

## 30 Years of Membrane Technology for Gas Separation

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Membrane technology applied to the separation of gaseous mixtures competes with conventional unit operations (e.g., distillation, absorption, adsorption) on the basis of overall economics, safety, environmental and technical aspects. Since the first industrial installations for hydrogen separation in the early eighties, significant improvements in membrane quality have been achieved in air separation as well as in CO<sub>2</sub> separation. However, beside the improvement in the materials as well as in membrane module design, an important point is represented by a correct engineering of these separation processes. The recovery of high value co-products from different industrial streams (e.g. organic vapours from off-gas streams, helium from natural gas) is an interesting application, which created a new market for gas separation membranes, coupling environmental and economic benefits. The opportunity to integrate membrane operations in ongoing production cycles for taking advantage from their peculiar characteristics has been proved as a viable approach. In this ambit, membrane systems in appropriate ranges of operating conditions meet the main requirements such as purity, productivity, energy demand of specific industrial processes. A critical discussion about the role of membrane material and engineering aspects is given. Finally, this work intends to give a brief overview of the development of the membrane technology for gas separation in the last 30 years, addressing open problems and strategies proposed in applications of industrial interest.

### 1. History and approach

Although since more than one century ago gas diffusion and mass transport principles through polymer films are known, only in the last 30 years membranes were applied on industrial scale in gas separation (GS). Since the first large industrial application of Prism membranes by Permea (Monsanto) for hydrogen separation from the purge gas stream of ammonia plants, membrane-based GS has grown exponentially. Membrane units do not require a phase change and have relatively small footprints, being smaller than conventional systems such as amine stripping towers. The lack of mechanical complexity in membrane systems is another advantage and their modularity allows an easy scale-up and results in a significant flexibility (Bernardo et al., 2009). Membrane devices for gas separation usually operate under continuous steady-state conditions. They are of special interest to chemical companies, industrial gas suppliers, petroleum producers and refiners (Bernardo and Drioli, 2010). Several applications have achieved commercial success: nitrogen production from air, hydrogen removal from ammonia purge gas, carbon dioxide removal from natural gas and in enhanced oil recovery.

A strong push to the technology to produce economically high-performance membranes was given by the development of the innovative concept of high-flux asymmetric membranes (Loeb and Sourirajan, 1962) initially for reverse osmosis and then adapted to gas separation. Thus, several companies investigated a limited number of polymers for specific separations. Milestones in the industrial application of membrane GS are shown in Figure 1. The largest membrane plant for natural gas processing (CO<sub>2</sub>/CH<sub>4</sub> separation), installed in Pakistan in 1995 with spiral wound modules is included. Its expansion is a clear example of the easy scale-up of the membrane technology.

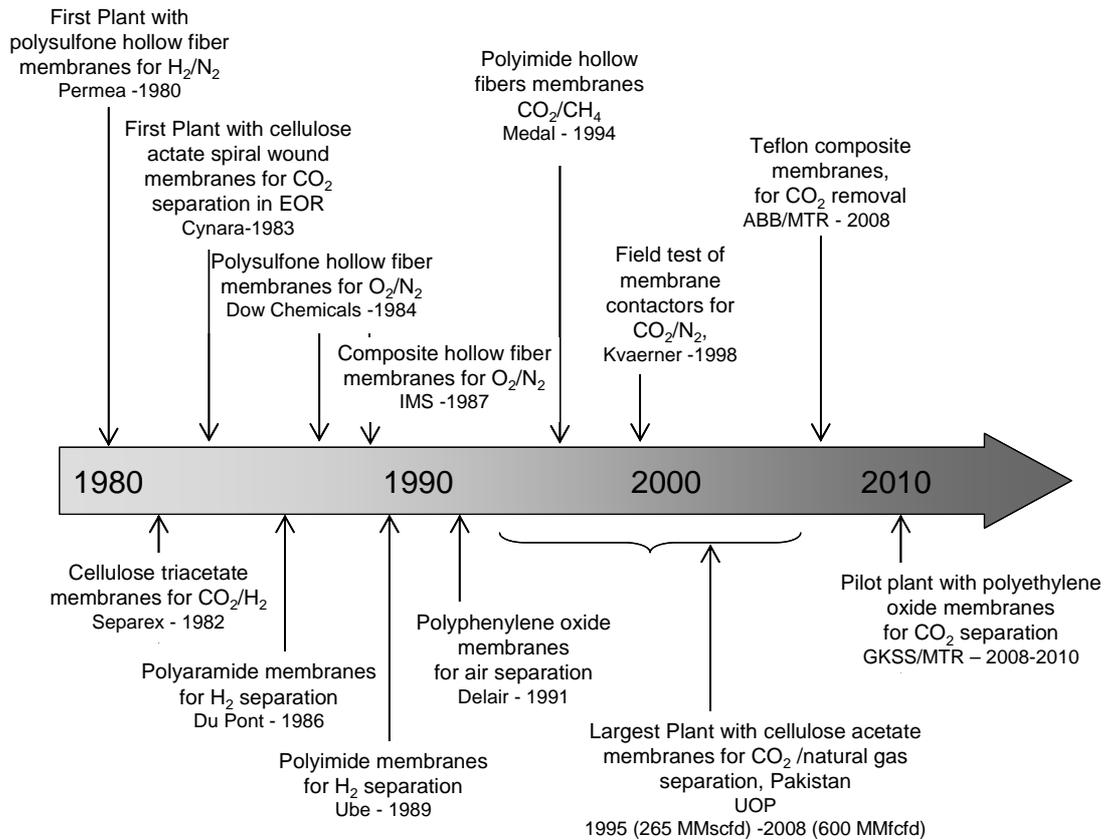


Figure 1: Milestones in the industrial application of membrane gas separation systems.

Different factors concurred in the rapid growth of membrane technology in GS (Figure 2). From a commercial point of view, a significant impetus was provided by the main companies operating in the gas sector which, via joint ventures or acquisitions, make available the potential of this emerging technology, favouring a direct access to the market. In addition, the implementation of new preparation methods (hollow fibre spinning) allowed to reduce significantly the effective thickness of the membrane selective layer with consequent increase of permeation rate and membrane surface area inside the membrane module. Other key aspects are represented by the progress achieved in material science (improved and tailored properties of the materials) and in the design of membrane units (patterns closer to ideal counter-current flow mode).

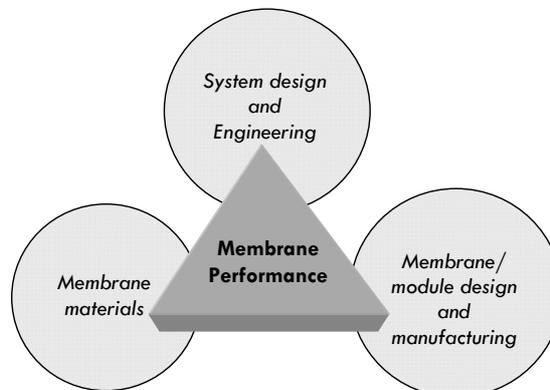


Figure 2: Main topics involved in membrane performance development.

## 2. Membrane material development

Gases dissolve and diffuse into polymeric films under a pressure gradient generating a mass transport through the film. Membrane GS is a pressure driven operation where gas species are separated by “dense” membranes in virtue of differences in solubility and diffusivity. The non-permeating molecules, that remain at the feed-stream side, leave the membrane unit as the retentate stream. A proper selection of the polymer comprising the membrane is extremely important. It determines the ultimate performance of the gas separation module.

### 2.1 Polymeric membranes

Permeability and selectivity are the two main parameters that characterise the performance of a membrane material. They are directly connected from an application point of view to productivity and purity, respectively. The trade off between permeability and selectivity in conventional membrane polymers was first evidenced by Robeson in 1991 and then updated (Robeson, 2008), illustrating the progress achieved by polymer science for the main gas separations ( $O_2/N_2$ ,  $CO_2/CH_4$ ,  $CO_2/N_2$ ,  $H_2/CH_4$ , etc.). Figure 3 combines the data of the last three decades for the air separation, evidencing a shift in the upper bound.

Similar shifts in the upper bound were achieved for other gas pairs. With very few exceptions, glassy polymers result less permeable and more selective occupying the left part of the Figure 3, whereas more permeable rubbery polymers are positioned in the right corner. High free volume polymers were lately introduced, providing very high permeability values. Perfluoropolymers composite membranes are produced by MTR for  $CO_2$  separation with improved resistance to contaminants (Baker and Lokhandwala, 2008). Innovative polymers, the so called polymers with intrinsic microporosity (PIM), were first synthesized ten years ago. They incorporate sites of contortion that force the polymer chains to form a loosely packed matrix. Their exceptional transport properties introduced significant novelty in the field. The family is now growing, with more rigid materials which are able to surpass the current upper-bound for different separations (Budd and Mc Keown, 2010).

In many applications further material requirements are the resistance to temperature and high pressure and to solvents. Thin-film, composite membranes consist of a thin polymer barrier layer formed on one or more porous support layers (almost always a different polymer from the surface layer). The skin layer determines the flux and separation characteristics of the membrane; the porous backing serves only as a support for the selective layer and has no effect on membrane transport properties. In these membranes it is possible to optimize the performance of the different materials independently (two steps). Composite membranes are less sensitive to the presence of humidity in the gas streams, avoiding the separate hydration step in their processing.

Polymeric membrane materials will continue to dominate the market because of their relatively low initial costs and their ability to be used in a variety of applications (Yampolskii, 2012). However, polymer-based membranes are subject to an increasing level of competition from nonpolymeric membranes, which are less likely to foul and can be more easily cleaned.

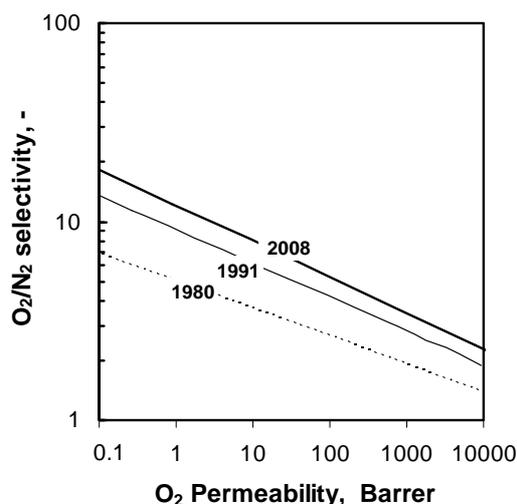


Figure 3: Time evolution of the upper bound for  $O_2/N_2$  separation.

## 2.2 Inorganic membranes

Inorganic membranes have a niche role in GS. Pd-based alloys have a strong potential in hydrogen separation but their very expensive cost limits their application on a very small scale.

Zeolites and carbon belong to molecular sieves and are more selective than polymers for specific gas components due to the important contribution of entropic selectivity to the global selectivity. However, drawbacks of these materials are the difficulty to produce defect-free thin films and manufacturing cost for the former, poor resistance to poisoning and stability for the latter.

## 2.3 Mixed matrix membranes

The combination of the superior performance of inorganic materials with handling properties of the polymers is offered by mixed matrix membranes (MMMs). In these composites inorganic fillers are embedded within a polymer matrix. Although MMMs have a great potential in gas separations, crucial issues are the homogeneous dispersion at high filler content and mainly the adhesion between heterogeneous phases. The functionalization of the filler surface and the use of additives can overcome both issues (Clarizia et al., 2008). Another aspect of interest is the stability of MMMs over time. The filler addition, in some cases can also help in controlling the polymer relaxation, typical of glassy materials which results in permeation decline over time.

## 2.4 Issues to be addressed

Some glassy polymers lose their gas selectivity and sometimes even productivity in presence of trace amounts of condensable hydrocarbons. Plasticization of the selective skin layer by high acid gases (e.g. CO<sub>2</sub>), partial pressure and temperature is also known. It decreases membrane separation ability and may also adversely affect the gas flux due to the compaction of the membrane sub-layer over which a thin gas separation film may be supported. Physical aging occurs in polymers as result of slow and gradual loosing of unrelaxed extra-volume under their glass transition temperature toward an equilibrium state. This phenomenon is more significant and quick for thin films and it causes a generalised decrease of permeability. Crosslinking prevents the material from swelling in presence of aggressive components as well as promotes chemical and thermal stability. The stabilised membrane has a lower permeability than the untreated one, but it also keeps its selective properties as feed pressure increases, thus assuring fibre integrity and performance reliability, key factors for membrane suitability in industrial applications.

## 2.5 Membrane contactors

Membrane contactors are a new membrane-based concept where a hydrophobic microporous membrane operates as contact medium between a feed stream and an extracting phase. This approach takes advantage from the more efficient mass transfer achievable through the membrane pores with respect to conventional packing absorption towers. Membrane modules based on this principle was adopted for different applications ranging from medical to petrochemical field (Klaassen et al., 2005).

## 3. Engineering aspects

Engineering of the membrane systems faces of different aspects ranging from membrane configuration to units arrangement passing from optimal operation modes. These features have to be developed in strict contact with evolution in membrane materials (Clarizia, 2009).

### 3.1 Membranes in modules

In previous section (Figure 1) differences in membrane material and configuration among the main membrane manufacturers were mentioned. Spiral wound modules based on planar membranes are less sensitive to fouling, whereas hollow fibres are characterised by the highest packing density up to 20000 m<sup>2</sup>/m<sup>3</sup>. Pressure drops inside the hollow fibre bundle can be significant at high feed pressure.

The uniformity of size and transport properties of the fibres in the bundle assures the best performance in terms of required driving force/energy and membrane surface. The gain is more important as product purity increases. Thus, the same purity level can be achieved with the lowest compression energy and membrane surface area if homogeneous and uniform fibres are used.

The thickness of the selective layer actually is less than 50 nm, four times lower than the first membranes used in GS. These extremely thin films are possible by virtue of "new generation" spinnerets that also allow to obtain composite structures where the few defects in the integrally skinned membrane are coated by a high permeable sealing polymer, according to Henis and Tripodi (1980).

In order to combine the highest permeation surface area, acceptable pressure drops inside the fibres and resistance to the applied pressure, optimal inner and outer fibre diameters were identified for admissible module length.

For minimising the gas mixing on permeate side with consequent worse concentration profiles, feed stream is sent on the support side of the membrane.

Lumen side or shell side configurations for gas feeding were selected according to fluidodynamic considerations.

Polarisation effects are present in plate-and-frame and spiral wound modules, while is negligible in hollow fibres where shear forces are emphasized. In the last option, as a consequence, high pressure drops and pumping energy are observed.

Industrial module producers (Cynara Group and UOP) achieved a substantial decrease in footprint, up to 70 %, by increasing the module diameter and doubling the length and by developing compact systems with lower weight and savings for support steel.

### 3.2 Operation modes

Two main operation modes are commonly used to impose the driving force in membrane systems: a) high pressure at feed side and permeate at atmospheric pressure; b) feed side at atmospheric pressure and permeate extracted under vacuum. Also a combination of the two modes can be used in specific applications to enhance the driving force.

High driving force means high energy cost for the compression but low membrane surface area. Thus, typically, a compromise between membrane and energy costs governs the membrane operation. The energy efficiency of the operation depends also on concentration of the separating species. In the case of nitrogen production from air the compression mode is mandatory, while for producing oxygen enriched air the solution to extract the permeate by vacuum pump is the appropriate choice because O<sub>2</sub> represents only one fifth of the feed stream and the compression of the whole feed stream is expensive. Similar considerations are valid to purify a gas streams removing traces of impurities.

In applications where a large amount of a stream has to be recovered as permeate, it is (strongly) suggested the use of a very permeable membrane material in order to reduce membrane area requirement. On the contrary, if high purity in a single stage is required a high selective material has to be used.

In addition to the selection of an appropriate membrane material and module design, the pretreatment of the raw feed before entering in membrane system to get rid of all particulates, aerosols, oil and organic condensable vapours is fundamental. It can consume up to 40% of the total separation cost, but it preserves the correct operation mode of the membrane unit. The feed stream may be heated or cooled depending on the feedstock and the separation type.

### 3.3 Membrane unit configurations

Concerning the membrane unit arrangement, the simple design of a single-stage may not yield needed purity. Thus, high product purity can be achieved in more complex cascade processes; they require inter-stage recompression to refine low-pressure permeate. Intermediate streams can be further purified. In order to combine good product purity and recovery, a series-parallel system can be the optimal compromise. A parallel arrangement favours an efficient turndown of the capacity keeping the performance if the load distribution on each membrane module is correct. On the other hand, a sensitive factor of series sequence is the control of the high pressure drop on feed side. Despite of higher complexity of the system, a recycle is widely used to reduce the loss of value components. More exotic solutions are represented by multi-membrane units where simultaneous recovery of more than one enriched product stream can be performed.

Membrane separation processes operated continuously, have few valves and control components which can cause unscheduled shutdowns. Thus, also by virtue of their intrinsic modularity, they result extremely reliable.

## 4. Membranes in hybrid process

Different unit operations can be combined to develop a better separation process where each unit is operating at its optimum domain. Hybrid separation systems in which membrane units are integrated in production cycles with conventional unitary operations were investigated for the petrochemical industry (Bernardo and Clarizia 2011). Hybrid systems are attractive for grass-roots as well as revamps. A typical application is for CO<sub>2</sub> separation and consists in a membrane system for the rough separation, followed by a reduced solvent absorption tower (Bernardo et al., 2004).

## 5. Conclusions

Today, membrane systems are profitably used in gas separation field due to significant improvements in membrane manufacturing methods and design of membrane modules. As a function of working conditions and purity level requested, the choice of membrane material is fundamental. However, an appropriate combination of material and engineering practice determines the achieving of good performance in membrane operations. Despite of outstanding development in material science, polymer membranes, already widely used at industrial level, remain the best option, particularly when shifting from ambient conditions is limited. More selective glassy polymers are preferred to achieve high purity levels also in single stage operations, whereas more permeable rubbery polymers can provide high recovery factors combined with a moderate purity. The whole knowledge of the main limits of membranes (e.g. plasticization, aging) allowed to find appropriate strategies such as crosslinking. The opportunity to integrate membrane with conventional unit operations in production cycles opened a bright scenario in the process intensification logic for a sustainable development.

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