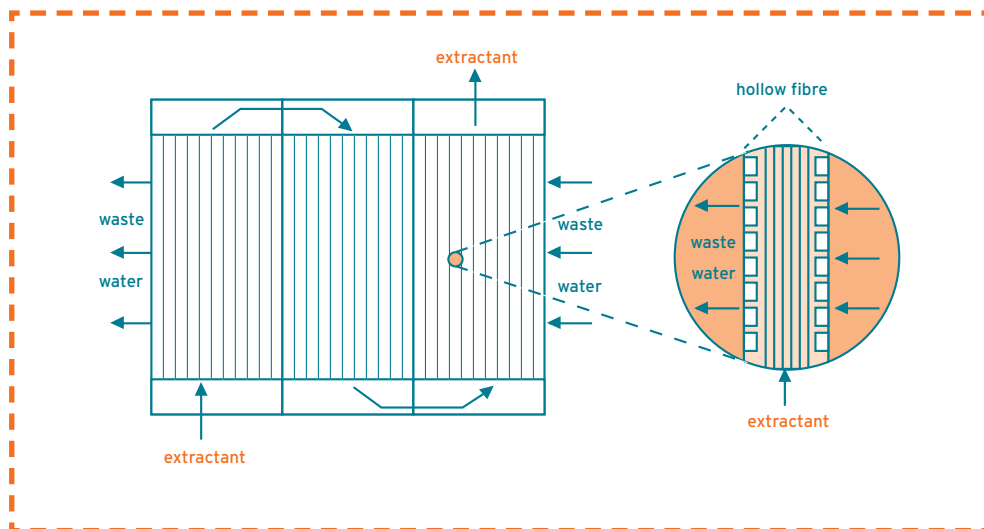
TECHNOLOGY MEMBRANE HYBRID SYSTEMS

SUBCODE 2.1.5.6

SUB-TECHNOLOGY MEMBRANE EXTRACTION

Description/Basic Features

In membrane extraction the treated solution and the extractant/solvent are separated from each other by means of a solid or liquid membrane. Currently, the technique is primarily applied in three areas: wastewater treatment (e.g. removal of pollutants or recovery of trace components), in biotechnology (e.g. removal of products from fermentation broths or separation of enantiomers) and in analytical chemistry (e.g. on-line monitoring of pollutants concentrations in wastewater).



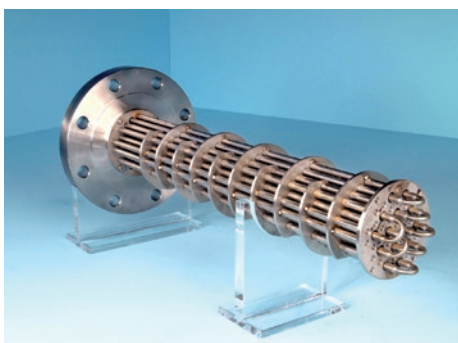
Hollow-fiber pertraction unit for wastewater treatment (Courtesy of TNO)

CODE 2.2.1

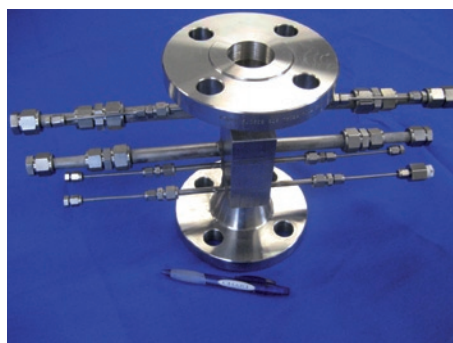
TECHNOLOGY HEAT EXCHANGERS (HEX) REACTORS

Description/Basic Features

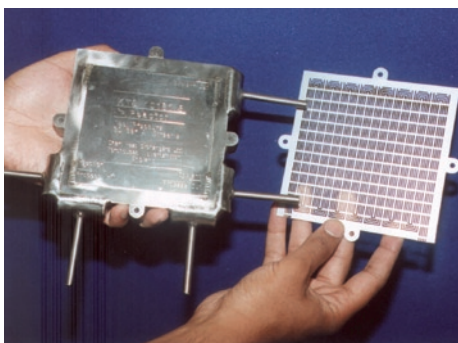
In a heat exchanger (HEX) reactor the reaction takes place adjacent to a heat exchange surface. In this way the heat generated in a reaction can be easily removed from the process (or supplied to the process in the case of an endothermic reaction). Close(r) control of the temperature at which the reactor occurs can be achieved. In millireactors, which usually have structure & scale similar to plate heat exchangers, typical channel size is in the millimetre range. In those reactors porous catalyst plates and/or profile plates are stacked in a sandwich-like structure. Co-current, counter-current and crossflow cooling is possible.



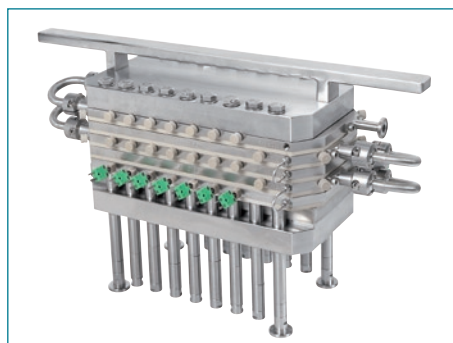
Static mixer-based FlexReactor from BHR Group Ltd. (Courtesy of BHR)



ShimTec™ reactor from Chart Energy & Chemicals (Courtesy of Chart)



Marbond HEX reactor from Chart Energy & Chemicals (Courtesy of BHR Group Ltd.)



ART® Plate Reactor from Alfa Laval (Courtesy of Alfa Laval)



Helix heat exchanger reactor (Courtesy of TNO)

Evaluation	
Potential for energy savings	Low
Potential for eco impact CO ₂	Low
Potential to improve cost competitiveness	High
Ripeness of application in X years	5-10
Ripeness of related technology fields	High
Likelihood of overcoming barriers	Medium
Potential for innovative high quality products	High
Character of required R&D	Applied

Review

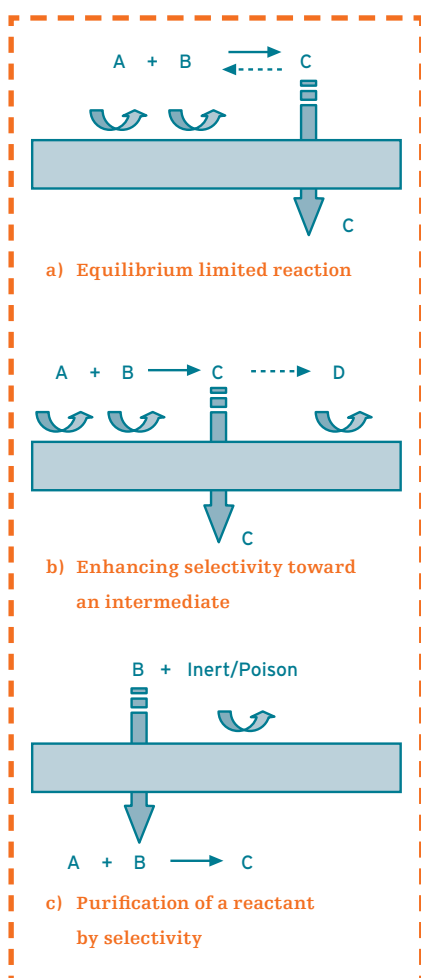
Heat-Exchanger Reactors have large potential for fast reactions with a high heat of reaction. HEX Reactors can be classified as micro reactors with characteristic dimensions >0.5 mm, so, diffusion is not the key transport. They can be divided in non-catalytic and catalytic reactors. In the latter case a catalyst has to be present. If this is integrated in the reactor and present as a catalytic coating development work is needed. Barriers are the manufacture of robust reactors, catalyst development, scale-up (inlet and outlet design), and lack of experience.

CODE 2.2.2

TECHNOLOGY MEMBRANE REACTORS (SELECTIVE, CATALYTIC)

Description/Basic Features

In most cases application of selective membranes in membrane reactors is considered to obtain a high(er) conversion in equilibrium limited reactions. Removing one of the products enables the reaction to proceed beyond the equilibrium. This application is shown in figure (a).



There are many different types of membranes and selectivity can be based on many different mechanisms. In dense membranes the functional layer is a gas-tight material which transports a specific component, usually in atomic or ionic form. Two well-known examples are hydrogen conducting membranes based on palladium and oxygen conducting membranes based on perovskites. Other separation principles include molecular sieving, capillary condensation and difference in adsorption and diffusion properties of gases. The wide range of principles and characteristics also leads to a wide range of operating conditions. Operating temperatures, for example, range from room temperature to $>800\text{ }^{\circ}\text{C}$ for oxygen conducting membranes.

CODE 2.2.3

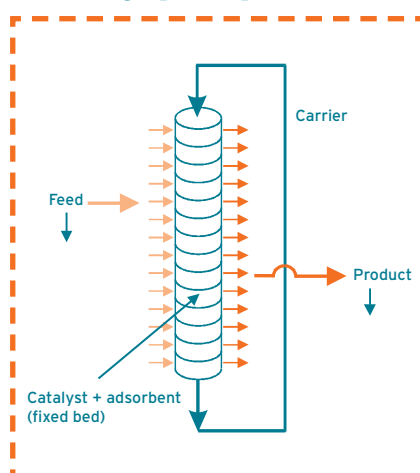
TECHNOLOGY REACTIVE ADSORPTION

SUBCODE 2.2.3.1

SUB-TECHNOLOGY SIMULATED MOVING BED REACTORS

Description/Basic Features

The simulated moving-bed reactor (SMBR) combines continuous countercurrent chromatographic separation with chemical reaction. It is a hybrid process, not



energy-intensive and is competitive with traditional processes in which reaction and separation are carried out in different devices. Higher conversions and better yield can be achieved by separating educts and products of an equilibrium reaction from each other. The (simulated) movement of the bed with regard to the reactants inlets/outlets is usually realized in a rotating system.

Working principle of SMB reactors

Evaluation	
Potential for energy savings	Low
Potential for eco impact CO ₂	Low
Potential to improve cost competitiveness	High
Ripeness of application in X years	5-10
Ripeness of related technology fields	Medium
Likelihood of overcoming barriers	Medium
Potential for innovative high quality products	High
Character of required R&D	Combination

Review

In this technology chromatographic separation and reaction are combined. The mode is counter-current. The technology can be applied for processes where chromatographic separation is a necessary step. The equilibrium can be 'shifted' allowing yields above the equilibrium value. Because of the (often) high quality of separation the resulting product quality can be high.

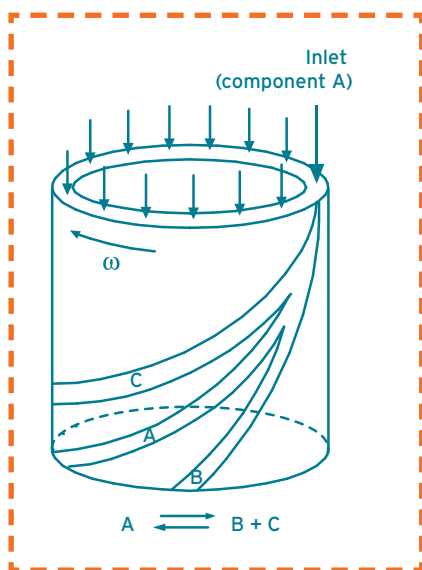
SMBRs could be applied in large-scale processes (higher fructose corn syrup) but in smaller scale processes for fine chemicals and pharmaceuticals is more realistic; industrial applications have not been reported. In every process development, design studies are a must. Development of adsorbent/ catalysts is a barrier.

CODE 2.2.3

TECHNOLOGY REACTIVE ADSORPTION

SUBCODE 2.2.3.2

SUB-TECHNOLOGY ROTATING ANNULAR CHROMATOGRAPHIC REACTORS

**Description/Basic Features**

In the Rotating Cylindrical Annulus Chromatographic Reactor the inlets of the mobile phase are uniformly distributed along the annular bed entrance, while the feed stream is stationary and confined to one sector. As a result of the rotation of reactor, the selectively adsorbed species take different helical paths through the bed and can be continuously collected at fixed locations. Alternatively, it is possible to hold the reactor stationary and rotate continuously the feed.

Evaluation	
Potential for energy savings	Low
Potential for eco impact CO ₂	Low
Potential to improve cost competitiveness	High
Ripeness of application in X years	10-15
Ripeness of related technology fields	Medium
Likelihood of overcoming barriers	Medium
Potential for innovative high quality products	High
Character of required R&D	Fundamental

Review

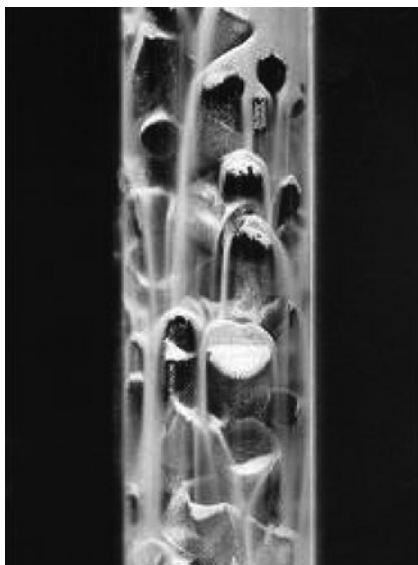
Similar to Simulated Moving Bed Reactors in Rotating Annular Chromatographic Reactors the (bio) chemical reaction is carried out together with a chromatographic separation. The difference is that the RACR works in the co-current mode. The name suggests that the bed rotates, but it is also common practice to apply a stationary bed and to rotate the feed and collector devices. The

advantages applying to Simulated Moving Bed Reactors also apply here.

No large-scale demonstration processes are known but a pilot plant scale

demonstration has been reported (sucrose inversion in a biochemical reaction).

Barriers are high solvent consumption, poor bed utilization and too broad peaks leading to overlapping.

CODE **2.2.3**TECHNOLOGY **REACTIVE ADSORPTION**SUBCODE **2.2.3.3**SUB-TECHNOLOGY **GAS-SOLID-SOLID TRICKLE FLOW REACTOR**

Gas-Solid-Solid Trickle Flow Reactor for methanol synthesis (Kuczynski, Ph.D. Disser., University Twente 1987)

Description/Basic Features

In the Gas-Solid-Solid Trickle Flow Reactor fine adsorbent trickles through the fixed bed of catalyst, removing selectively in-situ one or more of the products from the reaction zone. In case of the methanol synthesis this led to conversions significantly exceeding the equilibrium conversions under given conditions.

Evaluation	
Potential for energy savings	Low
Potential for eco impact CO ₂	Low
Potential to improve cost competitiveness	High
Ripeness of application in X years	10-15
Ripeness of related technology fields	High
Likelihood of overcoming barriers	Low
Potential for innovative high quality products	Medium
Character of required R&D	Fundamental

Review

In GSSTFRs a fine powder (adsorbent, catalyst) trickles down through a packed bed. Several hybrid operations are possible: heterogeneous catalysis with in-situ adsorption (e.g., in equilibrium limited reactions), heterogeneous catalysis with heat transfer, use as heat exchanger. Benefits are energy savings (less recirculation of reactants, although obviously the powdered solid has to be re-circulated), increased conversion. For heat exchange the technology has been demonstrated at a commercial scale, but apart from this, only university groups have been active experimentally. Benefits are energy savings and high potential for innovations (multifunctional catalysis, structured packing). A barrier is that recycling of solids in general is less attractive than recycling of liquids or gases.

CODE **2.2.4**TECHNOLOGY **REACTIVE CONDENSATION****Description/Basic Features**

Direct condensation of products from the reacting mixture can result in similar advantageous effects as it is in case of reactive distillation. So far, only catalytic methanol synthesis from carbon monoxide and hydrogen has been investigated in a spatially constructed reactor-condenser.

CODE **2.2.5**TECHNOLOGY **REACTIVE EXTRACTION****Description/Basic Features**

Reactive extraction processes involve simultaneous reaction and liquid-liquid phase separation. The immiscibility may occur naturally within the reactive system



Pulsed columns for metal extraction
(Courtesy of Bateman Litwin N.V.)

or may be introduced deliberately by addition of solvent(s). Reactive extraction can be effectively utilized to obtain significant improvements in yields of desired products and selectivities to desired products in multi-reaction systems, thereby reducing recycle flows and waste formation. The combination of reaction with liquid-liquid extraction can also be used for separation of waste by-products that are hard to separate using conventional techniques.

Evaluation	
Potential for energy savings	Medium
Potential for eco impact CO ₂	Medium
Potential to improve cost competitiveness	Low
Ripeness of application in X years	5-10
Ripeness of related technology fields	Medium
Likelihood of overcoming barriers	High
Potential for innovative high quality products	Medium
Character of required R&D	Combination

Review

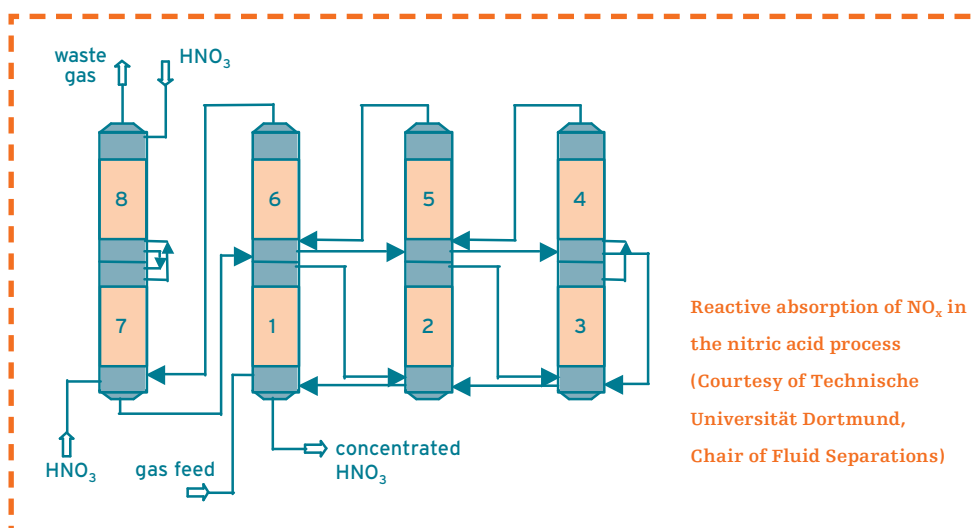
Commercial applications exist since the 60s in hydrometallurgy. Recent application is in pharma in producing optically pure isomers. The type equipment to be used is straightforward: agitated or non-agitated columns. More advanced techniques might be developed (centrifugal and membrane based systems have been studied occasionally). The mass transfer in the liquid-liquid dispersions might be an issue and should be studied in the laboratory.

CODE 2.2.6

TECHNOLOGY REACTIVE ABSORPTION

Description/Basic Features

Reactive absorption is a mature processing technique and has been used for production purposes in a number of classical bulk-chemical technologies, such as nitric or sulfuric acid. Carbon dioxide removal by reactive absorption in amine solutions is also applied on the commercial scale, for instance in the treatment of the flue gas. Another possible application field of the technique is gas desulfurization, in which H_2S is removed and converted to sulfur by means of reactive absorption. The separation of light olefins and paraffins by means of a reversible chemical complexation of olefins with $Ag(I)$ or $Cu(I)$ compounds in aqueous and non-aqueous solutions presents another interesting example of reactive absorption that could possibly replace the conventional cryogenic distillation technology.



Evaluation	
Potential for energy savings	High
Potential for eco impact CO_2	High
Potential to improve cost competitiveness	Low
Ripeness of application in X years	<5
Ripeness of related technology fields	High
Likelihood of overcoming barriers	High
Potential for innovative high quality products	Medium
Character of required R&D	Applied

Review

Reactive absorption is the most applied reactive separation technique. It is not surprising that modelling has drawn a lot of attention and the technique is relatively mature. In contrast to distillation reactive absorption is rate-controlled and occurs far from equilibrium. Several commercial applications are known in

several industrial sectors, viz., steel industry, refinery, energy, bulk chemistry, fine chemistry, environmental protection. The major applications are gas purification, gas drying and separation, olefin/ paraffin separation, chemical synthesis (sulfuric, nitric acid). Challenges still exist, e.g., tailored solvents, corrosion resistant internals.

CODE 2.2.7

TECHNOLOGY REACTIVE CRYSTALLIZATION/PRECIPITATION

Description/Basic Features

Reactive crystallization/precipitation plays a role in a number of industrially relevant processes, such as liquid-phase oxidation of para-xylene to produce technical grade terephthalic acid, the acidic hydrolysis of sodium salicylate to salicylic acid, and the absorption of ammonia in aqueous sulfuric acid to form ammonium sulphate. Reactive crystallization/precipitation is also widely applied in the pharmaceutical industry, to facilitate the resolution of the enantiomers (diastereomeric crystallization). Here, the racemate is reacted with a specific optically active material (resolving agent), to produce two diastereomeric derivatives (usually salts), that are easily separated by crystallization:



Diastereomeric crystallization is commonly used in the production of a number of pharmaceuticals, such as ampicillin, ethambutol, chloramphenicol, diltiazem, fosfomicin, and naproxen.

CODE 2.2.8

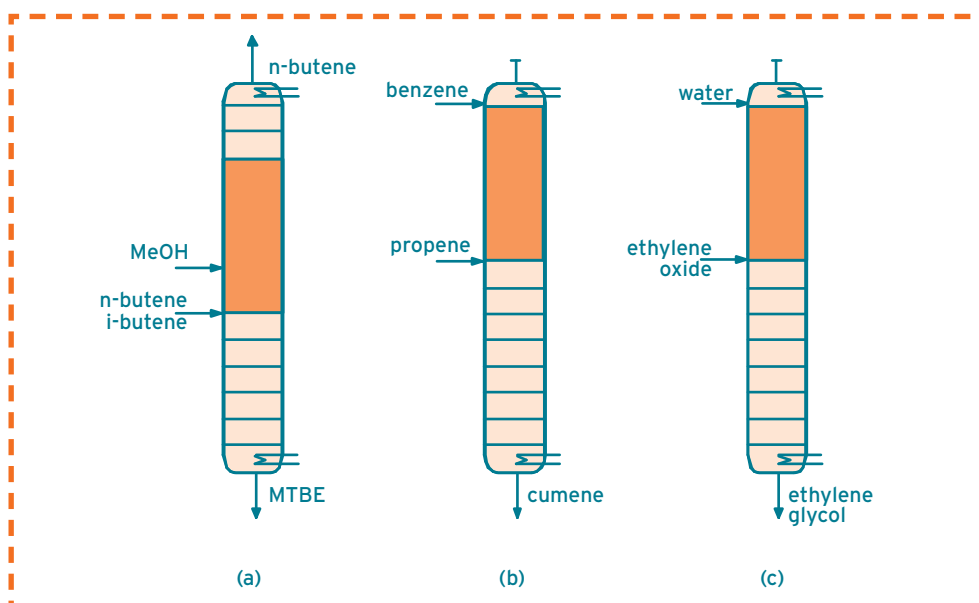
TECHNOLOGY REACTIVE DISTILLATION

SUBCODE 2.2.8.1

SUB-TECHNOLOGY REACTIVE DISTILLATION (CATALYTIC + NON-CATALYTIC)

Description/Basic Features

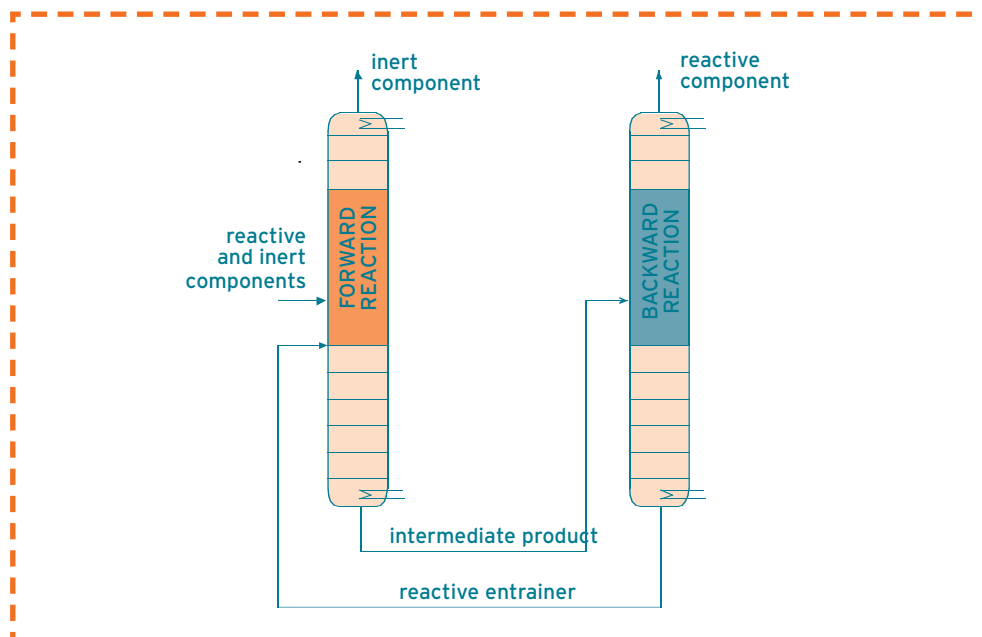
Continuous removal of reaction products is the distinct feature that gives reactive distillation its technical and economic advantages where it is applicable. The process takes place in a conventional distillation column. In the column chemicals are reacted in the presence of a structured catalyst and the products are continuously separated by fractionation (thus overcoming equilibrium limitations according to Le Chatelier's principle). Advantages include lower energy requirements, higher yields, good product purity and lower capital investment. Usually, the catalyst is incorporated into fibreglass and wiremesh supporting structure, which also provides liquid redistribution and disengagement of the vapour.



Examples of industrial processes employing reactive distillation:

(a) – MTBE, (b) – cumene, (c) – ethylene glycol

Reactive distillation with a reactive entrainer can also be used as a powerful separation method in case of mixtures containing reactive and non-reactive components with close boiling point.



Working principle of reactive distillation with entrainer
to separate closely boiling reactive and non-reactive components

Evaluation	
Potential for energy savings	High
Potential for eco impact CO ₂	High
Potential to improve cost competitiveness	High
Ripeness of application in X years	<5
Ripeness of related technology fields	High
Likelihood of overcoming barriers	High
Potential for innovative high quality products	Medium
Character of required R&D	Applied

Review

In this technique distillation and reaction are simultaneously carried out in the column. The equilibrium can be 'shifted' and higher or even total conversion can be reached; under normal operation conditions equilibrium would not allow that. Typically rates should be high enough to enable reaction times of 10 min at maximum because of the limited hold

up in the distillation column. Usually catalysts are essential. Both homogeneous and heterogeneous catalysis can be applied. In the former case the design of the catalyst morphology is essential. Commercial designs exist but tailored structures might be 'winners'. Benefits are 'shifting the equilibrium', increased yields and selectivity, simpler process, lower costs (capex). Further integration with other functions is feasible (Pervaporation).

Many commercial applications are known, e.g., production of ethers (MTBE, TAME) and the famous example of Eastman (methyl acetate).

There are still issues, catalyst development (performance, kinetics, stability against leaching, morphology, coating procedures). An issue is also lack of expertise, e.g., in fine chemistry, pharma.

CODE 2.2.8

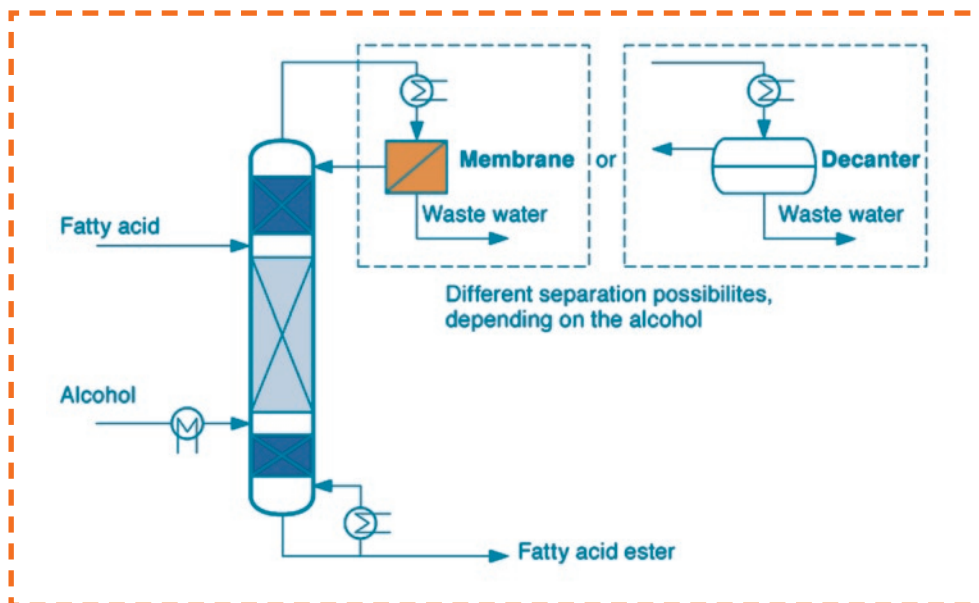
TECHNOLOGY REACTIVE DISTILLATION

SUBCODE 2.2.8.2

SUB-TECHNOLOGY MEMBRANE-ASSISTED REACTIVE DISTILLATION

Description/Basic Features

The combination of chemical reaction and distillation in one apparatus (Reactive Distillation, RD) is favourable to equilibrium limited reactions. In case of further limitations by e.g. azeotropes additional unit operations can be helpful. In the pervaporation-assisted reactive distillation a reactive distillation unit is coupled with a pervaporation module to further purify the distillate stream. As a result, no additional entrainer is needed as in e.g. extractive distillation processes.



Membrane-assisted reactive distillation for synthesis of fatty acid esters (Courtesy of Sulzer Chemtech)

Evaluation	
Potential for energy savings	High
Potential for eco impact CO ₂	High
Potential to improve cost competitiveness	High
Ripeness of application in X years	5-10
Ripeness of related technology fields	High
Likelihood of overcoming barriers	Medium
Potential for innovative high quality products	High
Character of required R&D	Applied

Review

In this technique reactive distillation is coupled with membrane separation. It is an extension of catalytic distillation and useful when the latter can not be applied, e.g., when azeotropes interfere. Two commercial applications have been reported, viz., the production of methyl borate and the production of fatty acid esters. Considerable energy savings and cost reductions are claimed. Barriers are the development of satisfactory membranes, catalysts and equipment/process design.

CODE **2.2.9**

TECHNOLOGY **OTHER REACTIVE SEPARATIONS**

SUBCODE **2.2.9.1**

SUB-TECHNOLOGY **REACTIVE COMMINATION**

Description/Basic Features

The concept of reactive comminution consists in carrying out chemical conversion in a mill. Performing of some non-catalytic gas-solid reactions in combination with a comminution process may lead to drastically reduced induction period in the starting phase of the gas-solid reaction and to essentially lowered temperature limit to run the reaction. This can be explained by the enlargement of the reactive solid surface during comminution and by the mechanical activation of the particles.

CODE **2.2.9**TECHNOLOGY **OTHER REACTIVE SEPARATIONS**SUBCODE **2.2.9.2**SUB-TECHNOLOGY **REACTIVE EXTRUSION****Description/Basic Features**

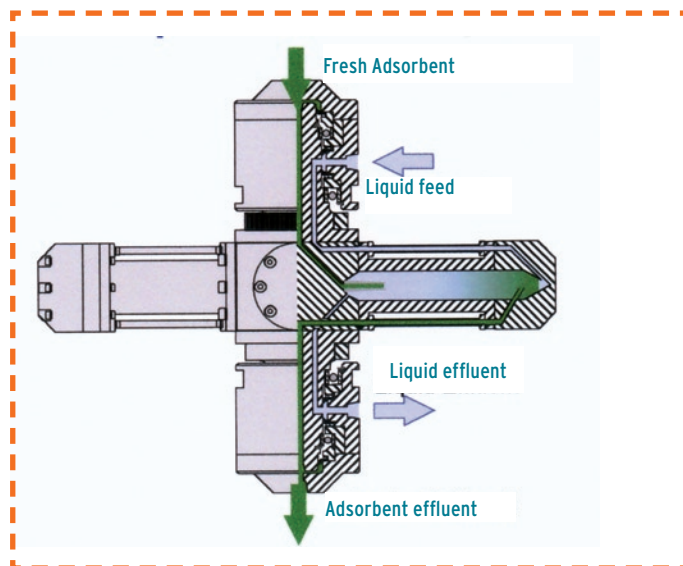
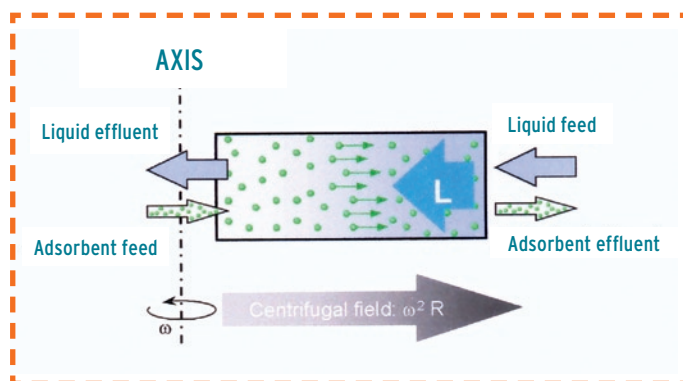
Reactive extruders have been increasingly used in polymer industries. They enable reactive processing of highly viscous materials without a need for using large amounts of solvents, as it is in the case of stirred-tank reactors. Particularly popular are twin-screw extruders, which offer effective mixing, possibility of operation at high pressures and temperatures, plug-flow characteristics and capability of multistaging. Most of the reactions carried out in extruders are single- or two-phase reactions. Only recently new types of extruders are investigated with catalyst immobilized on the surface of the screws, which enables carrying out three-phase catalytic reactions.

CODE 3.1.1

TECHNOLOGY CENTRIFUGAL ADSORPTION TECHNOLOGY

Description/Basic Features

Centrifugal adsorption technology is a continuous technique for carrying out ion exchange and adsorption processes. By using a centrifugal field for establishing countercurrent flow between the liquid phase and the adsorbent, very small adsorbent particles can be used. This allows for the design of extremely compact separation equipment with very short contact times.



Principle of centrifugal adsorption technology

(M. Bisschops, Ph.D. Dissert., TU Delft 1999)

CODE **3.1.2**TECHNOLOGY **CENTRIFUGAL LIQUID-LIQUID CONTACTORS****Description/Basic Features**

In 1945 Podbielniak modified a patented liquid-liquid contactor using a perforated spiral passageway as the rotor packing, to solve extraction problems with penicillin recovery - centrifugal solvent extractor achieved 98% product recovery by taking advantage of its low liquid hold-up, short residence time, high centrifugal force, and multistage countercurrent contacting. A more recent development is the so-called CINC Centrifugal Contactor/Extractor which provides intensive mixing and settling zones within a fast rotating apparatus. For a multistage contacting, however, several CINC devices in counter-current configuration have to be used.

Evaluation	
Potential for energy savings	High
Potential for eco impact CO ₂	Medium
Potential to improve cost competitiveness	Medium
Ripeness of application in X years	<5
Ripeness of related technology fields	High
Likelihood of overcoming barriers	High
Potential for innovative high quality products	Low
Character of required R&D	Applied

Review

In these devices for two liquids, mixing and separation can be performed in one piece of equipment. Because of the high centrifugal forces (> 1000g) phase separation goes very efficiently. The principle can be used in many applications. Mixing can be done at low severity enabling processing of shear sensitive liquids.

This technology has been developed for the nuclear fuel processing industry and there is over 30 years of operating experience. Compared to gravity driven settlers they provide for large process intensification. In principle they can be used generally, viz., fine and bulk chemistry, pharma, food industry. They can be used also on a small scale in the continuous mode.

CODE **3.1.3**TECHNOLOGY **ROTATING PACKED BEDS****Description/Basic Features**

The HIGEE technology consists in intensifying the mass transfer processes by carrying them in rotating packed beds in which high centrifugal forces occur. This way not only mass transfer, but also heat and momentum transfer can be intensified. The rotating bed equipment, originally dedicated to separation processes (such as absorption, extraction, distillation), can also be applied to



250t/h HiGee installation for seawater deoxygenation in offshore platform (Courtesy of Research Center of the Ministry of Education for High Gravity Engineering & Technology, University of Beijing)

reacting systems (especially those mass transfer limited). It can potentially be applied not only to gas-liquid but also to other phase combinations, gas-liquid-solid systems including. In a Rotating Packed Bed liquid (or heavy phase in the case of liquid-liquid systems) enters at the eye of the rotor, being distributed on the rotor packing at the inside diameter. Gas (or light phase in case of liquid-liquid systems) enters the stationary housing and passes through the rotor from outside to inside. Woven wire screen, randomly packed pellets, foam metal or structured packings are used as the RPB internals.

Evaluation	
Potential for energy savings	Medium
Potential for eco impact CO ₂	Medium
Potential to improve cost competitiveness	High
Ripeness of application in X years	5-10
Ripeness of related technology fields	High
Likelihood of overcoming barriers	Medium
Potential for innovative high quality products	Medium
Character of required R&D	Combination

Review

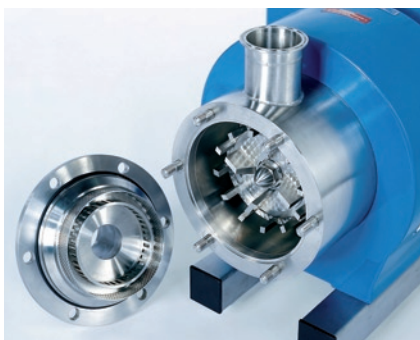
In this technology centrifugal forces lead to a high-gravity environment. It is also referred to as HIGEE technology. It has been invented by Ramshaw who coined the name "Process Intensification". It has been extensively explored for applications in absorption, stripping, liquid-liquid extraction, crystallization etc. The micro-mixing and mass transfer can be 1-3

orders of magnitude larger. Of course, the technique is not limited to packed beds, also foams or other structured packing can be used. Potential benefits are smaller catalyst particles (associated herewith higher activity and selectivity), smaller volumes and better product quality.

Several commercial applications have been reported, e.g., production CaCO₃ nanoparticles (Ca(OH)₂ with CO₂), production HOCl, removal O₂ in water processing plant. Barriers are reliability of rotating equipment, modelling reactor in multiphase systems (flooding, micro-mixing, solid/liquid systems).

CODE **3.1.4**TECHNOLOGY **ROTOR-STATOR DEVICES****Description/Basic Features**

A rotor/stator mixer contains a high-speed rotor spinning close to a motionless stator. Fluid passes through the region where rotor and stator interact and experiences highly pulsating flow and shear. In-line rotor/stator mixers resemble centrifugal pumps and may contribute significantly to pumping the fluid.



Multistage rotor-stator device
(Courtesy of Silverson Machines Ltd.)



Cavity transfer mixer rotor
(Courtesy of Maelstrom Advanced Process Technologies Ltd.)

Evaluation	
Potential for energy savings	High
Potential for eco impact CO ₂	Medium
Potential to improve cost competitiveness	Medium
Ripeness of application in X years	<5
Ripeness of related technology fields	High
Likelihood of overcoming barriers	High
Potential for innovative high quality products	High
Character of required R&D	Applied

Review

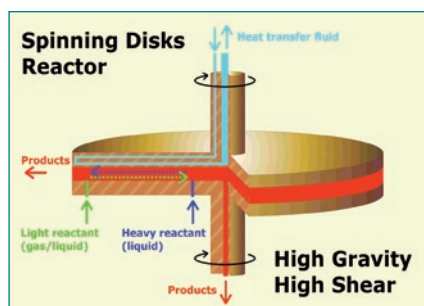
High speed rotor-stator devices are used for homogenization, emulsification, dissolution and other mixing applications. Very high shear rates are possible (tip speeds up to 50 m/s, shear rates up to 100.000 s⁻¹, energy dissipation 10⁴-10⁵ W/kg). They are applied in batch vessels and as continuous in-line devices. The former do not show favourable scale-up.

Benefits are low costs, the fact that they are very versatile and they constitute proven technology. They are important in product technology. Examples of sectors where this is applied are the food industry, cosmetics, fine chemistry, catalyst production, etc.

Rotor-stator devices are widely used in the industry. Nevertheless, there are still challenges for new ideas. In particular in producing nano-structured materials break-throughs' might be realized.

CODE **3.1.5**TECHNOLOGY **SPINNING DISC REACTOR****Description/Basic Features**

The Spinning Disc Reactor is particularly effective when high heat fluxes or viscous liquids are involved. The objective is to generate a highly sheared liquid film when a liquid is supplied to the unit at or near its centre. In SDR the smooth inner film always broke down into an array of spiral ripples and the liquid film flow over a surface is intrinsically unstable. High heat transfer rates present the most important feature of SDR's and heat transfer coefficients exceeding $20 \text{ kW/m}^2\text{K}$ are reported. Spinning Disc Reactors are particularly attractive for applications in fast, highly exothermic reactions, also involving highly viscous liquids.



Scheme of a Spinning Disc Reactor developed at Eindhoven University of Technology (Courtesy of TU Eindhoven)



Spinning Disc Reactor setup (Courtesy of Clarkson University)



Liquid flow on spinning disc surface (Courtesy of University of Newcastle)



Spinning Disc Reactor setup (Courtesy of University of Newcastle)

CODE **3.1.6**TECHNOLOGY **VISCOUS HEATING DEVICE****Description/Basic Features**

The device is based on the principle of heating by viscous dissipation of the energy in rotating machinery. It comprises of a plain stainless steel disc fully enclosed within a casing. Viscous dissipation is enhanced by using narrow clearances (ca. 1 mm in radial and axial directions) between the disc and the casing.

CODE **3.2.1**TECHNOLOGY **EJECTOR (VENTURI) - BASED REACTORS**

Ejector reactor
(Courtesy of BHR Group Ltd.)

Description/Basic Features

Gas-liquid ejector-based reactor utilizes high velocity jets to create suction in the gas chamber, entraining gas into the ejector. On leaving the gas chamber, the liquid causes a rapid dissipation of kinetic energy, creating an intensive mixing zone known as the “mixing shock” region

Reactors based on gas-liquid ejectors can be used for very fast gas-liquid reactions where high local mass transfer rates are required.

CODE **3.2.2**TECHNOLOGY **HYDRODYNAMIC CAVITATION REACTORS****Description/Basic Features**

Similarly to ultrasound, the energy of liquid flow can be utilized to purposefully create cavitation for intensifying reactions and other operations. Such a purposeful hydrodynamic cavitation can be created on two ways. One alternative is to let the liquid pass through a throttling valve, orifice plate or any other mechanical constriction. If the pressure in vena contracta falls below the cavitation pressure (usually the vapour pressure of the medium), millions of microcavities will be generated. Those cavities will subsequently collapse as the liquid jet expands and pressure recovers. Another possibility to create cavitation is to use the so-called liquid whistle, already applied in food industry for homogenization and emulsification. The characteristic feature of it is that the power here is transmitted from the medium to the device and not the other way round. The liquid is accelerated in a jet and then flows across a steel blade, which vibrates as liquid passes over it at high velocity. The frequency of those vibrations can be adjusted in such a way that cavitation is created. This way large liquid volumes could in principle be processed.

Evaluation	
Potential for energy savings	Medium
Potential for eco impact CO ₂	Low
Potential to improve cost competitiveness	Medium
Ripeness of application in X years	10-15
Ripeness of related technology fields	Medium
Likelihood of overcoming barriers	Medium
Potential for innovative high quality products	Medium
Character of required R&D	Fundamental

Review

Hydrodynamic Cavitation Reactors are applied for reaction (limited demonstration) or homogenization/emulsification and cell disruption (fair commercial demonstrations available). Main benefit is increased yield and selectivity (substantial) with limited positive effect on energy savings and safety (mild operation conditions).

Laboratory scale studies have given proof of concept, but major efforts are still required to develop rules for intensification and optimization, as well as modelling, scale up and design. A concerted effort by Academia and equipment manufacturers is needed to develop robust systems in the next 15 years. Hydrodynamic cavitation is a better choice over Sonochemical reactors (see 3.2.5).

CODE **3.2.3**TECHNOLOGY **IMPINGING STREAMS REACTORS****Subtechnologies covered**

- Two-Impinging-Streams Reactor
- Jet Impingement Reactor

Design 1: Two-Impinging-Streams Reactor**Description/Basic Features**

The Two-Impinging-Streams Reactor has been investigated for gas-solid as well as (gas)-liquid-solid operations. Here, two reacting streams are fed via two inlet pipes positioned symmetrically with respect to the annular upper portion of the reactor. Both streams impinge at certain point. The particles contained in two impinging streams may directly collide with each other or experience harmonic oscillations while moving along the perimeter. The reactor was claimed to provide the highest mass transfer coefficients among all the reactors designed for continuous operation.

Design 2: Jet impingement reactor**Description/Basic Features**

Jet impingement reactor is a high-intensity reactor for liquid-liquid reactions. After introducing the reactants in a suitable way, the combined flows are commingled and made to flow through a series of baffles having inlet and outlet ports. The mixed flow forms into a series of jets, which are in turn directed against another baffle, or in some cases against each other. The jet-impingement reactors have already been positively proven on the industrial scale in case of benzene nitration process. Other liquid/liquid and gas/liquid reactions, such as alkylations or sulfonations, should also potentially benefit from the high-intensity shear regions produced in the reactor.

Evaluation	
Potential for energy savings	Medium
Potential for eco impact CO ₂	Low
Potential to improve cost competitiveness	Medium
Ripeness of application in X years	<5
Ripeness of related technology fields	High
Likelihood of overcoming barriers	Medium
Potential for innovative high quality products	Low
Character of required R&D	Applied

Review

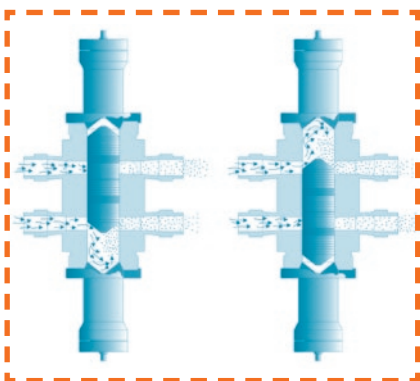
The concept of impinging streams provides a zone of high shear and turbulence resulting in excellent conditions for mixing, heat and/or mass transfer. Despite the large number of potential applications, it has not found wide application in reactor technology. The technology offers fair potential for energy savings, cost saving as well as

narrower product quality, but no direct eco or CO₂ reduction potential. The theoretical basis for impinging effects as well as design of reactors is well established. Ripeness for application of this technology as well as ripeness of technology related fields (separation, filtration etc) is good while barriers to be overcome in a specific application (e.g. modelling and design criteria) do not seem to be high or very fundamental. The technology is ready to be applied by industry. The technology will not create new innovative high quality products.

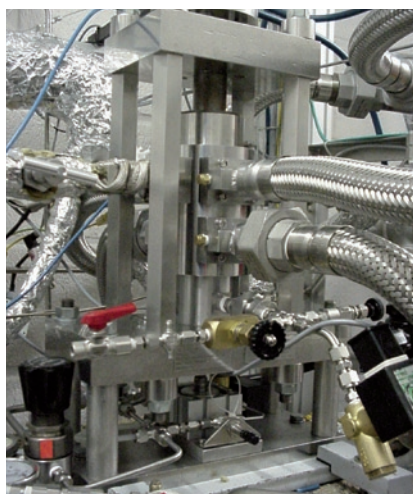
CODE **3.2.4**TECHNOLOGY **PULSED COMPRESSION REACTOR****Description/Basic Features**

A fundamentally new chemical reactor concept permits a breakthrough in synthesis gas production in terms of energy efficiency, capital costs, and portability. The novel reactor technology is totally opposite to the current trends. Instead of developing better catalysts and decreasing the process temperature no catalysts is used and the reactions occur at very high temperatures of 1500 - 3000 oC.

The reactor consists of a double-ended cylinder and a free piston, which divides the cylinder into two compression-reaction chambers. The cylinder has inlet and outlet ports in its wall for feeding the reactants and exhaust of the reaction products. The piston reciprocates compressing in turn the feed gas, until it reacts, in the lower and upper chamber. The reciprocation is maintained by the released reaction energy. An essential feature of the reactor is that the piston-cylinder assembly has no sealing rings. Gas leakage through the annular piston-cylinder gap is prevented by using contactless labyrinth seals.



Scheme of operation of
the Pulsed Compression Reactor
(Courtesy of Energy Conversion
Technologies BV)



Experimental setup of
the Pulsed Compression Reactor
(Courtesy of Energy Conversion
Technologies BV)

Evaluation	
Potential for energy savings	High
Potential for eco impact CO ₂	High
Potential to improve cost competitiveness	Medium
Ripeness of application in X years	>15
Ripeness of related technology fields	Low
Likelihood of overcoming barriers	Low
Potential for innovative high quality products	Medium
Character of required R&D	Fundamental

Review

This technology is fundamentally different from currently applied reaction technologies. No other chemical reactors can compete with compression reactors in terms of combinations of pressures, temperatures and the rate of their change. With this, new chemical processes will become feasible. This technology could provide a very

innovative and radically different approach towards current conventional bulk production of olefins, synthesis gas, hydrogen, acetylene etc.

The technology provides excellent potential for energy savings (reaction energy is directly applied) while, by avoiding feed heating, CO₂ and NO_x emissions are reduced. Cost competitiveness is potentially improved by narrower reaction product distribution (less downstream processing) and more compact reactor area design. However, the technology is yet in an early stage of development. Whilst benefits will be high, barriers to be overcome are many and high. Main hurdles are fundamental reaction data at extreme conditions, reaction/reactor control, construction materials, noise, vibration and scale up & design concepts.

CODE **3.2.5**TECHNOLOGY **SONOCHEMICAL REACTORS****Description/Basic Features**

In the liquid-phase systems, exposure to ultrasound results in formation, growth and subsequent collapse of microbubbles (microcavities), occurring in the extremely short period of time (milliseconds). The microimplosions are accompanied by an energy release with very high energy densities (order of up to 1018 kW/m³), which leads to local generation of extremely high temperatures and pressures, up to ca. 5000 K and ca. 2,000 bar, respectively, as well as release of free radicals due to pyrolysis of water.

Review

The use of ultrasound can (similar to microwaves) dramatically speed-up chemical reactions. Ultrasound creates micro cavitations in which, after implosion, extreme high temperatures and pressures occur. This positively influences reaction speed and increases the product yield. Energy savings and eco (CO₂) impact are limited, but yield increase can be substantial while safety is enhanced due to milder operating conditions. Main barriers are small irradiation depth and poor definition of acoustic energy distribution. Sonochemical reactor have come to age e.g. in water disinfection, although costs are very high. For chemical syntheses, this technology is in the early stages of development. Considerable R&D effort in a multi discipline manner is required in the next 5 years for reliable scale-up, but first full scale commercial application may need another 15 years for this niche application in food processing, biotechnology and environmental protection.

CODE **3.2.6**TECHNOLOGY **ULTRASOUND-ENHANCED CRYSTALLIZATION****Description/Basic Features**

Sonocrystallization is a non-invasive method of using ultrasound to control the point of nucleation and the number of nuclei formed. Combining technologies of



Prosonitron™ sonocrystallization technology at large scale in continuous flow
(Courtesy of Prosonix Ltd, Oxford UK)

sonochemistry (see 3.2.5) and crystallization, sonocrystallization provides “a route to better crystals”. Benefits of sonocrystallization can include controlled initiation of nucleation, enhanced yield, improved crystal habit, improved filtration characteristics, improved product properties including, handling, bulk density and appearance, reduced agglomeration crystals with fewer imperfections and increased process reproducibility.

Evaluation	
Potential for energy savings	Medium
Potential for eco impact CO ₂	Low
Potential to improve cost competitiveness	Medium
Ripeness of application in X years	10-15
Ripeness of related technology fields	Low
Likelihood of overcoming barriers	Low
Potential for innovative high quality products	Medium
Character of required R&D	Fundamental

Review

Acoustically induced cavitations are particularly effective at inducing nucleation in supersaturated liquids. The effect of power ultrasound on crystal suspensions is complex but strong effects have been reported on the growth of secondary nucleation and agglomeration rates. The primary benefit is the formation of ultra-fine, nano-structured

materials, with secondary benefits of energy and cost saving because expensive milling and/or recrystallisation steps can be avoided. No eco impact is reported. This niche technology is still in laboratory phase of development, with only a few industrial applications on pilot level. Barriers are understanding the interaction of cavities and crystals, optimizing the different effects, equipment development, modelling and scale-up issues as well as engineering and design concepts. This is a very promising technology for niche applications in pharma, food or other areas which need very fine matter, but it will probably take 10-15 years of fundamental research to reach full commercial applications.

CODE **3.2.7**TECHNOLOGY **ULTRASOUND REACTORS FOR ENHANCED
DISINTEGRATION/PHASE DISPERSION/MASS
TRANSFER****Description/Basic Features**

Acoustic irradiation appears to be able not only to boost chemical reactions, but also to intensify mass transfer processes in multiphase systems. In gas-liquid systems a circa twofold increase of kLa was observed when ultrasound was used. The effect was even stronger (up to 5 times increase) when NaCl (electrolyte) was added to the system. In the liquid-solid mass transfer, up to 20-fold increase of the mass transfer coefficient was observed. A reduction of the boundary layer thickness due to the micro-scale turbulence and reduction of the viscosity in the boundary layer were postulated as the mechanism behind the observed phenomenon.

Evaluation	
Potential for energy savings	Medium
Potential for eco impact CO ₂	Medium
Potential to improve cost competitiveness	Medium
Ripeness of application in X years	<5
Ripeness of related technology fields	High
Likelihood of overcoming barriers	High
Potential for innovative high quality products	Medium
Character of required R&D	Applied

Review

Ultrasound enhanced Process intensification is broadly applied in anaerobic digestion of biomass/sludge of waste water treatment plants. This technology offers chances for process intensification to produce biomass while reducing digested organic (waste) solids. This technology will become a major innovative contributor in emerging niche

“green” chemistry and “green” engineering e.g. intensive animal farming. Through better biogas production and resulting less organics (waste) solids energy gain and cost savings will be substantial, but technology could also be applied to disinfection of process water etc.

Barriers to be overcome are not only unfamiliarity for applications, but also material issues and modelling, scale up and design concepts. Nevertheless the technology is judged to be ripe for broad application in the next 5 years.

CODE **3.2.8**TECHNOLOGY **SUPERSONIC SHOCKWAVE FOR PHASE DISPERSION**SUBCODE **3.2.8.1**SUB-TECHNOLOGY **SUPERSONIC GAS-LIQUID REACTORS****Description/Basic Features**

Using the energy of the supersonic shockwave presents another promising alternative method for intensification of the phase contacting and transport processes. A high intensity tubular reactor has been developed by Praxair Inc. for fast plug-flow reactions between a gas and a liquid. According to Praxair, the reactor is also suitable for three-phase reactions involving solid phase. The basic part of the reactor is the supersonic in-line mixer. The supersonic gas-liquid reactor enables to achieve very high mass transfer fluxes within a limited volume by using the supersonic shockwave to disperse gas into tiny bubbles. Results of experiments carried out with oxygen-water system show that the oxygen transfer rate in a



Transonic oxygen injection in fermentation plant (Courtesy of DSM)

supersonic reactor is up to ca. 10 times higher than in a tee-mixer. Recently, DSM reported development and application of a transonic oxygen injection technology in one of its large-scale fermentation processes. New type of the supersonic injection system has doubled the yeast productivity of the fermenter.

Review

Very high mass transfer can be realized in gas-liquid contacting by utilizing a supersonic shock wave. Praxair uses this technology for oxygen injection in electric steel furnaces (>70 applications). Recently DSM commercialized it for fermenters. Mass transfer (volumetric mass transfer coefficient up to 6 s^{-1}) is enhanced by brute forces and, as a consequence, large energy savings are not to be expected. Benefits are robust, compact and safer reactors. A barrier is lack of experience in the chemical industry.

Evaluation	
Potential for energy savings	Low
Potential for eco impact CO ₂	Low
Potential to improve cost competitiveness	Low
Ripeness of application in X years	<5
Ripeness of related technology fields	High
Likelihood of overcoming barriers	High
Potential for innovative high quality products	Low
Character of required R&D	Applied

CODE 3.2.8**TECHNOLOGY SUPERSONIC SHOCKWAVE FOR PHASE DISPERSION****SUBCODE 3.2.8.2****SUB-TECHNOLOGY SUPERSONIC GAS-SOLID REACTORS****Description/Basic Features**

German company Messer Griesheim GmbH has patented and commercialized a supersonic nozzle for fluidized-bed applications. The concept was subsequently applied on the industrial scale in a fluidized-bed reactor for iron sulphate decomposition at Bayer AG. Supersonic injection of oxygen has increased the capacity of the reactor by 124%. The same technology has also been applied to the sludge combustion reactors increasing the throughput by approximately 40%.

CODE **3.3.1**TECHNOLOGY **ELECTRIC FIELD-ENHANCED OPERATIONS**SUBCODE **3.3.1.1**SUB-TECHNOLOGY **ELECTRIC FIELD-ENHANCED EXTRACTION****Description/Basic Features**

Electric fields are commercially employed to augment rate processes and to control droplet size in paint spraying, crop spraying and surface coating processes. Placement of an electric charge on droplets can substantially improve the required adhesion between the product and the target.

Electric fields can also enhance processes involving liquid/liquid mixtures, in particular liquid-liquid extraction where extraction rate enhancements of 200-300% were reported. In electric-field-induced emulsification - 200 to 500 times increase in the surface area per unit volume, compared to the millimetre-sized droplets in the conventional processes has been reported.

Evaluation	
Potential for energy savings	High
Potential for eco impact CO ₂	Low
Potential to improve cost competitiveness	Low
Ripeness of application in X years	<5
Ripeness of related technology fields	High
Likelihood of overcoming barriers	High
Potential for innovative high quality products	Low
Character of required R&D	Combination

Review

Attractiveness of this technology stems from very efficient direct application of electric energy in mass transfer operations as well as dispersion of fluids in liquids. It is a well known application in the mining industry, gas cleaning, emulsion breaking, ink-jet spraying, fuel spraying, car painting, crude oil desalting, and bulk chemical washing

(MTBE). Typical advantages are energy savings and equipment size reduction (cost savings). No specific eco (CO₂, waste) advantages are reported. Further optimization of equipment and applications are possible but no break-through new applications have been identified. Barriers for wider use are identified as modelling, design and scale up for larger commercial installations. Also social acceptance/ unfamiliarity of use of direct electricity in chemical processing plays a role. The Technology is well developed for broader use but no new innovative products are to be expected.

CODE 3.3.1**TECHNOLOGY ELECTRIC FIELD-ENHANCED OPERATIONS****SUBCODE 3.3.1.2****SUB-TECHNOLOGY ELECTRIC FIELD-ENHANCED HEAT TRANSFER****Description/Basic Features**

In boiling heat transfer electric fields have been successfully used to control nucleation rates and achieve a continuous rise in heat transfer coefficient. Up to a 7-fold heat transfer enhancement by the electric field in falling film evaporators has also been reported.

CODE **3.3.1**

TECHNOLOGY **ELECTRIC FIELD-ENHANCED OPERATIONS**

SUBCODE **3.3.1.3**

SUB-TECHNOLOGY **ELECTRIC FIELD-ENHANCED MIXING**

Description/Basic Features

Providing electric fields, both AC and DC in microchannels considerable shortens the mixing length. Shortening of the mixing length by factor 30 or more are reported.

CODE **3.3.1**TECHNOLOGY **ELECTRIC FIELD-ENHANCED OPERATIONS**SUBCODE **3.3.1.4**SUB-TECHNOLOGY **OTHER APPLICATIONS****Description/Basic Features**

Electric fields can be used for instance to reduce fouling phenomena in systems involving electrically charged macromolecules (e.g. proteins). In microsystems used for capillary zone electrophoresis external electric field applied across the capillary tube induces electrostatic repulsion between the macromolecules and the inner surface. The reduced adsorption of macromolecules enhances separation resolution and efficiency.

Some works have also been carried out o application of electric field in membranes, to reduce/prevent fouling.

CODE **3.3.2**TECHNOLOGY **INDUCTION + OHMIC HEATING****Description/Basic Features**

Inductive heating is a process wherein electric currents are induced within the food or other material due to the presence of oscillating electromagnetic fields generated by electric coils in the vicinity of this material; with the primary purpose of heating the said material. Such fields may be generated in various ways, including the use of the flowing food material as the secondary coil of a transformer. Inductive heating may be distinguished from microwave heating by the frequency (specifically assigned in the case of microwaves), and the nature of the source (the need for coils and magnets for generation of the field, in the case of inductive heating, and a magnetron for microwave heating).

Ohmic heating, also known as Joule heating, electro-conductive heating, or direct electrical resistance heating, involves the passage of electric current through a material for the purpose of heating it. James Prescott Joule, in 1840, recognized that an electric current passing through a material generated heat within it. The heat generation is more uniform than with microwave and induction heating. Ohmic heating necessarily involves electrodes that contact the product to create a continuous electrical circuit.

Evaluation	
Potential for energy savings	Low
Potential for eco impact CO ₂	Low
Potential to improve cost competitiveness	High
Ripeness of application in X years	5-10
Ripeness of related technology fields	Medium
Likelihood of overcoming barriers	Medium
Potential for innovative high quality products	High
Character of required R&D	Combination

Review (Ohmic heating)

Ohmic heating involves passage of electric current through a material for the purpose of heating it. It is an emerging technology and commercial application is at a relatively early stage. Most promising applications lie in continuous sterilization of foods containing particles by high temperature-short-time processing, thereby yielding

quality improvement. No firm data are as yet available on energy savings and cost savings, but potentials are identified as good. Barriers for this niche application for the food industry are establishing proof for the “safety” of sterilized food (e.g. microbiological testing, but also use of direct electricity in processing steps) as well as development of novel process equipment and systems. This technology could be ripe for use in 5-10 years and would create an innovative new way of food processing. But combined development efforts of Research and Industry are necessary.

CODE **3.3.3**TECHNOLOGY **MICROWAVE-ENHANCED OPERATIONS**SUBCODE **3.3.3.1 + 3.3.3.2**SUB-TECHNOLOGY **MICROWAVE DRYING + (PRE)HEATING****Description/Basic Features**

In general, microwave frequencies range from 0.3 to 300 GHz, which corresponds to the wavelength between approximately 1 mm and 1 m. Much part of this range is occupied by the radar and telecommunication applications and in order to avoid interference the industrial and domestic microwave appliances operate at several standard allocated frequencies, most often at 2.45 GHz. Molecules that have a permanent dipole moment (e.g. water) can rotate in a fast changing electric field of microwave radiation. Additionally, in substances where free ions or ionic species are present, the energy is also transferred by the ionic motion in an oscillating microwave field. As a result of both these mechanisms the substance is heated directly and almost evenly. Heating with microwaves is therefore fundamentally different from conventional heating by conduction. The magnitude of this effect depends on dielectric properties of the substance to be heated.

Also in solid materials microwaves are used on industrial scale for heating purposes. The ability of the solid material to absorb the microwave heating depends on two properties: the dielectric constant and the loss tangent. Some materials absorb the microwave energy very easily; others are transparent or impermeable to it.



Microwave hybrid continuous belt dryer

(Courtesy of Fricke und Mallach Microwave Technology GmbH)

The difference in sensitivity of various substances to microwaves makes the latter an interesting technology for the selective heating of materials/products. Microwave-enhanced drying is used on the industrial scale in food, wood, textile and pharmaceutical industries. Microwaves enable selective heating of the moisture contained in microwave-transparent materials. This way the whole process proceeds in lower bulk temperatures and allows for considerable energy savings. Also, the speed of the MW drying allows avoiding unwanted degradation of some less stable components of the dried materials.

Evaluation	
Potential for energy savings	High
Potential for eco impact CO ₂	Low
Potential to improve cost competitiveness	Medium
Ripeness of application in X years	<5
Ripeness of related technology fields	High
Likelihood of overcoming barriers	High
Potential for innovative high quality products	High
Character of required R&D	Applied

Review

Microwave heating is applied on the scale of the consumer but also on a large industrial scale. The mechanism of heating is different from conventional heating by conduction. Molecules with a dipole moment (water is the most important representative) and free ions and ionic species absorb the energy. This leads to even heating and, dependent on

the system, to selective heating. Commercial equipment for heating and drying is available from several vendors. The technology is widely applied: fine chemicals, pharma, food, polymers. New applications are in the field of materials production (nano-materials, zeolites). Energy savings and occasionally, because of the much shorter process times, space savings can be substantial. Barriers are investment costs, reactor design (increase of efficiency, irradiation depth in the scale of cm's, safety as the radiation is dangerous), limited know-how on physical properties of the materials to be processed (dielectric properties).

CODE **3.3.3**TECHNOLOGY **MICROWAVE-ENHANCED OPERATIONS**SUBCODE **3.3.3.3**SUB-TECHNOLOGY **MICROWAVE-ENHANCED SEPARATIONS****Description/Basic Features**

In general, microwave frequencies range from 0.3 to 300 GHz, which corresponds to the wavelength between approximately 1 mm and 1 m. Much part of this range is occupied by the radar and telecommunication applications and in order to avoid interference the industrial and domestic microwave appliances operate at several standard allocated frequencies, most often at 2.45 GHz. Molecules that have a permanent dipole moment (e.g. water) can rotate in a fast changing electric field of microwave radiation. Additionally, in substances where free ions or ionic species are present, the energy is also transferred by the ionic motion in an oscillating microwave field. As a result of both these mechanisms the substance is heated directly and almost evenly. Heating with microwaves is therefore fundamentally different from conventional heating by conduction. The magnitude of this effect depends on dielectric properties of the substance to be heated.

Microwave heating is shown to enhance some extraction operations, particularly extraction of pharmaceutical ingredients from plant material. Also, a limited number of papers have been published concerning the enhancement effects of microwaves on membrane separation and distillation.

CODE **3.3.3**TECHNOLOGY **MICROWAVE-ENHANCED OPERATIONS**SUBCODE **3.3.3.4.1**SUB-TECHNOLOGY **MICROWAVE REACTORS FOR NON-CATALYTIC AND
HOMOGENEOUSLY CATALYZED LIQUID-PHASE PROCESSES****Description/Basic Features**

In general, microwave frequencies range from 0.3 to 300 GHz, which corresponds to the wavelength between approximately 1 mm and 1 m. Much part of this range is occupied by the radar and telecommunication applications and in order to avoid interference the industrial and domestic microwave appliances operate at several standard allocated frequencies, most often at 2.45 GHz. Molecules that have a permanent dipole moment (e.g. water) can rotate in a fast changing electric field of microwave radiation. Additionally, in substances where free ions or ionic species are present, the energy is also transferred by the ionic motion in an oscillating microwave field. As a result of both these mechanisms the substance is heated directly and almost evenly. Heating with microwaves is therefore fundamentally different from conventional heating by conduction. The magnitude of this effect depends on dielectric properties of the substance to be heated.

Authors generally agree about the ability of microwave heating to accelerate organic reactions and acceleration factors from several to more than thousand are reported. Also, increase of the product yield has been reported in some cases as a result of microwave heating.



Modomode (left) and multimode (right) microwave reactors from CEM Corporation
(Courtesy of CEM)

Evaluation	
Potential for energy savings	Low (see review)
Potential for eco impact CO ₂	Low
Potential to improve cost competitiveness	Medium
Ripeness of application in X years	10-15
Ripeness of related technology fields	Low
Likelihood of overcoming barriers	Medium
Potential for innovative high quality products	
Character of required R&D	Fundamental

Review

This is a promising technology for niche applications in the fine chemical/ pharmaceutical and consumer products sector in small-to-medium scale applications. The technology is in its early stages of development. No firm data are available on energy savings, cost saving and/or eco impact but are judged to be considerable in specific applications. With the use of other than

fossil fuel for electricity generation this might become interesting.

Major barriers are the small irradiation depth of the microwave versus required scale of production, narrow applicability of media in the process as well as materials of construction. Next to that, design/engineering, scale-up and modelling remains major challenges. For the next 10-15 years a major effort in interdisciplinary R&D will be required to bring this technology closer to commercialization.

CODE **3.3.3**TECHNOLOGY **MICROWAVE-ENHANCED OPERATIONS**SUBCODE **3.3.3.4.2**SUB-TECHNOLOGY **MICROWAVE REACTORS FOR HETEROGENEOUS CATALYSIS****Description/Basic Features**

Dramatic effects of microwave irradiation have been reported in heterogeneous catalysis. For example, in microwave-assisted oxidative coupling of methane on alumina supported $\text{La}_2\text{O}_3/\text{CeO}_2$ catalyst conversion into the C_2 products occurred at temperatures about 250°C lower than during the conventional heating. The authors ascribed this dramatic effect to the CH_4 plasma formation and arcing. Other hypotheses concerning the MW effects in heterogeneous catalysts base on the selective heating of the metal nanoparticles, due to which the reaction sites become much hotter than the catalyst support.

Evaluation	
Potential for energy savings	Low
Potential for eco impact CO_2	Medium
Potential to improve cost competitiveness	High
Ripeness of application in X years	10-15
Ripeness of related technology fields	High
Likelihood of overcoming barriers	Medium
Potential for innovative high quality products	High
Character of required R&D	Combination

Review

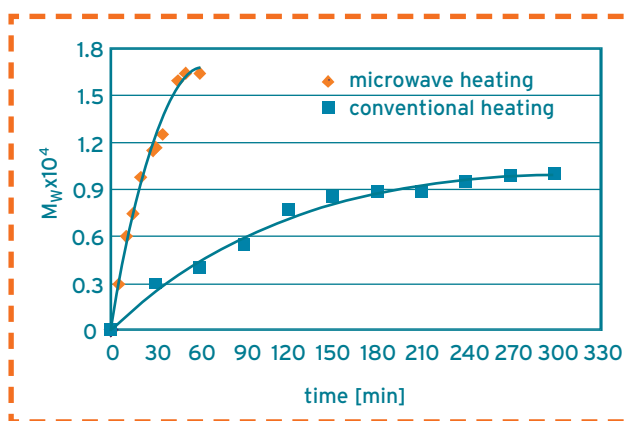
This topic is closely related to microwave heating/ drying (3.3.3.4.1/2). Microwave heating is applied on the scale of the consumer but also on a large industrial scale. The mechanism of heating is different from conventional heating by conduction. Molecules with a dipole moment (water is the most important representative) and free ions and ionic

species absorb the energy. This leads to even heating and, dependent on the system, to selective heating. In this respect there is no difference with heating/ drying by microwaves. However, in heterogeneous catalysis innovative ideas exist: the temperature of reactant and catalyst could be different, the same applies to nano-structured materials (e.g., a support does not heat up, whereas nano-particles do). Microwave-induced reforming has been studied. The reactor functioned as a plasma reactor. Laboratory-scale microwave reactors are offered by vendors but there might be room for innovations in designing tailored reactors. Barriers are reactor design, unknown materials properties.

CODE **3.3.3**TECHNOLOGY **MICROWAVE-ENHANCED OPERATIONS**SUBCODE **3.3.3.4.3**SUB-TECHNOLOGY **MICROWAVE REACTORS FOR POLYMERIZATION REACTORS & POLYMER PROCESSING****Description/Basic Features**

The use of microwave irradiation in polymerisation processes may lead to considerable increase of the process rates and can also influence product properties.

MW heating is already used on the industrial scale in the curing of various polymeric materials.



An example of microwave influence of a polyesterification reaction resulting in 1.6-fold molecular weight increase and 10-fold increase of the rate of polymerization

Evaluation	
Potential for energy savings	High
Potential for eco impact CO ₂	Low
Potential to improve cost competitiveness	Low
Ripeness of application in X years	10-15
Ripeness of related technology fields	Medium
Likelihood of overcoming barriers	Low
Potential for innovative high quality products	High
Character of required R&D	Fundamental

Review

Applying microwave reactors in Polymer processing (bonding/welding, curing and forming) is reasonably established, but this technology in polymerization reactions is in its early stages of development. No firm data are available on energy savings, cost saving and/or eco impact but are judged to be considerable in specific applications. In Processing

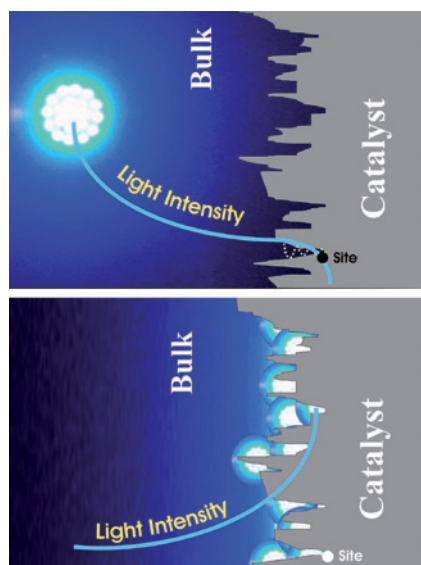
this offers a much better control over temperature compared to conventional heating (e.g. no baking, no deterioration due to high temperatures). Benefits for reaction are polymers with different mol weight and increase of selectivity compared to conventional heating. Major barriers are the small irradiation depth of the microwave versus required scale of production, narrow applicability of media in the process as well as materials of construction. Next to that, design/engineering, scale-up and modelling remains major challenges. For the next 10-15 years a major effort in interdisciplinary R&D will be required to bring this technology closer to commercialization.

CODE **3.3.4**TECHNOLOGY **PHOTOCHEMICAL REACTORS****Description/Basic Features**

Photochemical reactors use the energy of light to initiate or catalyze reactions. The basic principle is that light quanta are absorbed by chemical compounds (reagents, sensitizers or catalysts) which are electronically excited and become (more) reactive towards other compounds present. The wavelength of the light is in the range of 200



Stripped optical fibres used in photocatalytic reactor
(Courtesy of Delft University of Technology)



New concept of photocatalytic reactor with in-situ light generation via nano-scale illumination
(Courtesy of Delft University of Technology)

nm to 400 nm (UV) and 400 nm to 700 nm (visible light). IR induced photochemistry also exists, but is mainly used in analytical techniques and has not frequently been investigated for chemical process technology, except for some very specific applications in the USA. The light can originate either from the sun (4-5% UV) or from artificial sources (e.g., medium-pressure mercury or xenon lamp, excimer lamp). In the case of solar-driven photochemical reactors, the energy needs to be concentrated in order to reach sufficient efficiency.

In non-catalyzed photochemical reactions the light energy is absorbed by the reagent itself or by a sensitizer. A sensitizer transfers the electronic energy to the reagent or undergoes a reversible redox reaction with the reagent (which is then photocatalysis). The reagent becomes then electronically excited by the transfer of an electron to a higher energy band. Upon returning to its ground state, the molecule can either transfer its energy to another molecule (thus exciting this molecule) or produce reactive components such as radicals or ions.

Evaluation	
Potential for energy savings	High
Potential for eco impact CO ₂	Medium
Potential to improve cost competitiveness	Medium
Ripeness of application in X years	10-15
Ripeness of related technology fields	Medium
Likelihood of overcoming barriers	Medium
Potential for innovative high quality products	Medium
Character of required R&D	Fundamental

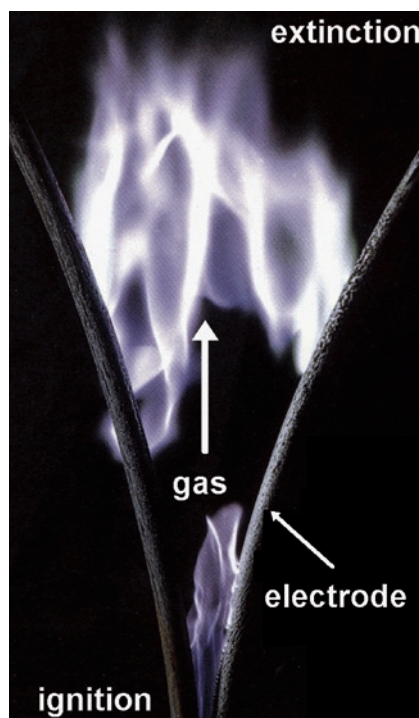
Review

These reactors use the energy of light to initiate or catalyze reactions. Today the main applications are in production of protective and decorative coatings, inks, packaging and electronic materials. Commercial applications in bulk chemical, pharma, and agro sectors are scarce. Major benefits are the use of low temperatures (room temps), thus

providing energy savings, cost savings and very high conversion/yield/selectivity. Major barriers are light penetration depth, the light source itself, light efficiency and wavelength. Also modelling, scale-up and optimal reactor configuration form a high hurdle. It probably will take another 10 years of interdisciplinary research before commercialization of this niche technology could start to develop.

CODE **3.3.5**TECHNOLOGY **PLASMA (GLIDARC) REACTORS****Description/Basic Features**

Gliding Arc technology is a new way of plasma generation by formation of electric “gliding discharges”. At least two electrodes diverging with respect to each other are placed in fast gas flow and in the flow direction. Gliding discharges are



Operating principle of GlidArc reactors
(Courtesy of A. Czernichowski, *Etudes Chimiques et Physiques*)

produced between the electrodes and across the flow. They start at the spot where the distance between the electrodes is the shortest, and spread by gliding progressively along the electrodes in the direction of flow until they disappear after a certain path. Possible applications of GlideArc tested so far include methane transformation to acetylene and hydrogen, destruction of N₂O, reforming of heavy petroleum residues, activation of organic fibres, CO₂ dissociation, air depollution from volatile compounds, valorisation of concentrated H₂S or H₂S + CO₂ mixtures, flue gas SO₂ reduction to elementary sulfur, natural gas conversion to the syngas etc. Gliding arc discharges are an inexpensive method to bring easy controllable energy, so that high energy consuming thermal processes at high temperatures can be substituted by this cold and catalytic plasma process at lower energy expense.

Evaluation	
Potential for energy savings	Low
Potential for eco impact CO ₂	Low
Potential to improve cost competitiveness	Medium
Ripeness of application in X years	5-10
Ripeness of related technology fields	Medium
Likelihood of overcoming barriers	Medium
Potential for innovative high quality products	Medium
Character of required R&D	Combination

Review

Gliding Arc electric discharges in a reactor generate ionized gas for further chemical reaction. A number of potential applications are discussed (partial oxidation of natural gas and bio methane, steam reforming of light hydrocarbons, N₂O to NO_x, SO₂ reductions to its elements) and to some extent demonstrated but no commercial

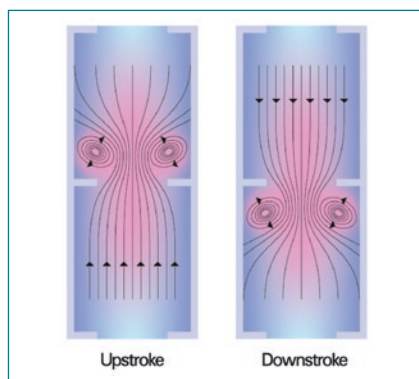
applications are known as of today. The technology could lead to a way to provide easily controllable and very active energy to various processes.

Barriers are engineering/design as well as control systems for commercial scale units. Also “fear” (applying high voltage devices) is a barrier. Although in the next 2-5 years these reactors will participate in the further growth of green distributed electric energy, it is not expected that major innovative breakthroughs will appear in the next 10 years, even with combined efforts from R&D and Industry.

CODE 4.1.1

TECHNOLOGY **OSCILLATORY BAFFLED REACTOR AND CONTINUOUS OSCILLATORY BAFFLED REACTOR TECHNOLOGIES****Description/Basic Features**

The Oscillatory Baffled Reactor (OBR) technology generally consists of a cylindrical column containing equally spaced orifice baffles and superimposing with fluid oscillation. Vortices are generated when fluid flow past through the baffles enabling significant radial motions where events at the wall are of the same magnitude as these at the centre. The generation and cessation of eddies creates uniform mixing in each baffled cell, collectively along the column. The degree of mixing is independent of the net flow, which makes it possible to realize a nearly plug-flow character (many CSTRs in series) in a flow system at long residence times.



Flow pattern in Oscillatory Baffled Reactor
(Courtesy of NiTech Solutions Ltd.)



Oscillatory Baffled Reactor (Courtesy of Ni-Tech Solutions Ltd.)

Evaluation	
Potential for energy savings	Medium
Potential for eco impact CO ₂	Low
Potential to improve cost competitiveness	High
Ripeness of application in X years	<5
Ripeness of related technology fields	High
Likelihood of overcoming barriers	High
Potential for innovative high quality products	Low
Character of required R&D	Combination

Review

OBR and COBR techniques offer enhanced mass and heat transfers over stirred tank reactors (the workhorse in chemicals and pharmaceuticals). The technology uses a cylindrical column containing equally spaced orifice baffles and superimposed fluid oscillation, thus allowing plug flow conditions even at low (laminar) flow rates. (changing batch to continuous

production). Major benefits are significant energy/utility savings, higher yields and less side products/high product consistency. In addition, capital cost savings are achieved through much more compact designs. This technology is a niche application for one company (NiTech Solutions Ltd). Through this company industrial applications (exothermic/explosive reaction; specialty chemicals, API

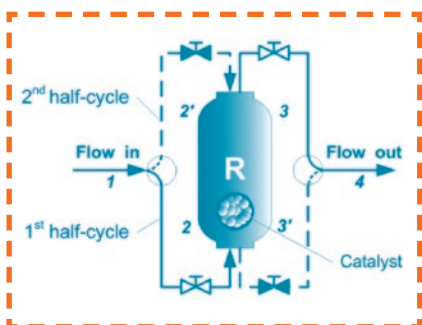
(active pharmaceutical ingredient) production involving solid, liquid and gas phase) are demonstrated. The technology is applicable to much broader fields such as chemicals, food drinks, pharma API's, bio fuels etc. Barriers (medium complexity) are dealing with high viscous or high-density liquids, high gas production in reaction and reactions with long intrinsic reaction times and its associated modelling techniques. Concerted efforts from academia, industry and NiTech Ltd will bring this technology to full broad commercialisation in the next 5 years.

CODE 4.1.2

TECHNOLOGY REVERSE FLOW REACTOR OPERATION

Description/Basic Features

A pretty widely known example of the integration of reaction and heat transfer in a multifunctional unit are reverse-flow reactors. In case of exothermic processes the periodic flow reversal in such units allows for almost perfect utilization of the heat of reaction by “keeping it” within the catalyst bed and, after reversion of the flow



Operating principle of the Reverse Flow Reactor (Courtesy of Y. Wibisono Budhi, Institute of Technology Bandung)

direction, using it for the pre-heating of the cold reactant gases. To date the reverse-flow reactors have been used in three industrial processes: the SO_2 oxidation, total oxidation of hydrocarbons in off-gases and the NO_x reduction. The reverse-flow principle has also been applied in rotating monolith reactors used industrially for removal of the undesired components from the gas streams and continuous heat regeneration. Studies are also carried out on the use of reversed-flow reactors for endothermic processes.

Evaluation	
Potential for energy savings	Medium
Potential for eco impact CO_2	High
Potential to improve cost competitiveness	Medium
Ripeness of application in X years	5-10
Ripeness of related technology fields	Medium
Likelihood of overcoming barriers	High
Potential for innovative high quality products	Medium
Character of required R&D	Combination

Review

In reverse flow reactor operation, one or more process variables are intentionally and permanently perturbed according to some schedule. This dynamic operation creates process improvements that cannot be achieved by steady state operation. The technology was first introduced for removal of pollutants (so good eco impact) but this novel concept of

catalytic reaction engineering get much more attention. Expected benefits are targeted at energy savings, increased conversion selectivity and productivity. Barriers are reaction kinetics (exothermic reactions, endothermic reactions as well as equilibrium reactions), energy storage, as well as reactor design operation and control. All these barriers stem from the dynamics of high flow reversal frequency. A concerted effort from Academia and Industry is needed to address this broad range of barriers, but this novel concept could be brought to commercialization in 5-10 years time.

CODE **4.1.3**TECHNOLOGY **PULSING OPERATION OF MULTIPHASE REACTORS****Description/Basic Features**

Forced dynamic (periodic, pulsing) operation of chemical reactors as a means for improving the reactor performance has been investigated since late 1960's. Usually the flow (rate or direction) or the inlet concentration are periodically varied. Via dynamic operation one can advantageously influence the kinetics of the adsorption-reaction-desorption processes on the catalyst surface (solid-catalyzed gas-phase reactions), increase interfacial mass transfer rates (e.g. pulsing operation of trickle-bed reactors), shift the process beyond the equilibrium limitation or improve heat transfer (e.g. reversed-flow operation of fixed-bed catalytic reactors), or improve mixing characteristics of the system (e.g. variable-volume operation of the stirred-tank reactors). This way spectacular improvements in the process rates (50% and more) have been achieved in the bench-scale experiments.

CODE 4.1.4

TECHNOLOGY PULSE COMBUSTION DRYING

Description/Basic Features

The term pulse combustion (PC) originates from the intermittent (pulse) combustion of the solid, liquid or gaseous fuel in contrast to the continuous combustion in conventional burners. Such periodic combustion generates intensive pressure,



Rotary-valve pulse combustor mounted at the top of the spray dryer

(Courtesy of Pulse Combustion Systems, San Rafael, CA, USA)

velocity, and to certain extent, temperature waves propagated from the combustion chamber via a tailpipe to the process volume (applicator) such as a drying chamber. Because of oscillatory nature of the momentum transfer, pulse combustion intensifies the rates of heat and mass transfer thus accelerates drying rates. The pulse combustion dryer consists of a pulse combustor fitted to a spray dryer, rotary kiln, pneumatic dryer, cyclone dryer or a fluid-bed dryer. Such a combination leads to increased heat and mass transfer rates (factor 2-5), increase combustion intensity (up to factor 10) and efficiency, and increased thermal efficiency (up to 40%).

Evaluation	
Potential for energy savings	Medium
Potential for eco impact CO ₂	Low
Potential to improve cost competitiveness	Medium
Ripeness of application in X years	5-10
Ripeness of related technology fields	Low
Likelihood of overcoming barriers	Medium
Potential for innovative high quality products	High
Character of required R&D	Combination

Review

Pulse combustion drying is a promising energy efficient and environmentally friendly technology for use in processing of minerals, chemicals, foods as well as wastes. These direct-heated dryers provide low energy consumption, lower capital cost and lower CO₂ emission over conventional spray dryers. Even though combustion dryers have been in the

market for years, they form an art rather than a science, and application is not wide spread.

Barriers are noise reduction, mechanical reliability, use of other energy sources then fossil fuels as well as design and scale up rules and mathematical models. A combined effort by interdisciplinary scientists and industry practitioners is needed to advance this technology to broader commercialization in the next 5-10 years.

CODE **5.1.1**TECHNOLOGY **SUPERCRITICAL REACTIONS****Description/Basic Features**

Supercritical reactions are reactions which utilize a fluid which is near- or supercritical. The potential advantage is based on the ability to tune the physical properties of the reaction medium with the objective to enhance reaction rate and strongly improve on selectivity.

A fluid is called supercritical when its temperature and pressure exceed their values at the critical point. Supercritical fluids (SCFs) can be attractive media for chemical reactions because of their unique properties. Many of the physical and transport properties of an SCF are intermediate between those of a liquid or a gas. For instance, the diffusivity in an SCF falling between that in a liquid and a gas suggests that reactions that are diffusion limited in the liquid phase could become faster in an SCF phase. SCFs have also unique solubility properties. Compounds that are largely insoluble in a fluid at ambient conditions can become soluble in the fluid at supercritical conditions. Conversely, some compounds that are soluble at ambient conditions can become less soluble at supercritical conditions.

CODE 5.1.2

TECHNOLOGY SUPERCRITICAL SEPARATION

Description/Basic Features

Supercritical fluids on the one hand possess properties that are quite similar to those of a liquid such as their density, which makes them a solvent, but on the other hand they behave like a gas, or as a fluidum between a gas and a liquid, e.g. they exhibit low viscosities, low surface tensions, high diffusivities for solutes and high compressibilities especially around the critical point. Supercritical fluids are attractive media for separations (e.g. extraction) because of their unique properties. Compounds that are largely insoluble in a fluid at ambient conditions can become soluble in the fluid at supercritical conditions. Conversely, some compounds that are soluble at ambient conditions can become less soluble at supercritical conditions.

Evaluation	
Potential for energy savings	Medium
Potential for eco impact CO ₂	High
Potential to improve cost competitiveness	High
Ripeness of application in X years	<5
Ripeness of related technology fields	Medium
Likelihood of overcoming barriers	High
Potential for innovative high quality products	Medium
Character of required R&D	Combination

Review

Supercritical fluids behave both like liquid and as gas since there is no difference between these phases above the supercritical point. Currently mainly CO₂ is used but other substances are very well possible (e.g. hexane, pentane, ammonia). By using the substance as “a liquid”

valuable compounds can be extracted from mixtures which, after flashing/pressure reduction of the supercritical fluid (which then becomes a gas), are recovered in a pure/ not dissolved form. Main benefit is an eco impact (and energy savings) through the avoidance of a “normal” solvent (organic and/or water) and its associated waste problems (e.g. emissions to the atmosphere and/or waste fluid treatment). Main (relatively low) barriers to overcome are mechanical challenges caused by high pressure, design of “low cost” equipment using alternative materials over steel but particularly prejudices against the used of pressurized systems compared to current solvent based atmospheric systems. Supercritical separations using CO₂ are well established in extraction of natural materials. Break through towards other fields e.g. replacing water as solvent is the next challenge. A combined effort of Academia and Industry could bring these break-throughs’ (thus making a step change in waste reduction and use of energy for waste disposal) within the next 5 years.

CODE **5.1.3**TECHNOLOGY **CRYOGENIC SEPARATIONS****Description/Basic Features**

Cryogenic separation techniques (distillation or distillation combined with adsorption) are nowadays almost exclusively used for production of industrial gases. They may in the future prove attractive for some specific separations in manufacturing of bulk or fine chemicals. In the production of argon, oxygen and nitrogen from air, the latter is compressed and cooled to cryogenic temperatures against the product gases and sent to double distillation column. The two columns in this system work at different pressures and are thermally linked. The reboil vapours from the low pressure column condense the overhead vapours in the high pressure column. Cryogenic adsorption can complement cryogenic distillation to remove impurities down to ppb level under cryogenic conditions.

Technology code	technology name	Criteria A			Criteria B			Criteria C	Criteria D
		Potential for energy savings	Potential for eco impact CO ₂	Potential to improve cost competitiveness	Ripeness application in X years	Ripeness related technology fields	likelihood of overcoming barriers	potential for innovative high quality products	Character required R&D: fundamental/combined/applied
1.1.1	Advanced plate-type heat exchangers	medium	medium	high	<5	high	high	low	applied
1.1.2	Advanced shell & tube type heat exchangers	medium	medium	medium	<5	high	high	low	applied
1.1.4	Static mixers	medium	medium	medium	<5	medium	medium	low	applied
1.2.1.1	Heterogeneously catalyzed solid foam reactors	low	low	low	5-10	high	high	medium	fundamental
1.2.1.2	Monolithic reactors	medium	medium	medium	5-10	high	high	high	applied
1.2.1.3	Millisecond (gauze) reactors	low	low	medium	5-10	medium	medium	low	combination
1.2.1.4	Structured reactors	medium	medium	medium	5-10	medium	medium	low	applied
1.2.2	Micro channel reactors	low	low	low	>15	medium	medium	high	fundamental
1.2.3	Membrane reactors (non-selective)	low	low	low	>15	low	low	medium	fundamental
1.2.4	Static mixer reactors for continuous reactions	high	high	medium	5-10	high	high	medium	applied
2.1.1	Adsorptive distillation	medium	medium	low	10-15	low	low	medium	fundamental
2.1.3	Extractive distillation	medium	low	low	5-10	medium	medium	medium	fundamental
2.1.4	Heat-integrated distillation	high	high	high	<5	high	high	low	applied
2.1.5.3	Membrane crystallization technology	medium	medium	medium	10-15	low	low	high	fundamental
2.1.5.4	Membrane distillation technology	medium	medium	medium	5-10	medium	medium	medium	combination
2.1.5.5	Distillation-Pervaporization	medium	medium	medium	<5	high	medium	medium	combination
2.2.1	HEX reactors	low	low	high	5-10	high	medium	high	applied
2.2.3.1	Simulated Moving Bed reactors	low	low	low	5-10	medium	medium	high	combination
2.2.3.2	Rotating Annular Chromatographic reactors	low	low	high	10-15	medium	medium	high	fundamental
2.2.3.3	Gas-Solid-Solid Trickle Flow reactors	low	low	high	10-15	high	low	medium	fundamental
2.2.5	Reactive extraction columns, HT and HS	medium	medium	low	5-10	medium	high	medium	combination
2.2.6	Reactive absorption	high	high	low	<5	high	high	medium	applied
2.2.8.1	Reactive distillation	high	high	high	<5	high	high	medium	applied
2.2.8.2	Membrane-assisted reactive distillation	high	high	high	5-10	high	medium	high	applied

Technology Matrix 1: General overview of the PI Technology reviews

Technology code	technology name	Criteria A			Criteria B			Criteria C	Criteria D
		Potential for energy savings	Potential for eco Impact CO ₂	Potential to improve cost competitiveness	Ripeness application in X years	Ripeness related technology fields	likelihood of overcoming barriers	potential for innovative high qual products	Character required R&D: fundamental/combined/applied
3.1.2	Centrifugal liquid-liquid contractors	high	medium	medium	<5	high	high	low	applied
3.1.3	Rotating packed beds	medium	medium	high	5-10	high	medium	medium	combination
3.1.4	Rotor stator devices	high	medium	medium	<5	high	high	high	applied
3.2.2	Hydrodynamic cavitation reactors	medium	low	medium	10-15	medium	medium	medium	fundamental
3.2.3	Impinging streams reactor	medium	low	medium	<5	high	medium	low	applied
3.2.4	Pulsed compression reactor	high	high	medium	>15	low	low	medium	fundamental
3.2.5	Sonochemical reactors (ultrasound and low frequency sonics)	medium	low	medium	10-15	medium	medium	medium	fundamental
3.2.6	Ultrasound enhanced crystallization	medium	low	medium	10-15	low	low	medium	fundamental
3.2.7	Ultrasound reactors for enhanced distillation/phase dispersion/mass transfer	medium	medium	medium	<5	high	high	medium	applied
3.2.8	Supersonic Gas-Liquid reactors	low	low	low	<5	high	high	low	applied
3.3.1.1	Electric field-enhanced extraction	high	low	low	<5	high	high	low	combination
3.3.2	Induction and ohmic heating	low	low	high	5-10	medium	medium	high	combination
3.3.3.1/2	Microwave heating/microwave drying	high	low	high	<5	high	high	high	applied
3.3.3.4.1	Microwave reactors for non-catalytic and homogeneously catalyzed liquid phase process	low	low	low	10-15	medium	low	medium	fundamental
3.3.3.4.2	Microwave reactors for heterogeneously catalyzed chemical processes	low	medium	high	10-15	high	medium	high	combination
3.3.3.4.3	Microwave reactors for polymerization reactors and polymer processing	low	low	low	10-15	medium	low	high	fundamental
3.3.4	Photochemical	high	medium	medium	10-15	medium	medium	medium	fundamental
3.3.5	Plasma (GlidArc) reactors	low	low	medium	5-10	medium	medium	medium	combination
4.1.1	Oscillatory	medium	low	high	<5	high	high	low	combination
4.1.2	Reverse flow reactor operation	medium	high	medium	5-10	medium	high	medium	combination
4.1.4	Pulse combustion drying	medium	low	medium	5-10	low	medium	high	combination
5.1.2	Supercritical separations	medium	high	high	<5	medium	high	medium	combination

Technology Matrix 1: General overview of the PI Technology reviews (continued)

Barriers					Benefits																			
most common		most common			most common																			
Table 5 Challenges		Table 4 development issues			Table 1 benefits																			
model+design+scale up simulation/modelling	control	cost	safety	Eng/Design concepts incl equip design modelling + scale up	CFD techniques	safety	control systems	new applications	code	technology name	energy savings	less CO ₂ emission	eco impact	increased yield + conversion	better quality product	cost/invest savings	higher selectivity	more compact plant	more compact reactors	catalyst savings	better heat transfer	fouling prevention	less waste	
									1.1.1	Advanced plate-type heat exchangers														
									1.1.2	Advanced shell-and-tube heat exchangers														
									1.1.4	Static mixers			na	na	na									
									1.2.1.1	Catalytic foam reactors				na							na		na	
									1.2.1.2	Monolithic reactors														
									1.2.1.3	Millisecond (gauze) reactors														
									1.2.1.4	Structured reactors												na		
									1.2.2	Micro channel reactors														
									1.2.3	Membrane reactors (non-selective)		na	na					na						
									1.2.4	Static mixer reactors for continuous reactions														
									2.1.1	Adsorptive distillation			na	na			na							
									2.1.3	Extractive distillation			na				na							
									2.1.4	Heat-integrated distillation														
									2.1.5.3	Membrane crystallization technology		na												
									2.1.5.4	Membrane distillation technology														
									2.1.5.5	Distillation-Pervaporization														
									2.2.1	HEX reactors							na							
									2.2.3.1	Simulated Moving Bed reactors		negl	negl						na					
									2.2.3.2	Rotating Annular Chromatographic reactors		na	na				na							
									2.2.3.3	Gas-Solid-Solid Trickle Flow reactors							na							
									2.2.5	Reactive extraction columns, HT and HS			na											
									2.2.6	Reactive absorption														
									2.2.8.1	Reactive distillation														
									2.2.8.2	Membrane-assisted reactive distillation			na			na						na		na

Technology Matrix 2: Common barriers and benefits of the PI Technology

Barriers					Benefits																					
most common		most common			most common																					
Table 5 Challenges		Table 4 development issues			Table 1 benefits																					
model+design+scale up simulation/modelling	control	cost	safety	Eng/design concepts incl equip design modelling + scale up	CFD techniques	safety	control systems	new applications	code	technology name	energy savings	less CO ₂ emission	eco impact	increased yield + conversion	better quality product	cost/invest savings	higher selectivity	more safe	more compact plant	more compact reactors	catalyst savings	better heat transfer	fouling prevention	less waste		
		■		■					3.1.2	Centrifugal liquid-liquid contactors				na					■							
		■							3.1.3	Rotating packed beds	■	■	■	■	■	■	■	■	■	■						
			■	■					3.1.4	Rotor stator devices	na	na			na	na										
			■	■					3.2.2	Hydrodynamic cavitation reactors	■	na		■	na	na	■	■				■		na		
									3.2.3	Impinging streams reactor	■				■	■						■	■			
									3.2.4	Pulsed compression reactor	■	■	■	■	na	■	■	■	na			■	■			
		■		■					3.2.5	Sonochemical reactors (ultrasound and low frequency sonics)	■	na		■	na				■			■				
									3.2.6	Ultrasound enhanced crystallization	■				■				■							
									3.2.7	Ultrasound reactors for enhanced disintegration/phase dispersion/mass transfer	■	■	■	■	■	■	■	■	na							
									3.2.8.1	Supersonic Gas-Liquid reactors	na	na							na							
		■		■					3.3.1.1	Electric field-enhanced extraction	■	■	na	na	na	na	na	na	na	■	na					
									3.3.2	Induction and ohmic heating	na	na			■	■	■	■	na						■	
		■							3.3.3.1/2	Microwave heating/ microwave drying	■				na	na				■						
		■							3.3.3.4.1	Micro wave reactors for non-catalytic and homogeneously catalyzed liquid phase process	■	na	na	■	na	na	na	na	■			■		na		
		■		■					3.3.3.4.2	Microwave reactors for heterogeneously catalyzed chemical processes	na	na		■	na	na			na			na				
		■							3.3.3.4.3	Microwave reactors for polymerization reactors and polymer processing	na		na		■				na			■		■		
									3.3.4	Photochemical reactors	■			■				■								
									3.3.5	Plasma reactors	■							■					■			
									4.1	Oscillatory baffled reactors and continuous osc baffled reactor techn	■			■	■	■				■	■					
									4.1.2	Reverse flow reactor operation	■		■	■	na	na	■	■				■	■			
									4.1.4	Pulse combustion drying	■		■													
									5.1.2	Supercritical separations	■		■													

Technology Matrix 2: Common barriers and benefits of the PI Technology (continued)