

## EUROPEAN ROADMAP OF PROCESS INTENSIFICATION

### - TECHNOLOGY REPORT -

TECHNOLOGY:

Membrane Reactors (non-selective)

TECHNOLOGY CODE: 1.2.7

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# 1. Technology

## 1.1 Description of technology / working principle

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

A membrane reactor, strictly speaking (according to the IUPAC), is an apparatus combining the accomplishment of a chemical or biochemical reaction with separation through a membrane in *one device* (“in the same physical enclosure”). However, as opposed to the usual understanding of a membrane acting as a barrier, most often a solid, which is permeable only to *one* component (or to a group of components) from a mixed fluid, in this report the use of *non-selective* membranes for enhanced reactor performance is discussed. The application of selective membranes in chemical reactors is covered in a separate report (technology code 2.2.2).

Non-selective membranes are used in reactors mainly to influence the contacting among the reactants and/or between the reactants and a solid wall, or to manipulate the concentration profiles of certain reactants along the reaction zone. There may be different aims: One is to maximise the reaction rate due to an accelerated heat and/or mass transfer, e.g., by profiting from special hydrodynamic conditions in confined structures, by establishing shorter transport paths within a reacting phase, or, in multiphase reactions, by providing a large interphase area. One may also want to improve the safety, e.g., by allowing mixing of reactive species not before the actual reaction zone, by quenching unwanted radical reactions due to the presence of a large inert wall area, or just by providing an excellent contact to a solid offering high thermal conductivity in order to keep the temperature constant. In addition, the membrane may serve to exert an improved control on the concentration profile of one of the reactants along the reaction zone by utilising its ability to fine-tune the mass transfer through it. The latter may target a uniform concentration of the dosed species, if this gives a higher selectivity or yield. If suitable membranes were available, or a design in sections was feasible, one might also go for a specific shape of the concentration profile, if this paid back in terms of improved reactor performance due to kinetic reasons. Another effect observed when distributing a fraction of the feed along the reactor length, is an increasing flow rate downstream the reactor. Together with the fact that fluid elements entering the reactor further downstream will have a reduced residence time compared to fluid elements supplied at the entrance, this severely alters the residence time distribution and may improve the yield of intermediate products in multiple reactions. Finally, a non-selective membrane can be used to provide the reaction zone. For reactions relying on a catalyst, an active material can be incorporated into the membrane. This can be done uniformly or only in a certain region, e.g., a thin surface layer.

## 1.2 Types and “versions”

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

Based on the main function of the membrane, three different types of non-selective membrane reactors (MR) may be distinguished (see also the report on technology code 2.2.2).

### 1.2.1 Distributor MR

In this concept, the membrane is first of all used to implement an advanced dosing strategy for one of the reactants to manipulate its concentration profile along the reaction zone. It has been proposed mainly for multiple reactions where the kinetics (and not the thermodynamics) controls the yield of the desired product, and the rates of the undesired reactions depend more strongly on the concentration of the reactant

supplied through the membrane than the rate of the target reaction. Selective oxidation of an alkane with oxygen in the gas phase is a typical example. These are exothermic reactions, for which a control of the reaction rate is important not only to preserve high selectivity, but also for safety reasons. If the limiting reactant is distributed along the reactor through a membrane, its concentration profile in the reaction zone will be flat, as opposed to an exponential decay with the highest concentration at the reactor inlet in conventional mixed-feed operation. The maximum concentration (in a mixed feed) is often dictated by the explosion limit, which also determines the maximum conversion in the reactor. With separate feeding of the reactants, one being supplied at the reactor entrance and the other distributed over the length, a higher amount of substance of the limiting reactant can be fed while staying safely below the explosion limit. In turn, higher conversion is expected without loss in selectivity. However, whereas this idea holds for parallel reactions where the undesired pathway has a higher kinetic order in respect of the limiting reactant, it is not *generally* applicable to consecutive reactions or parallel/consecutive reaction networks where the intermediate is the target product. This is because the rate of the subsequent reaction increases with increasing concentration of the intermediate, if not restricted by depletion of the limiting reactant. Thus, a flat concentration profile of the limiting reactant over the reactor length may significantly reduce the selectivity as conversion increases. A gradually decreasing trans-membrane flux downstream the reactor might offer a solution to this problem, as it allowed fine-tuning of the concentration profile to match the demands associated with the kinetics of the actual reaction system. This could be achieved by a design in sections or by gradual variation of the membrane properties, if this was technically feasible. Practically, adjusting the trans-membrane flux in a distributor MR with non-selective membranes to the requirements of the reaction poses a significant challenge to the reactor design, in particular for large-scale catalytic reactors, where the pressure drop on the catalyst side is likely to be much higher than on the side from which the limiting reactant is supplied. Also, unwanted backdiffusion of the other reactant may take place at moderate trans-membrane flux.

An interesting idea addressing the question of how to reach an optimal adaptation of the trans-membrane flux is the so-called “chemical valve membrane” (Julbe et al., 2001). It aims at adjusting the alkane/oxygen concentration ratio in a distributor MR for selective oxidation of alkanes by offering an oxygen permeance that actively changes depending on the alkane/oxygen ratio in the atmosphere the membrane is exposed to, i.e., the permeance is reduced as the alkane/oxygen ratio decreases. The principle has been demonstrated by placing a mixture of a crystalline red/ox material, which changes its morphology upon a change of the oxidation state, into the macropores of a porous membrane, but the technical feasibility of the concept is still to be demonstrated.

### 1.2.2 Contactor MR

In this version, the membrane serves to provide the reaction zone, e.g., by containing an active catalyst, either throughout the structure or only in a certain region, e.g., a thin surface layer. Two versions of contactor MRs may be further distinguished.

In a *catalytic diffuser (CD)*, two fluid streams are passed along the different sides of the membrane and mix in the catalytic zone by diffusion. One may mainly think of porous membranes and a solid active material coated to the pore walls for this kind of configuration due to the higher permeance such systems allow compared to dense membranes. But other types are also conceivable, e.g., a molecular catalyst dissolved in a liquid filling the pores of a support. Even if no catalyst is required, the same principle may be applied if the reaction is fast enough to reach complete conversion within the membrane. Moreover, membrane contactors applied to gas absorption also belong to this category provided that they involve chemically absorbing liquids (see also technology code 2.1.5). The same holds for other applications of membrane contactors for separations, e.g., liquid/liquid extraction

(see technology code 2.1.9) if they involve chemical reactions to provide enhanced selectivity or mass transfer. Yet membrane contactors for separation are not in the focus here, as it is understood that the accomplishment of a chemical reaction is the main purpose of a membrane *reactor*.

An alternative to relying on diffusion as the transport mechanism in a contactor MR is to push a (premixed) reactant stream through a catalytic membrane by a pressure difference. Such a system is referred to as a *pore-flow-through catalytic membrane (PFT)*. In the more likely case of a porous membrane, there is convection inside the pores resulting in a very efficient contact between the fluid and the active phase on the pore walls, e.g., present in the form of attached nano-sized particles. The pore size of such a membrane was chosen in the micrometer or sub-micrometer range, and the contact time per pass was short. Thus the arrangement can be viewed as a short contact time catalytic micro- or nanoreactor.

The aim of both principles, i.e. diffuser and forced through-flow membrane contactor, is to optimize the contact between the reactants and the active phase to exploit its intrinsic catalytic properties. Besides elimination of mass transfer resistances, improved isothermicity due to the enhanced heat transfer (porous solids with high thermal conductivity) may be targeted. In the pore-flow-through membrane contactor, the *membrane* has no dosing function and thus can be viewed as a special type of structured catalyst.

### 1.3 Potency for Process Intensification: possible benefits

*(In Table 1 describe the most important documented and expected benefits offered by the technology under consideration, focusing primarily on energy; CO<sub>2</sub> emission and costs, providing quantitative data, wherever possible. Add other benefits, if needed).*

Non-selective membrane reactors show significant potential for process intensification. For separations based on membrane contactors, reductions of the footprint and weight of the unit are considered as most important benefits.

Table 1: Documented and expected benefits resulting from technology application

Benefit	Magnitude	Remarks
Energy savings	No industrial data available so far, however, can be substantial.	For distributor MRs, energy savings are expected mainly in downstream processing which profit from higher conversion/yield in the reactor. The same holds for contactor MRs, whether in diffuser mode or in pore-flow-through mode. Membrane gas absorption, e.g., is expected to offer energy savings due to removal of constraints on the solvents (allowing their optimisation). Similar effects are expected for other separations based on membrane contactors.
CO <sub>2</sub> emissions	No industrial data available.	Membrane gas absorption is an advanced technology for carbon dioxide capture. If it is used on large-scale in the future, this would have a significant impact on CO <sub>2</sub> emissions. CO <sub>2</sub> emission reductions for other non-selective MR applications will be through improved energy efficiency (i.e., less energy consumption per ton of product).
Costs	ca. 30-40% (for membrane gas absorption of CO <sub>2</sub> )	Estimated reduction of the investment and operating costs for off-shore CO <sub>2</sub> capture by membrane gas absorption (based on field pilot testing). For other non-selective MR applications, more or less significant cost reductions are expected through increased space time yield, higher selectivity/yield, and lower catalyst needs.
More compact plants	70-75% in weight 65% in space (for membrane gas absorption of CO <sub>2</sub> )	Projected reduction of the installed weight and the required space for absorber and stripper in off-shore membrane gas absorption as compared to conventional absorption technology.

Increased yield and/or selectivity	modest effects for distributor MRs, e.g., up to 10-15%; higher benefit for pore-flow-through contactors	Typical yield improvements (conversion or selectivity), e.g., for selective oxidation of hydrocarbons, in distributor MRs compared to mixed-feed operation are 10-15%. In pore-flow-through mode, due to elimination of transport resistances, dramatic improvements of the activity (space-time-yield) can be achieved depending on the system.
Better product quality	ca. 50% reduction of unwanted trans-fatty acids	Pilot plant data for selective hydrogenation of edible oils in a contactor MR in pore-flow-through mode.
Improved safety	No data available	Significant improvements of the process safety are expected for distributor MRs and for catalytic diffusers mainly due to separate feeding of reactive species.

## 1.4 Stage of development

Membrane contactors with hydrophobic polymer membranes for gas/liquid contacting are commercially available from different suppliers. They are mainly used for degassing or gassing of liquids, but also for the removal of specific compounds from gas mixtures, for liquid/liquid extraction, emulsification, distillation and crystallisation. Commercial applications exist, e.g., in the semiconductor industry, power generation, the food industry, the medical industry and the pharmaceutical industry. More recently, membrane contactors were developed also for capture of carbon dioxide from flue gases, e.g., to provide high purity carbon dioxide to the horticultural industry. Other commercial applications are in the field of life support (spacecrafts, submarines, operating theatres, consumer products, biogas treatment). Membrane contactors have also been receiving much attention as compact systems for carbon dioxide capture for sequestration. Kvaerner developed a membrane gas absorption process for natural gas sweetening working at pressures as high as 88 barg, and one for capture of carbon dioxide from flue gases at atmospheric pressure. The latter was tested in a demonstration unit at a gas terminal in Norway, but, so far, not applied on full scale. Moreover, a commercial installation of a membrane contactor for removal of ammonia from the off-gas of a chemical production plant for dye intermediates in the Czech Republic is reported to be in operation since 1999, and a process using a membrane contactor for recovery of sulphur dioxide from flue gases is being developed.

Catalytic versions of membrane contactors relying on hydrophobic polymer membranes were studied for different applications, e.g., hydrogenation of dissolved oxygen in water and direct synthesis of hydrogen peroxide. Another reaction was hydration of propene which was studied in a hydrophobic carbon membrane contactor acting as a support for a dissolved molecular catalyst. As yet, these are mainly lab-scale developments. The same holds for catalytic contactors equipped with hydrophilic membranes, i.e., mostly ceramics or metals. These systems were applied to a number of hydrogenations, catalytic wet air oxidation of organic acids, and direct synthesis of hydrogen peroxide, to name a few examples. For wet air oxidation, experiments in a small pilot plant with 0.3 m<sup>2</sup> membrane area and a treatment capacity of 300 L·h<sup>-1</sup> are reported. And it also holds for catalytic membrane contactors in pore-flow-through mode, which were proposed mainly for selective hydrogenations, for selective oxidations, methanol to gasoline, olefin oligomerisation, and Fischer-Tropsch synthesis.

Non-selective distributor MRs have been studied by many groups in the lab-scale, and in a few collaborative research projects also in small pilot scale; commercial operation, however, has not been reported so far.

## 2. Applications

### 2.1 Existing technology (currently used)

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

Non-selective distributor MRs compete with conventional (mixed feed) reactors and staged reactors with split feed.

Non-catalytic membrane contactors for gas absorption contend with conventional gas absorbers, e.g., columns with internals, bubble columns, or other gas/liquid reactors. Catalytic membrane contactors in pore-flow-through operation face competition against other types of structured catalysts, e.g., monoliths, packings, foams and the like. The same holds for catalytic membrane contactors in diffuser mode, although they are slightly more unique due to their potential advantage of acting as a reactive interface between two reactants streams.

### 2.2 Known commercial applications

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

Membrane gas absorption presently is the only field where non-selective membrane reactors appear to have found commercial application, e.g., a membrane contactor for recovery of ammonia from an off-gas installed in the chemical company Aliachem in Pardubice, Czech Republic, is reported to be operational since 1999. The Dutch technology supplier TNO delivered the unit. This innovation won the Kirkpatrick honour award in 2001.

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

Sector	Company - Process/Product name/type	Short characteristic of application	Product ion capacity /Plant size	Year of application	Reported effects
Specialty chemicals	Aliachem - Recovery of ammonia from the offgas of pressurised reactors for production of dye intermediates by membrane gas absorption	A membrane gas absorption unit treats the total off-gas stream. Ammonia is recovered as an aqueous solution of up to 27 wt% which is reused in the process.	NH <sub>3</sub> capacity 50 kg·h <sup>-1</sup>	1999	<ul style="list-style-type: none"><li>• The installation proved easy operation</li><li>• Variations in the flow rate could be handled without any problems</li><li>• No detectable emissions of ammonia in the environment (99.9% removal)</li></ul>

### 2.3 Known demonstration projects

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

There has been a multi-year development effort on membrane contactors for off-shore carbon dioxide and water vapor removal from pressurised natural gas (sweetening) and for carbon dioxide removal from atmospheric flue gas by Kvaerner Process Systems together with W.L. Gore & Associates GmbH. Field pilot testing for natural gas sweetening took place from 1998 to 1999 at a large gas terminal north of Aberdeen, Scotland, with activated MDEA where 1 % of the process flow train was treated, i.e.,  $5000 \text{ m}^3_{\text{N}} \cdot \text{h}^{-1}$  gas flow,  $5 \text{ m}^3 \cdot \text{h}^{-1}$  liquid flow, 88 barg pressure, and at the Shell Fandango field in Zapata, Texas with a physical solvent; also, dehydration with glycol was tested there. The flue gas process was pilot tested at the Statoil gas terminal in Kårstø, Norway where  $2610 \text{ kg} \cdot \text{h}^{-1}$  exhaust flow was treated and 85% of the  $\text{CO}_2$  ( $195 \text{ kg} \cdot \text{h}^{-1}$ ) was separated.

As yet, however, large-scale commercial use of the technology for gas sweetening or carbon dioxide capture from combustion exhaust gases is not reported.

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

Sector	Who is carrying out the project	Short characteristic of application investigated, including product name/type	Aimed year of application	Reported effects
Natural gas production Power generation	Kvaerner Process System together with W.L. Gore and Associates	Natural gas sweetening ( $\text{CO}_2$ removal and dehydration) $\text{CO}_2$ removal from combustion exhaust gas	2000	<ul style="list-style-type: none"> <li>The results of the field tests were very good</li> <li>No degradation in 5000 h of operation</li> <li>Scale-up showed potential for 75-85% reduction in vessel size and weight for gas sweetening and 60-80% reduction for gas dehydration</li> </ul>

## 2.4 Potential applications discussed in literature

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

Membrane contactors for gas absorption using chemically absorbing solvents are being developed for removal of carbon dioxide, ammonia, sulphur dioxide, hydrogen sulphide, water and other gases that can be removed by chemical absorption (Drioli et al., 2005, Klaasen et al., 2005).

In addition, many applications of non-selective membrane contactors involving (mostly catalysed) chemical reactions were proposed in the literature.

For the distributor MR, selective oxidation of hydrocarbons forms a major class of reactions. Oxidative dehydrogenation of ethane to ethene, of propane to propene, oxidative coupling of methane to  $\text{C}_2$ -hydrocarbons, and partial oxidation of propane to acrolein as well as of n-butane to maleic anhydride may be named as examples (Coronas and Santamaria, 1999, Dittmeyer and Caro, 2008). Moreover, the concept has been suggested for polymerisations (Gilson and Sbardella, 1994, 1995).

For membrane contactors in diffuser mode, most of the proposed applications were hydrogenations:

- $\alpha$ -Methylstyrene to cumene
- Dehydrolinalool to linalool
- Nitrobenzene to anilin

- Cinnamaldehyde to hydrocinnamyl alcohol
- Methylenecyclohexane to methylcyclohexane
- Selective hydrogenation of edible oils
- Nitrate and nitrite to nitrogen
- Direct synthesis of hydrogen peroxide
- Hydrodechlorination of chlorobenzene to benzene
- Removal of trace oxygen from water through hydrogenation

followed by oxidations:

- Wet air oxidation of organic acids
- Wet air oxidation of phenols
- Selective oxidation of ethene to acetaldehyde
- Selective oxidation of light alkanes to oxygenates

Membrane contactors in pore-flow-through mode were also mainly applied to hydrogenations:

- Nitrate and nitrite to nitrogen
- 2-Hexyne and 1,3 hexadienes to hexenes
- Selective hydrogenation of edible oils
- 1-Octyne to octene
- Phenylacetylene to ethylbenzene
- Geraniol to citronellol
- Cyclooctadiene to cyclooctene
- $\alpha$ -Methylstyrene to cumene

as well as to selective oxidations:

- Preferential oxidation of carbon monoxide in presence of hydrogen
- Epoxidation of propene

and to several other reactions, e.g.:

- Photocatalytic oxidation of volatile organic compounds
- Olefin oligomerisation (*i*-butene to *i*-octene)
- Methanol conversion to olefins
- Fischer-Tropsch synthesis

A more complete list of applications and more details can be found in the reviews listed below, e.g., Sanchez Marcano and Tsotsis, 2002, Dittmeyer et al., 2004, or Dittmeyer and Caro, 2008, as well as in the references therein.



### 3. What are the development and application issues?

#### 3.1 Technology development issues

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

Table 4. Technology development issues

Issue	Description	How and by whom should be addressed?
Material selection and membrane design for high mass (and heat) transfer rate and, eventually, high catalyst efficiency	Non-selective membrane reactors aim for an optimised contacting of the reacting phases. The design, for gas/liquid or liquid/liquid applications, must therefore take into account the wetting behavior, i.e., a suitable pairing of membrane material and solvent is critical and the guiding of the fluid phases must allow good control of the differential pressure (as to avoid thick stagnant liquid layers in the pores). For applications involving a (solid) catalyst, the placement of the catalyst must guarantee short diffusion paths for the reactants from all phases involved.	<ul style="list-style-type: none"> <li>• Should be addressed through R&amp;D.</li> <li>• Membrane producers and research institutes or universities should work together on these issues.</li> <li>• Modelling of the relevant phenomena is essential.</li> </ul>
Membrane quality	A non-uniform pore size distribution, e.g., the occurrence of defects, and larger variations of important properties such as porosity and/or thickness of the membranes are critical for some distributor or contactor MR concepts and must be avoided.	<ul style="list-style-type: none"> <li>• Improved methods for manufacturing are required.</li> <li>• Should be addressed mainly by membrane producers.</li> </ul>
Sealing	Reliable seals for sealing inorganic membranes to modules and module housings must be developed which can withstand high temperature and aggressive chemicals and allow joining of different materials (ceramics, metals, glass, polymers, etc.).	<ul style="list-style-type: none"> <li>• Should be addressed by membrane producers and end users through collaborative R&amp;D.</li> </ul>
Membrane lifetime	Long membrane life must be demonstrated for key applications to build up confidence in the new technology. For catalytic membranes, strategies for regeneration and, eventually, recycling are needed.	<ul style="list-style-type: none"> <li>• Should be addressed by collaborative projects on key applications involving membrane producers, technology providers, and end users.</li> </ul>
Membrane reactor design and scale-up	MR performance depends on the kinetics of reactions and transport processes at various levels. MRs, like other reactors, should be designed based on such knowledge. Scale-up must be demonstrated to build up confidence in the new technology.	<ul style="list-style-type: none"> <li>• Should be addressed by research institutes, universities and companies when developing new applications.</li> <li>• Modelling combined with experimental data from various scales is essential.</li> </ul>

### 3.2 Challenges in developing processes based on the technology

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

Table 5. Challenges in developing processes based on the technology

Challenge	Description	How and by whom should the challenge be addressed?
Demonstration of key technical advantages	In order to find commercial application, MRs, like other novel technologies, must have the potential to achieve clear (step change) improvements over established techniques.	<ul style="list-style-type: none"> <li>• Development efforts should be focused on promising concepts.</li> </ul>
Membrane costs	Membrane materials, production technologies, and membrane module designs must generally be improved in respect of cost. This holds for all inorganic membranes, e.g., ceramics, metals, carbon, and also for non-conventional polymers (even PTFE).	<ul style="list-style-type: none"> <li>• Should be addressed through R&amp;D.</li> <li>• This is a domain of membrane producers, but research institutes, universities and engineering companies should be involved, e.g., in interdisciplinary research projects.</li> </ul>
Performance degradation	Degradation of the membranes must be kept within acceptable limits, or easily applicable techniques for regeneration (preferably <i>in place</i> ) must be provided. This can be critical because membrane cost is a major portion of the equipment cost and frequent replacement is not tolerable.	<ul style="list-style-type: none"> <li>• Strategies for preventing degradation and for in place cleaning must be developed.</li> <li>• Should be addressed through R&amp;D at universities and research institutes.</li> </ul>
Acceptance and awareness	Lack of knowledge or readiness to accept new developments in the process industry is a major barrier for success of novel technologies.	<ul style="list-style-type: none"> <li>• Universities should make students familiar with the pros and cons of MRs compared to conventional reactors.</li> </ul>

## 4. Where can information be found?

### 4.1 Key publications

(Provide the list of key publications in Table 6)

Since 1994 conferences devoted to catalysis in membrane reactors have been organised every two years (International Conference on Catalysis in Membrane Reactors, ICCMR) with both selective and non-selective membrane reactors in the focus. The next event of this series will take place in December 2007 in Kolkata/India (ICCMR-8); information can be found at the website <http://www.cgcri.res.in/iccmr8>.

Table 6. Key publications on the technology

Publication	Publication type (research paper/review/book/report)	Remarks
B.W. Reed, M.J. Semmens, E.L. Cussler, <i>Membrane Contactors</i> in: R.D. Noble, S.A. Stern (eds.), <i>Membrane Separation Technology: Principles and Applications</i> , Elsevier Science, Amsterdam, 1995, Chapter 10.	Review	Good introduction to membrane contactors.
E. Drioli, E. Curcio, G. Di Profio, <i>State of the art and recent progresses in membrane contactors</i> , Chem. Eng. Res. Des. 83 (2005) 223.	Review	Focus on innovative applications of membrane contactors.
R. Klaasen, P.H.M. Feron, A.E. Jansen, <i>Membrane Contactors in Industrial Application</i> , Chem. Eng. Res. Des. 83 (2005) 234.	Review	Perspectives for industrial use of membrane contactors.
J. Coronas, J. Santamaria, <i>Catalytic reactors based on porous ceramic membranes</i> , Catal. Today 51 (1999) 377.	Review	Main concepts and selected examples to illustrate the application of membrane reactors.
José Sanchez Marcano, Theodore T. Tsotsis, <i>Catalytic Membranes and Membrane Reactors</i> , Wiley-VCH, Weinheim, 2002, pp. 251.	Book	Whole field of membrane reactors. Contents are organized by reactions, not by membrane types.
R. Dittmeyer, K. Svajda, M. Reif, <i>A review of catalytic membrane layers for gas/liquid reactions</i> , Top. Catal. 29 (2004) 3.	Review	Various types and applications of catalytic membranes.
R. Dittmeyer, J. Caro, <i>Catalytic Membrane Reactors</i> in: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp (eds.), <i>Handbook of Heterogeneous Catalysis</i> 2 <sup>nd</sup> ed., Wiley-VCH, Weinheim, 2008, Chapter 10.7.	Review	Status of the most important types of catalytic membrane reactors.
J. Coronas, M. Menéndez, J. Santamaria, <i>Development of ceramic membrane reactors with a non-uniform permeation pattern. Application to methane oxidative coupling</i> , Chem. Eng. Sci. 49 (1994) 4749. J. Coronas, M. Menéndez, J. Santamaria, <i>Methane oxidative coupling using porous ceramic membrane reactors - II. Reaction studies</i> , Chem. Eng. Sci. 49 (1994) 2015.	Paper	Distributor MRs: First study where a decreasing permeance along the membrane reactor was established.
Y. Lu, A.G. Dixon, W.R. Moser, Y.H. Ma, <i>Analysis and optimization of cross-flow reactors with staged feed policies - isothermal operation with parallel-series, irreversible reaction systems</i> , Chem. Eng. Sci. 52 (1997) 1342.	Paper	Distributor MRs: Simulation study assessing the benefits and limitations of distributor MRs.
A. Julbe, D. Farusseng, D. Cot, C. Guizard, <i>The chemical valve membrane: a new concept for an auto-regulation of O<sub>2</sub> distribution in membrane reactors</i> , Catal. Today 67 (2001) 139.	Paper	Distributor MRs: Paper introducing the idea of a "chemical valve membrane"

Publication	Publication type (research paper/review/book/ report)	Remarks
P. Kölsch, Q. Smejkal, M. Noack, R. Schäfer, J. Caro, <i>Partial oxidation of propane to acrolein in a membrane reactor – Experimental data and computer simulation</i> , Catal. Commun. 3 (2002) 465.	Paper	Distributor MRs: Selectivity ca. 2-4 times higher in the membrane reactor compared to mixed feed.
A. Julbe, D. Farusseng, C. Guizard, <i>Limitations and potentials of oxygen transport dense and porous ceramic membranes for oxidation reactions</i> , Catal. Today 104 (2005) 102.	Review	Distributor MRs: Analysis of the achievements with both selective and non-selective membranes.
A. Tóta, C. Hamel, S. Thomas, M. Joshi, A. Seidel-Morgenstern: <i>Theoretical and Experimental Investigation of Concentration and Contact Time in Membrane Reactors</i> , Chem. Eng. Res. Des. 82 (2004) 236.	Paper	Distributor MRs: Good theoretical analysis; results are illustrated by example of oxidative dehydrogenation of ethane.
A.A. Lapkin, S.R. Tennison, W.J. Thomas, <i>A porous carbon membrane reactor for the homogeneous catalytic hydration of propene</i> , Chem. Eng. Sci. 57 (2002) 2357.	Paper	Contactor MRs (diffuser): Molecular catalyst dissolved in a liquid filling the pores of a carbon membrane.
R. van der Vaart, V.I. Lebedeva, I.V. Petrova, L.M. Plyasova, N.A. Rudina, D.I. Kochubey, G.F. Tereshchenko, V.V. Volkov, J. van Erkel, <i>Preparation and characterisation of palladium-loaded polypropylene porous hollow fibre membranes for hydrogenation of dissolved oxygen in water</i> , J. Membr. Sci. 299 (2007) 38.	Paper	Contactor MRs (diffuser): Catalytically enhanced membrane contactor for oxygen removal from water.
E.E. Iojoiu, S. Miachon, E. Landrison, J.C. Wamsley, H. Ræder, J.A. Dalmon, <i>Wet air oxidation in a catalytic membrane reactor: Model and industrial wastewaters in single tubes and multichannel contactors</i> , Appl. Catal. B: Environmental 69 (2007) 196.	Paper	Contactor MR (diffuser): Small pilot plant for Watercatox process.
A. Pashkova, K. Svajda, R. Dittmeyer, <i>Direct synthesis of hydrogen peroxide in a catalytic membrane contactor</i> , Chem. Eng. J. in press (available online 11. September 2007)	Paper	Contactor MR (diffuser): Improved safety due to separate supply of reactants.
M. Reif, R. Dittmeyer, <i>Porous, catalytically active ceramic membranes for gas-liquid reactions: a comparison between catalytic diffuser and forced through flow concept</i> , Catal. Today 82 (2003) 3.	Paper	Contactor MR (diffuser vs. pore-flow-through): Higher activity and selectivity in pore-flow-through mode due to elimination of mass transport resistances.

Publication	Publication type (research paper/review/book/report)	Remarks
M. Kobayashi, J. Togawa, T. Kano, J.-I. Horiuchi, K. Tada, <i>Dramatic innovation of propene epoxidation efficiency derived from a forced flow membrane reactor</i> , J. Chem. Technol. Biotechnol. 78 (2003) 303.	Paper	Contactora MR (pore flow-through): Membrane reactor gives higher selectivity and yield to propylene oxide due to improved concentration and temperature control.
A. Schmidt, R. Haidar, R. Schomäcker, <i>Selectivity of partial hydrogenation reactions performed in a pore-through-flow catalytic membrane reactor</i> , Catal. Today 104 (2005) 305.	Paper	Contactora MR (pore-flow-through): Membrane reactor performance close to intrinsic kinetics.
A. A. Khassin, A. G. Sipatov, T. M. Yurieva, G. K. Chermashentseva, N. A. Rudina, V. N. Parmon, <i>Performance of a catalytic membrane reactor for the Fischer–Tropsch synthesis</i> , Catal. Today 105 (2005) 362.	Paper	Contactora MR (pore-flow-through): Membrane reactor offers improved concentration and temperature control.
M.P. Rohde, D. Unruh, G. Schaub, <i>Membrane application in Fischer–Tropsch synthesis reactors-Overview of concepts</i> , Catal. Today 106 (2005) 143.	Review	Good analysis of different membrane reactor concepts (distributor, extractor, contactora) for FT synthesis.
D. Fritsch, G. Bengtson, <i>Development of catalytically reactive porous membranes for the selective hydrogenation of sunflower oil</i> , Catal. Today 118 (2006) 121.	Paper	Contactora MR (pore-flow-through): Membrane reactor reaches much lower trans fatty acid content.

## 4.2 Relevant patents and patent holders

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

Many patents and patent applications have been published describing the use of non-selective membranes in separators and reactors.

Celgard (former Hoechst Celanese) and Mykrolis/Entegris have been the two most active companies in patenting of membrane contactors for separations. Both companies are commercial suppliers of membrane contactors. The idea of using porous membranes to create a fixed interface between two immiscible fluid streams has been around for a while (e.g., US 4 789 468, US 4 750 918). More recent patents and pending applications document improvements and design variants as well as specific applications. Not all of the known documents are listed.

Concerning membrane contactor applications where chemical reactions are in the focus, a broad patent by Alcan on non-selective pore-flow-through catalytic membranes must be mentioned (EP 0 244 970). Although being focused on *selective*

permeation through micropores (i.e., pore diameter smaller than 1.2 nm) and therefore not being in the focus of this report, the patent(s) by Studiengesellschaft Kohle mbH, Mülheim an der Ruhr (DE), are listed here as well because they also refer to the pore-flow-through contacting mode. A more recent patent application related to the use of pore-flow-through catalytic membranes for hydrogenations is also reported below (WO 2006/094699 A1).

Catalytic membrane contactors in diffuser mode, from a system perspective, are rather close to membrane contactors for separations. Such concepts have been patented, e.g., for photocatalytic treatment of water (US 6 030 526), photochemical oxidation of organics in water or air (US 5 779 912, US 6 117 337, US 6 136 186, US 6 409 928 B1), for photochemical conversion of methane to methanol (US 6 156 211), and for removal of nitrate, nitrite, perchlorate and other harmful substances by catalytic reduction with hydrogen (DE 100 64 622 B4). Another recent example is the direct synthesis of hydrogen peroxide from hydrogen and oxygen (WO 2007/028375 A1).

Distributor MRs also were patented already more than a decade ago. Increased safety due to improved control of the reaction rate is the main motivation behind the patents by Asher et al. (WO 94/20207, US 5 583 240, US 5 936 106) which cover a wide range of exothermic liquid-phase and gas-phase reactions. One of the main benefits of a distributed feed along the reactor wall in polymerisation as claimed in US 5 319 120 and US 5 456 888 is the avoidance of building up of polymer on the wall. Oxidative coupling of methane (ES 2 079 996), on the other hand, is an application where selectivity control due to distributed feeding of oxygen is in the focus. Finally, distributor MRs have also been applied to the production of solid nanoparticles (FR 2 879 476 B1, FR 2 885 538 B1, WO 2007/000531A3).

Table 7. Relevant patents

Patent	Patent holder	Remarks, including names/types of products targeted by the patent
US 4 789 468 (filed: 28.08.1984) Immobilized-interface solute-transfer apparatus US 4 750 918 (filed: 28. May 1985) Selective-permeation gas-separation process and apparatus	The Trustees of the Stevens Institute of Technology, Boboken/NJ (US)	Early patents on membrane contactors
US 4 959 152 (filed: 24.03.1989) Hollow fiber separation module and method for the use thereof US 5 174 900 (filed: 25.09.1990) Apparatus for separation and for treatment of fluid feedstreams, wafers for the use therein and related methods	The Standard Oil Company, Cleveland/OH (US)	Early patents on hollow fiber-based designs for membrane contactors
US 5 104 535 (17.08.1990) Frameless array of hollow fiber membranes and module containing a stack of arrays	Zenon Environmental Inc., Burlington (CA)	Stacked design for hollow fibers
US 5 169 529 (filed: 22.04.1991) Liquid membrane modules with minimal effective membrane thickness and methods of making the same	Hoechst Celanese Corp., Charlotte/NC (US)	Special design to minimize liquid film thickness

US 5 328 610 (filed: 15.06.1993) Self-supported low pressure drop hollow fiber membrane panel and contactor module	Integrated Process Technologies Inc., Boulder/CO (US)	Short fiber stacked design for low pressure drop
US 6 149 817 (filed: 08.03.1999) Shell-less hollow fiber membrane fluid contactor	Celgard Inc., Charlotte/NC (US)	Shell-less design
EP 1 148 931 B1 (filed: 28.01.2000) Hollow fiber membrane contactor	Entegris Inc., Chaska/MN (US)	Membrane contactor based on perfluorinated membranes for low surface tension fluids
US 6 582 496 B1 (filed: 28.01.2000) Hollow fiber membrane contactor US 6 805 731 B2 (filed: 06.03.2003) Hollow fiber membrane contactor	Mykrolis Corp., Billerica/MA (US)	Membrane contactor based on perfluorinated membranes for low surface tension fluids
US 6 402 818 B1 (filed: 02.06.2000) Degassing a liquid with a membrane contactor	Celgard Inc., Charlotte/NC (US)	Membrane contactor for degassing a liquid
US 6 616 841 B2 (filed: 21.06.2001) Hollow fiber membrane contactor	Celgard Inc., Charlotte/NC (US)	Membrane contactor for degassing a liquid
US 7 264 725 B2 (filed: 04.03.2004) Hollow fiber membrane contactor and method of making same	Celgard Inc., Charlotte/NC (US)	Hollow fiber membrane contactor and its fabrication
US 7 273 549 B2 (filed 23.01.2004) Membrane contactor apparatus including a module having hollow fiber membranes	Geoscience Support Services Inc., Upland/CA (US)	Special multi-module contactor design
EP 0 244 970 (filed: 16.04.1986) Porous aluminium oxide membrane catalyst support	Alcan International Ltd., Montreal (CA)	Broad patent claiming inorganic membranes with pores larger than 2 nm and a catalytic material inside as well as their use in pore-flow-through mode
US 5 250 184 (filed: 13.05.1993) Procedure for the preparation of microporous ceramic membranes for the separation of gas and liquid mixtures	Studiengesellschaft Kohle mbH, Mülheim an der Ruhr (DE)	Microporous membranes with pores smaller than 1.2 nm and their use for gas and liquid separations as well as in a pore-flow-through catalytic contactor
WO 98/10865 (filed: 13.09.1996) Use of microporous inorganic membrane catalysts EP 0 949 971 B1 (filed: 13.09.1996) Use of microporous inorganic membrane catalysts	Studiengesellschaft Kohle mbH, Mülheim an der Ruhr (DE)	Pore-flow-through in microporous membranes for suppressing consecutive reactions
WO 2006/094699 A1 (filed: 05.03.2005) Catalytically active porous membrane reactor for reacting organic compounds	Bayer Technology Services GmbH, Leverkusen (DE)	Pore-flow-through membrane contactor for hydrogenation of organic compounds
WO 98/29346 (filed: 31.12.1996) Water treatment and purification US 6 030 526 (filed: 31.12.1996) Water treatment and purification	UV Technologies Inc., Medford/MA (US)	Photocatalytic generation of hydrogen peroxide and/or ozone on a TiO <sub>2</sub> coated porous wall for water treatment

<p>US 5 779 912 (filed: 31.01.1997) Photocatalytic oxidation of organics using a porous titanium dioxide membrane and an efficient oxidant</p> <p>US 6 117 337 (filed: 11.06.1998) Enhanced photocatalytic oxidation of organics using a porous titanium dioxide membrane</p> <p>US 6 136 186 (filed 14.07.1998) Photocatalytic oxidation of organics using a porous titanium dioxide membrane and an efficient oxidant</p> <p>US 6 409 928 B1 (filed: 5.10.2000) Photocatalytic oxidation of organics using a porous titanium dioxide membrane and an efficient oxidant</p>	<p>Lynntech Inc., College Station/TX (US)</p>	<p>Photochemical oxidation of organics in water or air on a porous TiO<sub>2</sub> membrane</p>
<p>US 6 156 211 (filed: 14.07.1998) Enhanced photocatalytic conversion of methane to methanol using a porous semiconductor membrane</p>	<p>Lynntech Inc., College Station/TX (US)</p>	<p>Photochemical conversion of methane in solution or in the gas phase in a unique two- or three-phase system inside the pores of a semiconductor membrane</p>
<p>DE 100 64 622 B4 Verfahren und katalytischer Kontaktor zur Entfernung von Nitrat, Nitrit, Perchlorat und anderen schädlichen Verbindungen aus verunreinigtem Wasser durch Wasserstoff</p>	<p>Venezia Technologie, Porto Marghera, Venezia (IT), Anjou Recherche, Paris (FR), CH2MHILL, San Fernando de Hanares, Madrid (ES)</p>	<p>Membrane contactor (diffuser) for catalytic nitrate reduction for water purification</p>
<p>WO 2007/028375 A1 (filed: 07.09.2006) Inherent and reliable selective method for directly synthesising hydrogen peroxide from oxygen and hydrogen with the aid of a catalytically coated wettable porous membrane</p>	<p>DECHEMA e.V., Frankfurt am Main (DE)</p>	<p>Small-scale process for hydrogen peroxide production based on a membrane contactor (diffuser)</p>
<p>WO 94/20207 (filed: 02.03.1994) Exothermic process with porous means to control reaction heat and exothermic heat</p> <p>US 5 583 240 (filed: 02.03.1994) Exothermic process with porous means to control reaction rate and exothermic heat</p> <p>US 5 936 106 (filed: 06.12.1996) Process with porous means to control reaction rate and heat</p>	<p>SRI International, Menlo Park/CA (US)</p>	<p>Broad patents covering distributed-feed reactor systems for many exothermic liquid-phase and gas-phase reactions involving two reactant streams</p>
<p>US 5 319 120 (filed: 07.07.1992) Polymerization reactor and polymerization process</p> <p>US 5 456 888 (filed: 16.11.1993) Polymerization reactor and polymerization process</p>	<p>Dow Corning S.A., Seneffe (BE)</p>	<p>Continuous static reactor with distributed feed for production of liquid polymers by condensation polymerization</p>



ES 2 079 996 (filed: 14.06.1993) Reactor con pared de cerámica porosa y método para obtener hidrocarburos a partir de metano	Universidad de Zaragoza, Zaragoza (ES)	Catalytic reactor with distributed feed for oxidative coupling of methane to C <sub>2+</sub> hydrocarbons
FR 2 879 476 (filed: 21.12.04) Nouveau procédé de préparation de particules dont au moins la surface périphérique est de nature polymérique, mettant en œuvre un réacteur membranaire  FR 2 885 538 (filed: 16.05.2005) Nouveau procédé de préparation de particules lipidiques solides, mettant en œuvre un réacteur membranaire  WO 2007/000531 A3 Method for preparing solid lipidic particles using a membrane reactor	Université Claude Bernard Lyon I, Etablissement public et Centre National de la Recherche Scientifique (FR)	Reactor with distributed feed for production of solid nanoparticles

### 4.3 Institutes/companies working on the technology

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

A significant number of universities and research institutes worldwide work on non-selective membrane contactors for reactive applications. Some membrane manufacturers (mainly SMEs) also started development activities, however, most often in cooperative, publicly funded research projects. As opposed to membrane contactors for enhanced gas absorption or other separations, catalytic versions of membrane contactors are not yet commercially available.

From the multitude of institutions active in the field, Table 8 lists those who have frequently shown their colours in the ICCMR (International Conference on Catalysis in Membrane Reactors) or other relevant conferences. Moreover, a certain focus on Europe must be admitted which is due to a lack of insight in the situation on other continents, in particular in Asia. The institutions' fields of activity, as far as *non-selective* membrane reactors are concerned, are also given.

Table 8. Institutes and companies working on the technology

Institute/Company	Country	Remarks
UNIVERSITIES / INSTITUTES		
Katholieke Universiteit Leuven, Department of Interphase Chemistry (Pierre Jacobs, Ivo Vancellecom)	Belgium	<ul style="list-style-type: none"> <li>• composite inorganic-organic membranes</li> <li>• ultrathin ceramic membranes</li> <li>• catalytic functionalization of polymer membranes</li> <li>• membrane-enhanced homogeneous catalysis</li> </ul>
Dalian Institute of Chemical Physics (Weishen Yang)	China	<ul style="list-style-type: none"> <li>• catalytic membrane reactors (distributor, diffuser)</li> </ul>
Institut Européen des Membranes, Montpellier (Jose Sanchez, Anne Julbe)	France	<ul style="list-style-type: none"> <li>• porous and dense ceramic and hybrid membranes</li> <li>• membrane contactors</li> <li>• enzymatic membrane</li> </ul>

		<ul style="list-style-type: none"> <li>reactors</li> <li>• catalytic membrane reactors (distributors, contactors)</li> <li>• modelling of membrane processes</li> </ul>
Institut de Recherches sur la Catalyse et l'Environnement (IRCE), Lyon (Jean-Alain Dalmon, Sylvain Miachon)	France	<ul style="list-style-type: none"> <li>• catalytic membrane contactors for gas-liquid reactions (diffuser and pore-flow-through)</li> </ul>
GKSS, Institute of Polymer Research, Geesthacht, Department of Polymer Chemistry 2 (Detlev Fritsch)	Germany	<ul style="list-style-type: none"> <li>• porous polymer catalytic membranes for membrane contactors (pore-flow-through)</li> </ul>
RWTH Aachen, Institute of Process Engineering (Thomas Melin)	Germany	<ul style="list-style-type: none"> <li>• membrane contactors for water purification</li> <li>• catalytic membrane contactors (diffuser and pore-flow-through)</li> </ul>
Max-Planck-Institut für Dynamik komplexer technischer Systeme, Magdeburg and Otto-von-Guericke Universität Magdeburg, Institut für Verfahrenstechnik (Andreas Seidel-Morgenstern)	Germany	<ul style="list-style-type: none"> <li>• catalytic membrane reactors (distributor) for selective oxidation</li> <li>• modelling of membrane reactors</li> </ul>
DECHEMA e.V., Karl-Winnacker-Institut, Frankfurt am Main (Roland Dittmeyer)	Germany	<ul style="list-style-type: none"> <li>• catalytic membrane contactors for gas-liquid reactions (diffuser and pore-flow-through)</li> </ul>
Università degli Studi di Genova, Laboratorio di Scienze e Tecnologie Chimiche e dei Materiali "SCITECHMA" (Gustavo Capannelli)	Italy	<ul style="list-style-type: none"> <li>• membrane contactors</li> <li>• catalytic membrane reactors (distributors, contactors)</li> <li>• modelling of membrane reactors</li> </ul>
Institute on Membrane Technology, Arcavacata di Rende (Enrico Drioli)	Italy	<ul style="list-style-type: none"> <li>• preparation and transport phenomena in inorganic, polymeric and biological membranes</li> <li>• membrane operations and integrated processes for chemicals production and biomedical applications</li> <li>• catalytic membranes and membrane reactors</li> </ul>
Twente University, Membrane Technology Group (Matthias Wessling)	The Netherlands	<ul style="list-style-type: none"> <li>• membrane microreactors</li> <li>• membrane contactors for gas absorption</li> <li>• biomedical membrane applications</li> </ul>
Netherlands Organisation for Applied Scientific Research TNO, Eindhoven (Erik Meuleman)	The Netherlands	<ul style="list-style-type: none"> <li>• membrane contactors for enhancing separations (gas absorption, extraction, distillation)</li> </ul>
SINTEF Materials and Chemistry, Functional Ceramics (Rune Bredesen, Henrik Raeder)	Norway	<ul style="list-style-type: none"> <li>• catalytic membrane contactors for gas-liquid reactions (diffuser)</li> </ul>
Universidade Nova de Lisboa, Departamento de Química, REQUIMTE/CQFB, Caparica (João G. Crespo, Joaquim Vital)	Portugal	<ul style="list-style-type: none"> <li>• polymeric catalytic membranes for fine chemistry applications</li> </ul>

A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow (Vladimir Teplyakov, Vladimir V. Volkov )	Russia	<ul style="list-style-type: none"> <li>• membrane contactors for gas absorption</li> <li>• catalytic membrane contactors for gas-liquid and gas-phase reactions (diffuser and pore-flow-through)</li> </ul>
Boreskov Institute of Catalysis, Novosibirsk (Valentin N. Parmon, Zinfer R. Ismagilov)	Russia	<ul style="list-style-type: none"> <li>• catalytic membrane contactors (pore-flow-through)</li> </ul>
National Institute of Chemistry Slovenia, Laboratory of Catalysis and Chemical Reaction Engineering, Ljubljana (Janez Levec, Albin Pintar)	Slovenia	<ul style="list-style-type: none"> <li>• catalytic membrane contactors for gas-liquid reactions (diffuser)</li> </ul>
University of Zaragoza, Department of Chemical and Environmental Engineering (Jesus Santamaria, Miguel Menéndez)	Spain	<ul style="list-style-type: none"> <li>• catalytic membrane reactors (distributors, contactors)</li> </ul>
University of Bath, Department of Chemical Engineering, (Alexei Lapkin)	United Kingdom	<ul style="list-style-type: none"> <li>• catalytic membrane reactors (distributors, contactors)</li> </ul>
<b>COMPANIES</b>		
Inocermic GmbH, Hermsdorf	Germany	<ul style="list-style-type: none"> <li>• supplier of porous and dense ceramic membranes</li> </ul>
Bayer Technology Services GmbH, Leverkusen	Germany	<ul style="list-style-type: none"> <li>• pilot-scale experiments with a ceramic multi-capillary pore-flow-through catalytic membrane contactor for hydrogenations</li> </ul>
Due Miljø, Oslo	Norway	<ul style="list-style-type: none"> <li>• pilot-scale experiments with a ceramic multi-channel tube catalytic diffuser for wet air oxidation of organic acids</li> </ul>
Lípidos Santiga S.A., Barcelona	Spain	<ul style="list-style-type: none"> <li>• pilot scale experiments with a polymeric pore-flow-through catalytic membrane contactor for hydrogenation of sunflower oil</li> </ul>
Kühni Ltd., Separation Processes and Technology, Allschwil	Switzerland	<ul style="list-style-type: none"> <li>• development of membrane contactors for membrane gas absorption (or aeration) and extraction</li> </ul>
Mast Carbon Ltd., Guildford	United Kingdom	<ul style="list-style-type: none"> <li>• supplier of porous carbon membranes</li> </ul>
CeraMem Corp., Waltham/MA	USA	<ul style="list-style-type: none"> <li>• supplier of porous ceramic membranes</li> <li>• development of a prototype monolithic loop catalytic membrane contactor for Fischer Tropsch-Synthesis</li> </ul>
Media and Process Technology Inc., Pittsburg/PA	USA	<ul style="list-style-type: none"> <li>• supplier of porous ceramic membranes</li> </ul>

## 5. Stakeholders

### 5.1 Suppliers and developers

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

Many suppliers of non-selective, i.e., mostly porous, membranes exist that may be used in distributor or contactor membrane reactors. Commercially available materials include polymeric, ceramic, carbon, metal, and silicon membranes and composites thereof. Catalytically active membranes for contactors, as yet, are not commercially available. Such materials are generally prepared *on purpose* in research institutes, universities, or small companies within R&D projects. However, catalytic modification of the membranes, in most cases, may be adopted rather easily by membrane producers, once technical feasibility and market demand look promising.

Apart from membrane manufacturers, engineering companies are involved in the development of new applications, often together with end users of the technology. In the following table, a list of membrane manufacturers and engineering companies is provided who have been involved in development activities in the field of non-selective membrane reactors (including contactors for gas absorption and other separations). The list is certainly not complete as much more projects have been executed.

Table 9. Supplier and developers

Institute/Company	Country	Remarks
MEMBRANE MANUFACTURERS		
Pall Exekia, Bazet	France	Manufacturer of porous ceramic membranes ( $\text{Al}_2\text{O}_3$ )
Tami Industries, Nyons	France	Manufacturer of porous ceramic membranes ( $\text{TiO}_2$ , $\text{ZrO}_2$ )
W.L. Gore & Associates GmbH, Munich	Germany	Manufacturer of PTFE-based membranes and partner of Kvaerner in the development of membrane contactors for natural gas sweetening and dehydration, and $\text{CO}_2$ removal from exhaust gases
Inocermic GmbH, Hermsdorf	Germany	Manufacturer of porous ceramic membranes ( $\text{Al}_2\text{O}_3$ , $\text{TiO}_2$ , $\text{ZrO}_2$ , $\text{SiO}_2$ ) and zeolite membranes
NGK Insulators Ltd., Nagoya	Japan	Manufacturer of ceramic substrates, particulate filters, catalyst supports, porous ceramic membranes
Noritake CO. Ltd., Ceramics & Materials Group, Nagoya	Japan	Manufacturer of porous ceramics and catalysts supports
Hyflux CEPAration B.V., Helmond	The Netherlands	Manufacturer of porous ceramic capillaries (mainly $\text{Al}_2\text{O}_3$ ).
Aquamarijn Microfiltration B.V., Zutphen	The Netherlands	Manufacturer of silicon nitride-based microsieves
FluXXion B.V., Eindhoven	The Netherlands	Manufacturer of silicon-based microsieves
Mast Carbon Ltd., Guildford	United Kingdom	Manufacturer of porous carbon membranes
Membrana (former Celgard Inc.), Charlotte/NC	USA	Manufacturer of LiquiCel® membrane contactors

Entegris Inc., Chaska/MN	USA	Manufacturer of pHasor® membrane contactors
Compact Membrane Systems Inc., Wilmington/DE	USA	Manufacturer of membrane contactors based on nonporous fluoropolymer thin film membranes acting as a highly gas transmissive barrier to liquids
Corning Inc., Environmental Technologies, Corning/NY	USA	Manufacturer of ceramic substrates, particulate filters, catalyst supports
TECHNOLOGY DEVELOPERS		
Haldor Topsoe A/S, Lyngby	Denmark	Pilot-scale experiments for a distributor MR for selective oxidation on n-butane to maleic anhydride
Netherlands Organisation for Applied Scientific Research TNO, Eindhoven	The Netherlands	Technology development for membrane-enhanced gas absorption, distillation, extraction, etc.
Bayer Technology Services GmbH, Leverkusen	Germany	Pilot scale testing of a pore-flow-through catalytic membrane contactor for hydrogenations
Aker Kvaerner Process Systems A/S, Lysaker	Norway	Membrane-enhanced gas absorption for natural gas sweetening and dehydrations and CO <sub>2</sub> removal from exhaust gases. Process development together with W.L. Gore & Associates as membrane manufacturer and different end users (Chevron Texaco, Statoil)
Kühni Ltd., Separation Processes and Technology, Allschwil	Switzerland	Technology development for membrane-enhanced gas absorption and extraction

## 5.2 End users

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

End users are engineering companies which may utilise the technology for the development of novel processes, the upgrading of proven processes or the revamping of existing installations. Chemical companies or other industries (e.g., electrical power generation) may license these processes or purchase the equipment for improving their production.

## 6. Expert's brief final judgment on the technology

*(maximum 5 sentences)*

Membrane *contactors* for enhancing separations (absorption, extraction, distillation, etc.), though not in the focus of this report, show great potential for improving chemical processes in respect of reducing plant size, investment and operating costs, and energy demand. As opposed to these devices, which do not target the accomplishment of chemical transformations but rather use them for intensifying the separation, non-selective membrane *reactors* are still in an early development stage and face more difficulties to find industrial application. Non-selective distributor MRs do not offer step change improvements in yield or selectivity, thus the benefits are

modest compared to the cost of the membranes and the additional efforts for integrating them into the design. Contactor MRs are more promising, i.e., diffusers may win recognition where their unique feature of being used as a reactive interface between two reactant streams provides an incentive, e.g., due to improved safety, and pore-flow-through MRs enable much higher space-time-yields and better selectivity in applications where mass (and heat) transport limitations are of major concern.