Already Used and Candidate Polymeric Membranes for CO_2 Separation Plants

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1. Membranes for Acid Gas Separation: Generalities

Synthetic polymer membranes have evolved rapidly in recent years and have become an industrial product of great importance. In the mid-1960s, the first membrane was commercialized based on the formulation of Loeb and Sourirajan (1962).

In recent decades, the use of polymer membranes significantly increased in applications of gas separation. In the 1980s, the initial industrial membrane systems were introduced mainly for the separation of hydrogen from different gaseous mixtures. Later, this technology was incorporated in the production of ammonia for the separation of nitrogen (N_2), methane (CH_4) from other components in petroleum processing, carbon dioxide (CO_2) from natural gas, N_2 from the air, CO_2 from postcombustion, and the removal of CO_2 and hydrogen sulfide (H_2S) from natural gas (Baker, 2007; Favre, 2007).

Membrane use and applications have notably increased since the big commercial introduction in the 1980s. According to different authors, the increasing interest in the membrane technology is due to the operation simplicity, start-ups, shutdowns, and maintenance. In addition, they proved to be economically competent, with lower operating costs and flexibility in the face of composition and conditions fluctuations, when compared with other conventional separation methods (Luis et al., 2012).

According to the literature, continuously improved materials and membrane process configurations offer better performances and more stability toward the removal of contaminants in natural gas streams. When selecting a membrane material for a specific purpose, factors to be considered include an efficient combination of the required permeability, proper selectivity, and mechanical and chemical properties of the membrane to be used.

Considering the importance of the natural gas as a primary raw material for the petrochemical industry and its energy capacity as a fuel, it is mandatory to develop a more efficient natural gas treatment processes. One of the indispensable stages during the natural gas conditioning is the sweetening process, for which the membrane technology represents an alternative of application because of the promising energy consumption, in some cases better performances, cleanness, energy requirements, operative costs, location flexibility, and separation global efficiency (Gutierrez et al., 2017).

Khoo and Tan (2006) stablish the membrane technology uses between 70 and 75 kWh/ton of removed CO_2 and what makes this technology more attractive than other technologies, such as adsorption (160−180 kWh), cryogenic distillation (600−800 kWh), or chemical absorption with amines (330−340 kWh). In terms of economics, amine-based absorption systems have a total cost of $40−100 per ton of captured CO_2, whereas in new commercial membrane schemes (e.g., Polaris membrane), the estimated capture costs around $23 per ton of captured CO_2 (Merkel et al., 2010).

Different types of membranes were adopted for the separation of CO_2 to date. For instance, polymer membranes (Powell and Qiao, 2006), inorganic membranes (Bredesen et al., 2004), and those with facilitated transport mechanism (Luis et al., 2009) have been extensively studied. From the commercial point of view, polymeric materials are preferred in the manufacture of membranes for their processing versatility (Hägg, 2009). The most used materials are organic polymers (polyamide (PA) and polysulfone (PS)) and cellulose acetate (CA) that is highly used in the membranes manufactured for gas sweetening.

In the next decades, the industry will have to exploit low-quality gas reserves under unfavorable conditions. For example, natural gas fields with high levels of acidity might cover the energy demands of the future population (Lee et al., 1995). In parallel to this situation, it is expected that membrane separation technology improves because membrane technology has proved excellent performances to eliminate high volumes of acid gases and also represents a good-positioned competitor to remove acid gases in bulk conditions. In addition to this, operating costs for most extended methods, such as those based on chemical absorption, are directly proportional to the concentration of acid gases in the gas to be treated (Li et al., 1990). Conversely, for membrane systems the concentration of acid gas in the feed gas affects only the investment cost of the design, while the operating cost is significantly lower respect to those conventional methods.

1.1 Permeable Membranes

A membrane is an extremely thin porous sheet mounted on a much thicker, highly porous layer that acts as a barrier. It allows the selective and specific passage of the components under appropriate conditions for the transport mechanism. In this respect, the separation of gases is due to diffusivity dissimilarities among gas components crossing the polymeric

material barrier. For acid gas separation purposes, a polymeric membrane has high affinity for the acidic components of a natural gas stream, increasing the speed with which these components pass through it. Water (H_2O), H_2S, and CO_2 are high diffusers, and thus they pass through a membrane more easily than hydrocarbons, with the same driving force. For the separation of a gas component in a mixture of gases, the driving force is the difference between its partial pressure across the membrane. The gas to be treated is sent to a vessel that has two different pressure zones, separated by the membrane. The gas enters the zone of higher pressure and selectively releases the components that can permeate through the membrane to the area of lower pressure. As it was introduced, the permeation of the gases through the film is not by filtration but is governed on the basis of a selective separation mechanism that includes the absorption, of the high pressure side, diffusion through the film, and desorption on the low pressure side.

Extended bibliography reports the application of membranes in industrial processes for the separation of acid gases, removal of heavy hydrocarbons, water removal, and separation and recovery of helium from N_2 mixtures (Scholes et al., 2012). Particularly, studies consider membrane technology as an alternative to separate CO_2 from various types of fluids such as natural gas, gas combustion from power generation or synthesis gas, carbon monoxide (CO), and hydrogen (H_2) (Lock et al., 2015a; Roussanaly et al., 2016; Vakharia et al., 2015).

In regard to the transportation mechanisms, the gas permeability (P) of dense polymeric films is usually expressed as the product of the gas solubility (S) in the polymeric material and its diffusivity (D). The selectivity $\alpha_{A/B}$ for a gas pair A/B is defined as the ratio of their permeabilities, Eq. (2.1) (Yave et al., 2010; Zhao et al., 2017).

$$\alpha_{A/B} = \frac{P_A}{P_B} = \left(\frac{S_A}{S_B}\right)\left(\frac{D_A}{D_B}\right) \tag{2.1}$$

The diffusion of gas molecules in a dense membrane is a thermally activated process and is described by the Arrhenius expression, according to Eq. (2.2) (Rezakazemi et al., 2018).

$$D_A = D_{0A} \exp\left(-\frac{E_{DA}}{RT}\right) \tag{2.2}$$

where E_{DA} is the diffusion activation energy, R is the universal gas constant, T is the absolute temperature, and D_{0A} the preexponential factor. The flow of component A crossing the porous barrier can be represented according to Eq. (2.3) (Gutierrez et al., 2017).

$$F_A = P_A \cdot \overline{A} \cdot N \left[\frac{P_{A_i} - P_{A_o}}{\ln\left(\frac{P_{A_i}}{P_{A_o}}\right)}\right] \tag{2.3}$$

where F_A is the permeate molar flow for component A (kmol/h), P_A is the permeability for component A (kmol/(1000 kPa h m^2)), $\bar{A}$ is the area per membrane unit (m^2), N is the total number of units, P_{A_i} is the partial pressure of component A in the membrane module input (kPa), and P_{A_o} is the partial pressure of component A in output (kPa).

As the separation is based on a difference in the permeation rates instead of physical barrier, the gas that is recovered by the membrane, permeate, is not completely pure. A quantity of the permeate remains in the residue, limiting the separation capacity of this technology. As can be inferred from these considerations, the membrane process is applied for removal of large quantities of acid gases, that is, for the treatment of large gas flows, with the energy required for the pressure gradient. For cases where this technology is unable to meet product specifications, a multistage membrane system or combined technologies are considered.

In general, as a challenge of process engineers, they are involved in developing membrane dispositions with an extremely thin porous layer mounted on a thicker and highly porous layer of the same material. We describe the most common structures in the following sections.

1.1.1 Porous Membranes

Porous membranes are solid membranes with micropores in which the separation of the gases depends on their molecular size, which diffuses through small pores through the membrane. This type of separation mechanism is restrictive to the commercial separation, and thus implies that they best fit to microfiltration and ultrafiltration instead of large-scale acid gas separation.

1.1.2 Nonporous Membrane

In this respect, the separation of a gas stream is dependent on the different permeation velocities through thin and nonporous films. In the course of the mechanism, the physicochemical properties, the characteristics of the membrane, and the differential partial pressure of the gases through it determine the permeation rate of each component. To reach a required flow, it is necessary to have a suitable membrane material and process conditions.

2. Existing Membrane Structures

Virtually all the existing gas separation membranes are based on the concept of phase inversion, which proves their commercial viability, thinness (i.e., in the order of 100 nm or less), and defect-freeness at large areas in practical applications (Sanders et al., 2013).

Phase inversion process was first used by Loeb and Sourirajan (1962), who produce desalination membranes of CA. Primarily, this technique can be used to produce asymmetric membranes with very thin, dense films on a porous substrate provided with a proper support to high material flows. Specifically, phase inversion has allowed membranes to be arranged at high-density areas and able to operate, for example, from 50 to 700 million SCFPD in some locations (Sanders, 2004).

Many commercial gas separation systems are produced according to the phase inversion process, based on hollow fibers (Kesting et al., 1989; Baker, 2002). During spinning, the bore of the hollow fiber often has a bore fluid to provide a compensating pressure to maintain the hollow interior, coagulate the spin dope, and stabilize the forming fiber. On the other hand, the spiral wound arrangement consists of successive layers of feed gas flow channels, separation membrane, permeable flow support material, and another separation membrane wound around an axially perforated tube (Lin et al., 2012).

The aim of such configurations is to maximize the membrane surface area that can be placed in a given volume. In this sense, the higher the surface to volume ratio, the lesser the amount of pressure vessels and, consequently, the required cost to install such membranes (Sanders et al., 2013).

A typical hollow fiber bundle contains approximately 105 hollow fibers, which are tightly disposed (packing fractions of 50% magnitude are commonly used) with both terminals embedded in a thermosetting polymer epoxy (Coker et al., 1998).

Contrary to this, the module of spiral wound membrane involves alternating layers of flat sheet asymmetric membranes, with porous spaces between the membrane sheets (Baker, 2007). The permeate and feed streams flow through alternate layers in a spiral wound module. The hollow fiber module is much more common than spiral wound systems for gas separation because of the cost of production (Baker, 2002), higher membrane surface area to module volume, and generally easier fabrication methods (Henis, 1994). A pressured vessel, normally metal or polymeric depending on the pressure magnitude, is the confining unit for the hollow fiber bundle or the spiral wound module.

3. *Polymeric Membranes for CO_2 Separation*

Separation and capture of carbon dioxide are the greatest expense in the overall capture and storage processes. However, improvements in this area are of great potential regarding the global awareness to mitigate CO_2 emissions. In this regard, polymeric membranes represent a significant alternative for their applicability ranges, operability, energy demand, cleanness, and capital and total annual costs (Falbo et al., 2014; Gutierrez et al., 2017).

3.1 Already Used Materials in Industrial Scale Applications

In the following sections, a review of already in use membranes for the separation of CO_2 from mixtures gases is given. In addition, some comments on the applicability, their main conditions to be employed, performance, and particular characteristics are given in each case.

First materials to separate CO_2 from natural gas were introduced in the market in the mid-1980s, mainly anisotropic polymeric membranes made of CA. However, the selectivity of CO_2/CH_4 from such membranes remains equal to 12, value under the reported for the same pure gases. An effect known as plasticization explains the decrease in the selectivity values when natural gases are considered instead of pure gases. During the phenomenon, the CO_2 concentration increases, blocking the interaction between polymer adjacent segments and increasing the gas permeability. It is well known that the high-pressure (concentration) CO_2 induces the plasticization of most of the glass materials and, thus, different studies to enhance the membrane characteristics were performed. A proper selection of a polymeric material for the industrial separation of CO_2 is based on the intrinsic permeability and selectivity. After the selection, the polymer is arranged in either hollow fiber membranes or spiral wound membranes, with a high specific surface area.

In accordance with the industrial scale use of membranes for CH_4/CO_2 separation, diverse studies have evaluated the permeabilities and selectivities of the mixture through commercially used polymer membranes. Koros and Fleming (1993), Sanders et al. (2013), George et al. (2016), Naylor (1996), and Alcheikhhamdon and Hoorfar (2017) report the permeability and selectivity of common gases for representative commercially used polymers in the process of gas separation with membranes.

3.1.1 Cellulose Acetates

Chatterjee et al. (1997), George et al. (2016), and Dai et al. (2016) state that the CA is the most extended material for acid gas separation, with CO_2/CH_4 mixture selectivity of 20, under real industry operation conditions. According to Sridhar et al. (2007), polyimides and CA were found to be the best polymeric materials for CO_2/CH_4 separation. Even though the CA still remains as the most popular polymer in the industry, many other polymeric materials, including polyimides, are available this period (Kosuri and Koros, 2008). One of the reasons that CA-based membranes have found success in the field is their resistance to contaminants found in natural gas streams (White et al., 1995). Fig. 2.1 shows the basic structure of the CA.

Available polymer membranes are highly selective to CO_2 relative to CH_4, and reductions of the CO_2, concentration from 20−25 mol% to 2 mol% pipeline specification, are feasible (Lee et al., 1995). Some of the representative suppliers of membrane systems using CA for CO_2 separation from natural gas are UOP and NATCO, in different dispositions. UOP offers a

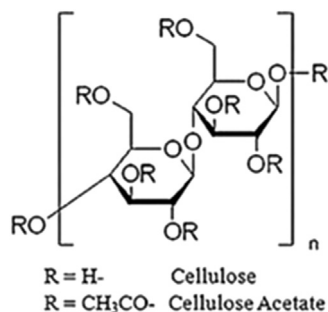R = H-　　　　Cellulose
R = CH₃CO-　Cellulose Acetate

Figure 2.1
Chemical structure of cellulose acetate (Mischnick and Momcilovic, 2010).

spiral wound configuration under the name Separex, whereas NATCO presents an alternative configuration of hollow fiber membrane, under the name Cynara (He et al., 2014).

Separex membrane systems prove good location flexibility for CO_2 separation; literature reports both onshore and offshore applications using this technology. It is particularly suitable for the use in remote locations where logistics make it difficult to transport supplies to a site, says UOP. Among other advantages, they demonstrate robustness during continuous operation, reduce number of utilities to employ, and are easy to start after shutdowns. The UOP Separex membrane technology is applied in the treatment of natural gas streams by removing CO_2, H_2S, and water vapor in a single process. The aim of this process is to meet the quality standards specified by pipeline transmission companies, as well as end users of the natural gas (Bessarabov et al., 2010).

Cynara system operates on the basis of selective permeation; this phenomenon consists of a combination between the gases dissolution and diffusion into the polymeric material. Owing to a subsequent differential pressure imposed on one side of the polymeric membrane, a selective transport across the film occurs. In this mechanism, the rate of permeation is determined by the product between the solubility and diffusion coefficients. Highly soluble molecules and small molecules (CO_2 and H_2S) permeate faster than large molecules. Cynara removal membrane systems efficiently and selectively permeate acid gases to remove them from produced gas streams, with a concentration between 5 and 95 mol% of acid gas (Product Sheet Cynara Sample, 2016).

In industrial applications using CA membranes, aromatic hydrocarbon exposure causes serious performance declines (Ratcliffe et al., 1999). It is observed that these plasticized glassy polymer membranes are often unstable, and the evaluating factors show that CA performance declines over time, as suggested by Wind et al. (2004). However, CA membranes are sensitive to water vapor, and a pretreatment collector must be introduced to use them for the separation of gaseous streams (Datta and Sen, 2006).

The Generon membrane, developed by Dow Chemical in 1985, has a great sweetening power but a great loss of methane (Matsuura, 1993). Separex and CA-2.45 have a very good methane recovery but a low performance with respect to the reduction of CO_2 from the CH_4/CO_2 mixture. For these types of materials, a two-stage membrane system is required in most of the industrial plant applications.

One limitation of CA is that it plasticizes in the presence of CO_2 (Schell et al., 1989). Plasticization can cause the CO_2/CH_4 selectivity of CA to decrease in mixed gas environments (Suleman et al., 2016). For example, the CO_2/CH_4 selectivity decreased from 35 to 31 as CO_2 partial pressure increased from roughly 4.1 to 12.7 bar in a 30% CO_2 mixture (Donohue et al., 1989). This decrease of selectivity reduces methane recovery in natural gas separations, but it implies an increase of CO_2 permeability, which reduces the membrane area required for removing CO_2 (Maroto-Valer, 2010). These changes, which vary with feed gas concentration, mean that the separation performance of CA depends on feed composition and feed pressure (Lee et al., 1988).

3.1.2 Polycarbonates

Polycarbonates (PCs) are polyesters of carbonic acid, specially derived from phosgene or diphenyl carbonate (Sanders et al., 2013). PCs are tough and glassy thermoplastic polymers of particular interest for gas separation. Specifically, bisphenol-A polycarbonate, which is the product of reaction between bisphenol-A and phosgene, has been widely studied for gas separation (Muruganandam et al., 1987; Sanders and Overman, 1991; Puri, 2011; Hamrahi and Kargari, 2017). Shafie et al. (2017) concluded that mixed matrix membranes might present better performances when compared with pure PC membranes in CO_2/CH_4 separation. However, although the combination of PC and tetrabromo bisphenol A polycarbonate (TB-Bis-PC) has proved low CH_4 loss, the percentage of CO_2 obtained in the residue gas is higher than 2%, for a single-stage membrane arrangement. Fig. 2.2 presents the polymer structures related to PCs (Koros and Fleming, 1993).

3.1.3 Polyethylene Oxide

Recently, poly(ethylene oxide) (PEO) membranes have garnered interest as their performance for CO_2 removal can be controlled by the solubility of the diverse gases in the membranes. Pure PEO has demonstrated simplicity in membrane fabrication and a high affinity toward CO_2 (Liu et al., 2013). In addition, this polymembrane exhibits low permeability owing to its crystallinity and has a poor film-forming ability (Lin and Freeman, 2004). Examples of commercially available PEO membranes are Pebax and Arkema (Pebax-1657) (Zhao et al., 2017). Pebax copolymers are composed by two well-distinguished phases, the amorphous PEO phase and the crystalline PA phase. Gas permeability through the PEO is higher than that of its selectivity, whereas in the PA phase the selectivity is predominant (Estahbanati et al., 2017). To obtain free-standing
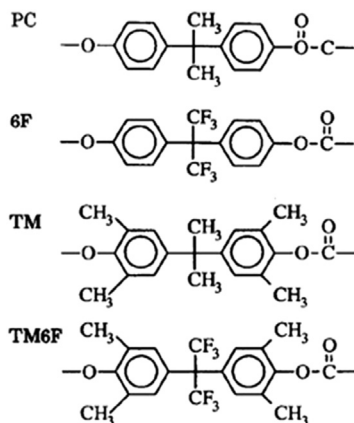
Figure 2.2
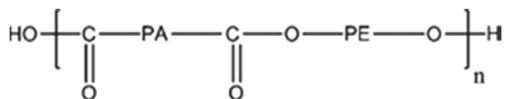Polymer structure related to polycarbonates (Koros and Fleming, 1993).

Figure 2.3
Chemical structures of Pebaxs (Vaughn and Koros, 2014).

membranes, amorphous short PEO has been applied as segments in copolymers. As a result, Charmette et al. (2004) introduce a number of polymeric structures such as cellulose nitrate, polyurethanes, polyimides, PAs, and polymethacrylates. Fig. 2.3 shows the chemical structures of Pebaxs.

With the aim of improving CO_2 separation performance, recent contributions have introduced polymer membranes containing PEO, poly(ethylene glycol) (PEG), or other groups bearing polar ether segments that can interact positively with acid gases (Favvas et al., 2017). PEO-containing polyurethanes were also objects of study for acid gas separation (Teo et al., 1996, 1998).

3.1.4 Polyimides

Aromatic polyimides (PIs) are attractive polymers for membrane gas separation. Sanders et al. (2013) and Guzmán-Lucero et al. (2015) attributed to the high permeability, high intrinsic selectivity, chemical stability, and applicability of PI in a broad range of temperatures. All polyimide membranes have a very good CH_4 recovery from the CH_4/CO_2 mixture, 6F-ODA and 6F-TADPO, and achieve a CO_2 concentration $<1\%$, thus the CO_2 purity is over 96 mol% in most of the cases.

Matrimid is an already in use PI material for gas separation. Chemically, it is a combination of the polymers 3,30-4,40-benzophenone tetracarboxylic dianhydride (BTDA) and diaminophenylindane (DAPI) (Bateman and Gordon, 1974; Falcigno et al., 1989; Farr et al., 2000). Matrimid PI membranes need a second stage to achieve a CO_2 concentration of less than 2 mol% and a high purity CO_2 in the permeate.

In pure Matrimid, a slight decrease in CO_2 permeability is observed when increasing the inlet gas pressure. More precisely, the plasticization of Matrimid starts at 10 bar. For most glassy polymers, the phenomenon tends to be the same: the CO_2 permeability is inversely proportional to feed gas pressure. For instance, Matrimid 5218 is a prominent aromatic PI, derived from $3,3',4,4'$-benzophenone tetracarboxylic dianhydride and DAPI, a gas separation membrane of polymeric material with thermal and mechanical properties adequate for the CO_2 industrial separation (Loloei et al., 2015). For the pure Matrimid, Li et al. (2015) report a pure gas permeability of 8.84 ± 0.40 for the CO_2 and 0.26 ± 0.01 for CH_4. In addition, authors purpose new formulation for mixed matrix membranes (MMMs) by incorporating carbon nanotubes (CNTs) and graphene oxide (GO) into the pure Matrimid, increasing the performance of CO_2 permeability 331% in one of the cases. Similar to Li et al. (2015), Amooghin et al. (2015) assess the performance of the pure Matrimid in respect to the embedded of aminosilane grafting on microsized nanoporous sodium zeolite Y particles for the mixture CO_2/CH_4. Their results show that CO_2 permeability increases from 8.34 Barrer for Matrimid to 9.70 Barrer (about 16%) and the related CO_2/CH_4 selectivity increases considerably from 36.3 to 57.1 (about 57%). The chemical structure of Matrimid PI is represented in Fig. 2.4.

Also Upilex (Type R) and Kapton, developed by UBE and DuPont manufactures, respectively, are significant examples of PI materials for gas separation. The first derives from the polymerization of biphenyl tetracarboxylic dianhydride and 4,40-oxydianiline, whereas the second derives from pyromellitic dianhydride and $4,4'$-oxydiphenylamine (Sasaki et al., 1981; Thomas and Visakh, 2011).

Additionally, polyethersulfone (PES) and polyimides blends were reported for separation of natural gas and N_2/O_2 (Kapantaidakis et al., 2003; Yates et al., 2011). Sanders et al. (2013)
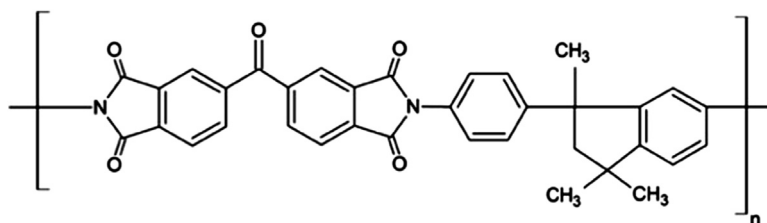

Figure 2.4
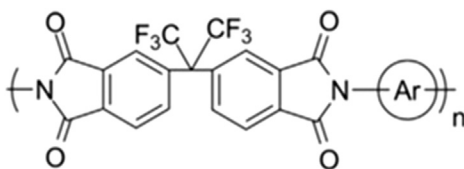Chemical structure of the repeating unit of Matrimid (Castro-Muñoz et al., 2018).

Figure 2.5
Structure of hexafluoroisopropylidene diphthalic anhydride—based aromatic polyimides
(Sanders et al., 2013).

define the composition of this blend as a 90 wt% PI, 3,30-4,40-diphenylsulfone tetracarboxylic dianhydride, and 3,30-5,50-tetramethyl-4,40-methylene dianiline and a 10% of PES.

PIs made from the carbon substitution of the hexafluoro group have also been objects of research; they are significantly more selective, toward the CO_2/CH_4 mixture, than other glassy polymers with comparable permeabilities. The hexafluoro group in the dianhydride moieties (hexafluoroisopropylidene diphthalic anhydride [6FDA]) produces clear, flexible, and rigid support materials, soluble in a broad range of boiling point solvents (Al-Masri et al., 1999), suitable for CO_2/CH_4 separation.

6FDA-based polymers are known as the first generation of polyimides (Bernardo et al., 2009; Xiao et al., 2009). Trend membranes of PI polymers are synthesized from 6FDA and diaminofluorene (DAF), isorpopylidenedianiline (IPDA), and 2,3,5,6-tetramethyl-1,4-diaminobenzene durenediamine (TMPD) (Wang et al., 2007; García et al., 2011a). Fig. 2.5 shows the general structure of 6FDA-based PIs (Ar = aromatic moieties in the diamine).

3.1.5 6FDA-IPDA

The polymer made from the condensation of 6FDA has been identified as a polyamide material with high selectivity for CO_2/CH_4. White et al. (1995) report a solubility ratio of CO_2/CH_4 for the combined 6FDA/IPDA of 5.4, 3.8, and 3.5, to 2.0, 6.8 and 10.0 atm, respectively. In addition, they present ratio permeability factors for 6FDA/IPDA dense films (at 10 atm and 35°C), P_{CO_2/CH_4}, S_{CO_2/CH_4}, and P_{CO_2/CH_4} of 49.2, 3.5, and 14.1, respectively.

This type of membranes showed higher permeability values, 15—55 Barrer for CO_2 (35°C and 3.5 bar), and moderate selectivity, 17—53 for CO_2/CH_4 (35°C and 3.5 bar), than common CA and PC membranes (Sen and Banerjee, 2010).

6F-IPDA, 6FPC, and 6F-6FDA demonstrate to sweeten the gas, molar composition of CO_2 in the residue below 2%, but methane losses are important. In this case, a two-stage membrane system is also necessary to recover a higher percentage of CH_4. Fig. 2.6 shows the chemical structure of polyimides 6F-IPDA, 6FPC, and 6F-6FDA.
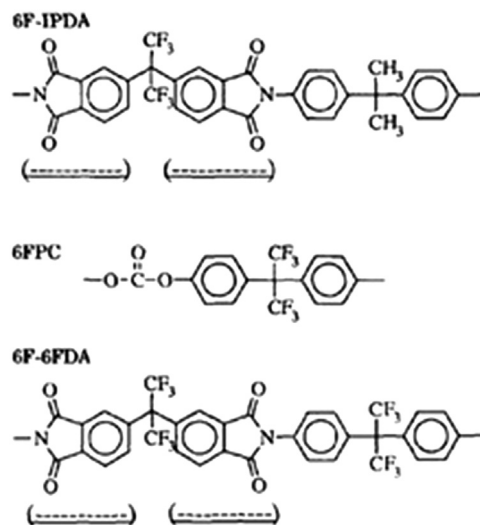
Figure 2.6
Structure of polyimides 6F-IPDA, 6FPC, and 6F-6FDA (Koros and Fleming, 1993).

3.1.6 Polysulfones

Repeated diphenylene sulfone units (eAreSO2eAr'e) characterize the structure of PS polymers. PS represents chemically and thermally stable blend membranes and is durable and thermoplastic (Guo and McGrath, 2012). Because of the particular molecular structure, PS also provides mechanical strength, tough support, compaction resistance, dimensional stability, molecular immobility, and thermal resistance. These properties allowed the use of PS materials for industrial and commercial membranes. Also because of the low levels of plasticization, they proved good performances for the separation of CO_2 at high pressures (McGrail, 1996; Junaidi et al., 2014).

Vitrex PES, Ultrason E, Udel, Ultrason S, Radel R, and Radel A are extended examples of common PS, commercialized for gas separation. Guo and McGrath (2012) state that PI is a significant marketable material for industrial scale application because of the mechanical properties; operating range; resistance; easy production; and versatility respect to number of stages, process disposition, and configuration. Fig. 2.7 shows the chemical structures of several PS.

3.1.7 Poly(phenylene Oxides)

Hay (1967) patented the poly(phenylene oxide) (PPO), poly(2,6-dimethyl-1,4-phenylene oxide), for gas separation. General Electric and AKZO (van Dort, 1968) were in charge of their commercialization. PPO shows excellent mechanical properties and thermal and chemical stabilities (Aycock, 1974; Robeson et al., 1978). However, researching trends on
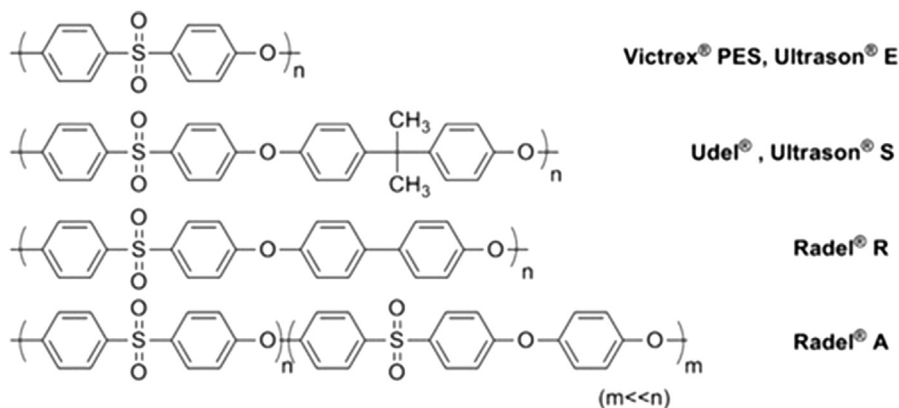
Figure 2.7
Chemical structures of several polysulfones (Sanders et al., 2013).
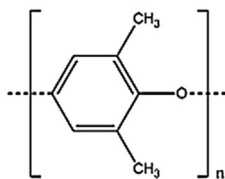

Figure 2.8
Basic chemical structure of poly(phenylene oxide) (Zhang et al., 2017).

PPO has studied the chemical modification of this polymer's family with a range of functional groups. Fig. 2.8 represents the chemical structure of the PPO (Zampini and Malon, 1985; Chern et al., 1987, 1990; Percec and Li, 1988; Story and Koros, 1991, 1992; Ghosal and Chern, 1992; Hamad et al., 2002; Sridhar et al., 2006).

PPO has been modified to improve gas transport properties, selectivity, and permeability, toward the gas of interest, under different conditions. In most of the cases, results show a strong dependence on the characteristics of the chemical alteration, such as the type of the molecular substitution, and the position of the replaced structure, either on the ring or on the methyl groups. Promising tests to improve such material have been proposed; however, more economical and controllable intensification procedures are continuously under study (Story and Koros, 1991; Hamad et al., 2002; Sridhar et al., 2006).

3.1.8 Aramids

Aromatic polyamides (APs), aramids, are high-performance materials with high levels of thermal and chemical stabilities and mechanical resistance. Basically, their molecular structure is composed of an aromatic structure together with amide leakages, which increase their rigidity, which make them useful in technologies for gas separation, such as CO_2/CH_4 (García et al., 2011b). Chemical structures for the family of APs are shown in Fig. 2.9.
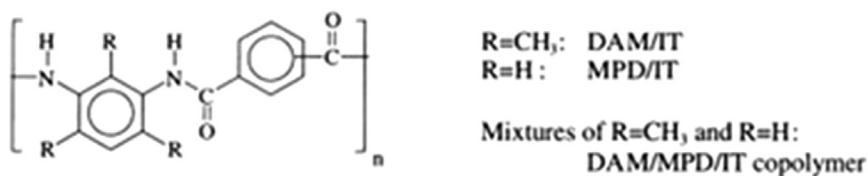
Figure 2.9
Structures of the family of polyaramides (Ekiner and Vassilatos, 2001).

The production of aramids involves the step polymerization (or the polycondensation reaction) of aromatic diamines with aromatic diacid chlorides. Examples of aramids include poly(p-phenylene terephthalamide) (Kevlar) and poly(m-phenylene isophthalamide) (Nomex) (Ekiner and Vassilatos, 2001), these last extensively used for advanced applications in a wide range of industries (García et al., 2011b).

3.2 Developing Membrane Materials

Research related to membrane science and manufacturing has focused attention to the development of new materials, improvement of existing mixed matrixes, and new combinations of the already in use family materials.

For instance, Park et al. (2007) reported a new group of polymeric membranes for CO_2/CH_4 separation, which are the thermally rearranged (TR) polymers. These materials have increased the CO_2 permeability and the CO_2/CH_4 selectivity; in addition, they have shown considerable resistance to plasticization and high chemical stability. In recent years, TR polymer membranes proved to have growing gas permeability, particularly in the separation of CO_2 from postcombustion flue gas and, also, in the process of natural gas sweetening, where CO_2 is taken from a gaseous hydrocarbon mixture (Kim and Lee, 2012).

The use of polymerized room temperature ionic liquids (poly(RTIL)s) has attracted the attention of active researchers to create ionic liquid membranes. Poly(RTIL) can be used as a complementary material for porous materials, as result for the CO_2/CH_4 separation a selectivity of 11 has been reported (Gin and Noble, 2011; Sanders et al., 2013).

Finally, Budd et al. (2005) introduced a novel concept of nonnetwork polymers of intrinsic microporosity (PIMs). This hybrid material is able to reproduce the structure of the zeolites. PIMs are of special interest in the industry of gas separation because of their high permeability and their solid and contorted chain structure. Nevertheless, the effect of contaminants on mixed gas permeation properties is controversial, and thus efforts to enhance their performance are still being studied (Wang et al., 2017).

4. Process Design Configurations

When the use of membranes is applied to separate the mixture CO_2/CH_4, the permeate stream is low concentrated in the hydrocarbon and high concentrated in the acid gas. For applications where a high-purity CO_2 stream is required, this permeate represents a great potential to be exploited, increasing economic benefits. For instance, high-purity CO_2 streams at high pressures are injected as enhanced oil recovery (EOR), a double-purpose technology: increase the crude oil production while capturing geologically thousands of tonnes of this greenhouse gas (Gallo and Erdmann, 2017). For natural gas conditioning, the molar fraction of CO_2 in the residue product must be lower than 2%, to meet most of the pipeline specifications (Behroozsarand and Zamaniyan, 2011). Flow sheet configurations with two or three stages are usually used to reach the conditions for the natural gas to be transported, the proper configuration must minimize the total annual cost.

Qi and Henson (2000) carry out a study on the optimal design of the configuration for the acid gas separation, using mixed integer nonlinear programming (MINLP) design strategy. According to them, the membrane system design for gas separation considers the selection of minimum cost permeators and recycle compressors that separate the inlet gas stream, of known conditions, into two products of a certain composition. The process design problem involves the determination of the optimal system configuration, as well as defines the process unit sizes and operating conditions. They perform the study of the configurations shown in Fig. 2.10.

The problem is solved considering the same operating conditions, with a membrane that has a CO_2/CH_4 selectivity equal to 20 and CO_2 molar percentage of the sweet gas lower than 2%. In addition, the associated costs to each configuration and the operative cost considering the compression power were taken into account.

4.1 Process Variable Analysis

For the sake of simplicity, we present the main aspects that describe the impact of important variables on the performance of a CO_2 separation plant. For instance, the total area of the membrane increases with the increment of the CO_2 in the inlet gas stream. However, Lock et al. (2015b) prove the existence of a limit point where the declination of the membrane surface declines with the increment of the acid gas to be separated.

Additionally, increments on the CO_2 in the inlet gas to be treated make the total compression work to rise. This general conclusion would lead the process designer to choose either the increment or the power of the compressor but with the corresponding increment of the operating expenses.
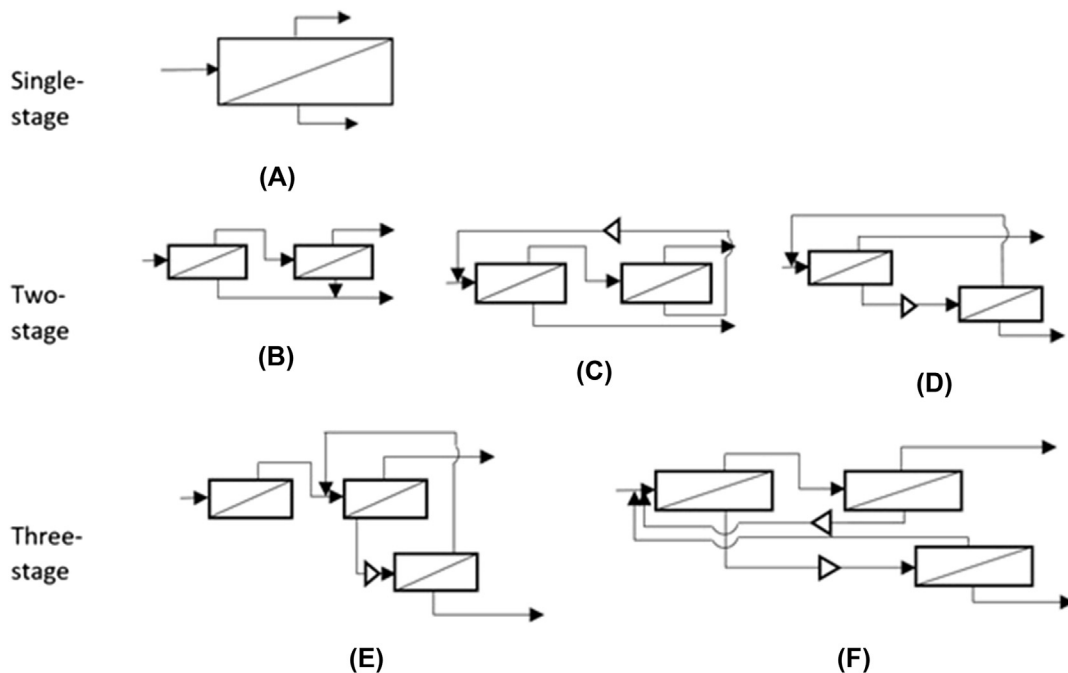
Figure 2.10
Different configurations for the CH_4/CO_2 separation mixture: (A) single-stage; (B–D) two-stage; (E and F) three-stage.

As it can be noticed, the increment of selectivity of the membrane is crucial when purposing new materials. With the increment of the selectivity, the membrane area could remain the same and the compressor power increases minimally, even though having the same permeate composition. This characteristic could also improve the hydrocarbon recovery.

Depending on the feed composition, the operating conditions, and the type of membrane material, the increase of the CO_2/CH_4 selectivity can cause the compressor power to decrease. This sensitivity could be explained knowing that the reduction of the compressor demand implies a decreasing flow rate of the permeate to be recycled.

Feed pressure is a decisive variable in membrane system design. Authors have reported considerable variations on hydrocarbon recovery, total membrane surface, and compressor capacity for single-, two-, and three-stage membrane processes for the separation (Palomeque-Santiago et al., 2016). When considering the type of system that best fits the system capacity, the compressor ratio and power are the main variables affecting both the annual operating cost and the total plant investment.

5. Conclusion and Future Trends

The selection of membranes for the separation of acid gases must consider the conditions of the gas to treat, the products specification, and the permeability and selectivity of the material to be employed. The challenge of material developers is to obtain better performances regarding the transport properties, pressure resistance, stability, hydrocarbon recovery, and energetic and economic viability. Eventually, all of these enhancements might be carried out with the support of modeling and simulation tools. Finally, the increasing world awareness toward the capture of CO_2 will also promote new insights and will contribute to the improvement of existing membrane materials.

List of Acronyms and Abbreviations

6FDA	(Hexafluoroisopropylidene) diphthalic anhydride
AKZO	Algemene Koninklijke Zout Organon, merger of AKU and KZO
APs	Aromatic polyamides
BTDA	Benzophenonetetracarboxylic dianhydride
CAs	Cellulose acetates
CNT	Carbon nanotube
DAF	Diaminofluorene
DAPI	Diaminophenylindane
EOR	Enhanced oil recovery
IPDA	Isorpopylidenedianiline
MINLP	Mixed integer nonlinear programming
NATCO	National Tank Company
ODA	Oxydianiline
PAES	Poly(aryl ether sulfone)
PC	Polycarbonates
PEO	Poly(ethylene oxide)
PES	Polyethersulfone
PI	Aromatic polyimides
PIM	Polymers of intrinsic microporosity
PPOs	Poly(phenylene oxides)
PS	Polysulfone
RTIL	Room temperature ionic liquids
TADPO	Tetraaminodiphenyl ether
TMPD	Tetramethyl-diaminobenzene durenediamine
TR	Thermally rearranged
UBE	City of Japan
UOP	Universal Oil Products

List of Symbols

α	Selectivity
$\overline{A}$	Area
D	Diffusivity

E	Activation energy
F	Molar flow
N	Number of units
P	Permeability
P_A	Partial pressure of A
R	Universal gas constant
S	Solubility
T	Absolute temperature

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