

APPLICATION OF MEMBRANE IN GAS SEPARATION PROCESSES: ITS SUITABILITY AND MECHANISMS

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Received April 30, 2010, Accepted June 15, 2010

Abstract

In separation of gases, membranes offer the greatest potential. In interaction with a membrane, a high degree of permeability coupled with a large selectivity of a specific gaseous species ensures superior performances in the gas processing industry. Economically, the advantage of membrane separation technology is immense. The separation of natural gas by thin barriers termed as membranes is a dynamic and rapidly growing field, and it has been proven to be technically and economically superior to other emerging technologies. This superiority is due to certain advantages which membrane technology benefits from, including low capital investment, low weight, and space requirement and high process flexibility. In the past ten years, the membrane gas separation technology has advanced greatly and can now be regarded as a competitive industrial gas separation method. The benefits of "Membrane Technology" also include higher recovery of the desired gaseous effluent that can be reused for multiple purposes. This article discusses various experimental and analytical models related to current membrane technologies.

Keywords: Gas Separation; Polymeric Membrane; Inorganic Membrane; Mixed Matrix Membrane; Mechanism.

1. Introduction

Solution gases are gaseous hydrocarbons that exist under increased pressure in oil reservoirs. They are "in solution" with the liquid hydrocarbon phase in equilibrium to a separate vapor phase. These gases are mostly conserved, but approximately 8% of the solution gases are considered uneconomical to be stored and are routinely flared. Gas flaring in crude oil production is a malpractice as substantial volumes of carbon dioxide are emitted during the process. Flaring has impacts on global warming, ozone depletion, and acidification. It also leads to resource depletion due to the combustion of the materials used in the flare construction. Flaring gases to the atmosphere can cause harmful side effects to the environment ^[1]. They include:

(1) Carbon dioxide and methane emission. The main gaseous emissions responsible for "Global Warming" are carbon dioxide and methane. Methane gas possesses 35 times global warming potential than carbon dioxide. The only feasible method for reduction of the volume of the wasted gases without constraining oil production is to improve electrical power generation efficiency and minimize flaring by exploiting gas conservation opportunities.

(2) Hydrogen sulfide/sulfur dioxide emissions, Sulfur dioxide does not contribute to the greenhouse effect. The main environmental concern with sulfur dioxide (SO₂) is that it is a source of acid rain. Hydrogen sulfide (H₂S) is a toxic and corrosive gas, which is rapidly oxidized to sulfur dioxide in the atmosphere.

(3) NO_x emissions. In the presence of volatile organic compounds, the nitrogen oxides can lead to the formation of ozone and other powerful respiratory irritants. Ozone, in addition to its impact on human health, can significantly reduce plant growth. Nitrogen oxides also contribute to the formation of acid rain and may contribute to global warming.

Flaring is prevented only when the impurities in the gases are removed before transportation to the pipeline. The components to be removed from the flare gas include hydrogen sulfide, sulfur dioxide, carbon dioxide, and nitrogen. In the last few years, many efforts have been made to develop effective means to separate the impurities in

natural gases. Ongoing research is being conducted to develop new membrane materials and improve pressure swing adsorption techniques to separate the gaseous mixtures. Membrane separation processes has become one of the emerging technologies, which have undergone a rapid growth during the past few decades. A membrane is defined as a selective barrier between two fluid phases [2-4]. Gas separation became a major industrial application of membrane technology only during the past 15 years, but the study of gas separation actually began long before that period [5]. Gas separation processes require a membrane with high permeability and selectivity that is the asymmetric membrane [6]. Asymmetric membranes that are suitable for gas separation should have thin and dense skin layers supported by thick porous sub-layers [7-9]. Membrane structures can be classified according to the cross section microstructure as shown in Figure 1. There are six major membrane processes, which are widely used, in industrial application. They are microfiltration, ultrafiltration, reverse osmosis, electrodialysis, gas separation and pervaporation. Gas separation is known as a developing process and most gas separation membranes are of the solution-diffusion mechanism type. The key membrane performance variables are selectivity, permeability and durability. For solution-diffusion membranes, permeability is defined as the product of the solubility and diffusivity. Traditionally, there has been a tradeoff between selectivity and permeability; high selectivity membranes tend to exhibit less permeability and vice versa.

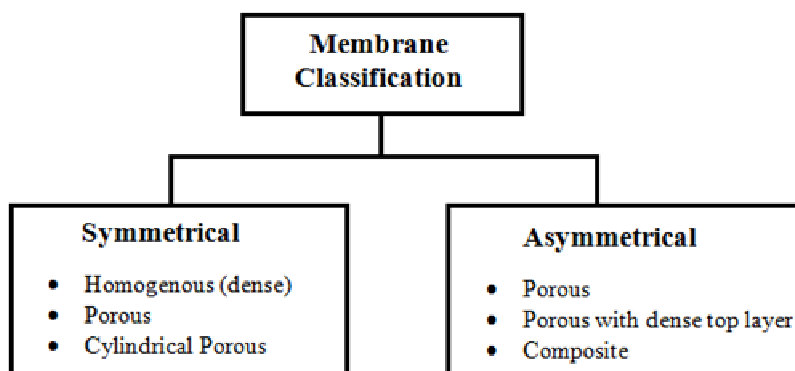


Fig 1. Membrane classifications.

2. Membrane Technology for Gas Separation

Membrane can be defined as a selective barrier between two phases, the "selective" being inherent to a membrane or a membrane process [10]. The membrane gas separation technology is over 15 years old and is proving to be one of the most significant unit operations. The technology inherits certain advantages over other methods that include compactness and light weight, low labor intensity, modular design permitting easy expansion or operation at partial capacity, low maintenance, low energy requirements, low cost, and environmental friendly.

The progress in membrane science and technology was accelerated during the 1980s by the development and refinement of synthetic polymeric membranes. Membrane gas separation emerged as a commercial process on a large scale during the 1980s. During this period, significant progress was made in virtually every aspect of membrane technology, including improvements in membrane formation process, chemical and physical structures, configurations and applications. Chemical structures coupled with subtle physical properties of the membrane material influence the permeability and selectivity of a gas. The responses of a polymeric material to permeation are strongly influenced by the polarity and steric characteristics of the polymer and permeate. The size and shape of bulky groups in both the polymer main chains and side chains determine certain fundamental properties like packing, density, and rigidity. These, in turn, influence the accessibility. An absence of such groups tends to increase the structural regularity, which favors increased density. The effect of lateral substituents on the backbone of aliphatic polyamides has a strong bearing on the gas separation properties. Bulky hydrocarbon groups force parallel chain segments further apart, thereby increasing free volume and diminishing hydrogen bonding and rigidity, and increasing the permeability [11].

In the concept of membrane science, a synthetic membrane behaves as a thin barrier between two phases through which differential transport can occur. Driving forces that facilitate this transport are pressure, concentration, and electrical potential across the

medium [12]. The transport itself is a non-equilibrium process and the separation of chemical species results from differences in transport rates through the membrane.

Gas membranes are now widely used in variety of application, as shown in Table 1.

Table 1. Gas separation membrane application

Common gas separation	Application
O ₂ /N ₂	Oxygen enrichment, inert gas generation
H ₂ /Hydrocarbons	Refinery hydrogen recovery
H ₂ /N ₂	Ammonia Purge gas
H ₂ /CO	Syngas ratio adjustment
CO ₂ / Hydrocarbons	Acid gas treatment, landfill gas upgrading
H ₂ O/ Hydrocarbons	Natural gas dehydration
H ₂ S/ Hydrocarbons	Sour gas treating
He/ Hydrocarbons	Helium separation
He/N ₂	Helium recovery
Hydrocarbons/Air	Hydrocarbons recovery, pollution control
H ₂ O/Air	Air dehumidification

3. Polymeric (Organic) Membranes

Polymeric membranes have been developed for variety of industrial applications including gas separation. For gas separation, the selectivity and permeability of the membrane material determines the efficiency of the gas separation process. Based on flux density and selectivity, a membrane can be classified broadly into two classes: (a) porous and (b) nonporous. A porous membrane is a rigid, highly voided structure with randomly distributed inter-connected pores. The separation of materials by porous membrane is mainly a function of the permeate character and membrane properties, such as the molecular size of the membrane polymer, pore-size, and pore-size distribution. A porous membrane is very similar in its structure and function to the conventional filter. In general, only those molecules that differ considerably in size can be separated effectively by microporous membranes. Porous membranes for gas separation do exhibit very high levels of flux but inherit low selectivity values. Microporous membranes are characterized by the average pore diameter d , the membrane porosity, and tortuosity of the membrane.

There are several ways to prepare porous polymeric membranes, such as solution casting, sintering stretching, track etching, and phase separation. The final morphology of the membrane obtained will vary greatly, depending on the properties of the materials and the process conditions utilized. Nonporous or dense membranes have high selectivity properties but the rates of transport of gases through the medium are usually low. An important property of a nonporous dense membrane is that even permeants of similar sizes may be separated if their solubility in the membrane differs significantly. A dense membrane can be prepared by melt extrusion, where a melt is envisioned as a solution in which the polymer is both solute and solvent. In the solution-casting method, dense membranes are cast from polymer solutions prepared by dissolution of a polymer in a solvent vehicle to form a sol. This is followed by complete evaporation of the solvent after casting. Polymer membranes have gained popularity in isolating carbon dioxide from other gases [13]. These membranes are elastomers formed from crosslinked copolymers of high molecular weights. They are prepared as thin films by extrusion or casting. They demonstrate unique permeability properties for carbon dioxide together with high selectivity towards H₂, O₂, N₂, and CH₄. These elastomers are very thin membranes (5–10 μm) and can be easily prepared by extrusion, solvent casting, or impregnation. The membranes are hydrophilic and the introduction of hydrophobic monomers provides regulation of water absorption. They are thermally stable up to 250°C and are biodegradable and nontoxic and their applications include food packaging, natural or industrial gas treatment of confined atmospheres (airplane cabins, air conditioned rooms), decarbonation of gases used in fuel cells, biomass treatment, medical uses.

4. Different Polymeric (Organic) Membranes

The effects of flexible hetero-atoms and cyclic structures, with nonlinear orientation in the polymer backbone lead to a decreased structural regularity, on permeation behavior [14].

The structural regularity favors close packing of molecules which improve density and rigidity in both crystalline and amorphous phases. All these changes have some bearing on the effects of permeability and selectivity. Polyether sulfones (PES) have a relatively more regular structure and inherits a higher bulk density (1.37 g/cm^3), and an elevated glass transition T_g , (220°C). It also acquires a lower free volume when compared to polysulfone (PSF) which contains an aliphatic isopropylidene group contributing to less regularity, lower bulk density (1.23 g/cm^3), and lower T_g (190°C).

Isotropic Polyethersulfone (PESF) dense film have been proven to exhibit better selectivity for the commercially important gas pairs (CO_2/CH_4 , He/CH_4 , H_2/N_2 , O_2/N_2) compared to bisphenol-A polysulphone and cellulose acetate [15].

Wang et al. (1990) reports that similar to PSF, PESF possesses properties of high mechanical and thermal stabilities [16]. Moreover, it is generally easy to prepare the dried asymmetric membranes by the immersion phase inversion method using water as a coagulant. This polymer has only a moderate permeability. In order to use this polymer to prepare commercially attractive gas separation membranes, fabrication of ultrathin-skinned asymmetric hollow fiber membranes will be needed so as to increase permeation flux. Only a few studies on the preparation of PESF asymmetric hollow fiber membranes for gas separation have been reported in the literature. The PESF hollow fibers prepared at various spinning conditions exhibit reduced gas permeation behavior. The observed CO_2 pressure-normalized flux is less than 12GPU at 24°C . In the later 1980s, PESF hollow fiber membranes with good permeance and selectivity were prepared from spinning solution containing 1:1 molar mixtures of propionic acid: NMP and high polymer concentration (more than 35 wt%) [17]. The oxygen pressure-normalized flux was prepared to be 13.1GPU with O_2/N_2 selectivity of 5.1 at 50°C . Fritzsche et al. (1990) examined the skin layer structure of membrane [18].

Wang et al. (2000) made studies on the preparation and characterization of PESF hollow fiber membranes spun from moderate polymer concentration (25–30 wt %) and solvent systems containing various alcohols as non-solvent additives (NSA) [19]. This NSA plays a dominant role in determining membrane structure and gas separation properties.

They prepared the PESF hollow fiber membranes with the best combination of gas permeability and selectivity by using ethanol as an additive in the various studies. Their studies also demonstrated that effective NSAs possess high affinities and diffusivities with the coagulant. It is also known that a certain amount of water can be added to the polymer solution before phase separation occurs. In addition, water and N, N-substituted amides (solvents) can form a complex through multiple hydrogen bonding. Therefore, the influence of water as a NSA on the structure and gas permeation properties of PESF hollow fiber membranes is of immediate interest. The authors demonstrated that silicon-coated PESF asymmetric hollow fiber membranes with high pressure-normalized fluxes and ideal selectivities for gas pairs of He and N_2 were fabricated from NMP/ H_2O solvent system with mass ratio of 8.4:1. In the presence of water as an additive, the viscosity of spinning solutions increased dramatically due to the formation of NMP: H_2O hydrogen-bonding complex. The observed pressure-normalized fluxes and ideal selectivities of the PESF membranes were higher than those of the hollow fiber membranes fabricated from NMP/alcohol and NMP/ propionic acid systems reported in literature.

Saha and Chakma (1995) suggested attaching a liquid membrane in a microporous polymeric membrane [20]. They immobilized mixtures of various amines such as monoethanolamine (MEA), diethanolamine (DEA), amino-methyl-propanol (AMP), and polyethylene glycol (PEG) in an icroporous polypropylene film and placed it in a permeator. They tested the mechanism for the separation of carbon dioxide from some hydrocarbon gases and obtained separation factors as high as 145.

Fuertes (2001) reported that when the size of micropores in the carbon membranes is in the 3–5 Å range, gas molecules with effective diameters smaller than 4Å display significant differences in gas diffusivity, and mixtures of these gases can be effectively separated according to a molecular sieving mechanism [21]. In this case, the gas transport rate through the membrane depends on the effective size of the gas molecules instead of the adsorption effects. Membranes with these characteristics are identified as Molecular Sieve Carbon Membrane (MSCM). Polymers (polyvinylidene chloride, polyimides, polyfurfuryl alcohol, phenolic regins) that are used to prepare MSCM are initially cross-linked or become cross-linked during pyrolysis. This prevents the formation of large graphite-like crystals during carbonization and leads to the formation of disordered structures (non-graphiting carbons) with a very narrow porosity formed by

micropores in the 3–5 Å range (molecular sieve carbons). In this sense, an MSCM can be described as a thin molecular sieve carbon film. If the micropores in the carbon membrane are enlarged from 3 to 5 Å, gas permeation through the membranes with enlarged micropores is governed by the adsorption strength instead of molecular size. This kind of membrane would be effective for separation of non-adsorbable or weakly adsorbable gases from adsorbable gases.

5. Inorganic Membranes

The efficiency of polymeric membranes decreases with time due to fouling, compaction, chemical degradation, and thermal instability. Because of this limited thermal stability and susceptibility to abrasion and chemical attack, polymeric membranes have found application in separation processes where hot reactive gases are encountered. This has resulted in a shift of interest toward inorganic membranes.

Inorganic membranes are increasingly being explored to separate gas mixtures. Besides having appreciable thermal and chemical stability, inorganic membranes have much higher gas fluxes as compared to polymeric membranes. There are basically two types of inorganic membranes - dense (nonporous) and porous membranes. Examples of commercial porous inorganic membranes are ceramic membranes, such as alumina, silica, titanium, and glass and porous metals, such as stainless steel and silver. These membranes are characterized by high permeabilities and low selectivities. Dense inorganic membranes are very specific in their separation behaviors, for example Pd-metal based membranes are hydrogen specific and metal oxide membranes are oxygen specific. Palladium and its alloys have been studied extensively as potential membrane materials. Air products and Chemical Inc. developed the selective surface flow (SSF) membranes. It consists of a thin layer (2–3 mm) of nanoporous carbon supported on a macroporous alumina tube [22]. The effective pore diameter of the carbon matrix is 5–7 Å [23]. The membrane separates the components of a gas mixture by selective adsorption–surface diffusion–desorption mechanism [24]. The larger polar molecules of a feedgas mixture at the high-pressure zone of the membrane are selectively adsorbed on the carbon pore walls followed by their selective diffusion along the pore walls to the low pressure side of the membrane where they desorb into the low pressure gas phase. Thus, a gas stream enriched in the smaller and less polar components of the feed-gas stream mixture is produced as a low pressure effluent gas from the Selective Surface Flow (SSF) membrane system. However, a gas stream enriched in the larger and more polar components of the feed-gas mixture is produced as a low-pressure effluent gas. The performance of the SSF membrane for the separation of hydrocarbons from H₂, CO₂ from H₂, CO₂ and CH₄ from H₂, H₂S from H₂, and H₂S from CH₄ are found in the literature [25]. Gas separation by means of microporous carbon membrane is based on interaction differences existing between components of a gas mixture with respect to the carbon membrane.

Materials that are thermally stable at temperatures above 400°C include ceramic membranes that are used to separate hydrogen from gasified coal [26]. With ceramic materials, very high separation factors have been achieved based on the ratios of individual gas permeances. This work focuses on the development of alumina membranes having nanopores that can separate gases based on the molecular size. A layer of alumina having a mean pore diameter of about 7nm is deposited on a stainless steel tube. Methods have been developed to reduce the pore diameter to values in the range between 0.5 and 3.0 nm. The membranes having the smallest estimated mean pore diameters have shown very high separation factors for helium and hydrogen with other gases. These separation factors are determined from pure gas separations in these pore diameter ranges. For pure molecular flow, separation factors should increase with decreasing pore size, but in many cases, the separation factor decreases. This decrease occurs because of adsorption and surface flow of the heavier molecule. The separation factor continues to decrease until the pore size becomes small enough that the entrance into the membrane is restricted for the larger molecule. At this point, the separation factor increases rapidly as pore size is decreased. It is observed that the separation factors are directly proportional to temperature. This is because with increase of temperature, an unexpected large increase of permeance of hydrogen and helium is observed.

6. Mixed Matrix Membranes (MMMs)

An upper limit for the performance of polymeric membranes in gas separation was predicted by Robeson [27] in early 1990. The performance of various membrane materials available for the separation of O_2/N_2 is depicted in Figure 2. The figure presents the permeability of the fast gas O_2 on the abscissa on a logarithmic scale and the O_2/N_2 selectivity on the ordinate, again on a logarithmic scale. For the polymeric materials, a rather general trade-off exists between permeability and selectivity, with an "upper-bound" evident in Figure 2.

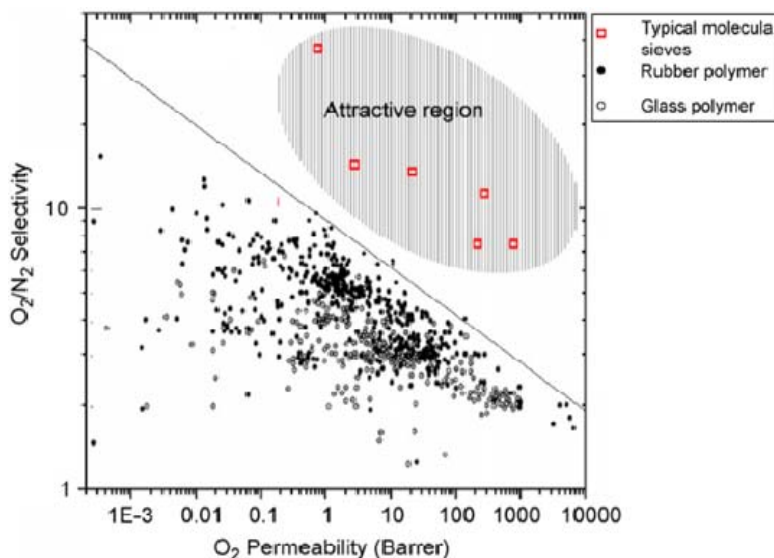


Fig 2. Relationship between the O_2/N_2 selectivity and O_2 permeability for polymeric membranes and inorganic membranes [27] (the dots indicates the performance of polymeric materials).

When materials with separation properties near this limit were modified based on the traditional structure – property relation, the resultant polymers have permeability and selectivity tracking along this line instead of exceeding it. On the other hand, as may be seen in Figure 2, the inorganic materials have properties lying far beyond the upper-bound limit for the organic polymers [28–32]. Though tremendous improvements had been achieved in tailoring polymer structure to enhance separation properties during the last two decades, further progress exceeding the trade-off line seems to present a severe challenge in the near future. Similarly, the immediate application of inorganic membranes is still seriously hindered by the lack of technology to form continuous and defect-free membranes, the extremely high cost for the membrane production, and handling issues (e.g., inherent brittleness) [33,34]. In view of this situation, a new approach is needed to provide an alternate and cost-effective membrane with separation properties well above the upper-bound limit between permeability and selectivity.

The latest membrane morphology emerging with the potential for future applications involves MMM, consisting of organic polymer and inorganic particle phases, as shown schematically in Figure 3. The bulk phase (phase A) is typically a polymer; the dispersed phase (phase B) represents the inorganic particles, which may be zeolite, carbon molecular sieves, or nano-size particles. MMMs have the potential to achieve higher selectivity, permeability, or both relative to the existing polymeric membranes, resulting from the addition of the inorganic particles with their inherent superior separation characteristics. At the same time, the fragility inherent in the inorganic membranes may be avoided by using a flexible polymer as the continuous matrix.

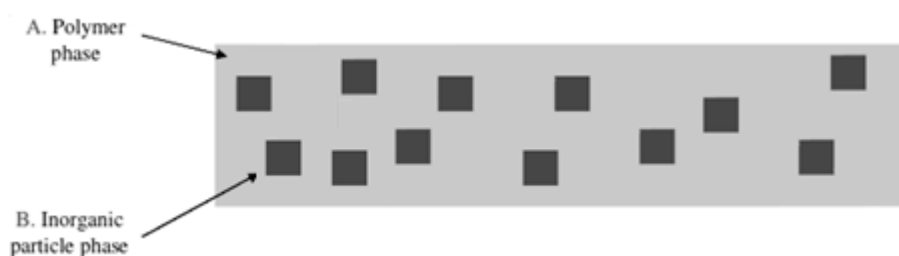


Figure 3. Schematic of a mixed matrix membrane (MMM)

The investigation of MMMs for gas separation was first reported in 1970s with the discovery of a delayed diffusion time lag effect for CO₂ and CH₄ when adding 5A zeolite into rubbery polymer polydimethyl siloxane (PDMS) [35]. In this work, Paul and Kemp found that the addition of 5A into the polymer matrix caused very large increases in the diffusion time lag but had only minor effects on the steady-state permeation. Researchers at UOP were the first to report that that mixed matrix systems of polymer/adsorbent might yield superior separation performance to that of pure polymeric system [36]. They observed an enhanced O₂/N₂ selectivity from 3.0 to 4.3 when increasing silicalite content in the polymer cellulose acetate (CA) matrix. The concept of MMM has been also demonstrate at UOP LLC in the mid-1980s using CA/silicalite MMMs for CO₂/H₂ separation [37]. In the demonstration, a feed mixture of 50/50 (mol%) CO₂/H₂ with a differential pressure of 50 psi was used. The calculated separation factor for CO₂/H₂ was found to be 5.15±2.2. In contrast, a CO₂/H₂ separation factor of 0.77±0.06 was found for CA membrane. This indicates that silicalite in the membrane phase has reversed the selectivity from H₂ to CO₂.

Many studies have demonstrated that the remarkable separation properties of MMMs accord with this design, exhibiting performance well beyond the intrinsic properties of the polymer matrix. The most prominent work involved the application 4A zeolite [38-40]. Figure 4 shows the O₂/N₂ transport properties of these membranes in comparison with the Robeson, 1991 O₂/N₂ upperbound limit curve, indicating that MMMs are promising candidates for the next generation of membranes.

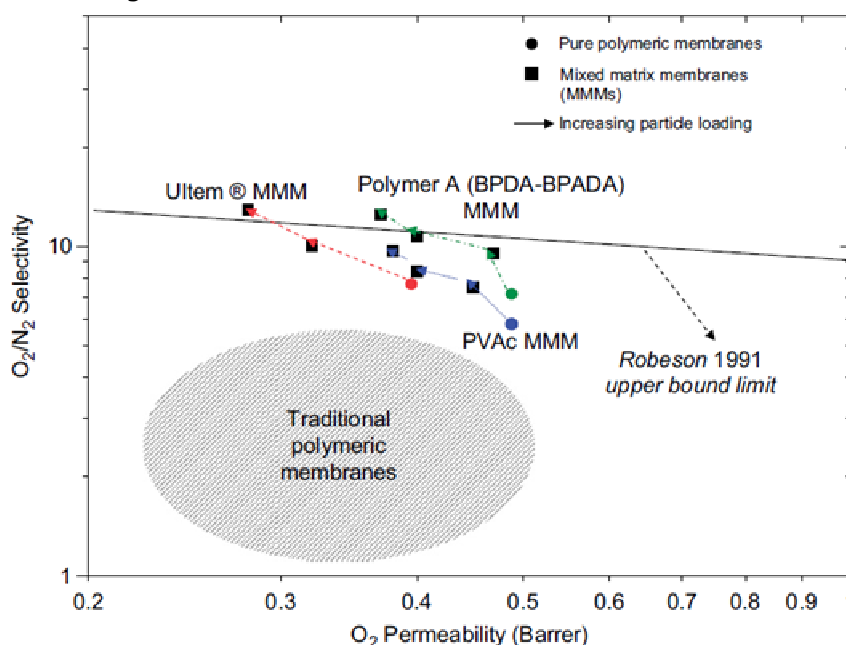


Fig 4. Mixed matrix membranes performance compared to the Robeson, 1991 upper-bound limit [54, 56].

7. Mechanisms for Gas Separation

Various mechanisms for gas transport across membranes have been proposed depending on the properties of both the permeant and the membrane. These include Knudsen diffusion, the molecular sieve effect and a solution diffusion mechanism. Most of these models, however, have been found to be applicable only to a limited number of gas/ material systems. Different mechanisms (a–d) may be involved in the transport of gases across a porous membrane gives a schematic representation of the mechanisms for the permeation of gases through porous as well as dense membranes (Baker, 1995).

Mechanism (a): The permeation of gas through porous membrane consists of Knudsen diffusion and Poiseuille flow. The properties of Knudsen to Poiseuille flow are governed by the ratios of the pore radius (r) to the mean free path (λ) of the gas molecules. The mean free path is given by

$$\lambda = \frac{3\eta(\pi RT)^{0.5}}{2P(2M)} \quad (1)$$

Where η is the viscosity of the gas, R the universal gas constant, T the temperature, M the molecular weight, and P the pressure.

If $\lambda/r \ll 1$ viscous or Poiseuille flow predominates then the gas flux through the pore is described by the following expression:

$$G_{vis} = \frac{r^2(P_1 - P_2)}{16LuRT} \quad (2)$$

where, r is the pore radius, P_1 the partial pressure of the gas on the feed side, P_2 the partial pressure of the permeate side, L the pore length, u the gas viscosity, Gives the viscous flow, and R the universal gas constant.

In Knudsen flow, λ/r is considerably less than unity, and therefore, there are more collisions with the pore walls than with other gas molecules. At every collision with the pore walls, the gas molecules are momentarily absorbed and then reflected in a random direction. As there is less number of collisions among molecules than pore walls, each molecule will move independent of others. Hence, the separation is achieved because different gaseous species are moving at different velocities.

The gas flux in such a case is described by the expression:

$$G_{mol} = \frac{8r(P_1 - P_2)}{3L(2\pi MRT)^{0.5}} \quad (3)$$

where G_{mol} is the molecular flow of the gas, r the pore radius, P_1 the partial pressure of the gas on the feedside, P_2 the partial pressure of the gas on the permeate side, L the pore length, M the molecular weight, R the gas constant, and T absolute temperature.

For Knudsen flow, the selectivity ratio or the separation factor for binary gas mixtures can be estimated from the square root of the ratio of the molecular weights. Knudsen separation can be achieved with membranes having pore sizes smaller than 50 nm. Based on Knudsen flow, separation factors for several gas pairs have been calculated and they represent ideal separation factors.

Mechanism (b): In order to function as a molecular sieve, membranes must have pore diameters that are in between those of the gas molecules to be separated. Separation factors greater than 10 should be achievable as the pores become smaller than approximately 0.5 nm. If the membrane has pore sizes between the diameter of the smaller and the larger gas molecules, then only the smaller molecule can permeate and a very high separation would be achieved. In practical situations, there will be a distribution of pore size in the membranes, and thus the gas permeability is actually influenced by a combination of transport mechanisms. From a practical standpoint, as the pore size decreases, the membrane porosity is expected to decrease, resulting in a lower gas flow through the membrane. Therefore, the pore size and porosity must be balanced to produce an efficient membrane.

Mechanism (c): Gas separation can also be affected by partial condensation for some component of a gas mixture in the pores, with the exclusion of others, and the subsequent transport of the condensed molecules across the pore.

Mechanism (d): Selective adsorption of the more strongly adsorbed components of a gas mixture onto the pore surface followed by the surface diffusion of the adsorbed molecule across the pore can also facilitate the separation of gases. A proper concentration gradient for the diffusing species must be imposed across the porous membrane to provide the driving force for transport by all four mechanisms.

The selectivity of separation achieved by Knudsen mechanism (a) is generally very low. Mechanism (b) exhibits high selectivity and high permeability for the smaller components of a gas mixture. Mechanism (c) requires the pore size of the membrane to be in the mesoporous size range (diameter > 30 Å) so that condensation of the component of a gas mixture can take place. A very high selectivity of separation of the condensable component can be achieved by this mechanism. The condensation partial pressure of the component at the system pressure, the pore size and the geometry of the membrane limit the extent of removal of that component from the gas mixture. Mechanism (d) provides the most flexible and attractive choice for the practical separation of gaseous mixtures. The reason is that the separation selectivity is determined by the preferential adsorption of certain components of the gas mixture on the surface of the membrane pores as well as by the selective diffusion of the absorbed molecules.

In meso- and microporous media, as in the case of inorganic membranes, if the relative pressure is increased, the adsorbed and capillary condensed materials permeate together. The porous media behave, as a semipermeable membrane through which the adsorbed permeate will flow freely while the weakly adsorbed component will be blocked. Thus, both the pore size and the physical-chemical nature of the pore surface play key roles in determining the separation efficiency of these membranes. Consequently, appropriate molecular engineering of their surface chemistries can alter the properties of the membranes.

The transport of gases through a dense polymeric membrane is usually described by the solution-diffusion mechanism. The important feature of dense membranes that are used in separation applications is the ability to control the permeation of different species. In the solution diffusion mechanism, the permeants dissolve in the membrane material and then diffuse through the membrane down a concentration gradient.

A separation is achieved between the different permeants because of differences in the amount of material diffusing through the membranes.

The solution-diffusion mechanism is considered to consist of three steps: (1) the absorption or adsorption at the upstream boundary, (2) activated diffusion (solubility) through the membrane, and (3) desorption or evaporation on the other side. These solution-diffusion mechanisms are driven by a difference in thermodynamic activity at the upstream and downstream faces of the membrane as well as the interacting forces between the molecules of the membrane material and permeate molecules. The activity difference causes a concentration difference that leads to diffusion in the direction of decreasing activity. As in microporous membranes, differences in permeability of dense membranes also result from differences in the physical-chemical interactions of the gas species within the polymer. The solution-diffusion model assumes that the pressure within a membrane is uniform and the chemical gradient across the membrane is expressed only as a concentration gradient.

The schematic diagram shown in Fig. 5 illustrates mass transfer across a regular membrane and a liquid membrane. In a regular membrane, the solute A passes through the membrane under pure diffusion mechanism, leaving the other gas behind. In the liquid membrane, the enhanced effect of having the liquid solvent, B, can be seen by the additional flux of species AB. This system, with the additional flux, is known as facilitated transport. Without the effects of the liquid, mass transfer would be reduced to that of the regular diffusion membrane system whereby the total flux only consists of the flux of species A including pressure, concentration, and electrical potential across the membranes.

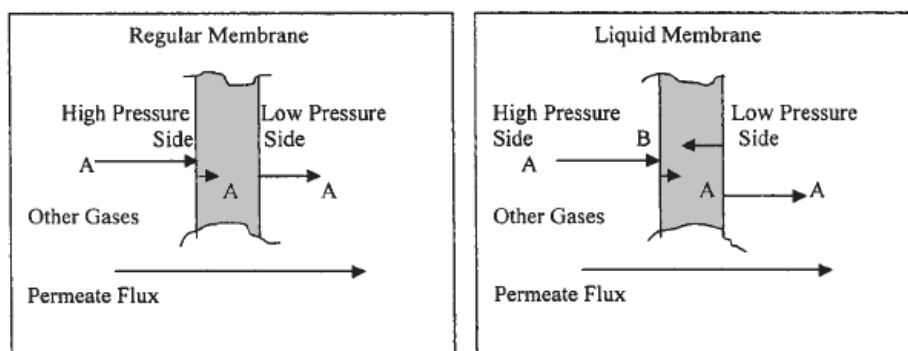


Figure 5. Facilitated transport in a membrane.

Pressure difference across the membrane can facilitate RO (reverse osmosis), ultra-filtration, micro-filtration, gas separation, and pervaporation. Temperature difference across the membrane can facilitate distillation, whereas concentration difference can be used for dialysis and extraction. Electro-dialysis can also be performed with the help of membranes when an electric potential across the membrane is maintained. Differential transport occurs when the membrane restricts the transport of different species in some specific way. The transport is a non-equilibrium process and the separation of chemical species results from differences in transport rates through the membranes. Membrane separation is considered a non-equilibrium process because it is based on the selective permeation rate of the feed components. If a membrane system is allowed to move

toward equilibrium, permeation would continue until the pressure and concentration of gases on both sides are equal (Koros et al., 1996) [12].

The two main parameters defining the performance of a membrane are separation factor and permeance. In a binary system consisting of gases "a" and "b" with gas "a" as the fast permeating gas, separation factor is defined as the concentration ratio of "a" to "b" in the permeate, and X_a and X_b are the concentration of the gases "a" and "b" in the feed.

$$\alpha_{a/b} = \frac{(Y_a / Y_b)}{(X_a / X_b)} \quad (4)$$

Where α is the separation factor, Y_a and Y_b are the concentration of the gases "a" and "b" in the permeate and X_a and X_b are the concentrations of gases "a" and "b" in the feed.

Permeance is defined as the volume of the feed passing through a unit area of membrane at unit time and under unit pressure gradient and is expressed as:

$$P = \frac{V}{At\Delta p} \quad (5)$$

Where P is permeance, V is volume of gas, A is area, t is time, and Δp is pressure difference (Tabe-Mahammadi, 1999) [41].

8. Conclusion

Membrane systems are highly applicable for separation of gases from a mixture. Continuing enhancements in technology developments of membrane systems is a natural choice for the future. Gas separation modules operate on the basis of selective permeation. The technology takes advantage of the fact that gases dissolve and diffuse into polymeric materials. If a pressure differential is set up on opposing sides of a film (membrane), transport across the film (permeation) will occur. The product of a solubility coefficient and a diffusion coefficient determines the rate of permeation. High performance zeolite materials as a filler for mixed-matrix membranes can further take gas separation membranes into uncharted areas. Membrane separations employing mixed-matrix materials have the potential to meet demanding gas separation in a world with shrinking energy resources and increasing environmental concerns. Any membrane will separate gases to some extent. However, proper selection of the polymeric material comprising the membrane is extremely important as it determines the ultimate performance of the gas separation module. Membrane productivity for a given base material is determined by three factors: partial pressure difference across the membrane, membrane thickness, and membrane surface area. The partial pressure difference is typically determined by the specifics of the application. The membrane manufacturer can address the other two factors determining membrane productivity.

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