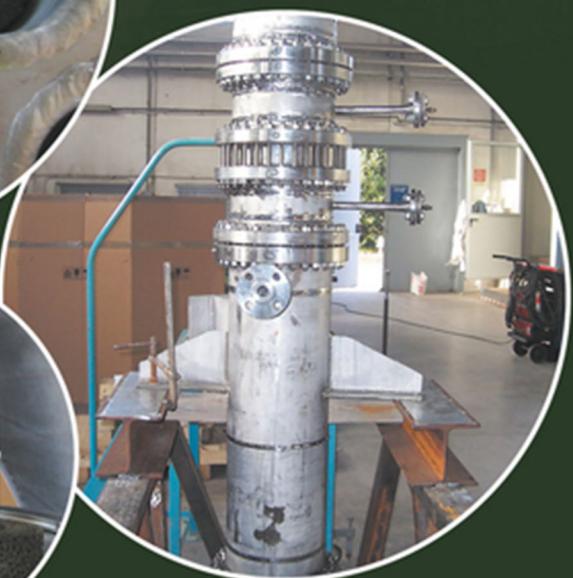


Edited by

Angelo Basile • Marcello De Falco

Gabriele Centi • Gaetano Iaquaniello

# MEMBRANE REACTOR ENGINEERING APPLICATIONS FOR A GREENER PROCESS INDUSTRY



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# **Membrane Reactor Engineering**



# Membrane Reactor Engineering

Applications for a Greener Process Industry

Edited by

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*Library of Congress Cataloging-in-Publication Data*

Names: Basile, Angelo (Angelo Bruno), editor. | Falco, Marcello de, editor. | Centi, G. (Gabriele), 1955– editor. | Iaquaniello, Gaetano, editor.

Title: Membrane reactor engineering : applications for a greener process industry / edited by Angelo Basile, University of Calabria, Marcello De Falco, University of Rome, Gabriele Centi, University of Messina, Gaetano Iaquaniello, KT-Kinetics Technology S.p.A.

Description: Chichester, West Sussex, United Kingdom : John Wiley and Sons, Inc., [2017] | Includes bibliographical references and index.

Identifiers: LCCN 2016013562 (print) | LCCN 2016021091 (ebook) | ISBN 9781118906804 (cloth) | ISBN 9781118906828 (pdf) | ISBN 9781118906811 (epub)

Subjects: LCSH: Membrane reactors.

Classification: LCC TP248.25.M45 M444 2017 (print) | LCC TP248.25.M45 (ebook) | DDC 660/.2832–dc23

LC record available at <https://lccn.loc.gov/2016013562>

A catalogue record for this book is available from the British Library.

Cover image: Courtesy of the author

Set in 10/12pt Times by SPi Global, Pondicherry, India

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# Preface

‘Process Intensification’ and ‘Resource and Energy Efficiency’ are two of the key concepts around which there has been an increased research effort, because these are elements that develop innovative process schemes and engineering. Smaller, cleaner, safer and more energy-efficient technologies are required for the future of energy and chemical production. Several of these objectives could be realized by a new process design based on the integration of membrane units. Membrane reactor technologies or coupling reactor and membrane units play an important role in advanced process engineering, going beyond the combination of just a membrane-based separation unit and a catalytic chemical reaction. Many catalytic industrial processes can potentially benefit from the introduction of advanced membranes and membrane-based process schemes.

There is an increasing industrial interest in these solutions, but there are still several limitations in the actual membranes in terms of flux, separation factor, conditions of operation and stability. There have been several recent advancements and new concepts in membrane design to overcome these limitations. At the same time, process design should account for these limitations and define the targets for new developments.

For the relevance of these concepts, an advanced school was run entitled ‘Engineering of Membrane Reactors for the Process Industry’ in the frame of activities by two EU projects, with core activities about the integration of membranes in advanced process schemes:

- COMETHY – Compact Multifuel-Energy to Hydrogen converter;
- NEXT-GTL – Innovative catalytic technologies and materials for the next gas-to-liquid processes.

The School was organized in Sarteano (Siena, Tuscany) – Italy on 3–6 October, 2013. This book is based, although not limited, to the presentations and discussions made during this School, and has been updated by considering more recent developments, as well as selected results



**Figure 1** A picture of 'Teatro degli Arrischianti' (Sarteano, Tuscany, Italy) during the school on 'Engineering of Membrane Reactors for the Process Industry' held on 3–6 October, 2013

from other EU projects also on the integration of membrane units in process industry, such as the CARENA (Catalytic membrane reactors based on new materials for C1–C4 valorization).

The School was organized by KT (currently Kinetics Technology SpA) and Processi Innovativi, in collaboration with the European Research Institute of Catalysis (ERIC AISBL) and with the financial support of the Maire Tecnimont group and COMETHY/NEXT-GTL projects. The aim of the Summer School was to focus on (i) the different types of membranes that could be employed in membrane reactors depending on the specific application, and (ii) the different applications that could be considered such as syngas production, hydrocarbon dehydrogenation and the water gas shift.

The School was held in the impressive 'Teatro degli Arrischianti'; a picture of which is presented in Figure 1. The origin of this theatre dates back to the seventeenth century and it is an excellent example of the possibility to use the beauty of culture to inspire scientific discussion to go beyond traditional limits and hold brainstorm-type discussions.

The organization of this school would have been impossible without great efforts by KT and Processi Innovativi staff, particularly Marta Borrillo, Maria Luce Brusco, and the ERIC AISBL staff, particularly Serena Orsi. The chairs of the School (G. Iaquaniello and G. Centi) would really like to thank their invaluable contribution to the successful realization of the school. The 'Comune di Sarteano' is also really thankful for the chance to use the 'Teatro degli Arrischianti' as the location for the school.

This book goes beyond this school, which was used as an inspiration to collect about 15 chapters, nearly half of which are on fundamental aspects of membrane reactor engineering and half on application examples. The realization of the book was impossible without the great work of M. De Falco and A. Basile collecting and revising these chapters. The result, however, is a book that could inspire the next generation of chemical engineers to look at the field from a different perspective for the future of process engineering.

*Gabriele Centi and Gaetano Iaquaniello*

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# **Part 1**

## **Fundamental Studies on Membrane Reactor Engineering**



# 1

## Membrane Reactors: The Technology State-of-the-Art and Future Perspectives

*Gaetano Iaquaniello<sup>1</sup>, Gabriele Centi<sup>2</sup>, Marcello De Falco<sup>3</sup> and Angelo Basile<sup>4</sup>*

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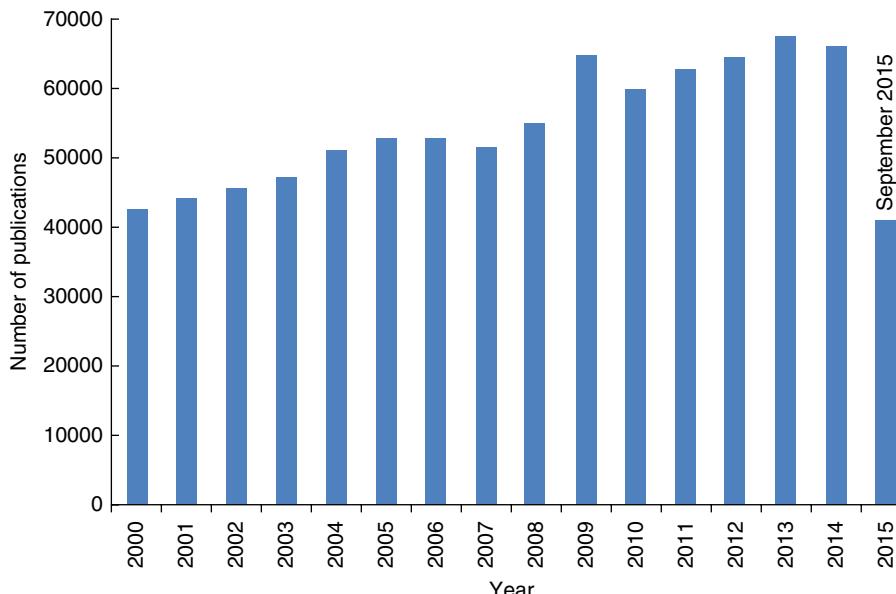
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### 1.1 Selective Membranes: State-of-the-Art

IUPAC [1] defines membranes as structures having lateral dimensions much greater than their thickness, with the mass transfer regulated by a driving force, expressed as gradient of concentration, pressure, temperature, electric potential, and so on. In other words, a membrane is a permeable phase between two fluid mixtures, which allows a preferential permeation to at least one species of the mixture. So, the membrane acts as a barrier for some species whereas for other species it does not. In effect, the main function of the membrane is to control the relative rates of transport of the various species through its matrix structure giving a stream (permeate) concentrated in (at least) one species and another stream (retentate) depleted with the same species.

The performance of a membrane is related to two simple factors: flux and selectivity. The flux through the membrane (or permeation rate) is the amount (mass or molar) of fluid



**Figure 1.1** Number of publications about “membranes” versus time. (Scopus database: [www.scopus.com](http://www.scopus.com))

passing through the membrane per unit area of membrane and per unit of time. Selectivity measures the relative permeation rates of two species through the membrane, in the same conditions (pressure, temperature, etc.). The fraction of solute in the feed retained by the membrane is the retention. Generally, as a rule, a high permeability corresponds to a low selectivity and, vice versa, a low permeability corresponds to a high selectivity and an attempt to maximize one factor is compromised by a reduction of the other one. Ideally membrane with a high selectivity and with high permeability is required.

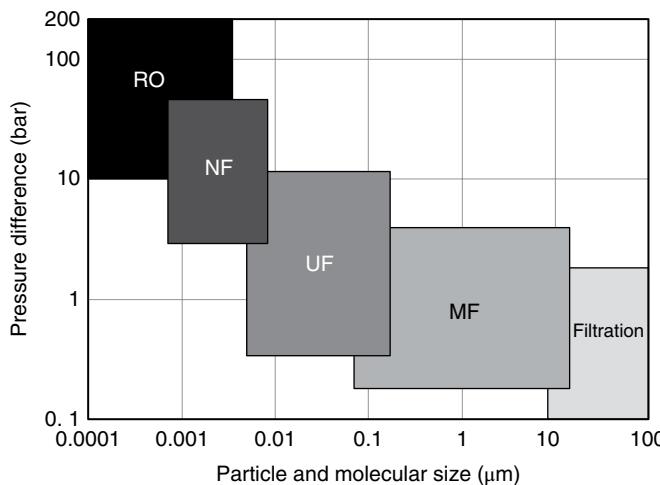
Membranes are used for many different separations: the separation of mixtures of fluids (gas, vapor, and miscible liquids such as organic mixtures and aqueous/organic ones) and solid/liquid and liquid/liquid dispersions, and dissolved solids and solutes from liquids [2].

Membrane processes are a well-established reality in various technology fields, as testified, for example, by Figure 1.1, which describes the trend in scientific publications regarding “membranes” in the last 15 years.

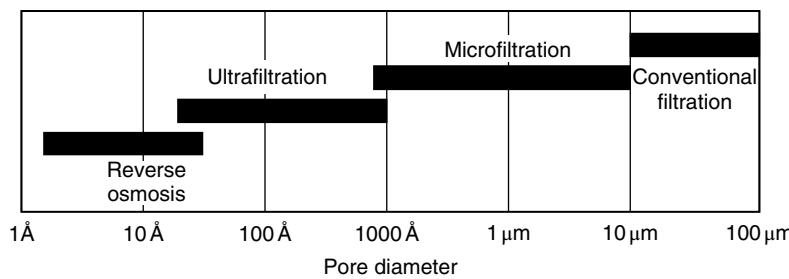
Membranes are applied to fluid treatment and they can be involved in different processes such as Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF), Pervaporation (PV), Gas Permeation (GP), Vapor Permeation (VP), and Reverse Osmosis (RO) processes.

To briefly summarize [2]:

1. MF is related to the filtration of micron and submicron size particulates from liquid and gases.
2. UF refers to the removal of macromolecules and colloids from liquids containing ionic species.
3. PV refers to the separation of miscible liquids.



**Figure 1.2** Separation capabilities of pressure driven membrane separation processes



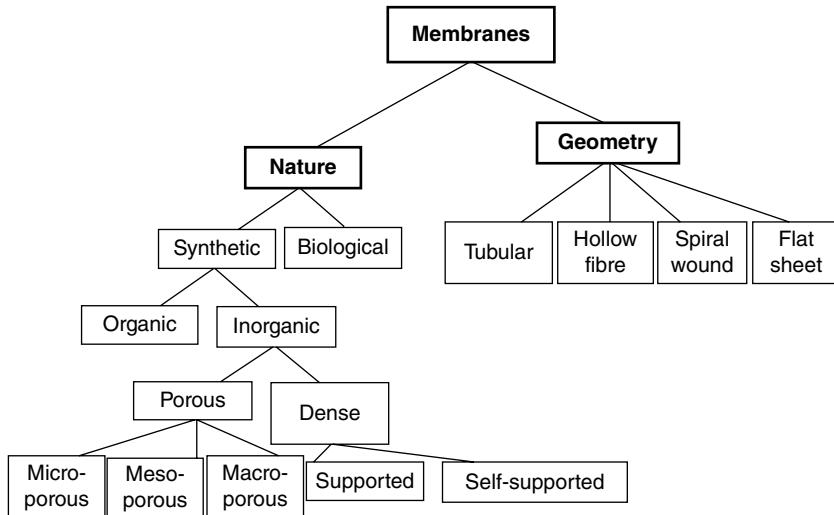
**Figure 1.3** Separation process as a function of the membrane pore diameter

4. The selective separation of mixtures of gases and vapor and gas mixtures are called GP and VP, respectively.
5. RO refers to the (virtual) complete removal of all material, suspended and dissolved, from water or other solvents.

The selective separation of species among others is related, in the aforementioned cases, to molecular size dimensions (see Figure 1.2). Furthermore, as reported in Figure 1.3, the pore size of useful membranes sets which kind of processes they can be applied for.

Nowadays, membranes are also applied in many other important technological fields such as dialysis, electrodialysis, hemodialysis, electrofiltration, liquid membrane contactors, and membrane reactors. A schematic view to classify membranes is shown in Figure 1.4, in which they are subdivided by nature and geometry.

Membranes subdivided by their nature can be distinguished into biological and synthetic, differing completely by functionality and structure [4]. Biological membranes are simple to manufacture, presenting, however, a limited operating temperature (below 100°C) and pH range, and are difficult to clean-up besides having a consistent exposure to microbial attacks.



**Figure 1.4** Schematic classification of the membranes. Adapted from [3]

Synthetic membranes can be further classified into organic and inorganic. The organic membranes are limited under operation up to 250°C, whereas the inorganic ones show great stability in the range 300–800°C, sometimes up to 1000°C [5].

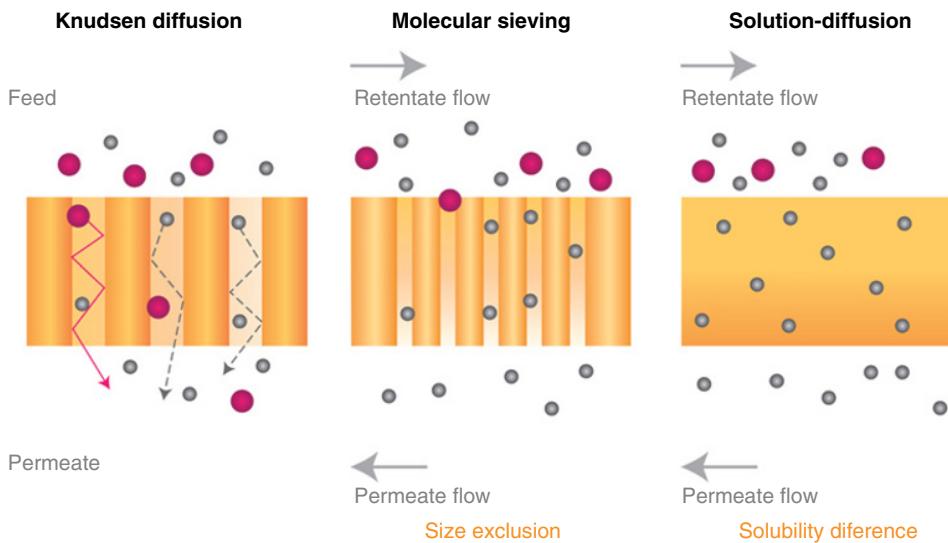
With particular reference to the fields of gas separation and membrane reactors, inorganic membranes can be *porous* [then classified according to their pore diameter in microporous ( $d_p < 2$  nm), mesoporous ( $2 \text{ nm} < d_p < 50$  nm), macroporous ( $d_p > 50$  nm)] and *dense*. Moreover, microporous membranes may have “small pores” ( $d_p \approx 0.5$  nm), “large pores” ( $d_p = 0.5 – 2$  nm), and a metal organic framework [6]. Inorganic membranes are defined as *dense* when  $d_p < 0.5$  nm.

Various mechanisms may regulate mass transport through membranes; some of them are very important and shown in Figure 1.5.

The *Poiseuille (viscous flow)* takes place in cases where the average pore diameter is bigger than the average free path of fluid molecules. A high number of collisions among different molecules is more frequent and consistent than that between the molecules and the porous wall, with the consequential absence of selective separation [7]. The *Knudsen mechanism* regulates mass transport when the average pore diameter is similar to the average free path of fluid molecules. In this case, the collisions between the molecules and the porous wall are very frequent and the permeating flux of such species is calculated by Eq. 1.1 [7]:

$$J_i = \frac{G}{\sqrt{2 \cdot M_i \cdot R \cdot T}} \cdot \frac{\Delta p_i}{\delta} \quad (1.1)$$

$J_i$  is the flux of the  $i$ -species permeating through the membrane,  $G$  is the factor depending on the membrane porosity and the pore tortuosity,  $M_i$  the molecular weight of the  $i$ -species,  $R$  the universal gas constant,  $T$  the absolute temperature,  $\Delta p_i$  pressure difference of species, and  $\delta$  the membrane thickness. The *surface diffusion* takes place if



**Figure 1.5** Representation of some mass transport mechanism through membranes

the permeating molecules are adsorbed on the pore wall due to the active sites present in the membrane. This mechanism can be present when combined with Knudsen transport, even though it becomes less significant at higher temperatures because of the progressive decrease in the bond strength between molecules and surface. *Capillary condensation* occurs in the case of condensation of a species within pores because of capillary forces. This is possible only at low temperature and in the presence of small pores. *Multi-layer diffusion* occurs in presence of strong interactions between molecule and surface, involving an intermediate flow regime between surface diffusion and capillary condensation [8]. The *molecular sieve* takes place in the case of very small pore diameters, allowing the permeation of only smaller molecules.

Regarding dense membranes, palladium and/or its alloys are the dominant materials in the field of hydrogen separation over a number of alternative materials such as tantalum, vanadium, nickel, titanium, and so on (cheaper than palladium and its alloys), particularly due to their characteristics of high hydrogen solubility in the membrane lattice, see Figure 1.6. Indeed, hydrogen molecular transport in dense membranes, with particular reference to palladium, takes place as a solution/diffusion mechanism developed for dense film thicker than  $5\text{ }\mu\text{m}$  in six different activated steps [10] (see Figure 1.7):

1. dissociation of molecular hydrogen at the gas/metal interface,
2. adsorption of the atomic hydrogen on membrane surface,
3. dissolution of atomic hydrogen into the palladium matrix,
4. diffusion of atomic hydrogen through the membrane,
5. re-combination of atomic hydrogen to form hydrogen molecules at the gas/metal interface,
6. desorption of hydrogen molecules.

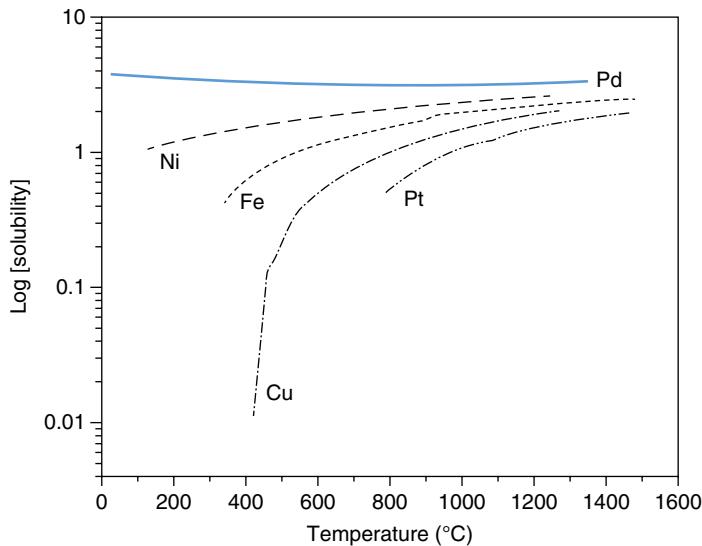


Figure 1.6 Solubility of hydrogen in various metals. Adapted from [9]

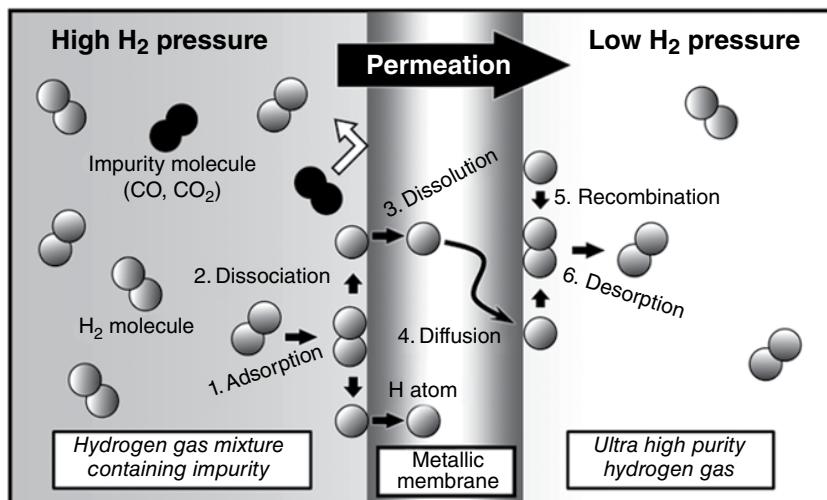


Figure 1.7 Permeation of hydrogen through a metallic membrane. Adapted from [11]

In the case of full hydrogen perm-selective palladium membranes, the equation regulating hydrogen permeating flux may be expressed by the Sieverts–Fick law:

$$J_{H_2} = \frac{Pe_{H_2}(p_{H_2,\text{retentate}}^{0.5} - p_{H_2,\text{permeate}}^{0.5})}{\delta} \quad (1.2)$$

where  $J_{H_2}$  is the hydrogen flux permeating through the membrane,  $Pe_{H_2}$  the hydrogen permeability, and  $p_{H_2,\text{retentate}}$  and  $p_{H_2,\text{permeate}}$  the hydrogen partial pressures in the retentate and permeate zones.  $\delta$  indicates the membrane thickness.

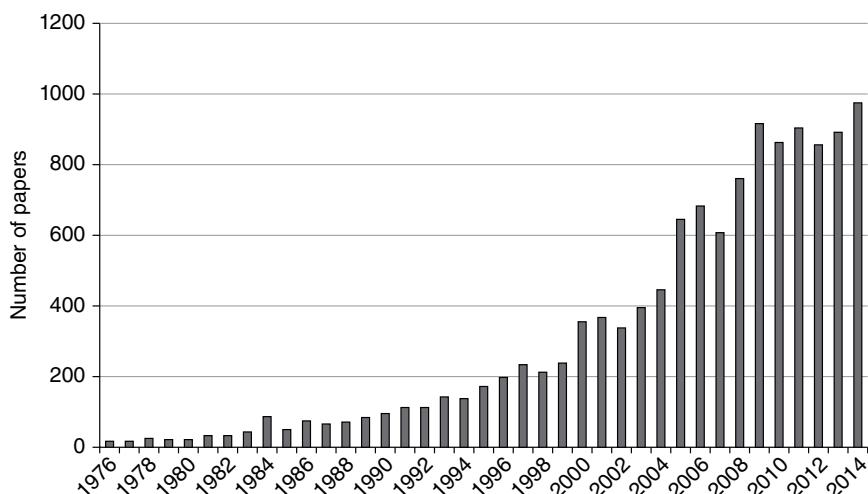
## 1.2 Membrane Reactors Technology: State-of-the-Art

A Membrane Reactor (MR) combines a chemical reaction with the separation process of a reactant or a product. MR technology perfectly fits the Process Intensive (PI) strategy focused on the reduction in the unit number in the chemical processes, boosting efficiency and reducing environmental impact and installation costs: in fact, coupling a reaction with the separation step allows the development of more compact units, replacing the conventional energy-intensive separation techniques. Globally, compared to the traditional reactors coupled with a separation step, a MR requires a lower amount of energy, leading to an increased productivity and easier downstream processing.

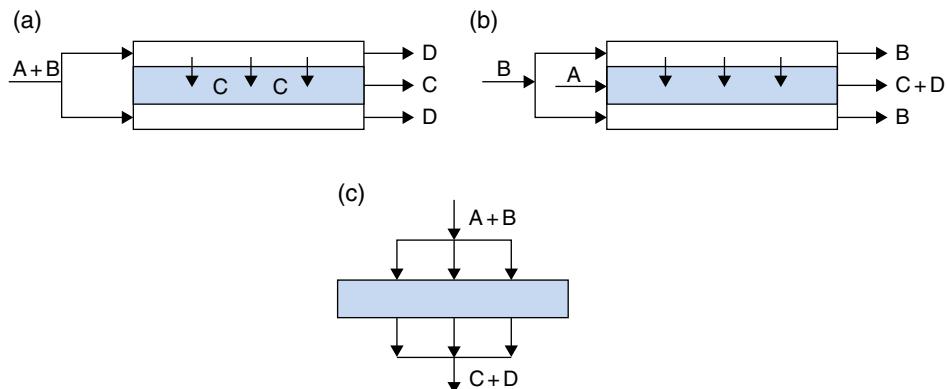
The interest on the MR technology is continuously growing. Inserting the keyword “Membrane Reactor” in the Scopus database, 13144 documents are listed with growing trends years by years (16 papers in 1976, 95 in 1990, 355 in 2000, 866 in 2010, and 980 in 2015, refer to Figure 1.8). The main topics of interest for MR applications are bioreactors, hydrogen production and separation, and wastewater treatments, as confirmed by refining the search on Scopus database: the keywords “Membrane Bioreactor” produce 7946 documents, “Hydrogen Membrane Reactor” 3227, “Wastewater Membrane Reactor” 2641, and “Enzymatic Membrane Reactor” 652. Moreover, the keywords “Industrial Membrane Reactor” give 1384 documents, demonstrating that technology industrial scale-up is progressing.

Generally, MRs are classified into extractor, distributor, and contactor types [12]. Figure 1.9 reports a layout of the three MR typologies: in the extractor type, the membrane removes one or more products from the reactor, thus promoting the reaction and shifting thermodynamic equilibrium; in the distributor configuration, the membrane’s role is to distribute one or more reactants along the reaction environment to ensure more uniform reactions and avoid cold and hot spots; in the contactor MR, a catalytic membrane is installed in order to improve contact of reactants, thus increasing catalyst activity.

Concerning the extractor-type, which is the most diffused and interesting configuration for industrial applications, two different layouts have been proposed [13]: The Integrated



**Figure 1.8** Number of documents found by using the keywords “Membrane Reactor” in the Scopus database (period 1976–2014)



**Figure 1.9** Extractor, distributor, and contactor membrane reactor types for the general reaction  $A+B \leftrightarrow C+D$

**Table 1.1** Selected papers on membrane reactor applications

Process	Membrane Typology	Reference
Pervaporation assisted esterification	Zeolite membranes for selective removal of water	[18, 19]
Direct synthesis of phenol by benzene oxidation	Microporous hydrophobic polypropylene membrane	[20]
Natural gas steam reforming	Pd-Ag membrane	[21, 22]
Autothermal hydrocarbons reforming	Pd-based membrane	[23]
Cyclohexane to benzene and ethylbenzene to styrene	Glass or alumina membranes	[24–26]
Selective oxidation and selective hydrogenation reactions	Solid electrolyte membrane	[27]
Water gas shift reaction	Pd or silica membrane	[27–30]
$H_2S$ decomposition	Silica membrane	[31]
Oxidation of dissolved compounds in wastewater	Pt – porous ceramic membrane	[32]
Oxidation of propane	Polymeric membranes	[33]
Partial hydrogenation of propyne to propylene.	PAA membrane functionalized with Pd nanoparticles	[34]
Alkane dehydrogenation	Pd-Ag membrane or molecular-sieve carbon membrane	[35]

Membrane Reactor (IMR), where the selective membrane is directly assembled in the reaction environment, thus allowing the reaction and products separation in one single compact device, and the Staged Membrane Reactor (SMR) composed of a series of reactor and separation module steps. Details about the benefits and drawbacks of the two configurations are reported in Chapter 4.

Concerning the membrane reactor technology industrial scale-up, Table 1.2 reports the most interesting applications already implemented worldwide: it is worth noting that

**Table 1.2** Selected applications already implemented worldwide of membrane reactors

Application	Company	Description
MR for pure hydrogen production through natural gas steam reforming [22].	Processi Innovativi	The pre-industrial plant, located at Chieti (Italy), has a pure hydrogen capacity of $20\text{ Nm}^3/\text{h}$ and is composed of 2 stages of reforming + hydrogen separation module with a Pd-Ag selective membrane (Staged Membrane Reactor configuration).
MR for pure hydrogen production through natural gas steam reforming [36].	Tokyo Gas Co.	The hydrogen capacity is $40\text{ Nm}^3/\text{h}$ , with a purity of 99.99% and a hydrogen production efficiency of 70% approx. The reformer is composed of 112 reactor tubes, each of which has two planar-type membrane modules with a selective layer of Pd-Y(Gd)-Ag alloy ( $20\mu\text{m}$ thick) and stainless steel support.
Membrane bio-reactor for wastewater treatment [37].	Veolia Water Solutions & Technologies	The Bellville plant features the largest membrane bio-reactor (MBR) in South Africa, with a capacity of 20 Ml/day. The water produced meets strict quality requirements with regards to organic matter, virus and bacteria removal, ammonia, and suspended solids content.
Treatment of municipal/industrial wastewater, production of tap water and industrial water [38]. Treatment of urban and industrial wastewater [39].	United Envirotech Ltd.	Effective membrane area = $10\text{--}27\text{ m}^2$ , selective material.
	Degremont SA	The ULTRAFOR process incorporates the following stages: (i) retention of solid waste by straining; (ii) activated sludge biological treatment; (iii) ultrafiltration by submerged hollow fiber membranes. The maximum unit capacity is $1750\text{ m}^3/\text{day}$ .
MRs are studied for a high number of applications and various experimental works are published reporting promising results and crucial improvements in respect to the traditional reactors. Excellent reviews about MRs have appeared in 2002 [14], in 2004 [15], in 2007 [16] and in 2014 [17]. Some of the most interesting papers on membrane reactor applications are listed in Table 1.1. Biological waste-water treatment process [40].	Wehrle Umwelt GmbH	Bioreactor with external membranes, with a global process energy consumption of 150W per $\text{m}^2$ of membrane area.

*(continued)*

**Table 1.2** (cont'd)

Application	Company	Description
Wastewater treatment [41].	Koch Membrane Systems	Pre-engineered modular MBR systems for flow rates up to 6840 m <sup>3</sup> /day.
Industrial wastewater treatment [43].	Dynatec Systems Inc.	Industrial membrane bioreactor (MBR) applied to: (i) Landfill Leachate; (ii) Hazardous Landfill Leachate with metal removal; (iii) Automotive Manufacturing Wastewater; (iv) Food Manufacturing Wastewater; (v) Titanium Processing Wastewater.
Enzyme membrane reactors [44].	Degussa	Pilot scale enzyme membrane reactor for the production of L-amino acids.
Stereoselective hydrolysis of racemic amino acid esters [45].	Sepracor Inc.	Large scale hydrolysis plant for stereoselective hydrolysis of racemic amino acids esters resulting in purification of the desired L-amino acids. The racemic mixture of amino acids is esterified and fed in an organic solvent to the membrane reactor, where an enzyme is supported in a polymer membrane, able to catalyze the hydrolysis of the L-amino acid ester. The aqueous recovery stream is separated from the hydrophobic D-amino ester.

membrane bioreactors for wastewater treatment are already in an industrial phase, while other applications, such as MR for hydrogen production and enzyme membrane reactors, are in a pre-industrial phase.

### 1.3 Main Barriers to Moving into the Commercialization Phase

This section will mostly deal with metallic MR application with an operating range between 350 and 550°C. Such relatively high temperatures offer the opportunity to run chemical processes – such as natural gas steam reforming (NGSR), water gas shift (WGS), or hydro-carbon dehydrogenation – at their optimum conditions, which at the moment seem to be the most interesting and promising applications.

There are several key obstacles to move into an industrial/commercial phase:

- Membrane stability under the process conditions and during accelerated aging test for membrane life. The operating test of membranes is still reduced to less than 5000 h, which is quite a limited timeframe for commercial application.

- Current lack of an emerging technology for membrane manufacturing to which high fabrication costs and no commercial-scale production unit are associated. Although membrane cost manufacturing is less than the cost of Pd and is more related to labor, the fact that no membrane manufacturing technology has clearly emerged with the last few years is a major problem for large-scale, low cost membrane manufacturing.
- Missing the chemical process that acts as a “white knight” to move metallic MR architecture into the real world of commercial use. WGS is an essential step in the emerging Integrated Gasification Combined Cycle (IGCC) technology to convert coal or biomass wastes into H<sub>2</sub> and zero CO<sub>2</sub> emissions. NGSR is a leading technology for H<sub>2</sub> production in refining and fertilizer industries. Hydrocarbon dehydrogenation is already (although through limited technology) able to convert propane into propylene. But, nevertheless, none of these processes have really taken the lead in shifting to such a new scheme.

In the previous section, the recent advances in substrate development were cited; Pd layer deposition, module modelling and design, together with beneficial efficiencies offered by this technology for quite few chemical processes. However, if the “scientific commitment” in the last 5 years is undeniable and progress to date has been impressive, major effort is still required in the nearby future in order to remove the listed key obstacles. A more strategic alliance with a strong commitment between universities and industry is then required to move ahead.

## 1.4 Conclusions and Future Perspectives

It is without doubt that the grand challenge of a better use of resource and energy efficiency (as well as a reduced impact on the environment) in future production requires development of new process architectures and technologies that reduce process stages, unit operations, recycling in equilibrium-driven reactions, and energy-intensity in product recovery. It is thus evident from this perspective that integration of membrane technology within process schemes is a necessary direction to proceed along. While membrane technology is well established in liquid-phase operations and in part in low-temperature gas-phase operations, the high-temperature gas-phase separation is still problematic. However, this is one of the challenges in this area, as also outlined in the previous sections.

Membrane gas separation has been discussed in various reviews, for example that of Drioli and collaborators [46] and the more recent Baker and Low review [47]. Both remark that membrane processes for gas separation are of increasing interest, but it is remarkable how, even 6 years ago, there was still a gap for moving from lab/pilot scale to industrial realization. It is thus evident, as remarked upon by Baker and Low [47], the need to overcome the barriers that have inhibited the development of these membranes. It is also necessary to have a more open-minded approach and turn in part to the perspective of use membrane, for example no longer as a separation element integrated in a reactor, but as element to achieve a nanoscale-organized material flow and a catalytic reaction in a confined space.

On the other hand, there are new driving forces to enable the use of membrane technology and concepts in novel process architectures, from the energy saving factor mentioned to the

need to develop intensified and efficient small-scale technologies for distributed solutions (for energy, but not only). In addition, there are new factors such as an efficient recovery of CO<sub>2</sub> integrated within the process stimulating the development of CO<sub>2</sub>-separation membranes and thus working typically at relatively high temperatures. Advances in both the science of material preparation and in characterization have also opened new possibilities to understand and control the preparation of membranes. It is thus a combination of different pushing and pulling forces opening new possibilities for membranes, notwithstanding that development was certainly slower than expected in the past, particularly for the area of membrane gas separation at high temperatures.

In CO<sub>2</sub> separation, for example, membrane technology shows undoubtedly interesting opportunities, even if it is still not yet at a commercial scale. Membranes with high permeability and selectivity, better thermal/chemical resistance, and improved mechanical stability for withstanding harsh environments need to be developed [40–50]. Glassy polymers such as cellulose acetate, polyamides, polyarylates, polycarbonates, polysulfones, or polyimides have dominated industrial CO<sub>2</sub> separation applications due to their good selectivities and mechanical properties [50].

Mixed Matrix Membranes (MMMs) have also gained interest recently. Their structure consists of an inorganic material, in the form of micro- or nano-filters incorporated into a polymeric matrix, in order to combine the mechanical properties and economical processing capabilities of polymers with the high separation performance of molecular sieving materials [51]. MMMs are typically less expensive than inorganic membranes and show enhanced thermal and mechanical properties for aggressive environments with respect to polymeric-only ones. Therefore, they can be used in an extended temperature range, although not for temperatures above about 200–250°C where ceramic membranes should be used. In addition, still challenging is their large-scale manufacture, as well as the elimination of interfacial defects between the organic matrix and the inorganic fillers [47].

Despite the large effort in developing new materials for membranes, most (more than 90%) current commercial membranes are still made from about 10 membrane materials, most of which have been used for decades [47]. It is thus evident that to target the challenge of a sustainable future (for example, for making CO<sub>2</sub> separation more reliable with respect to current technologies, e.g., adsorption swing technology), it is necessary to develop new concepts in membranes rather than only novel materials.

One of the emerging possibilities regards the use of functional membranes containing ionic liquids (ILs). ILs combine negligible volatility to other worthwhile properties, such as thermal stability, low flammability, and high-ion conductivity. Their characteristics, including selective adsorption of gases, can be tuned within a relatively wide range. Their use in preparing functional membranes, for example for CO<sub>2</sub> separation, has been known about for many years [52–56], but still the practical implementation is challenging. In using ILs for preparing functional membranes for gas separation, the case of CO<sub>2</sub> capture/separation is the most widely studied application, due to the fact that the quadrupole moment of the CO<sub>2</sub> molecules interacts with the electrical charges of the ILs, thus enhancing the possibility of selective adsorption and transport.

The concept may be extended, for example using the properties of ILs not only to selectively capture CO<sub>2</sub>, but also as a reaction medium to host a catalyst and transform CO<sub>2</sub>. It may be thus possible, in principle, to capture CO<sub>2</sub> and directly convert it (e.g., to methanol) and thus combine CO<sub>2</sub> capture and its conversion at the same time.

The simplest approach in realizing these functional and perhaps catalytic membranes is as supported ionic liquid membranes (SILMs) where the desired IL is immobilized into the pores of a solid membrane by capillary forces [57]. A broad diversity of ILs has already been used to develop SILM systems. SILMs show good  $\text{CO}_2$  separation performances, with permeabilities/perm-selectivities that are close or above the upper bounds for  $\text{CO}_2/\text{CH}_4$  and  $\text{CO}_2/\text{N}_2$  [57]; that is, SILMs are competitive with polymer membranes. Nevertheless, the industrial application of SILMs is limited due to their inadequate long-term stability since they are susceptible to failure if the pressure differential across the membrane is high enough to push out the IL phase from the pores of the membrane support. Presence of impurities or other components may also deteriorate their behavior. SILM stability is still an open issue as different behaviors have been found depending on the nature of both the IL and the membrane support, as well as the pore size [58, 59].

Nano-membranes (NMs) are free-standing structures with a thickness in the range of 1–100 nm and an aspect ratio of over 1,000,000. NM is close to a real 2D structure. With respect to conventional membranes, these NMs show more defined and often narrow size pores. An example is based on ordered arrays of aligned nanotubes either based on oxides or carbon. They were initially developed for material integration. For example, oxide NMs hybrids show enhanced mechano- and thermo-sensitivity for semitransparent epidermal electronics. The use of nanomaterials (single wall nanotubes and silver nanoparticles) embedded in the oxide NMs significantly enhances mechanical and thermal sensitivities [60].  $\text{Fe}_2\text{O}_3$  NMs enabling ultra-long cycling life and high rate capability for Li-ion batteries [61]. However, NMs are gaining increasing interest and even more so in the classical area of separation. The reason is the different flow, which may be obtained when an ordered array of small-size straight-channels is present. For example, ceramic NMs were used recently to separate humidity from natural gas in gas refining processes. The produced NMs has high thermal and chemical resistance and increases the efficiency of dehydration of gas while decreasing the amount of energy consumption [62].

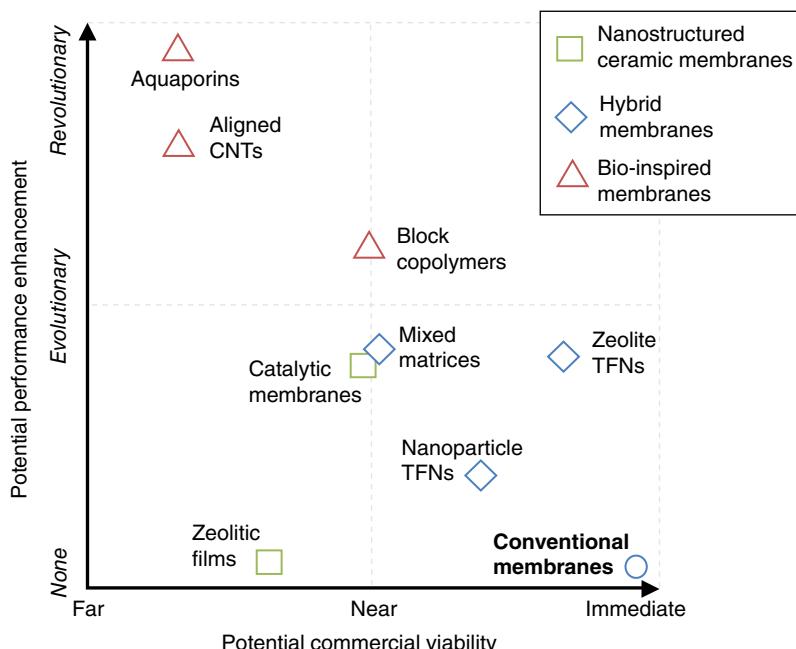
Carbon nanotube (CNT) membranes have received increasing interest for water purification, in particular water desalination [63]. The tip-functionalized nonpolar interior home of CNTs provides a strong invitation to polar water molecules and rejects salts and pollutants. Low energy consumption, antifouling and self-cleaning functions have made CNT membranes extraordinary compared to the conventional ones. The hydrophobic hollow structures encourage friction less movement of water molecules without formal need of any energy-driven force to push water molecules through hollow tubes. The cytotoxic effects of CNT membranes decrease biofouling and increase membrane life by killing and removing pathogens. Fabrication and functionalization of CNT membranes selectively reject particular pollutant from water mixture. Finally, CNT membranes can be made highly reusable, less complex, durable, scalable, and ecofriendly without the need for complicated chemical transformation. There is thus a great potential for CNT membranes in sea and brackish water desalination. Functionalization of CNT membranes with other antimicrobial nanoparticles, such as silver nanoparticles and  $\text{TiO}_2$ , is a further possibility for decreasing biofouling and increasing self-cleaning capacities. There are, however, still various hurdles, such as the still-complex methods for synthesis of CNTs with uniform pore size and distribution and the need to obtain smaller pores with better desalination properties.

Titania NMs, obtained by anodic oxidation derived processes [64] and characterized from straight channels and vertically aligned nanotubes of  $\text{TiO}_2$ , offer the possibility of

combining flow-through characteristics of NMs to photocatalytic and self-cleaning ones. The photo-stimulated current created upon illumination generates an electrical field around the channels, which in combination with the superhydropilicity created by illumination, allows us to obtain some behavior complementary to that of CNT NMs.

Zeolite-coated ceramic membranes are another of the many examples of the application of nanotechnology in developing novel membranes [65]. In this case, the objective is to form membranes with water permeability in the range of UF membranes, but with solute selectivity like that of NF or RO membranes. For RO applications, ceramic alternatives offer the clear advantage of mechanical stability under high pressures and chemical stability to withstand disinfectants. In many wastewater treatment applications, ceramic membranes are more foul-resistant and chemically stable than current polymeric membranes.

There are many other examples of the use of nanotechnology to develop novel or improved membranes, between which hybrid inorganic–organic nanocomposite membranes and bio-inspired membranes, such as hybrid protein–polymer biomimetic membranes, aligned nanotube membranes, and isoporous block copolymer membranes [65], may also be cited. Pendergast and Hoek [65] ranked the membrane nanotechnologies, with particular reference to those promising significant performance improvements over current industry standard membranes. Figure 1.10 summarizes the results for water treatment technologies. There is no equivalent ranking for gas-separation because this is an area far less developed in terms of the novel concepts proposed. In Figure 1.10, performance enhancement relates to permeability,



**Figure 1.10** Comparison of the potential performance and commercial viability of nanotechnology-enabled membrane advances based on review of current literature. Adapted from [65]