

Strong and weak points of membrane systems applied to gas separation

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Membrane operations are being asserted as a tangible option to conventional technologies in gas separation due to an advanced flexibility to tolerate fluctuations in feed composition and flow rate, operational simplicity and reliability, absence of moving parts, particularly when weight and space requirements are important. Most of the commercial synthetic membranes are made of polymers, characterised by specific transport properties according to their physical state. However, in order to keep the economic competitiveness also in aggressive environments and severe operating conditions, it is necessary to manufacture membranes starting from robust materials with intrinsic high permselective properties. Nanoporous inorganic molecular sieves are potential interesting materials for their peculiar transport, mechanical and physical properties significantly higher than polymers. Processing difficulties, reproducibility problems during the preparation step and high costs still hinder their direct application as membranes at an industrial level.

Although the development of new permselective materials is fundamental to meet the purification request, the correct combination of multiple membrane stages in integrated systems can improve significantly the performance. Therefore, according to the specific separation requests, it is possible to select the appropriate membrane material arranging a sequence of membrane units that maximises the purity and the recovery of a component with a right share of the separation load on each stage.

1. Introduction

The growing interest at an industrial level for novel systems suitable to operate successfully in separation and reaction processes is wholly satisfied by membrane technology in applications ranging from biomedical and food fields to environmental and energy ones. Nowadays, the applications of membrane technology in the gas separation field covers the supply of pure gases, particularly N_2 from air, the separation of acid gases such as CO_2 and H_2S in the natural gas treatment, the separation of H_2 from refinery industrial gases, VOC separation and a variety of smaller applications (Baker, 2002 and 2008). In gas separation, membranes compete successfully with conventional technologies such as adsorption, absorption, cryogenic distillation but, in

order to improve their efficiency, the aspects concerning material properties and module/stage engineering have to be properly taken into account according to the operation conditions.

In this study the attention has been focussed on the discussion of some peculiar features of the membrane systems.

2. Membrane materials for gas separation

According to the Robeson's analyses (1991 and 2008), the performance of polymeric membranes are limited by a trade-off between productivity and selectivity. Typically glassy polymers are characterised by high permselectivity combined to a moderate permeability, whereas rubbery polymers are less selective for discriminating permanent gases, but more permeable. If polymers are the materials more widely used for membrane manufacturing in virtue of their simple processability, intrinsic transport properties and low cost, on the other hand, some inorganic materials present a strong capability to discriminate gas species also in severe temperature and pressure conditions and aggressive environments. However, their use is still limited for reproducibility problems in the preparation step, as well as life time and high cost (Lin et al., 2005; Mc Leary et al., 2006).

Crosslinking of the polymer membranes is an effective method to reduce the plasticization phenomena, occurring in presence of components that strongly interact with the membrane material, and to control the physical aging affecting the selective thin layers of the membrane modules (Wind et al., 2002; McCaig et al., 1999).

Pd-based metallic membranes at certain operating conditions result virtually permeable only to hydrogen, but their high cost and life time still suggest their use for high temperature chemical reactions limited by thermodynamic equilibrium.

Mixed matrix membranes seem a promising and efficient way to combine the high selectivity of the molecular sieving materials with the high processability of the polymers. However, sample stiffness and adhesion problems between organic and inorganic phases still remain an unsolved problem without an appropriate filler functionalisation for improving the reciprocal affinity, particularly as glassy polymers are involved (Clarizia et al., 2008).

Promising recent studies on carbon nanotubes carried out by Sholl et al. (2006) should be confirmed on the larger samples since an appropriate and stable filler alignment along the flow direction is a fundamental requirement to achieve superior transport properties otherwise not possible in presence of a random dispersion of the nanotubes within the polymer matrix.

3. Material properties and driving force

Considering that intrinsic membrane properties such as permeability and, consequently, permselectivity can be significantly influenced by the operating conditions (e.g. temperature and pressure), it is important to establish when the use of a more permselective material is recommended at a fixed value of the driving force. For a gaseous binary mixture containing 10 vol% of the more permeable species, as the net driving force (defined as pressure ratio between permeate and feed streams, PR) is low ($PR \rightarrow 1$), an increase of the permselectivity (defined as ratio between the permeability

value of the two components, α) does not modify the achievable purity, whereas α becomes determinant at a high driving force ($PR \rightarrow 0$), as shown in Figure 1. Therefore, according to the results of the model based on mass balance equations, the use of an expensive highly permselective material is justified only if a substantial driving force between feed and permeate sides can be applied.

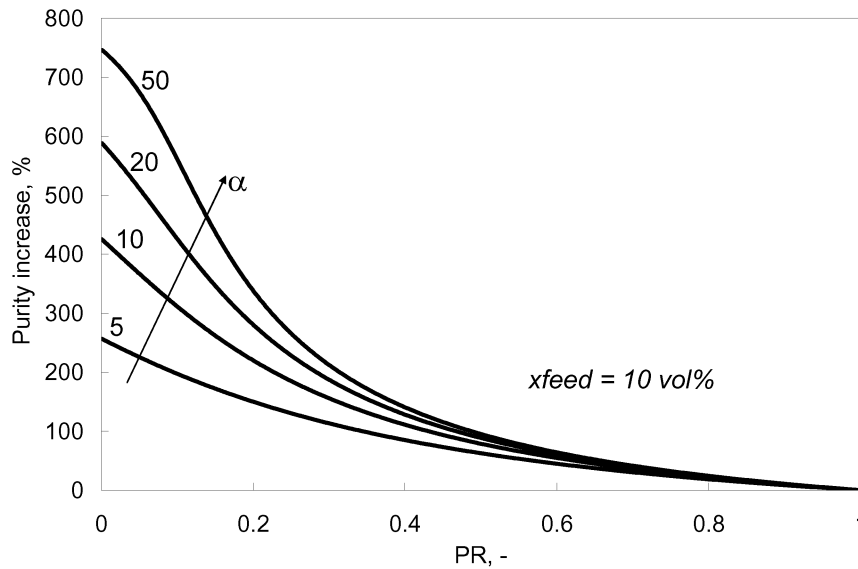


Figure 1. Maximum increment percentage of purity vs. pressure ratio at different permselectivity values (α) for a feed concentration (x_{feed}) equal to 10 vol%.

The influence of the permselectivity on the purity, measured with respect to the concentration of the more permeable component in the feed stream, results less important as the feed concentration increases. Although the increase of the purity achievable starting from a higher x_{feed} is lower, a lower driving force is requested to get it (as shown in Figure 2). In addition, can be observed how at $x_{feed} = 80$ mol%, a ten times increase of permselectivity (dotted line in Figure 2) affects more significantly the threshold value of PR than the final achievable purity.

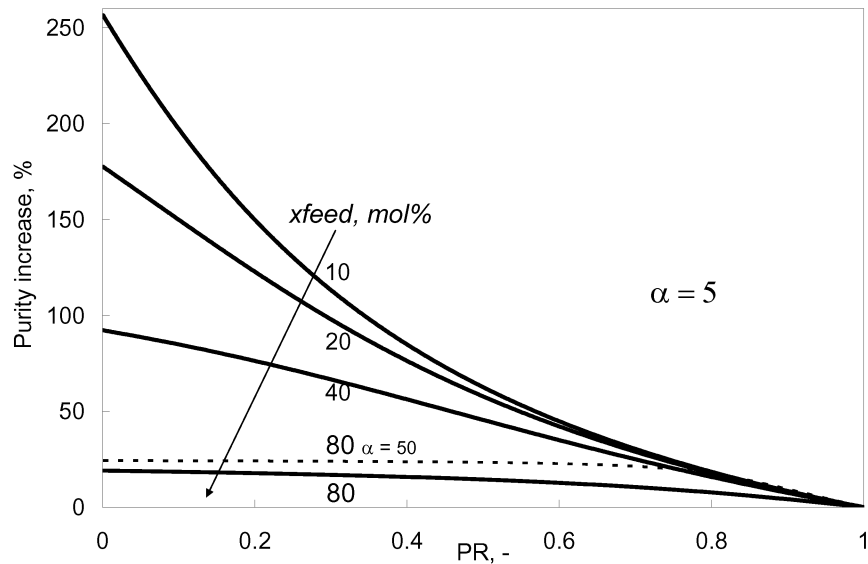


Figure 2. Maximum increment percentage of purity vs. pressure ratio at different feed concentration (x_{feed}) values at a permselectivity (α) equal to 5.

4. Arrangement of membrane stages

A gas separation plant may require several stages of separation to obtain the desired purity of the permeate. In the design of a whole gas separation system, each stage must be considered in terms of driving force and pressure drops, flow rates, permselectivities, and recycling of gas streams in order to achieve the highest possible cost efficiency. Different schemes may therefore be used by combining membrane modules (typically in hollow fibre configurations, when permanent gases are involved in the separation) in series and parallel for an optimised system.

In the logic of the process intensification, the opportunity to design integrated membrane operations opens new scenarios for the gas separation. The combination of membrane and absorption units in a hybrid scheme can be the best solution in a more large range of operating conditions and typically expands the economical area of operability of membrane units, as stated by Stern (Stern et al., 1998). This combination takes the advantages of the two constituent units lowering the costs because each unit can work in its better conditions, but loses the characteristics of working simplicity of membrane unit alone.

Referring to natural gas treatment, the presence of acid gases different of CO_2 at high concentration does not determine further problems in the separation. In fact, for natural gas containing H_2S (~1%) these systems have shown to offer cost savings compared to stand-alone membrane and amine units (Baker et al., 2008).

Some of the drawbacks of the membrane operations such as the necessity of accurate pretreatments, might be solved by combining, as already proposed in ethylene process, various membrane operations in the same industrial process (Bernardo et al., 2004).

With reference to CO₂ separation from ternary mixtures in natural gas processing, Clarizia and Drioli (2005) demonstrated how a proper distribution of the separation load in a two membrane stages in cascade can improve the performance of the operation. In particular at low recovery levels, the maximum of the CO₂ purity in the permeate stream is achieved sharing uniformly the separation load on the membrane stages with a moderate expense in terms of membrane surface areas and compression energy.

5. Conclusions

Problems related to the pre-treatment of the streams, to the membranes life time, to their selectivity and permeability still exist slowing down the growth of large scale industrial applications. However, the success of membrane science and membrane engineering are mainly related to the work of researchers able to face the basic problems related to the control of the structure of the membranes, their transport mechanism, and to develop new membrane-based units capable to perform the operation task also taking advantage of synergic effects of integrated systems. Thus, according to the specific separation target and working conditions, it is essential to select a suitable membrane material for improving the purity and the recovery of a component sharing appropriately the separation load on each membrane stage.

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