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Polymer-based membranes applied to gas separation: material and engineering aspects

Gabriele Clarizia*

Institute on Membrane Technology, via P. Bucci 17/C, 87030 Arcavacata di Rende (CS) Italy
Email: g.clarizia@itm.cnr.it

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Abstract

Polymers are widely used as membrane material to perform the separation of various gaseous mixtures due to their attractive permselective properties and high processability. Although the development of new robust materials is fundamental to enlarge the economic competitiveness in aggressive environments and severe operating conditions, the correct combination of multiple membrane stages in appropriately designed systems can improve significantly the performance, achieving the separation target by using existing materials. In fact, a single membrane stage requires the lowest membrane area but also produces the lowest purity in the permeate stream, whereas multiple membrane stages provide higher purity values with higher membrane surface areas. According to the specific transport properties of rubbery and glassy polymer membranes, it is possible to select an appropriate material in a sequence of membrane units that maximises the purity and the recovery of a species by means of a right share of the separation load on each stage. In this framework, some examples of gas separations of industrial interest are discussed to support this methodology.

Keywords: Polymer membranes; Gas separation; Separation load distribution

1. Introduction

All separation methods take advantage from differences concerning some specific chemical or physical properties of the mixture components that can be enhanced acting opportunely on the operating conditions [1]. As the differences are minimal, in order to make the process more efficient, it is possible to modify the system by means of an additive extraneous to the mixture. In this case, as suggested by euristics, it is better to eliminate the extraneous compound as soon as it has been used in order to avoid any contamination of the products [2]. The growing interest at an industrial level for novel systems suitable to operate

*Corresponding author.

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successfully in separation and reaction processes is wholly satisfied by membrane technology in applications ranging from biomedical and food to environmental and energy fields. Membrane technology is an innovative direct method to carry out fluid separations and it is less affected by scale factors and fluctuation of the feed composition than the conventional separation techniques. In fact, membrane units are intrinsically modular (easy scale-up) and compact, working continuously without any chemical damage of the involved species. In gas separation, they compete successfully with conventional technologies (e.g. adsorption, absorption, and cryogenic distillation) in virtue of a high flexibility to tolerate feed fluctuations in composition and flow-rate and as weight and space requirements are important [3]. In order to achieve a high efficiency in membrane systems, the aspects connected to the material properties and those relating to module and stage engineering have to be properly combined according to the operating conditions. The deep understanding of problems related to the pretreatment of gaseous streams, to the aging and plasticization phenomena occurring with polymer membranes, can strongly improve the performance of membrane units in large scale industrial applications. The opportunity to develop integrated membrane operations also in petrochemical industry, according to a process intensification strategy, has been successfully investigated in the ethylene production cycle, opening new frontiers for gas separation membrane systems [4]. Thus research and development, design and manufacturing steps have to be pursued in an appropriate way, taking into account also safety aspects and economic feasibility of the process.

In this work the performance of a membrane unit has been analysed as a function of the main process variables of interest for the separation of gas mixtures. Furthermore, the attention has been mainly focused on how a proper distribution of the separation load on each membrane stage can make more efficient the operation.

2. Influence of material permselectivity and driving force

The transport isothermal of a gas species in a membrane unit can be described by means of a mass balance equation Eq. (1) and an equation that relates the permeation flux through the membrane medium to the applied driving force Eq. (2):

$$x_{f_i} \cdot F = y_{p_i} \cdot P + x_{r_i} \cdot R \quad \forall i \tag{1}$$

$$-dF_i = \frac{Pe_i}{l} \cdot dS \cdot \left(p_i^F - p_i^P \right) \tag{2}$$

where x_f, y_p, and x_r represent the composition of the *i* species in feed (*F*), permeate (*P*), and retentate (*R*) streams respectively, dF_i the differential amount of the *i* species that permeates through the differential membrane surface (*dS*) under a driving force represented by a pressure difference $\left(p_i^F - p_i^P \right)$. Finally, Pe_i/l is the permeance of the *i* species through the membrane, obtained as ratio between its permeability value and effective membrane thickness.

By combining opportunely these fundamental equations, it is possible to determine, as demonstrated by Hwang and Kammermeyer [5], the effect of some main variables on the performance of a membrane separation system. It is important to point that intrinsic membrane properties such as permeability and, consequently, permselectivity are significantly influenced by the operating conditions (e.g. temperature and pressure).

Therefore, the maximum purity level of the more permeable species, achievable in a single membrane unit (y_p), is mainly affected by two concurrent parameters the intrinsic permselectivity of the material, defined as ratio between the permeation rate of the gas species through the membrane ($\alpha_{ij} = Pe_i/Pe_j$), and the applied driving force, expressed as pressure ratio between permeate and feed streams ($PR = p_p/p_f$).