

Polymeric Gas Separation Membranes

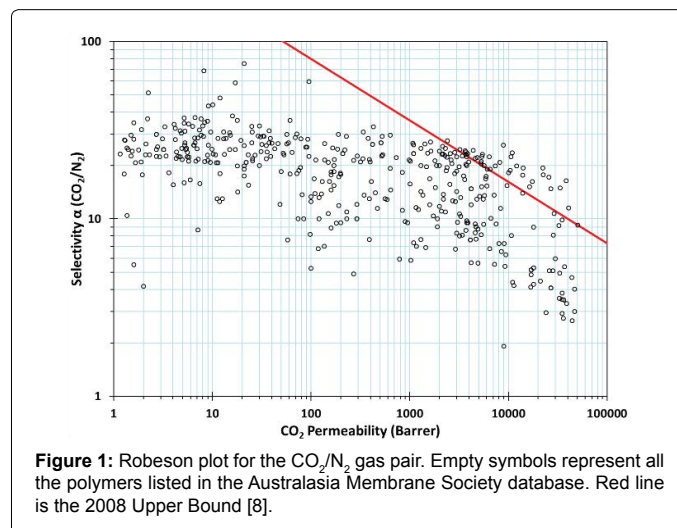
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Membrane gas separation technology was used in the early 1940s for the development of the atomic bomb during the Second World War to separate the much more fissionable U-235 from its abundant relative, U-238 [1]. However, its exploitation in industrial/commercial markets took several decades and only in 1980s the first industrial membrane gas separation process was built. The latter was a hydrogen separation process developed by Permea (currently an Air Products brand). Nowadays, hydrogen recovery, together with natural gas treatment, N₂ production and vapour recovery are the most exploited gas separation applications, with a total market of about 1.4 billion \$ per year [2]. In these applications, the advent of better performing membranes is not likely to cause a big expansion of the membrane gas separation market, while there is a number of challenges that could open completely new markets. Possible new applications are CO₂ capture from flue gas or syngas, CO₂ removal from biogas and several vapour/vapour separations [2]. The current membrane gas separation processes are not economically competitive with the traditional technologies. However, there are two main possible routes for the exploitation of the gas separation technology in new applications: synthesis of better performing new materials, and process optimizations. Most likely, a breakthrough into new markets will be given by a combination of both routes.

Even if hundreds of polymers have been synthesized and tested in the past, only few of them reached the market. Most of the actual commercial membranes are based on polymers with high selectivity and low permeability. Since the latter can be associated to the productivity of the membrane gas separation process, low permeability makes these polymers not suitable for the treatment of huge amount of gas such as the treatment of flue gas. However, the preparation of membranes with high selectivity and high permeability is challenging due to the well-known trade-off between these two quantities. This trade-off has been proposed for the first time by Robeson [3], and it is visible in the famous log-log plot where the selectivity of a gas pair (e.g. CO₂/N₂) is reported as a function of the permeability of the most permeable gas e.g. CO₂ (Figure 1). For instance, a suitable membrane to be used for the CO₂ capture from power plant flue gas would require a polymer with a permeability of at least 1000 barrer and a CO₂/N₂ selectivity over 30 [4]. Nowadays, only few polymers are close to this target. Polymers of intrinsic microporosity (PIMs) and thermally rearranged (TR) polymers are the most promising among the newly synthesized polymers [5-7]. Despite their very high permeability, their expensive multi-step synthesis and their physical ageing are two main drawbacks of these materials that should be solved before their potential application of in real industrial process.

An alternative for the synthesis of new polymers is the preparation of mixed matrix membranes (MMMs). They combine the process ability and stability of traditional polymers with the good performances of inorganic, organometallic or organic fillers such as zeolites, MOFs and ionic liquids. However, also in this case several drawbacks should be addressed before their possible commercialization. The most challenging issue to be solved is the compatibility between the organic polymeric phase and the dispersed fillers, since a low compatibility would lead to the presence of defects or poor mechanical properties



which decrease the separation performances or lifetime of the membranes.

The research of new materials is usually not the most critical step that needs to be solved for the exploitation of polymeric gas separation membranes in new markets. In fact, even an ideal material cannot perform an industrial separation in a one-step process, and multiple-stage processes are necessary. For instance, last year, Evonik Industries Ag has patented a three-step membrane process for raw biogas upgrading [9]. Moreover, the traditional processes configuration should be optimized on the performance of new materials. New opportunities could come also from the optimization of processes based on traditional polymers, for instance with the addition of a pre-treatment step before the real separation module. It goes without saying that the pre-treatment could be also performed using membrane module.

In conclusion, polymeric membrane gas separation membrane is at the same time a mature but expanding field. Opportunities are coming from both new membrane materials and process optimization, but a synergy between these two fields is essential to bring a new product from lab-scale to market.

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