

8

Gas Separation

8.1 Introduction and History

Gas separation only became a major industrial application of membrane technology in the past 30 years, but the study of gas permeation through membranes has a long history. Systematic studies began with Thomas Graham who, over a period of 20 years, measured the permeation rates of all the gases then known, through every diaphragm available to him [1]. This was no small task because his experiments had to start with synthesis of the gas. Graham gave the first description of the solution-diffusion model, and his work on porous membranes led to Graham's law of diffusion. Through the remainder of the nineteenth and the early twentieth centuries, the ability of gases to permeate membranes selectively had no industrial or commercial use. The concept of the perfectly selective membrane was, however, used as a theoretical tool to develop physical and chemical theories, such as Maxwell's kinetic theory of gases.

From 1943 to 1945, Graham's law of diffusion was exploited for the first time, to separate $U^{235}F_6$ from $U^{238}F_6$ as part of the Manhattan project. Finely microporous metal membranes were used. The separation plant, constructed in Knoxville, Tennessee, represented the first large-scale use of gas separation membranes and remained the world's largest membrane separation plant for the next 40 years. However, this application was unique and so secret that it had essentially no impact on the long-term development of gas separation.

In the 1940s to 1950s, Barrer [2], van Amerongen [3], Stern [4], Meares [5], and others laid the foundation of the modern theories of gas permeation. The solution-diffusion model of gas permeation developed then is still the accepted model for gas transport through membranes. However, despite the availability of interesting polymer materials, membrane fabrication technology was not sufficiently advanced, at that time, to make useful membrane systems from these polymers.

The development of high-flux anisotropic membranes and large-surface-area membrane modules for reverse osmosis applications in the late 1960s and early 1970s provided

the basis for modern membrane gas separation technology. The first company to establish a commercial presence was Monsanto, which launched its hydrogen-separating Prism[®] membrane in 1980 [6]. Monsanto had the advantage of being a large chemical company with ample opportunities to test pilot- and demonstration-scale systems in its own plants before launching the product. The economics were compelling, especially for the separation of hydrogen from ammonia-plant purge-gas streams. Within a few years, Prism systems were installed in many such plants [7].

Monsanto's success encouraged other companies to advance their own membrane technologies. By the mid-1980s, Cynara, Separex, and Grace Membrane Systems were producing membrane plants to remove carbon dioxide from methane in natural gas. This application has grown significantly over the years. At about the same time, Dow launched Generon[®], the first commercial membrane system for nitrogen separation from air. Initially, membrane-produced nitrogen was cost-competitive in only a few niche areas, but the development by Dow, Ube, and Du Pont/Air Liquide of materials with improved selectivities has since made membrane separation much more competitive. This application of membranes has expanded very rapidly and has now captured more than half of the nitrogen production market. More than 30 000 small- to medium-sized nitrogen production systems have been installed worldwide. Gas separation membranes are also being used for a wide variety of other, smaller applications ranging from dehydration of air and natural gas to organic vapor removal from air and nitrogen streams. Application of the technology is expanding rapidly, and further growth is likely to continue for the foreseeable future. Figure 8.1 provides a summary of the development of gas separation technology.

8.2 Theoretical Background

Porous or dense membranes can be used as selective gas separation barriers; Figure 8.2 illustrates the mechanism of gas permeation. Three types of porous membranes, differing in pore size, are shown. If the pores are relatively large – from 0.1 to 10 μm – gases permeate the membrane by convective flow, and no separation occurs. If the pores are smaller than 0.1 μm , then the pore diameter is smaller than the mean free path of the gas molecules. Diffusion through such pores is governed by Knudsen diffusion, and the transport rate of a gas is inversely proportional to the square root of its molecular weight. This relationship is called Graham's law of diffusion. Finally, if the membrane pores are extremely small, of the order 5–20 \AA , then gases are separated by molecular sieving. Transport through this type of membrane is complex and includes both diffusion in the gas phase and diffusion of adsorbed species on the surface of the pores (surface diffusion). These very-small-pore membranes have not been used on a large scale, but carbon, ceramic, and ultramicroporous glass membranes with extraordinarily high selectivities for similar molecules have been prepared in the laboratory.

Although microporous membranes are topics of research interest, almost all current commercial gas separations are based on the dense polymer membrane also shown in Figure 8.2. Separation through dense polymer films occurs by a solution-diffusion mechanism.

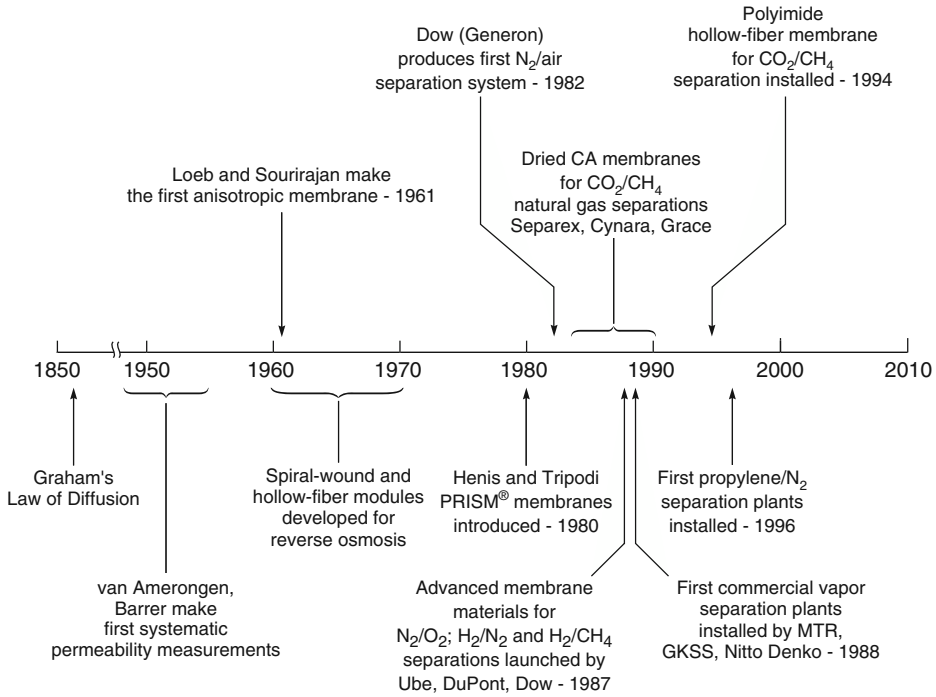


Figure 8.1 Milestones in the development of gas separation

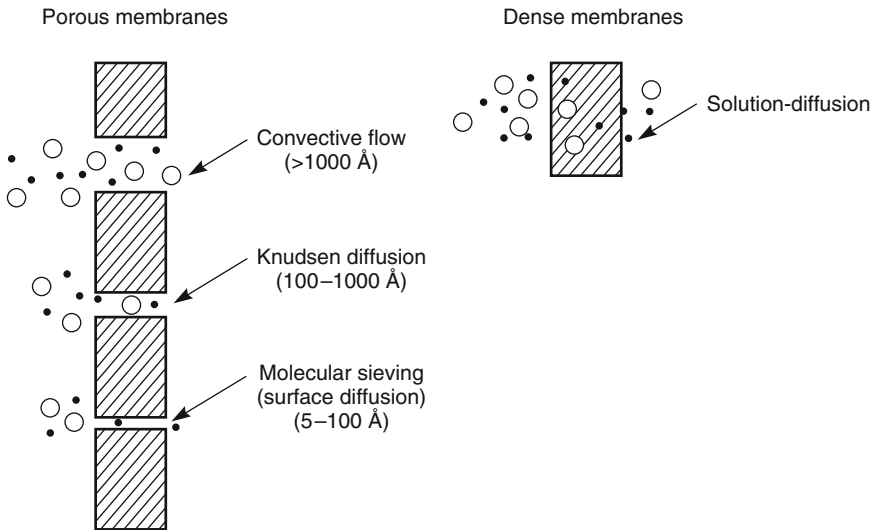


Figure 8.2 Mechanisms for permeation of gases through porous and dense gas separation membranes

In Chapter 2 (Equation 2.59), it was shown that gas transport through dense polymer membranes is governed by the expression

$$J_i = \frac{D_i K_i^G (p_{i_o} - p_{i_\ell})}{\ell} \quad (8.1)$$

where J_i is the flux of component i ($\text{g}/\text{cm}^2 \cdot \text{s}$), p_{i_o} and p_{i_ℓ} are the partial pressures of the component i on either side of the membrane, ℓ is the membrane thickness, D_i is the permeate diffusion coefficient, and K_i^G is the Henry's law sorption coefficient ($\text{g}/\text{cm}^3 \cdot \text{pressure}$). In gas permeation it is much easier to measure the volume flux through the membrane than the mass flux, and so Equation 8.1 is usually recast as

$$j_i = \frac{D_i K_i (p_{i_o} - p_{i_\ell})}{\ell} \quad (8.2)$$

where j_i is the volume (molar) flux expressed as ($\text{cm}^3(\text{STP})$ of component i)/ $\text{cm}^2 \cdot \text{s}$ and K_i is a sorption coefficient with units ($\text{cm}^3(\text{STP})$ of component i)/ cm^3 of polymer·pressure). The product $D_i K_i$ can be written as \mathcal{P}_i , which is called the membrane permeability, and is a measure of the membrane's ability to permeate gas, normalized for pressure driving force, and membrane thickness.¹ A measure of the ability of a membrane to separate two gases, i and j , is the ratio of their permeabilities, α_{ij} , called the membrane selectivity

$$\alpha_{ij} = \frac{\mathcal{P}_i}{\mathcal{P}_j} \quad (8.3)$$

8.2.1 Polymer Membranes

The relationship between polymer structure and membrane permeation was discussed in Chapter 2 and is revisited only briefly here. Permeability can be expressed as the product $D_i K_i$ of two terms. The diffusion coefficient, D_i , reflects the mobility of the individual molecules in the membrane material; the gas sorption coefficient, K_i , reflects the number of molecules dissolved in the membrane material. Thus, Equation 8.3 can also be written as

$$\alpha_{ij} = \left[\frac{D_i}{D_j} \right] \left[\frac{K_i}{K_j} \right] \quad (8.4)$$

The ratio D_i/D_j is the ratio of the diffusion coefficients of the two gases and can be viewed as the mobility selectivity, reflecting the different sizes of the two molecules. The ratio K_i/K_j is the ratio of the sorption coefficients of the two gases and can be

¹ The permeability of gases through membranes is most commonly measured in Barrer, defined as $10^{-10} \text{ cm}^3(\text{STP}) \cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$ and named after R.M. Barrer, a pioneer in gas permeability measurements. The term $j_i/(p_{i_o} - p_{i_\ell})$, best called the permeance or pressure-normalized flux, is often measured in terms of gas permeation units (gpu), where 1 gpu is defined as $10^{-6} \text{ cm}^3(\text{STP}) \cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$. One gpu is therefore one Barrer/ μ . Occasional academic purists insist on writing permeability in terms of $\text{mol} \cdot \text{m}/\text{m}^2 \cdot \text{s} \cdot \text{Pa}$ (1 Barrer = $0.33 \times 10^{-15} \text{ mol} \cdot \text{m}/\text{m}^2 \cdot \text{s} \cdot \text{Pa}$), but fortunately this has not caught on.

viewed as the sorption or solubility selectivity, reflecting the relative solubilities of the two gases.

In all polymers, the *diffusion coefficient* decreases with increasing permeant molecular size, because large molecules interact with more segments of the polymer chain than do small molecules. Hence, the mobility selectivity always favors the passage of small molecules over large ones. However, the magnitude of the mobility selectivity term depends greatly on whether the membrane material is above or below its glass transition temperature (T_g). If the material is below the glass transition temperature, the polymer chains are essentially fixed and segmental motion is limited. The material is then called a glassy polymer and is tough and rigid. Above the glass transition temperature, segments of the polymer chains have sufficient thermal energy to allow limited rotation around the chain backbone. This motion changes the mechanical properties of the polymer dramatically, and it becomes a rubber. The transition is quite sharp and occurs over a temperature change of just a few degrees. As characterized by their diffusion coefficients, the relative mobilities of gases differ significantly in rubbers and glasses, as illustrated in Figure 8.3 [8]. Diffusion coefficients in glassy materials are small and decrease much more rapidly with increasing permeate size than diffusion coefficients in rubbers. This means the mobility selectivity term for rubbery membranes is smaller than the mobility selectivity of glassy membranes. For example, the mobility selectivity for nitrogen over pentane in natural rubber is approximately 10. The mobility selectivity for nitrogen over pentane in poly(vinyl chloride), a rigid, glassy polymer, is more than 100 000.

The *sorption coefficient* of gases and vapors increases with increasing condensability of the permeant. This dependence on condensability means that the sorption coefficient also increases with molecular diameter, because large molecules are normally more condensable than smaller ones. The gas sorption coefficient can, therefore, be plotted against boiling point or molar volume. As shown in Figure 8.4 [9], sorption selectivity favors larger, more condensable molecules, such as hydrocarbon vapors, over permanent gases, such as oxygen and nitrogen. However, the difference between the sorption coefficients of permeants in rubbery and glassy polymers is far less marked than the difference in the diffusion coefficients.

It follows from the discussion above that the balance between the mobility selectivity term and the sorption selectivity term in Equation 8.4 [10] is different for glassy and rubbery polymers. This difference is illustrated by the data in Figure 8.5. In glassy polymers, the mobility term is usually dominant, permeability falls with increasing permeate size, and small molecules permeate preferentially. Therefore, when used to separate organic vapors from nitrogen, glassy membranes preferentially permeate nitrogen. In rubbery polymers, the sorption selectivity term is usually dominant, permeability increases with increasing permeate size, and larger molecules permeate preferentially. Therefore, when used to separate organic vapor from nitrogen, rubbery membranes preferentially permeate the organic vapor. The separation properties of polymer membranes for a number of the most important gas separation applications have been summarized by Robeson [11]. A review of structure/property relations has been given by Stern [12]. Properties of some representative and widely used membrane materials are summarized in Table 8.1.

An important tool to rationalize the properties of different membrane materials is the plot of membrane selectivity versus membrane permeability popularized by Robeson [11, 13]. A Robeson plot for the separation of oxygen and nitrogen is shown in Figure 8.6.

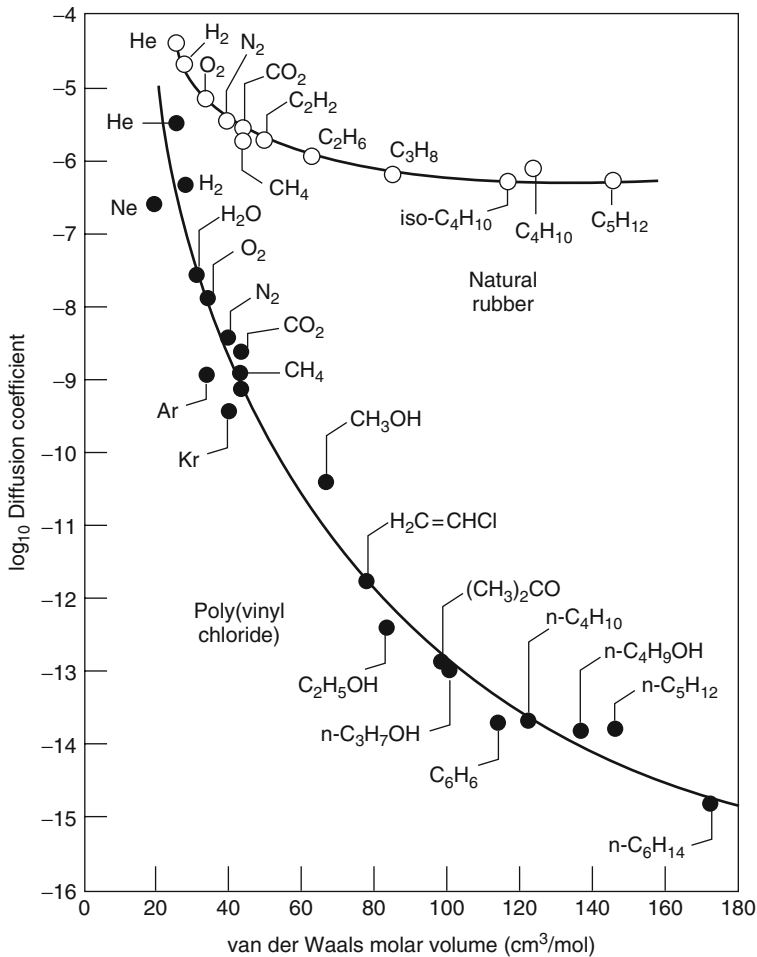


Figure 8.3 Diffusion coefficient as a function of molar volume for a variety of permeants in natural rubber and in poly(vinyl chloride), a glassy polymer. This type of plot was first drawn by Gruen [8], and has been used by many others since

Each point on the figure represents a different membrane material. A wide range of selectivity/permeability combinations are provided by different polymers, but for gas separation applications, only the most permeable polymers at a particular selectivity are of interest. The line linking these polymers is called the upper bound, beyond which no better material is currently known. There is a strong inverse relationship between permeability and selectivity. The most permeable membranes with a selectivity of 6–7 have 1% of the permeability of membranes with a selectivity of 2–3. The relative positions of the upper bound in 1991 and in 1980 show the progress that was made in producing polymers specifically tailored for this separation. Development of better materials is a continuing research topic at the major gas separation companies and in

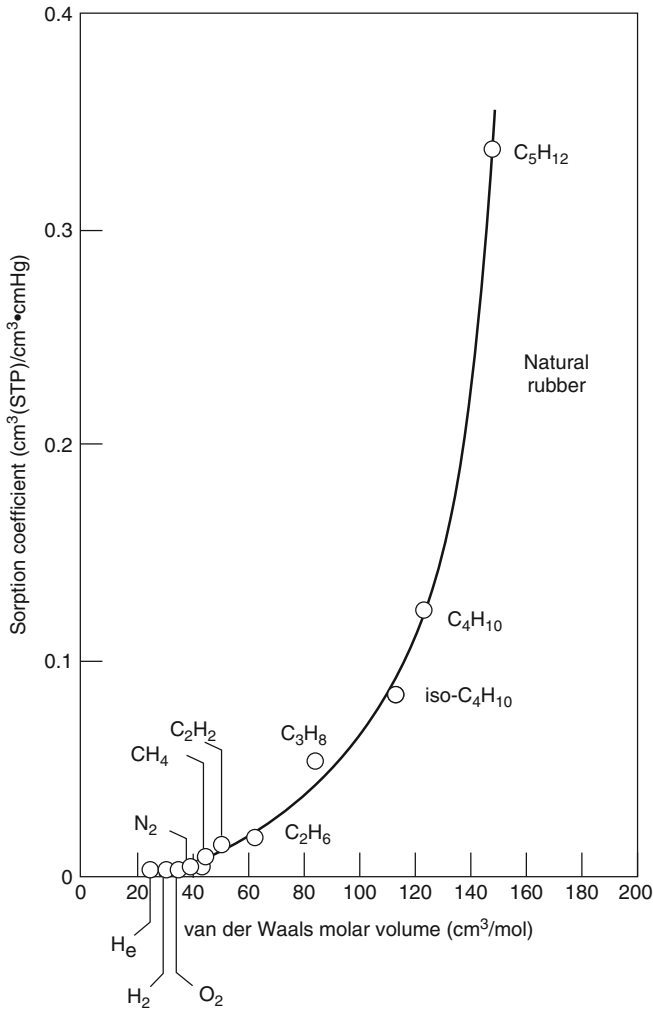


Figure 8.4 Gas sorption coefficient as a function of molar volume for natural rubber membranes. Larger permeants are more condensable and have higher sorption coefficients [9]

some universities, so further but slow movement of the upper bound may be seen in the future.

Robeson plots similar to that shown in Figure 8.6 have been created for a number of other gas pairs. The position of the upper bound lines for a number of gas pairs of commercial interest are shown in Figure 8.7. This type of plot is useful in estimating the permeability and selectivity that can be expected for the best membrane materials.

Figure 8.7 also shows that with some gas pairs it is possible to switch the selectivity of the separation by choice of the membrane material. For example, the separation of nitrogen/methane gas mixtures is of interest in the processing of natural gas [14].

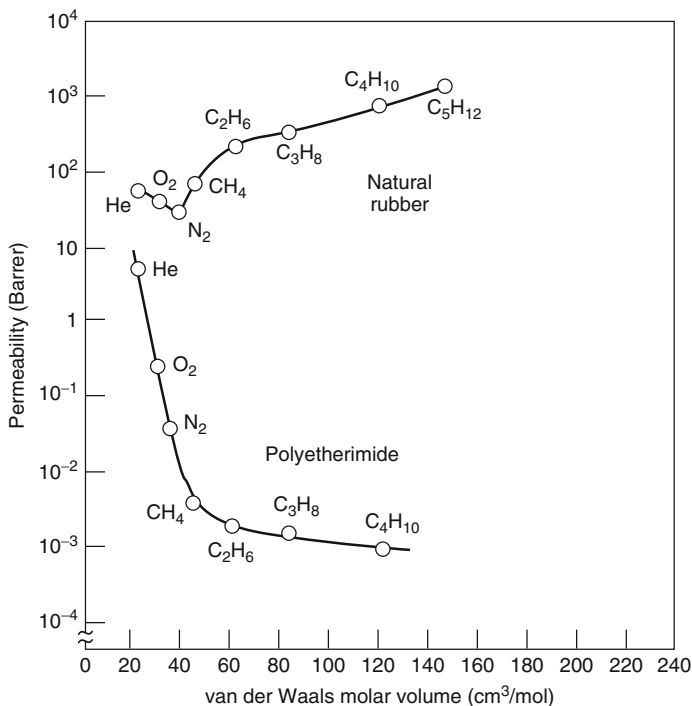


Figure 8.5 Permeability as a function of molar volume for a rubbery and a glassy polymer, illustrating the different balance between sorption and diffusion in these polymer types. The natural rubber membrane is highly permeable; permeability increases rapidly with increasing permeant size because sorption dominates. The glassy polyetherimide membrane is much less permeable; the permeability decreases with increasing permeant size because diffusion dominates [10]. Reprinted from R.D. Behling, K. Ohlrogge, K.-V. Peinemann and E. Kyburz, *The Separation of Hydrocarbons from Waste Vapor Streams*, in *Membrane Separations in Chemical Engineering*, A.E. Fouda, J.D. Hazlett, T. Matsuura and J. Johnson (eds), AIChE Symposium Series Number 272, Vol. 85, p. 68 (1989). Reproduced by permission of the American Institute of Chemical Engineers. Copyright © 1989 AIChE. All rights reserved.

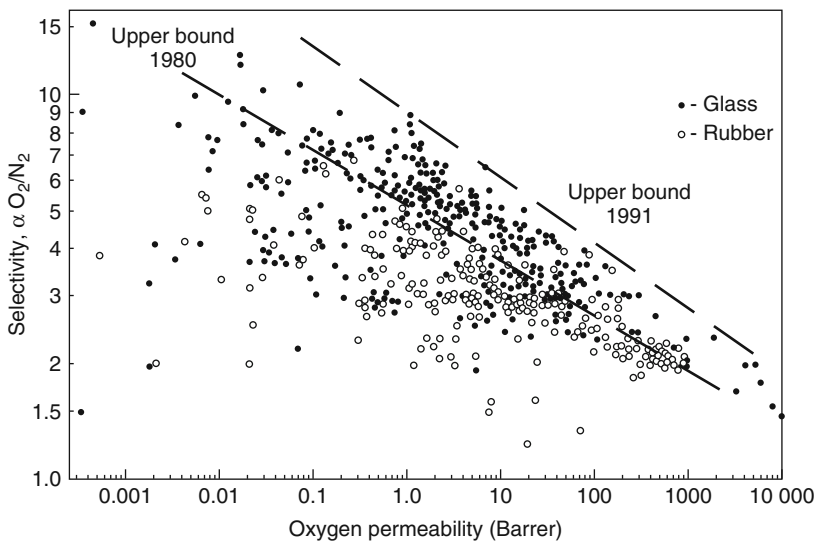
The mobility selectivity term D_{N_2}/D_{CH_4} favors permeation of the small molecule nitrogen (kinetic diameter 3.64 Å) over the larger methane (kinetic diameter 3.80 Å). On the other hand, the sorption selectivity K_{N_2}/K_{CH_4} favors sorption of the more condensable gas methane (boiling point 111 K) over the less condensable gas nitrogen (boiling point 77 K). It follows that the effects of the mobility and sorption selectivity terms in Equation 8.4 are opposed. Glassy polymers generally have low permeability and will preferentially permeate nitrogen ($\alpha_{N_2/CH_4} > 1$) because the diffusion mobility selectivity term is dominant. Rubbery polymers have higher permeabilities and preferentially permeate methane ($\alpha_{N_2/CH_4} < 1$) because the sorption selectivity term is dominant.

The upper bound lines shown in Figure 8.7 can be expressed mathematically as

$$\ln \alpha_{A/B} = \ln \beta_{A/B} - \lambda_{A/B} \ln P_A \quad (8.5)$$

Table 8.1 Pure-gas permeabilities (Barrer ($10^{-10} \text{ cm}^3(\text{STP})\cdot\text{cm}/\text{cm}^2\cdot\text{s}\cdot\text{cmHg}$)) of widely used polymers

Gas	Rubbers		Glasses		
	Silicone rubber at 25°C T_g = -129°C	Natural rubber at 30°C T_g = -73°C	Cellulose acetate at 25°C T_g = 124°C	Polysulfone at 35°C T_g = 186°C	Polyimide (Ube Industries) at 60°C T_g > 250°C
H ₂	550	41	24	14	50
He	300	31	33	13	40
O ₂	500	23	1.6	1.4	3
N ₂	250	9.4	0.33	0.25	0.6
CO ₂	2700	153	10	5.6	13
CH ₄	800	30	0.36	0.25	0.4
C ₂ H ₆	2100	—	0.20	—	0.08
C ₃ H ₈	3400	168	0.13	—	0.015
C ₄ H ₁₀	7500	—	0.10	—	—

**Figure 8.6** Oxygen/nitrogen selectivity as a function of oxygen permeability. This plot by Robeson shows the wide range of selectivity and permeability combinations achieved by current materials. Reprinted with permission from [11]. Copyright (1991) Elsevier.

or

$$\alpha_{A/B} = \beta_{A/B} / P_A^{\lambda_{A/B}} \quad (8.6)$$

where A and B represent the two gases, $\lambda_{A/B}$ is the slope of the line in Figure 8.7, and $\ln \beta_{A/B}$ is the intercept at $\ln P_A = 0$. Freeman [15] has shown that these parameters have physical significance and can be calculated with reasonable accuracy from first

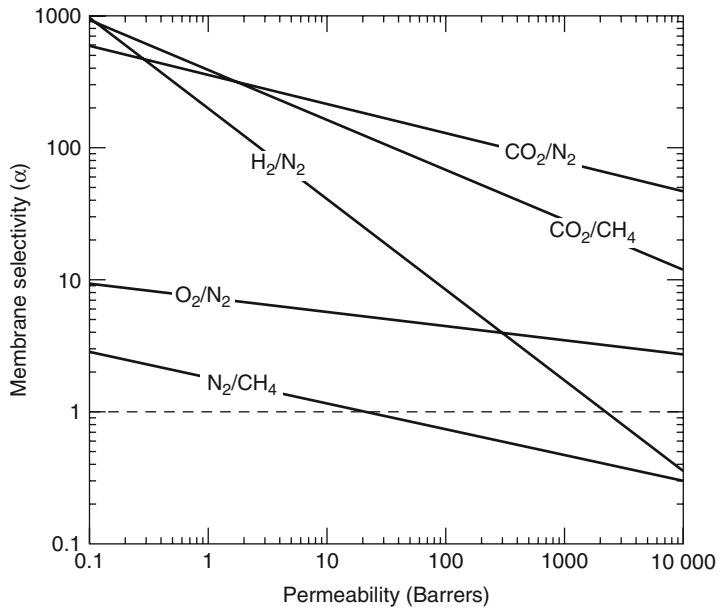


Figure 8.7 Upper bound Robeson selectivity/permeability lines for a number of commercially important gas separations. This figure allows the trade-off between selectivity and permeability to be estimated for the best available membrane materials

principle considerations. The slope $\lambda_{A/B}$ depends only on the size of the gas pair, and $\beta_{A/B}$ depends on the gas condensabilities.

Despite all of the above considerations, applying the permeability and selectivity data shown in Robeson plots to actual gas separation problems must be approached with caution. Permeabilities used to prepare Robeson plots are measured with pure gases; the selectivity obtained from the ratio of pure gas permeabilities gives the ideal membrane selectivity. However, practical gas separation processes are performed with gas mixtures. If the gases in a mixture do not interact with the membrane material, the pure gas selectivity and the mixed gas selectivity will be equal. This is usually the case for mixtures of oxygen and nitrogen, for example. In many other cases, such as the separation of carbon dioxide/methane mixtures, one of the components (carbon dioxide) is sufficiently sorbed by the membrane to affect the permeability of the other component (methane). The selectivity measured with a gas mixture may then be one-half or less of the selectivity calculated from pure gas measurements. Pure gas selectivities are much more commonly reported in the literature than gas mixture data because they are easier to measure. However, neglecting the difference between these two values has led many membrane users to seriously overestimate the ability of a membrane to separate a target gas mixture. Figure 8.8 [16] shows selected data for the separation of methane and carbon dioxide using cellulose acetate membranes. The calculated pure gas selectivity is very good, but in gas mixtures, enough carbon dioxide dissolves in the membrane to increase the methane permeability far above the pure gas methane permeability value. As a result,

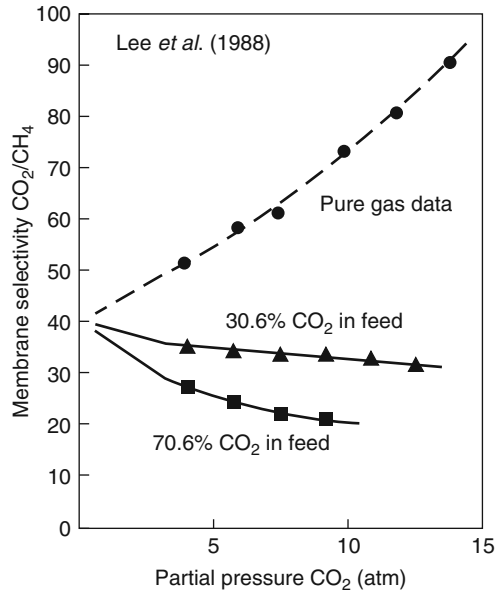


Figure 8.8 The difference between selectivities calculated from pure gas measurements and selectivities measured with gas mixtures can be large. S.Y. Lee, B.S. Minhas and M.D. Donohue, *Effect of Gas Composition and Pressure on Permeation through Cellulose Acetate Membranes*, in *New Membrane Materials and Processes for Separation*, K.K. Sirkar and D.R. Lloyd (eds), AIChE Symposium Series Number 261, Vol. 84, p. 93 (1988). Reproduced with permission of the American Institute of Chemical Engineers. Copyright © 1988 AIChE. All rights reserved.

the selectivities measured with gas mixtures are much lower than those calculated from pure gas data.

Most gas separation processes using polymer membranes require that the selective membrane layer be extremely thin to achieve economical fluxes. Typical membrane thicknesses are less than 0.5 μm and often less than 0.1 μm . Early gas separation membranes [17] were made by modifying cellulose acetate membranes produced for reverse osmosis by the Loeb–Sourirajan phase separation process. These membranes are produced by precipitation in water, and the water must be removed before the membranes can be used to separate gases. However, the capillary forces generated as the liquid evaporates cause collapse of the finely microporous substrate of the cellulose acetate membrane, destroying its usefulness. This problem has been overcome by a solvent-exchange process in which the water is first exchanged for an alcohol, then for hexane. The surface tension forces generated as liquid hexane evaporates are much reduced, when a dry membrane is produced. Membranes produced by this method are still used by Separex and Cynara to separate carbon dioxide from methane in natural gas.

Experience has shown that gas separation membranes are far more sensitive to minor defects in the selective membrane layer than membranes used in reverse osmosis or ultrafiltration. Even a few tiny defects can easily allow an unseparated gas flow equal

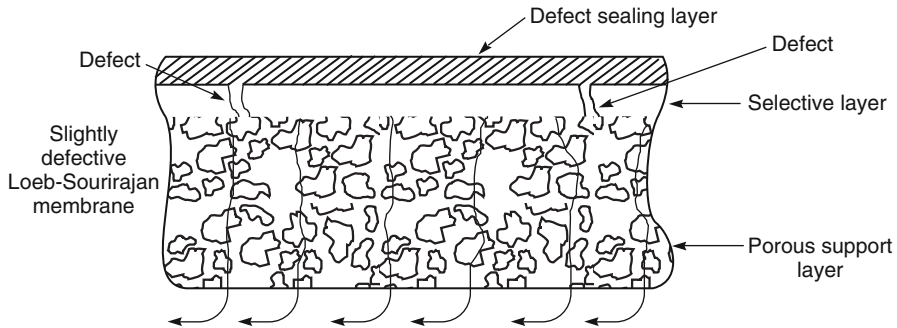


Figure 8.9 The technique devised by Henis and Tripodi [18] to seal defects in their selective polysulfone Loeb–Sourirajan membrane

to 1–2% of the total flux through the membrane. The sensitivity of gas separation membranes to defects posed a serious problem to early developers. Generation of a few defects is very difficult to avoid during membrane preparation and module formation.

In 1978, Henis and Tripodi [6, 18] at Monsanto devised an ingenious solution to the membrane defect problem; their approach is illustrated in Figure 8.9. The Monsanto group made Loeb–Sourirajan-type hollow fiber membranes (principally from polysulfone), then coated the membranes with a thin layer of silicone rubber. Silicone rubber is extremely permeable compared to polysulfone, but has a much lower selectivity; thus, the silicone rubber coating did not significantly change the selectivity or flux through the defect-free portions of the polysulfone membrane. However, the coating plugged membrane defects in the polysulfone membrane and eliminated convective flow through these defects. The silicone rubber layer also protected the membrane during handling. The development of silicone rubber-sealed anisotropic membranes was a critical step in the production of the first successful gas separation membrane for hydrogen/nitrogen separations by Monsanto.

Another type of gas separation membrane is the multilayer composite structure shown in Figure 8.10. The preparation of these membranes is described in Chapter 3. The base material that provides the mechanical strength is a finely microporous support membrane. This support is then coated with a series of thin polymer coatings. A gutter

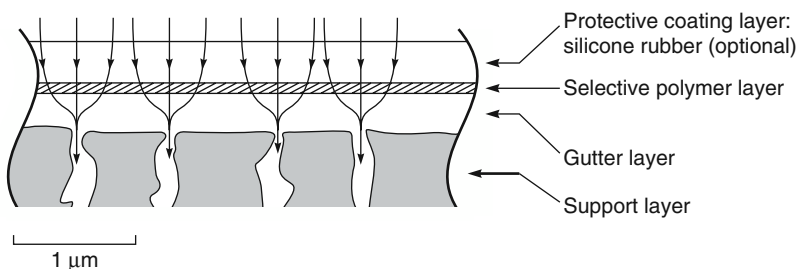


Figure 8.10 Multilayer composite membrane formed by coating thin layers of polymer on a microporous support membrane that provides mechanical strength

layer is often applied first to provide a defect-free, smooth surface onto which the ultrathin selective layer is applied. A final protective layer of silicone rubber or other highly permeable polymer is then applied to seal any defects. It is difficult to make composite membranes with glassy selective layers as thin and high-flux as good-quality Loeb–Sourirajan membranes. However, composite membranes can be made from a much wider range of materials than the Loeb–Sourirajan process allows. It is also possible to make composite membranes that use rubbery soft polymers as the selective layer, while the microporous support that provides mechanical strength is made from a tough, glassy polymer. Rubbery composite membranes of this type can withstand pressure differentials of 100 bar or more.

8.2.2 Metal Membranes

Although almost all industrial gas separation processes use polymeric membranes, interest in metal membranes continues, mostly for the high-temperature membrane reactor applications discussed in Chapter 13 and for the preparation of pure hydrogen for fuel cells. Hydrogen-permeable palladium and palladium alloy membranes are extraordinarily selective, being permeable to hydrogen, but essentially impermeable to all other gases. Membrane permeation rates are extremely high, usually 10–100 times higher than permeation rates measured with polymeric membranes. Hydrogen also permeates a number of other metals including tantalum, niobium, vanadium, nickel, iron, copper, cobalt, and platinum [19]. However, in most cases, metal membranes must be operated at high temperatures ($>300^{\circ}\text{C}$) to obtain useful permeation rates and to prevent embrittlement and cracking of the metal by sorbed hydrogen. Poisoning of the membrane surface by oxidation or sulfur deposition from trace amounts of hydrogen sulfide also occurs. The preparation and properties of these membranes are described in more detail in Chapter 3.

Despite their extraordinary permeation and selectivity properties, metal membranes have found very limited industrial application [20]. In the 1970s and early 1980s, Johnson Matthey built a number of systems to produce on-site hydrogen by separation of hydrogen/carbon dioxide mixtures made by reforming methanol. This was not a commercial success, but the company and others still produce small systems using palladium–silver alloy membranes to generate ultrapure hydrogen from 99.9% hydrogen for the electronics industry and as feed gas to fuel cells.

8.2.3 Ceramic and Zeolite Membranes

During the last few years, ceramic- and zeolite-based membranes have begun to be used for a few commercial separations. These membranes are all multilayer composite structures formed by coating a thin selective ceramic or zeolite layer onto a microporous ceramic support. Ceramic membranes are prepared by the sol-gel technique described in Chapter 3; zeolite membranes are prepared by direct crystallization, in which the thin zeolite layer is crystallized at high pressure and temperature directly onto the microporous support [21, 22] (also described in Chapter 3).

Both Mitsui [23] and ECN [24] have commercialized these membranes for dehydration of alcohols by pervaporation or vapor/vapor permeation. The membranes are made in tubular form. Extraordinarily high selectivities have been reported for these membranes, and their ceramic nature allows operation at high temperatures, so fluxes are high. These

advantages are, however, offset by the costs of the membrane modules, currently in excess of US\$3000/m² of membrane.

8.2.4 Thermally Rearranged/Microporous Carbon Membranes

When heated in a vacuum or inert atmosphere, many polymers will thermally rearrange, crosslink and, at temperatures above 300–400°C, begin to carbonize. Of particular interest are polymers that undergo these changes before they soften or melt. It is then possible to form an anisotropic or composite membrane and to partially or completely carbonize the membrane by heating it to a high temperature. The membrane left has the original asymmetric structure, but the selective layer is changed to a highly crosslinked or carbonized finely microporous film.

Koresh and Soffer were the first to prepare this type of membrane, and in 1983, reported a carbonized membrane with an oxygen/nitrogen selectivity of 7–8 [25]. Later, membranes with selectivities of 10–20 and good permeances were made. Since then, the process has been the subject of considerable development by Soffer, Lee [26, 27], Koros and Williams [28], Ube Industries in Japan [29, 30], and many others. Carbonized membranes can have exceptional separation properties. Membranes with oxygen/nitrogen selectivities of more than 10 and carbon dioxide/methane selectivities of 50–100 with good permeances have been reported many times. Membranes with propylene/propane selectivities of more than 20 have also been made [29]. These membranes, if successfully scaled up, would find use in many petrochemical applications.

Unfortunately, carbon membranes are brittle, and difficult to produce as high-surface-area membrane modules. More importantly, the finely microporous structure of the polymers can also be plugged by trace amounts of heavy hydrocarbons or even water present in the feed gas. Until these problems are solved, these membranes are likely to remain in the laboratory despite their outstanding permeation properties.

8.2.5 Mixed-Matrix Membranes

The ceramic microporous carbon and zeolite membranes described above are far too expensive for most separation applications. For this reason, despite their exceptional selectivities, these membranes are not yet used on an industrial scale. One solution to this problem is to prepare membranes from materials consisting of the inorganic particles dispersed in a polymer matrix. These mixed-matrix membranes are expected to combine the selectivity of the inorganic membranes with the low cost and ease of manufacture of polymer membranes. The development of these membranes has been described in Chapter 3. Despite a very significant effort over more than 20 years, these membranes have not left the laboratory. Low permeances are one problem, because it is difficult to make thin mixed-matrix membranes. Another problem is fouling of the membranes by minor, easily absorbed components in the feed mixture to be separated.

8.3 Membrane Modules

Gas separation membranes are formed into spiral-wound or hollow fiber modules. Particulate matter, oil mist, and other potentially fouling materials can be completely and

Table 8.2 Module designs used for various gas separation applications

Application	Typical membrane material	Selectivity (α)	Pressure-normalized flux of most permeable component ($10^{-6} \text{ cm}^3 \text{ (STP)/cm}^2 \cdot \text{s} \cdot \text{cmHg}$)	Commonly used module designs
O ₂ /N ₂	Polyimide	6–7	10–30	Hollow fiber–bore-side feed
H ₂ /N ₂	Polysulfone	100	100–200	Hollow fiber–shell-side feed
CO ₂ /CH ₄	Cellulose acetate	15	100–200	Spiral or hollow fiber–shell-side feed
VOC/N ₂	Silicone rubber	10–30	1000–2000	Spiral
H ₂ O/Air	Polyimide	>200	2000–5000	Capillary–bore-side feed

economically removed from gas streams by good-quality coalescing filters, so membrane fouling is generally more easily controlled in gas separation than with liquid separations. Therefore, the choice of module design is usually decided by cost and membrane flux. The high pressures used in gas separation applications require that the hollow fiber membranes used are very fine, with lumen diameters of 50–200 μm . The pressure drop required to circulate gas on the lumen side of the membrane of these small-diameter fibers can become large enough to seriously affect membrane performance. In the production of nitrogen from air, membrane permeances are relatively low, from 1 to 2 gpu, and parasitic pressure drops are not a problem. However, in the separation of hydrogen from nitrogen or methane and carbon dioxide from natural gas, membrane permeances are higher, and hollow fine fiber modules can develop excessive permeate-side pressure drops. The solution is to use capillary fibers or spiral-wound modules for this type of application. Nonetheless, these disadvantages of hollow fiber membranes may be partially offset by their lower cost per square meter of membrane. These factors are summarized for some important gas separation applications in Table 8.2.

8.4 Process Design

The three factors that determine the performance of a membrane gas separation system are illustrated in Figure 8.11. The role of membrane selectivity is obvious; not so obvious are the importance of the ratio of feed pressure (p_o) to permeate pressure (p_ℓ) across the membrane, usually called the pressure ratio, φ , and defined as

$$\varphi = \frac{p_o}{p_\ell} \quad (8.7)$$

and of the membrane stage-cut, θ , which is the fraction of the feed gas that permeates the membrane, defined as

$$\theta = \frac{\text{permeate flow}}{\text{feed flow}} \quad (8.8)$$

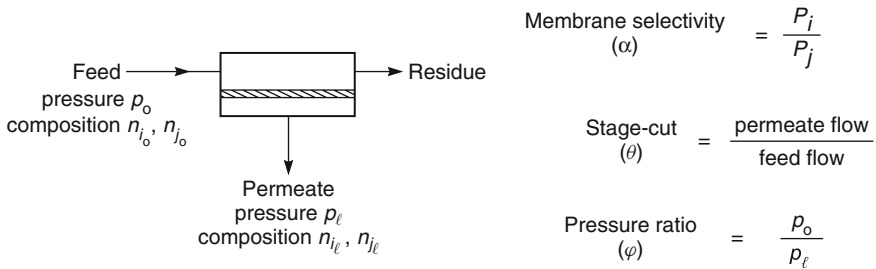


Figure 8.11 Parameters affecting the performance of membrane gas separation systems

8.4.1 Pressure Ratio

The importance of pressure ratio in the separation of gas mixtures can be illustrated by considering the separation of a gas mixture with component concentrations of n_{i_o} and n_{j_o} at a feed pressure p_o . A flow of component i across the membrane can only occur if the partial pressure of i on the feed side of the membrane ($n_{i_o} p_o$) is greater than the partial pressure of i on the permeate side of the membrane ($n_{i_l} p_l$), that is,

$$n_{i_o} p_o > n_{i_l} p_l \quad (8.9)$$

It follows that the maximum separation achieved by the membrane can be expressed as

$$\frac{p_o}{p_l} \geq \frac{n_{i_l}}{n_{i_o}} \quad (8.10)$$

That is, the separation achieved can never exceed the pressure ratio ϕ , no matter how selective the membrane:

$$\frac{n_{i_l}}{n_{i_o}} \leq \phi \quad (8.11)$$

The relationship between pressure ratio and membrane selectivity can be derived from the Fick's law expression for the fluxes of components i and j

$$j_i = \frac{\mathcal{P}_i (p_{i_o} - p_{i_l})}{\ell} \quad (8.12)$$

and

$$j_j = \frac{\mathcal{P}_j (p_{j_o} - p_{j_l})}{\ell} \quad (8.13)$$

The total gas pressures on the feed and permeate side are the sum of the partial pressures. For the feed side

$$p_o = p_{i_o} + p_{j_o} \quad (8.14)$$

and for the permeate side

$$p_\ell = p_{i_\ell} + p_{j_\ell} \quad (8.15)$$

The volume fractions of components i and j on the feed side and permeate side are also related to partial pressures. For the feed side

$$n_{i_o} = \frac{p_{i_o}}{p_o} \quad n_{j_o} = \frac{p_{j_o}}{p_o} \quad (8.16)$$

and for the permeate side

$$n_{i_\ell} = \frac{p_{i_\ell}}{p_\ell} \quad n_{j_\ell} = \frac{p_{j_\ell}}{p_\ell} \quad (8.17)$$

while from mass balance considerations

$$\frac{j_i}{j_j} = \frac{n_{i_\ell}}{n_{j_\ell}} = \frac{n_{i_\ell}}{1 - n_{i_\ell}} = \frac{1 - n_{j_\ell}}{n_{j_\ell}} \quad (8.18)$$

Dividing Equation 8.12 by Equation 8.13 and using the definition of α , Equation 8.3, and Equations 8.16–8.18 lead to

$$n_{i_\ell} = \frac{1}{2} \times \frac{n_{i_o} + \frac{1}{\varphi} + \frac{1}{\alpha - 1} - \sqrt{\left(n_{i_o} + \frac{1}{\varphi} + \frac{1}{\alpha - 1}\right)^2 - \frac{4 \times \alpha \times n_{i_o}}{(\alpha - 1) \times \varphi}}}{\frac{1}{\varphi}} \quad (8.19)$$

This somewhat complex expression breaks down into two limiting cases, depending on the relative magnitudes of the pressure ratio and the membrane selectivity. First, if the membrane selectivity (α) is very much larger than the pressure ratio (φ), that is,

$$\alpha \gg \varphi \quad (8.20)$$

then Equation 8.19 becomes

$$n_{i_\ell} = n_{i_o} \varphi \quad (8.21)$$

This is called the pressure-ratio-limited region, in which the performance is determined only by the pressure ratio across the membrane and is independent of the membrane selectivity.

If the membrane selectivity (α) is very much smaller than the pressure ratio (φ), that is,

$$\alpha \ll \varphi \quad (8.22)$$

then Equation 8.19 becomes (after some manipulation and the application of the rule of l'Hôpital)

$$n_{i_e} = \frac{\alpha \cdot n_{i_o}}{n_{i_o} \cdot (\alpha - 1) + 1} \quad (8.23)$$

This is called the membrane-selectivity-limited region, in which the membrane performance is determined only by the membrane selectivity and is independent of the pressure ratio. There is, of course, an intermediate region between these two limiting cases, in which both the pressure ratio and the membrane selectivity affect the membrane system performance. These three regions are illustrated in Figure 8.12, in which the calculated permeate concentration (n_{i_e}) is plotted versus pressure ratio (φ) for a membrane with a selectivity of 30 [31]. At a pressure ratio of 1, the feed pressure is equal to the permeate pressure, and no separation is achieved by the membrane. As the difference between the feed and permeate pressure increases, the concentration of the more permeable component in the permeate gas begins to increase, first according to Equation 8.21 and then, when the pressure ratio and membrane selectivity are comparable, according to Equation 8.19. At very high pressure ratios, that is, when the pressure ratio is four to five times higher than the membrane selectivity, the membrane enters the membrane-selectivity-controlled region. In this region the permeate concentration reaches the limiting value given by Equation 8.23.

The relationship between pressure ratio and selectivity is important because of the practical limit to the pressure ratio achievable in gas separation systems. Compressing the feed stream to very high pressure or drawing a very hard vacuum on the permeate side

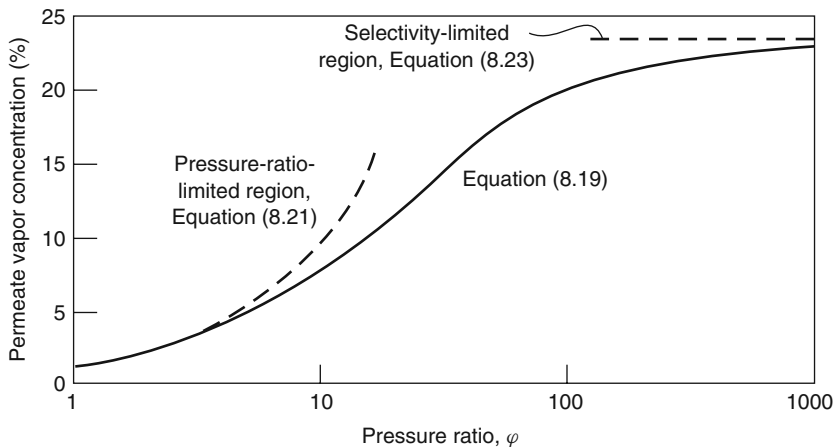


Figure 8.12 Calculated permeate vapor concentration for a vapor-permeable membrane with a vapor/nitrogen selectivity of 30 as a function of pressure ratio. The feed vapor concentration is 1%. Below pressure ratios of about 10, separation is limited by the pressure ratio across the membrane. At pressure ratios above about 100, separation is limited by the membrane selectivity [31]

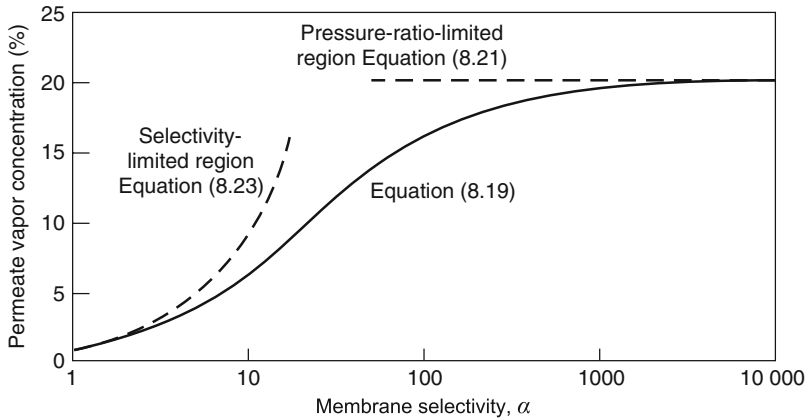


Figure 8.13 Calculated permeate vapor concentration as a function of selectivity. The feed vapor concentration is 1%; the pressure ratio is fixed at 20. Below a vapor/nitrogen selectivity of about 10, separation is limited by the low membrane selectivity; at selectivities above about 100, separation is limited by the low pressure ratio across the membrane [31]

of the membrane to achieve large pressure ratios both require large amounts of energy and expensive pumps. As a result, typical practical pressure ratios are in the range 5–20.

Because the attainable pressure ratio in most gas separation applications is limited, the benefit of very highly selective membranes is often less than might be expected. For example, as shown in Figure 8.13, if the pressure ratio is 20, then increasing the membrane selectivity from 10 to 20 will significantly improve system performance. However, a much smaller incremental improvement results from increasing the selectivity from 20 to 40. Increases in selectivity above 100 will produce negligible improvements.

8.4.2 Stage-Cut

Another factor that affects membrane system design is the degree of separation required. The usual target of a gas separation system is to produce a residue stream essentially stripped of the permeable component and a small, highly concentrated permeate stream. These two requirements cannot be met simultaneously; a trade-off must be made between removal from the feed gas and enrichment in the permeate. The system attribute that characterizes this trade-off is called the stage-cut. Analytical expressions linking the membrane and the operating conditions expressed in Equation 8.19 with the performance of a module have been developed for simple binary mixtures [32]. These expressions are clumsy for routine use, so industrial membrane producers have all developed differential element computer programs to calculate the performance of these modules. The techniques used to create these programs have been described in the literature [33, 34], but the programs themselves are not generally available.

The effect of stage-cut on module performance calculated with a differential element computer program is shown in Figure 8.14.

In the example calculation shown, the feed gas contains 50% of a permeable gas (i) and 50% of a relatively impermeable gas (j). Under the assumed operating conditions

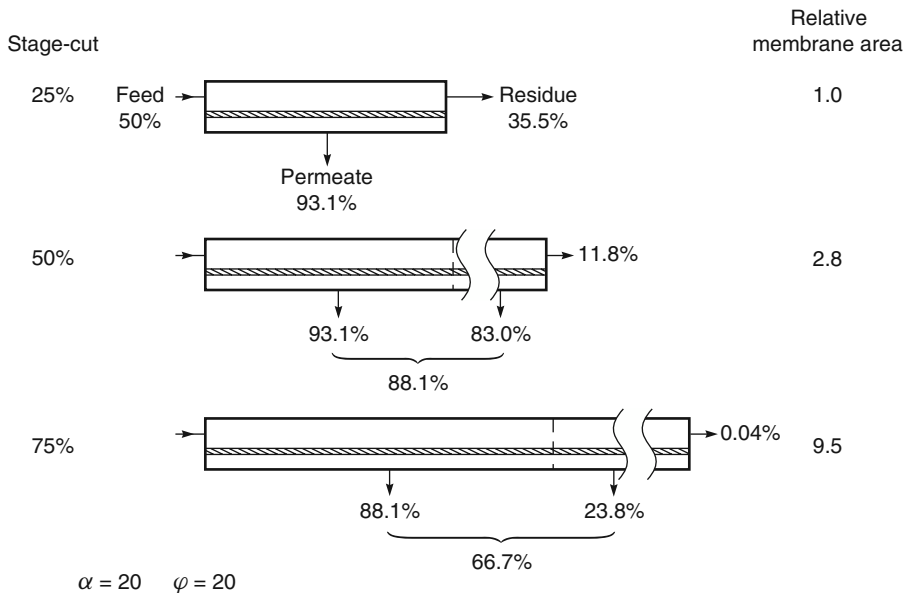


Figure 8.14 The effect of stage-cut on the separation of a 50/50 feed gas mixture (pressure ratio, 20; membrane selectivity, 20). At low stage-cuts a concentrated permeate product, but only modest removal from the residue, can be obtained. At high stage-cuts almost complete removal is obtained, but the permeate product is only slightly more enriched than the original feed

of this system (pressure ratio 20, membrane selectivity 20), it is possible at zero stage-cut to produce a permeate stream containing 94.8% of component i . But the permeate stream is tiny and the residue stream is still very close to the feed gas concentration of 50%. As the fraction of the feed gas permeating the membrane is increased by increasing the membrane area, the concentration of the permeable component in the residue and permeate streams falls. At a stage-cut of 25%, the permeate gas concentration has fallen from 94.8% (its maximum value) to 93.1%. The residue stream concentration of permeable gas is then 35.5%. Increasing the fraction of the feed gas that permeates the membrane to 50% by adding more membrane area produces a residue stream containing 11.8% of the permeable gas. However, the gas permeating the added membrane area only contains 83.0% of the permeable component, so the average concentration of permeable component in the permeate stream is reduced from 93.1 to 88.1%. If the fraction of the feed gas that permeates the membrane is increased to 75% by adding even more membrane area, the concentration of the permeable component in the residue stream is reduced to only 0.04%. However, the gas permeating the added membrane area only contains 23.8% of the permeable component, *less than the original feed gas*. The average concentration of the permeable component in the feed gas is, therefore, reduced to 66.7%. This means that half of the less permeable component has been lost to the permeate stream.

The calculations shown in Figure 8.14 illustrate the trade-off between recovery and purity. A single-stage membrane process can be designed for either maximum recovery or maximum purity, but not both. The calculations also show that membranes can produce very pure residue gas streams enriched in the less permeable component, although at low recoveries. However, the enrichment of the more permeable component in the permeate can never be more than the membrane selectivity, so a membrane with low selectivity produces an only slightly enriched permeate. This is why membranes with an oxygen/nitrogen selectivity of 4–6 can produce very pure nitrogen (>99.5%) from air on the residue side of the membrane, but the same membranes cannot produce better than 50–60% oxygen on the permeate side. If the more permeable component must be pure, very selective membranes are required or multistage or recycle membrane systems must be used.

Finally, the calculations in Figure 8.14 show that increasing the stage-cut to produce a pure residue stream requires a disproportionate increase in membrane area. As the feed gas is stripped of the more permeable component, the average permeation rate through the membrane falls toward the permeation rate of the slow gas. In the example shown, this means that permeating the first 25% of the feed gas requires a relative membrane area of 1, permeating the next 25% requires a membrane area increment of 1.8, and permeating the next 25% requires an increment of 6.7.

8.4.3 Multistep and Multistage System Designs

Because the membrane selectivity and pressure ratio achievable in a commercial membrane system are limited, a one-stage membrane system may not provide the separation desired. The problem is illustrated in Figure 8.15. By way of example, the process designs are calculated for the removal of a volatile organic compound (VOC), which is the permeable component, from a nitrogen feed gas, which contains 1 vol% of this component. Rubbery membranes such as silicone rubber permeate the VOC preferentially because of its greater condensability and hence solubility in the membrane. In this calculation, the pressure ratio is fixed at 20 by compressing the feed gas, and the permeate is maintained at atmospheric pressure. The membrane VOC/nitrogen selectivity is assumed to be 20.

Figure 8.15 shows that when 90% of the VOC in the feed stream is removed, the permeate stream will contain approximately 4% of the permeable component. In many

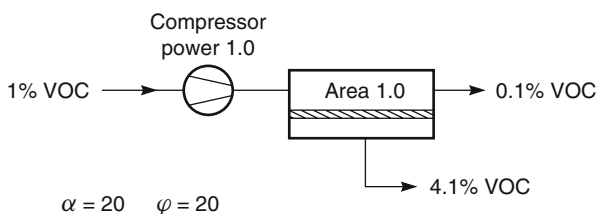


Figure 8.15 A one-stage vapor separation operation. The performance of this system was calculated for a cross-flow module using a vapor/nitrogen selectivity of 20 and a pressure ratio of 20

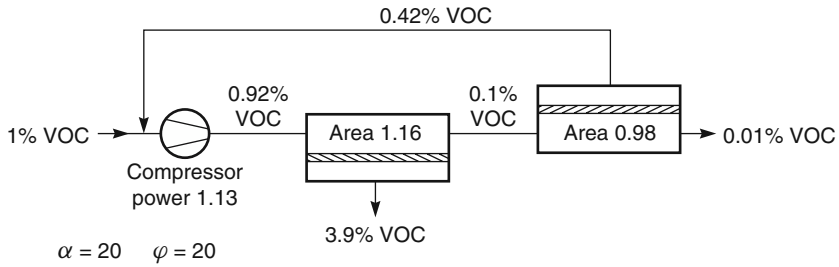


Figure 8.16 A two-step system to achieve 99% vapor removal from the feed stream. Selectivity, 20; pressure ratio, 20

cases, 90% removal of VOC from the feed stream is insufficient to allow the residue gas to be discharged, and enrichment of the component in the permeate is also insufficient.

If the main problem is insufficient VOC removal from the feed stream, a two-step system as shown in Figure 8.16 can be used. In a two-step system, the residue stream from the first membrane unit is passed to a second unit, where the VOC concentration is reduced by a further factor of 10, from 0.1 to 0.01%. Because the concentration of VOC in the feed to the second membrane unit is low, the permeate stream is relatively dilute and is recirculated to the feed stream.

A multistep design of this type can achieve almost complete removal of the permeable component from the feed stream to the membrane unit. However, greater removal of the permeable component is achieved at the expense of increases in membrane area and power consumption by the compressor. As a rule of thumb, the membrane area required to remove the last 9% of a component from the feed equals the membrane area required to remove the first 90%.

Sometimes, 90% removal of the permeable component from the feed stream is acceptable for the discharge stream from the membrane unit, but a higher concentration is needed to make the permeate gas usable. In this situation, a two-stage system of the type shown in Figure 8.17 is used. In a two-stage design, the permeate from the first

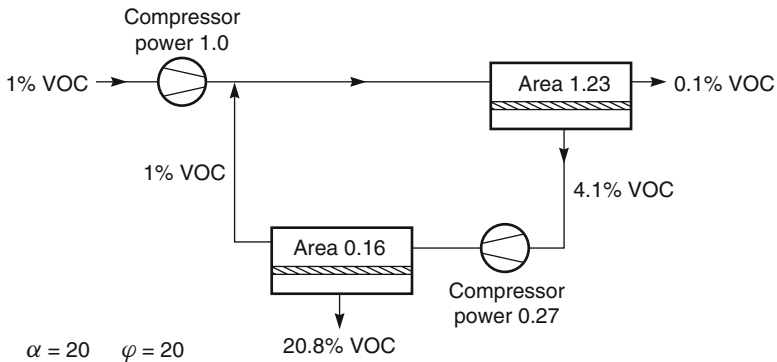


Figure 8.17 A two-stage system to produce a highly concentrated permeate stream. Selectivity, 20; pressure ratio, 20

membrane unit is recompressed and sent to a second membrane unit, where a further separation is performed. The final permeate is then twice enriched. In the most efficient two-stage designs, the residue stream from the second stage is reduced to about the same concentration as the original feed gas, with which it is mixed. In the example shown in Figure 8.17, the permeate stream, concentrated a further fivefold, leaves the system at a concentration of 21%. Because the volume of gas treated by the second-stage membrane unit is much smaller than in the first stage, the membrane area of the second stage is relatively small. Thus, incorporation of a second stage only increases the overall membrane area and power requirements by approximately 30–40%.

More complex multistage/multistep combination processes can be designed, but are seldom used in commercial systems – their complexity makes them uncompetitive with alternative separation technologies. More commonly, some form of recycle design is used.

8.4.4 Recycle Designs

A simple recycle design, sometimes called a two-and-one-half-stage system, proposed by Wijmans and Baker [35] is shown in Figure 8.18. In this design, the permeate from the first membrane stage is recompressed and sent to a two-step second stage, where a portion of the gas permeates and is removed as enriched product. The remaining gas passes to another membrane stage, which brings the gas concentration close to the original feed value. The permeate from this stage is mixed with the first-stage permeate, forming a recycle loop. By controlling the relative size of the two second stages, any desired concentration of the more permeable component can be achieved in the product. In the example shown, the permeable component is concentrated to 50% in the permeate. The increased performance is achieved at the expense of a slightly larger second-stage compressor and more membrane area. Normally, however, this design is preferable to a more complex three-stage system.

Figure 8.19 shows another type of recycle design in which a recycle loop increases the concentration of the permeable component to the point at which it can be removed

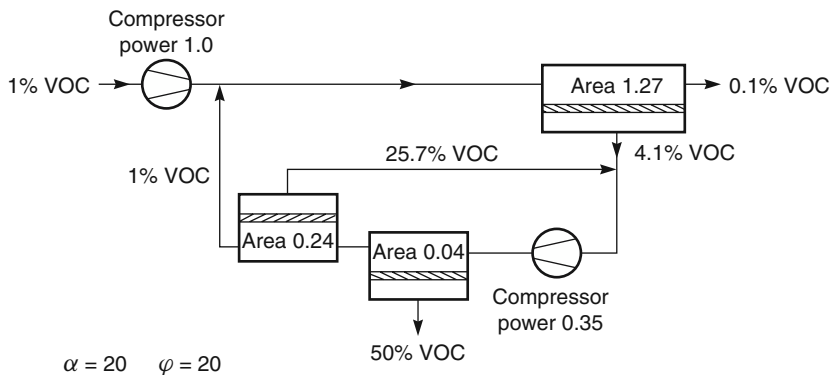


Figure 8.18 Two-and-one-half-stage system: by forming a recycle loop around the second stage, a small, very concentrated product stream is created. Selectivity, 20; pressure ratio, 20 [35]

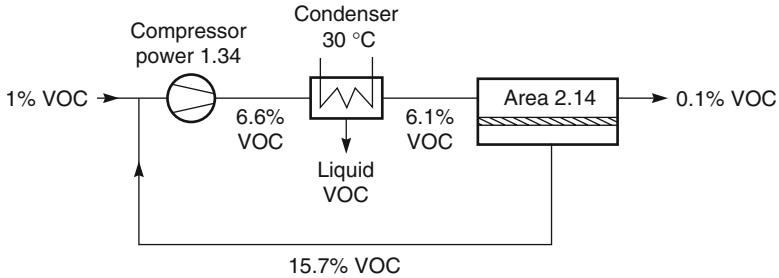


Figure 8.19 Recycle system design using one membrane stage, preceded by a compressor and condenser: feed stream, 1% vapor in nitrogen; selectivity, 20; pressure ratio, 20. The VOC is assumed to be pentane

by a second process, most commonly condensation [36]. The feed stream entering the recycle loop contains 1% of the permeable component as in Figures 8.15–8.18. After compression to 20 atm, the feed gas passes through a condenser at 30°C, but the VOC content is still below the condensation concentration at this temperature. The membrane unit separates the gas into a VOC-depleted residue stream and a vapor-enriched permeate stream, which is recirculated to the front of the compressor. Because the bulk of the vapor is recirculated, the concentration of vapor in the loop increases rapidly until the pressurized gas entering the condenser exceeds the vapor dew point of 6.1%. At this point, the system is at steady state; the mass of VOC entering the recirculation loop is equal to the mass discharged in the residue stream plus the mass removed as liquid condensate.

Recycle designs of this type are limited to applications in which the components of the gas mixture, if sufficiently concentrated, can be separated from the gas by some other technique. With organic vapors, condensation is often possible; adsorption, chemical scrubbing, or absorption can also be used. The process shown in Figure 8.19 is used to separate VOCs from nitrogen and air, or to separate propane, butane, pentane, and higher hydrocarbons from natural gas (methane).

All the example process designs illustrated in Figures 8.15–8.19 used cross-flow membrane modules. This is because the improvement in separation performance achieved by a counter-flow module does not normally compensate for the extra cost of fabrication and use of this type of module. However, some special cases do exist where this type of module can offer real benefits. The dehydration of air and natural gas with counter-flow sweep modules was discussed in Chapter 4. Counter-flow modules were also used in the continuous membrane column popularized by Hwang and Thorman [37].

Hwang's device is shown in Figure 8.20, applied to the separation of oxygen and nitrogen in air. Pressurized air is introduced at the middle of the high-pressure side of the unit. As the air travels down the bottom membrane section, the more permeable component (oxygen) permeates the membrane. The feed gas is thus continually depleted of oxygen. At the bottom of the unit, the nitrogen-enriched residue gas is removed. The permeate gas, enriched in oxygen, travels up the column on the permeate side of the membrane, countercurrent to the feed gas. A portion of this gas is removed at the top of the column while the remainder is compressed and recycled on the high-pressure side of

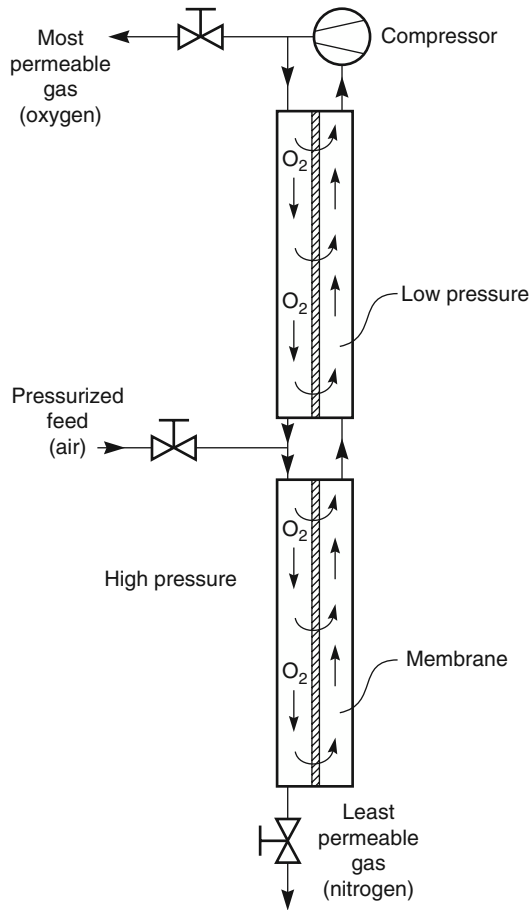


Figure 8.20 Schematic illustration of a continuous membrane column popularized by Sun-Tak Hwang and used here to separate oxygen and nitrogen in air. Reprinted with permission from [54]. Copyright (1980) John Wiley and Sons.

the top membrane section. Oxygen in this recycle gas permeates through the membrane, so the more permeable oxygen accumulates at the top of the column. The process has features in common with the reflux operation of a distillation column and, when developed by Hwang, was described in similar language. The Hwang group demonstrated that a number of spectacular separations could be achieved with the device. Unfortunately, the energy cost of the recycle operation meant the system could not compete economically with more conventional multistep/multistage membrane designs.

8.5 Applications

The membrane gas separation industry is still growing and changing. Two of the largest industrial gas companies now have membrane affiliates: Air Products (Permea) and

Air Liquide (Medal). The affiliates focus mainly on producing membrane systems to separate nitrogen from air, but also produce some hydrogen separation systems. Ube (Japan) and Aquillo (The Netherlands) are also active in these markets. Another group of companies – UOP (GMS/Separex), Cameron (Cynara), and MTR – produce membrane systems for natural gas separations. A third group of smaller independents are focusing on new applications, including vapor separation, air dehydration, and oxygen enrichment. The final size and form of this industry is still changing. The following section covers the major current applications. Overview articles on the main gas separation applications can be found in Paul and Yampol'skii [38], in Koros and Fleming [39], and elsewhere [40].

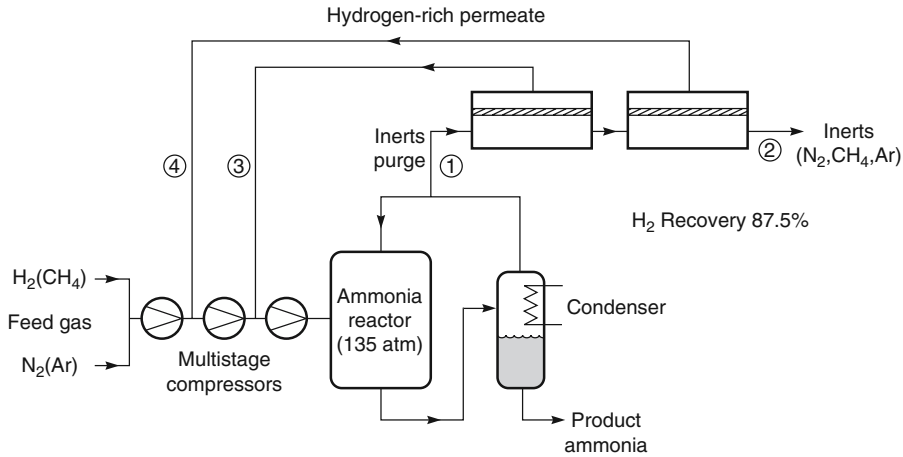
8.5.1 Hydrogen Separations

The first large-scale commercial application of membrane gas separation was the separation of hydrogen from nitrogen in ammonia purge gas streams. The process, launched in 1980 by Monsanto, was followed by a number of similar applications, such as hydrogen/methane separation in refinery off-gases and hydrogen/carbon monoxide adjustment in oxo chemical synthesis plants [7]. Hydrogen is a small, noncondensable gas, which is highly permeable compared to all other gases. This is particularly true with the glassy polymers primarily used to make hydrogen-selective membranes; fluxes and selectivities of hydrogen through some of these materials are shown in Table 8.3. With fluxes and selectivities as high as these, it is easy to understand why hydrogen separation was the first gas separation process developed. Early hydrogen membrane gas separation plants used polysulfone or cellulose acetate membranes, but now a variety of specifically synthesized materials, such as polyimides (Ube), polyaramide (Medal), or brominated polysulfone (Permea), are used.

A typical membrane system flow scheme for recovery of hydrogen from an ammonia plant purge gas stream is shown in Figure 8.21. A photograph of such a system is shown in Figure 8.22. During the production of ammonia from nitrogen and hydrogen, argon enters the high-pressure ammonia reactor as an impurity with the nitrogen stream, and methane enters the reactor as an impurity with the hydrogen. Ammonia produced in the reactor is removed by condensation, so the argon and methane impurities accumulate until they represent as much as 15% of the gas in the reactor. To control the concentration of these components, the reactor must be continuously purged. The hydrogen lost with this purge gas can represent 2–4% of the total hydrogen consumed. Ammonia plants are very large, so recovery of purged hydrogen for recycle to the reactor is economically worthwhile.

Table 8.3 *Hydrogen separation membranes*

Membrane (developer)	Selectivity			Hydrogen pressure-normalized flux (10^{-6} cm ³ (STP)/cm ² ·s·cmHg)
	H ₂ /CO	H ₂ /CH ₄	H ₂ /N ₂	
Polyaramide (Medal)	100	>200	>200	100
Polysulfone (Permea)	40	80	80	100
Cellulose acetate (Separex)	30–40	60–80	60–80	200
Polyimide (Ube)	50	100–200	100–200	80–200



	Stream Composition (%)			
	Membrane Feed ①	Membrane Vent ②	High-Pressure Permeate ③	Low-Pressure Permeate ④
Hydrogen	62	21	87.3	84.8
Nitrogen	21	44	7.1	8.4
Methane	11	23	36	4.3
Argon	6	13	2.0	2.5
Pressure (atm)	135	132	70	28
Flow (scfm)	2000	740	830	430

Figure 8.21 Simplified flow schematic of the PRISM[®] membrane system to recover hydrogen from an ammonia reactor purge stream. A two-step membrane system is used to reduce permeate compression costs

In the process shown in Figure 8.21, a two-step membrane design is used to reduce the cost of recompressing the hydrogen permeate stream to the very high pressures of ammonia reactors. In the first step, the feed gas is maintained at the reactor pressure of 135 atm, and the permeate is maintained at 70 atm, giving a pressure ratio of 1.9. The hydrogen concentration in the feed to this first step is about 62%, high enough that even at this low pressure ratio, the permeate contains about 90% hydrogen. However, by the time the feed gas hydrogen concentration has fallen to 30%, the hydrogen concentration in the permeate is no longer high enough for recycle to the reactor. This remaining hydrogen is recovered in a second membrane step operated at a lower permeate pressure of 28 atm; the resulting pressure ratio is 4.7. The increased pressure ratio increases the hydrogen concentration in the permeate significantly. By dividing the process into two steps operating at different pressure ratios, maximum hydrogen recovery is achieved at minimum permeate hydrogen recompression costs.

A second major application of hydrogen-selective membranes is recovery of hydrogen from waste gases produced in refinery operations [7, 41, 42]. A typical separation – treatment of the high-pressure purge gas from a hydrotreater – is shown in



Figure 8.22 Photograph of an Air Products and Chemicals, Inc. PRISM[®] membrane system installed at an ammonia plant. The modules are mounted vertically

Figure 8.23. The hydrogen separation process is designed to recycle the hydrogen to the hydrotreater. As in the case of the ammonia plant, there is a trade-off between the concentration of hydrogen in the permeate and the permeate pressure and subsequent cost of recompression. In the example shown, a permeate of 96.5% hydrogen is considered adequate at a pressure ratio of 3.9.

Another example of the use of highly hydrogen-selective membranes in the petrochemical industry is the separation of hydrogen from carbon monoxide/hydrogen mixtures to obtain the correct ratio of components for subsequent synthesis operations.

8.5.2 Oxygen/Nitrogen Separation

The largest gas separation process in current use is the production of nitrogen from air. The first membranes used for this process were based on poly(4-methyl-1-pentene) (TPX) and ethyl cellulose. These polymer materials have oxygen/nitrogen selectivities of 4; the economics of the process using these membranes were marginal. The second-generation materials now used have selectivities of 6–7, providing very favorable economics, especially for small plants producing 5–500 scfm of nitrogen. In this range, membranes are the low-cost process, and most new small nitrogen plants use membrane systems.

Table 8.4 lists the permeabilities and selectivities of some of the materials that are used or have been used for this separation. There is a sharp trade-off between permeability

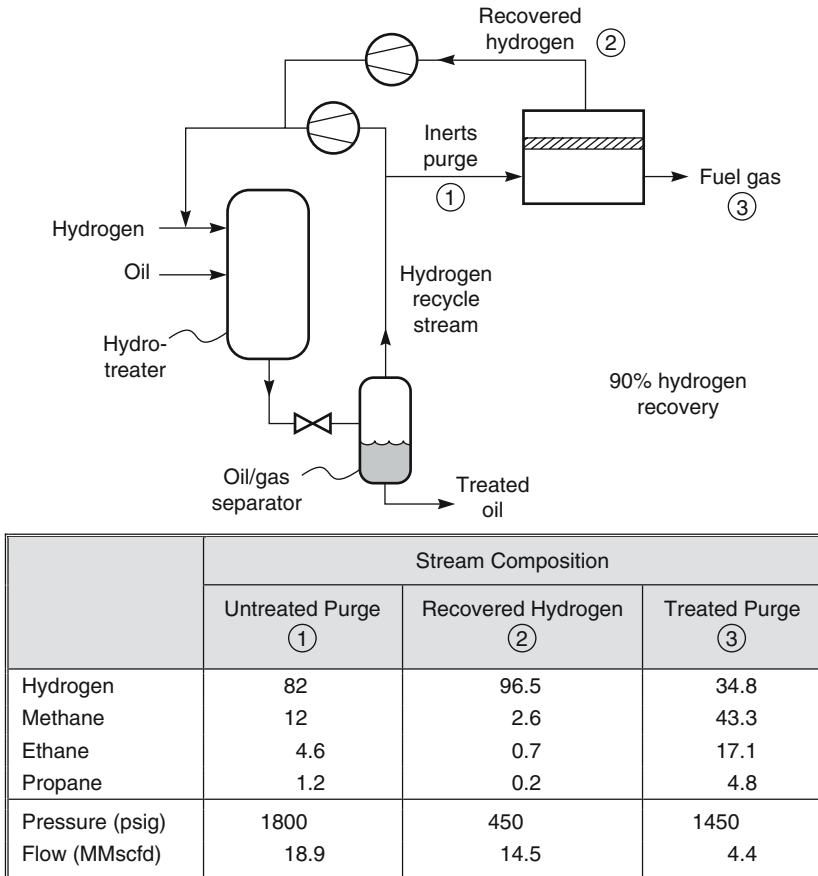


Figure 8.23 Hydrogen recovery from a hydrotreater used to lower the molecular weight of a refinery oil stream. Permea polysulfone membranes (PRISM[®]) are used [41]

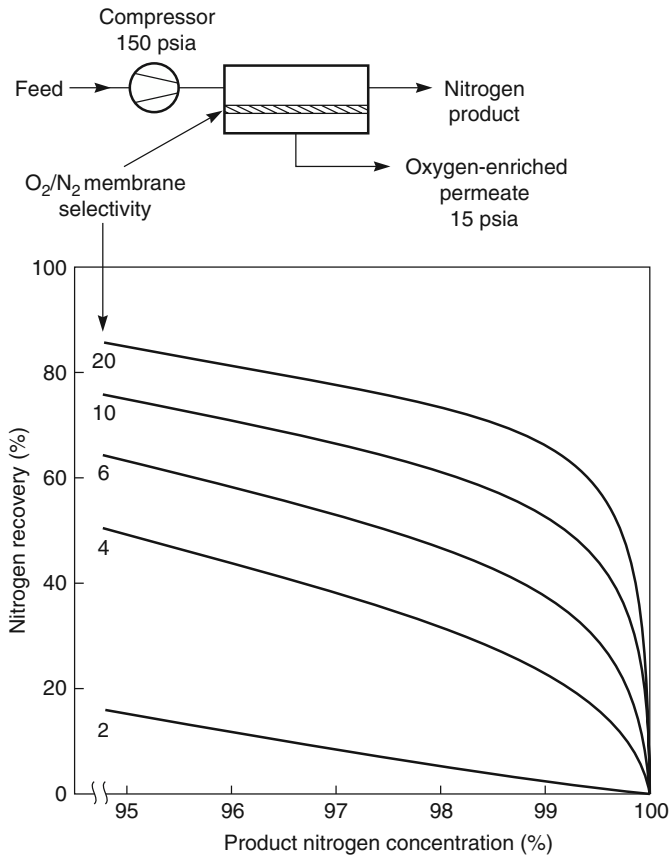
and selectivity. This trade-off was illustrated in the Robeson trade-off plot shown in Figure 8.6 [11].

High oxygen/nitrogen selectivity is required for an economical nitrogen production process. The effect of improved membrane selectivities on the efficiency of nitrogen production from air is illustrated in Figure 8.24. This figure shows the trade-off between the fraction of nitrogen in the feed gas recovered as nitrogen product gas as a function of the nitrogen concentration in the product gas. All oxygen-selective membranes, even membranes with an oxygen/nitrogen selectivity as low as 2, can produce better than 99% nitrogen, albeit at very low recoveries. The figure also shows the significant improvement in nitrogen recovery that results from an increase in oxygen/nitrogen selectivity from 2 to 20.

The first nitrogen production systems used membranes made from TPX with a selectivity of about 4. These membranes were incorporated into one-stage designs to produce 95% nitrogen used to render flammable-liquid storage tanks inert. As membranes

Table 8.4 Permeabilities and selectivities of polymers of interest in air separation

Polymer	Oxygen permeability (Barrer)	Nitrogen permeability (Barrer)	Oxygen/nitrogen selectivity
Poly(1-trimethylsilyl-1-propyne) (PTMSP)	7600	5400	1.4
Teflon AF 2400	1300	760	1.7
Silicone rubber	600	280	2.2
Poly(4-methyl-1-pentene) (TPX)	30	7.1	4.2
Poly(phenylene oxide) (PPO)	16.8	3.8	4.4
Ethyl cellulose	11.2	3.3	3.4
6FDA-DAF (polyimide)	7.9	1.3	6.2
Polyaramide	3.1	0.46	6.8
Tetrabromobisphenol A polycarbonate	1.4	0.18	7.5
Polysulfone	1.1	0.18	6.2

**Figure 8.24** Nitrogen recovery as a function of product nitrogen concentration for membranes with selectivities between 2 and 20

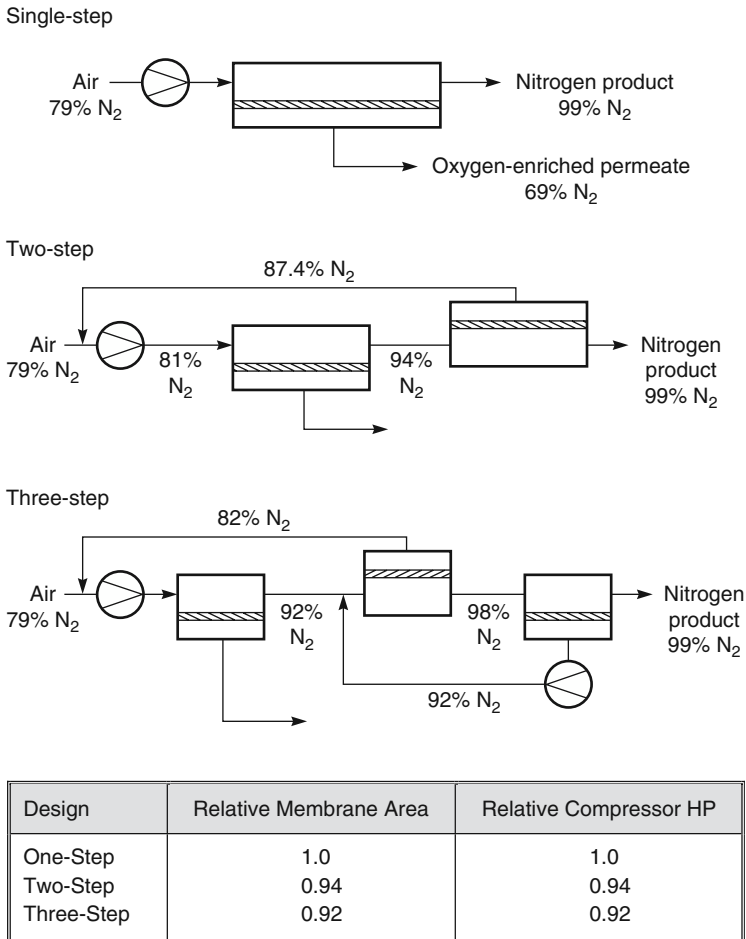


Figure 8.25 Single-, two-, and three-step designs for nitrogen production from air

improved, more complex process designs, of the type shown in Figure 8.25, were used to produce purer gas containing >99% nitrogen. The first improvement was the two-step process. As oxygen is removed from the air passing through the membrane modules, the oxygen concentration in the permeating gas falls. At some point, the oxygen concentration in the permeate gas is less than the concentration in normal ambient feed air. Mixing this oxygen-depleted gas permeate with the incoming air then becomes worthwhile. The improvement is most marked when the system is used to produce high-quality nitrogen containing less than 1% oxygen. In the example shown in Figure 8.25, the second-step permeate gas contains 12.5% oxygen, and recycling this gas to the incoming feed air reduces the membrane area and compressor load by about 6%. This relatively small saving is worthwhile because it is achieved at essentially no cost by making a simple piping change to the system. In the two-step design, the 12.5% oxygen permeate recycle stream

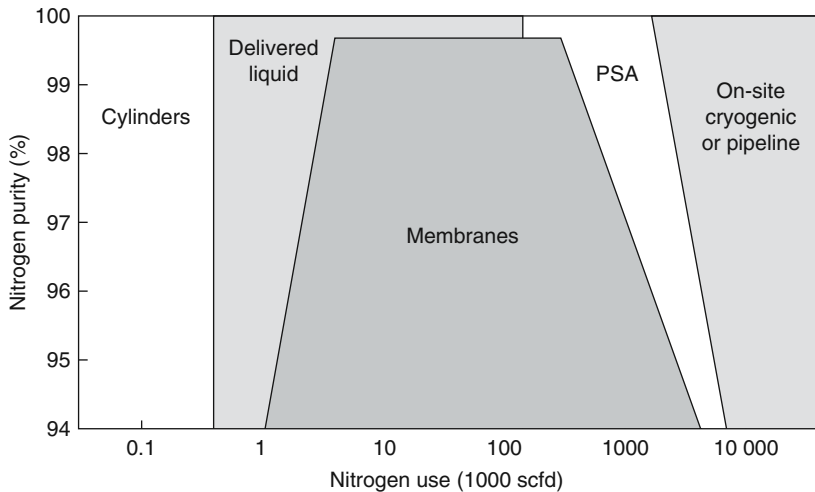


Figure 8.26 Approximate competitive range of current membrane nitrogen production systems. Many site-specific factors can affect the actual system selection

is mixed with ambient air containing 21% oxygen. A more efficient design would be to combine the recycle and feed gas where the feed gas has approximately the same concentration. This is the objective of the three-step process shown in Figure 8.25. This design saves a further 2% in membrane area and some compressor power, but now two compressors are needed. Three-step processes are, therefore, generally not used. A discussion of factors affecting the design of nitrogen plants is given by Prasad *et al.* [43, 44].

Membrane nitrogen production systems are now very competitive with alternative technologies. The competitive range of the various methods of obtaining nitrogen is shown in Figure 8.26. Very small nitrogen users generally purchase gas cylinders or delivered liquid nitrogen, but once consumption exceeds 5000 scfd of nitrogen, membranes become the low-cost process. This is particularly true if the required nitrogen purity is between 95 and 99% nitrogen. Membrane systems can still be used if high quality nitrogen (up to 99.9%) is required, but the cost of the system increases significantly. Very large nitrogen users – above 10 MMscfd of gas – generally use pipeline gas or on-site cryogenic systems. Pressure swing adsorption (PSA) systems are also used in the 1–10 MMscfd range.

A membrane process to separate nitrogen from air inevitably produces oxygen-enriched air as a by-product. Sometimes this by-product gas, containing about 35% oxygen, can be used beneficially, but usually it is vented. A market for oxygen or oxygen-enriched air exists, but because oxygen is produced as the permeate gas stream, it is much more difficult to produce high-purity oxygen than high-purity nitrogen with membrane systems. Figure 8.27 shows the maximum permeate oxygen concentration that can be produced by a one-step membrane process using membranes of various selectivities. Even at zero stage-cut and an infinite pressure ratio, the best currently available membrane, with an oxygen/nitrogen selectivity of 8, can only produce 68% oxygen. At useful stage-cuts and achievable pressure ratios, this concentration falls.

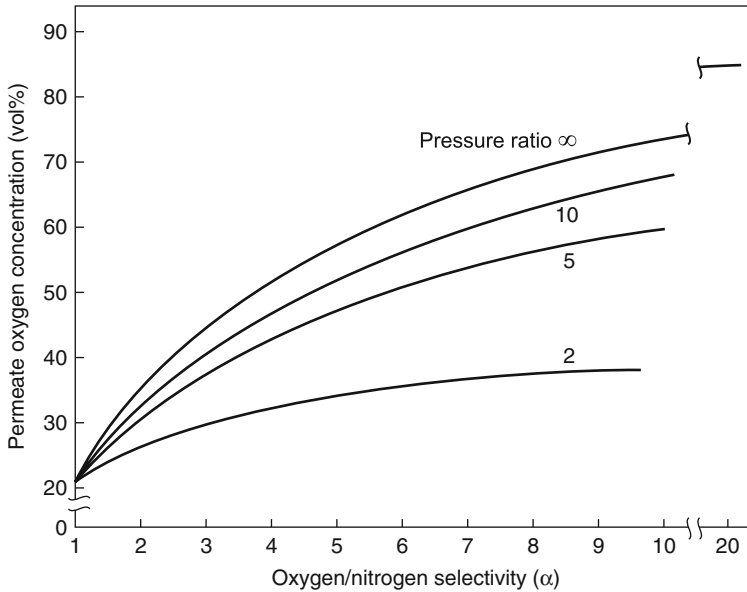


Figure 8.27 The maximum possible oxygen concentration in the permeate from a one-step membrane process with membranes of various selectivities (assumes zero stage-cut). Even the best current membrane materials, with a selectivity of 8, only produce 68% oxygen in the permeate at an infinite pressure ratio

These constraints limit membrane systems to the production of oxygen-enriched air in the 30–50% oxygen range.

Oxygen-enriched air is used in the chemical industry, in refineries, and in various fermentation and biological digestion processes, but it must be produced very cheaply for these applications. The competitive technology is pure oxygen produced cryogenically, then diluted with atmospheric air. The quantity of pure oxygen that must be blended with air to produce the desired oxygen enrichment determines the cost. This means that in membrane systems producing oxygen-enriched air, only the fraction of the oxygen above 21% can be counted as a credit. This fraction is called the equivalent pure oxygen (EPO₂) basis.

A comparison of the cost of oxygen-enriched air produced by membranes and by cryogenic separation shows that current membranes are generally uncompetitive. The only exception is for very small users in isolated locations, where the logistics of transporting liquid oxygen to the site increase the oxygen cost to US\$80–100/ton.

In the early 2000s in Japan and China, a market developed for small oxygen enrichment systems as a component in high-end room air conditioners, and in small personal oxygen-enriching devices for students working in smoke-filled rooms. These devices produced 25–28% oxygen and were filled with silicone rubber- or polyacetylene-based membranes.

Development of better membranes for producing oxygen-enriched air has been, and continues to be, an area of research because of the potential application of the gas in combustion processes. When methane, oil, and other fuels are burned with air, a large

amount of nitrogen passes as an inert diluent through the burners and is discarded as hot exhaust gas. If oxygen-enriched air were used, the energy lost with the hot exhaust gas would decrease considerably and fuel consumption would decrease. In the last few years, a market has developed in China for this type of system in regional cement plants. The high cost of natural gas in China makes the process economic. Carbon dioxide separation from the exhaust gas would also be easier – an advantage if CO₂ separation and sequestration ever becomes a real market. Use of oxygen-enriched air also improves the efficiency of diesel engines. The useful energy that can be extracted from the same amount of fuel increases significantly even if air is enriched only to 25–35% oxygen.

To make these oxygen-enrichment applications widely used, the fuel savings achieved must offset the cost of the oxygen-enriched air used. Calculations show that the process would be cost-effective for some applications at an EPO₂ cost as high as US\$60/ton and, for many applications, at an EPO₂ cost of US\$30–40/ton. Bhide and Stern [45] have published an interesting analysis of this problem, the results of which are shown in Figure 8.28. The figure shows the cost of oxygen-enriched air produced by a membrane process for membranes of various permeabilities and selectivities. The assumptions were optimistic – low-cost membrane modules (US\$54/m²) and membranes with extremely

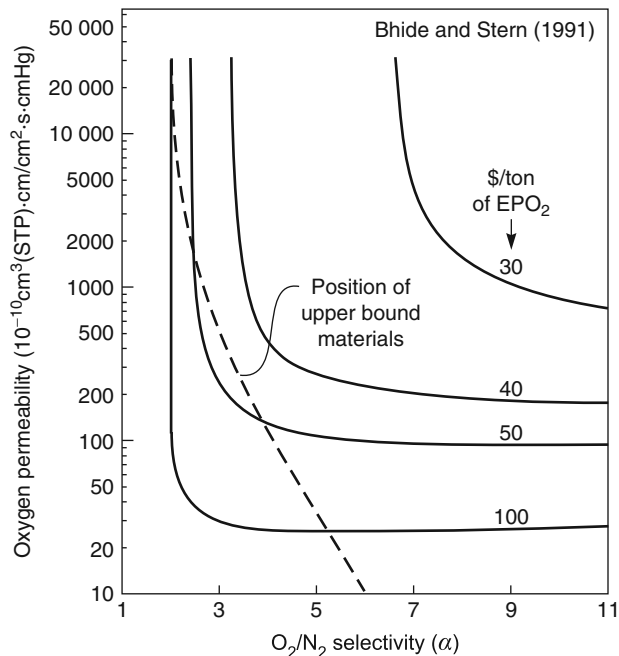


Figure 8.28 Cost of oxygen-enriched air produced by membrane separation on an EPO₂ basis as a function of the oxygen permeability and oxygen/nitrogen selectivity of the membrane. The performance of today's best membranes is represented by the upper bound performance line from Robeson's plot (Figure 8.6) [45]. Reprinted from *J. Membr. Sci.* 62, B.O. Bhide and S.A. Stern, *A New Evaluation of Membrane Processes for the Oxygen-Enrichment of Air*, p. 87. Copyright 1991, with permission from Elsevier.

thin selective separating layers (1000 Å). Also shown in Figure 8.28 is the portion of the upper-bound curve obtained from the permeability/selectivity trade-off plot shown in Figure 8.6. As the figure shows, a number of materials at the upper-bound limit, with oxygen/nitrogen selectivities of 3–4 and permeabilities of 50–500, are within striking distance of the US\$30–40/ton target. Production of these very high-performance membrane modules is at the outer limit of current technology, but improvements in the technology could open up new, very large applications of membranes in the future.

8.5.3 Natural Gas Separations

US production of natural gas is about 20 trillion scf/year; total worldwide production is about 100 trillion scf/year. All of this gas requires some treatment, and approximately 20% of the gas requires extensive treatment before it can be delivered to the pipeline. As a result, several billion dollars' worth of natural gas separation equipment is installed annually worldwide. The current membrane market share is about 5%, essentially all for carbon dioxide removal. However, this fraction is expected to increase as better carbon dioxide-selective membranes are developed and the application of membranes to other separations in the natural gas processing industry becomes more widespread [46–48].

Raw natural gas varies substantially in composition from source to source. Methane is always the major component, typically 75–90% of the total. Natural gas also contains significant amounts of ethane, some propane and butane, and 1–3% of other higher hydrocarbons. In addition, the gas contains undesirable impurities: water, carbon dioxide, nitrogen, and hydrogen sulfide. Although raw natural gas has a wide range of compositions, the composition of gas delivered to the pipeline is tightly controlled. Typical US natural gas specifications are shown in Table 8.5. The opportunity for membranes lies in the processing of gas to meet these specifications.

Natural gas is usually produced and transported to the gas processing plant at high pressure, in the range 500–1500 psi. To minimize recompression costs, the membrane process must remove impurities from the gas into the permeate stream, leaving the methane, ethane, and other hydrocarbons in the high-pressure residue gas. This requirement determines the type of membranes that can be used. Figure 8.29 is a graphical representation of the factors of molecular size and condensability that affect selection of membranes for natural gas separations.

As Figure 8.29 shows, water is small and condensable; therefore, it is easily separated from methane by both rubbery and glassy polymer membranes. Both rubbery and glassy

Table 8.5 Composition of natural gas required for delivery to the US national pipeline grid

Component	Specification
CO ₂	<2%
H ₂ O	<120 ppm
H ₂ S	<4 ppm
C ₃₊ content	950–1050 Btu/scf Dew point, –20°C
Total inerts (N ₂ , CO ₂ , He, etc.)	<4%

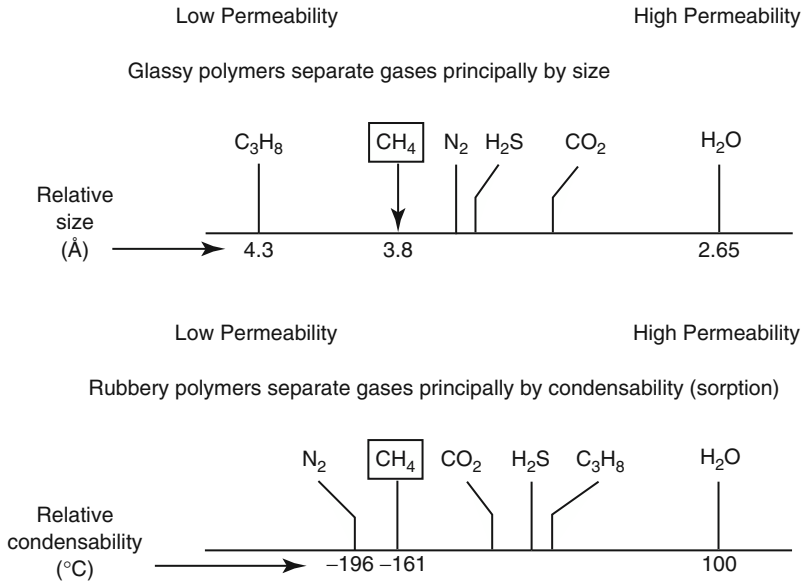


Figure 8.29 The relative size and condensability (boiling point) of the principal components of natural gas. Glassy membranes generally separate by differences in size; rubbery membranes separate by differences in condensability

membranes can also separate carbon dioxide and hydrogen sulfide from natural gas. However, in practice, carbon dioxide is best separated by glassy membranes (utilizing size selectivity) [49], whereas hydrogen sulfide, which is larger and more condensable than carbon dioxide, is best separated by rubbery membranes (utilizing sorption selectivity) [50, 51]. Nitrogen can be separated from methane by glassy membranes utilizing the difference in size, or rubbery membranes using the difference in sorption. In both cases, the differences are small, so the membrane selectivities are low. Finally, propane and other hydrocarbons, because of their condensability, are best separated from methane with rubbery sorption-selective membranes. Table 8.6 shows typical membrane materials

Table 8.6 Membrane materials and selectivities for separation of impurities from natural gas under normal operating conditions

Component to be permeated	Category of preferred polymer material	Typical polymer used	Typical selectivity over methane
CO ₂	Glass	Cellulose acetate, polyimide	10–20
H ₂ S	Rubber	Ether-amide block copolymer	20–30
N ₂	Glass	Polyimide, perfluoro polymers	2–3
N ₂	Rubber	Silicone rubber	0.35
H ₂ O	Rubber or glass	Many	>200
Butane	Rubber	Silicone rubber	7–10

and the selectivities that can be obtained with good-quality membranes under normal natural gas processing conditions.

8.5.4 Carbon Dioxide Separation

Removal of carbon dioxide is the only membrane-based natural gas separation process currently practiced on a large scale – several hundred plants have been installed, some very large. Most were installed by Grace, Separex (UOP), and Cynara, and all use cellulose acetate membranes in hollow fiber or spiral-wound module form. More recently, hollow fiber polyaramide and polyimide membranes have been introduced by Ube and Air Liquide, but their use has been slow to take off.

The designs of two typical carbon dioxide removal plants are illustrated in Figure 8.30. One-stage plants, which are simple, contain no rotating equipment, and require minimal maintenance, are preferred for small gas flows. In such plants methane loss to the permeate is often 10–15%. If there is no fuel use for this gas, it must be flared, which represents a significant revenue loss. Nonetheless, for gas wells producing 1–2 MMscfd, one-stage membrane units with their low capital and operating costs may still be the optimum treatment method.

For all but very small plants, the methane loss from a one-stage system becomes prohibitive. Often the permeate gas is recompressed and passed through a second membrane stage. This second stage reduces the methane loss to a small percentage. However,

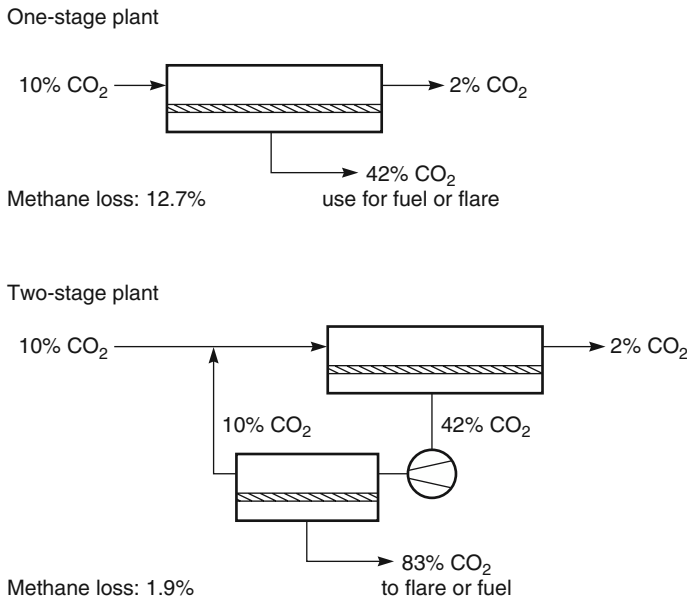


Figure 8.30 Flow scheme of one-stage and two-stage membrane separation plants to remove carbon dioxide from natural gas. Because the one-stage design has no moving parts, it is very competitive with other technologies, especially if there is a use for the low-pressure permeate gas. Two-stage processes are more expensive because a large compressor is required to compress the permeate gas. However, the loss of methane with the fuel gas is much reduced

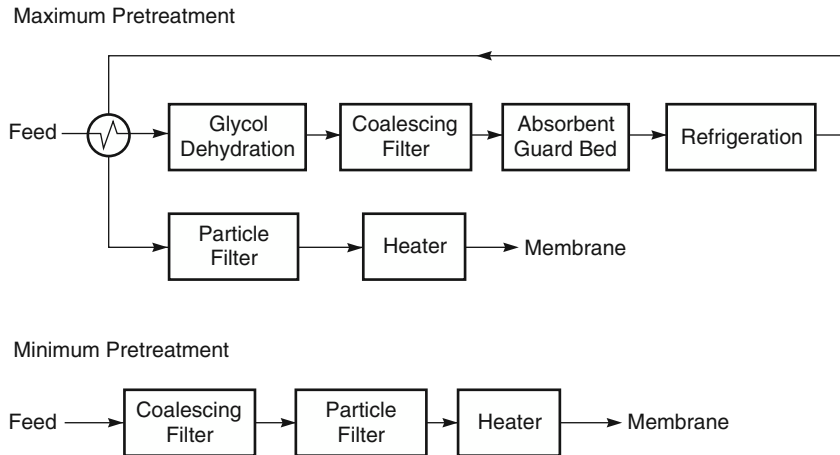


Figure 8.31 Natural gas pretreatment trains used in front of carbon dioxide membrane separation systems

because the cost of recompression is considerable, the membrane system may no longer compete with amine absorption, the alternative technology. In general, membrane systems have proven to be most competitive for gas streams containing high concentrations of carbon dioxide.

Natural gas contains a range of contaminants that can seriously affect the system performance. All carbon dioxide membrane separation units require some sort of pretreatment. Two possible pretreatment trains are illustrated in Figure 8.31. The amount of pretreatment is dependent on the membranes used and the nature of the gas to be treated. Cellulose acetate membranes, for example, are particularly sensitive to water, and therefore, glycol dehydration followed by silica bed drying would be used for most streams.

In Figure 8.31, the design labeled “maximum pretreatment” would be used for a gas that contains high levels of carbon dioxide and a high concentration of heavy hydrocarbons (for example, gas produced as a by-product of carbon dioxide flood-enhanced oil recovery projects). The pretreatment train labeled “minimum pretreatment” would be used for relatively hydrocarbon-lean gas that contains much smaller amounts of carbon dioxide [52].

The importance of adequate pretreatment was not appreciated by the builders of some of the first-generation membrane plants. Several early systems were damaged by plant upsets, which caused high levels of contaminants or liquids to reach the membranes. Better plant designs are now used to control membrane damage, and today’s membranes are also more robust.

Spillman [46], and more recently White [48], have reviewed the competitive position of membrane systems for this application. Currently the market for membrane carbon dioxide gas separation systems can be summarized as follows:

1. **Very small systems (less than 3 MMscfd).** At this flow rate, membrane units are very attractive. Often the permeate is flared or used as fuel, so the system is a simple bank of membrane modules.

2. **Small systems (3–30 MMscfd).** Two-stage membrane systems are used to reduce methane loss. In this gas flow range, amine and membrane systems compete; the choice between the two technologies depends on site-specific factors.
3. **Medium to large systems (greater than 30 MMscfd).** In general, membrane systems are too expensive to compete head-to-head with amine plants if the gas contains less than 10% CO₂. However, a number of large membrane systems have been installed on offshore platforms, where the small footprint and low weight of membrane systems are important. Membrane systems are also used in carbon dioxide enhanced oil recovery operations, or on other gas streams containing high concentrations of carbon dioxide, that favor membrane technology. As membranes improve, their market share is increasing.

In principle, the combination of membranes for bulk removal of the carbon dioxide with amine units as polishing systems offers a low-cost alternative to all-amine plants for many streams. However, this approach has not been generally used, because the savings in capital cost are largely offset by the increased complexity of the plant, which now contains two separation processes. The one exception has been in carbon dioxide flood-enhanced oil recovery projects [53, 54], in which carbon dioxide is injected into an oil formation to lower the viscosity of the oil. Water, oil, and gas are removed from the formation; the carbon dioxide is separated from the gas produced and reinjected. In these projects, the composition and volume of the gas changes significantly over the lifetime of the project. The modular nature of membrane units allows easy retrofitting to an existing amine plant, allowing the performance of the plant to be adjusted to meet the changing separation needs. Also, the capital cost of the separation system can be spread more evenly over the project lifetime. An example of a membrane/amine plant design is shown in Figure 8.32. In this design, the membrane unit removes two-thirds of the carbon dioxide, and the amine plant removes the remainder. The combined plant is usually significantly less expensive than an all-amine or all-membrane plant.

8.5.4.1 Dehydration

All natural gas must be dried before entering the national distribution pipeline, to control corrosion of the pipeline and to prevent formation of solid hydrocarbon/water hydrates

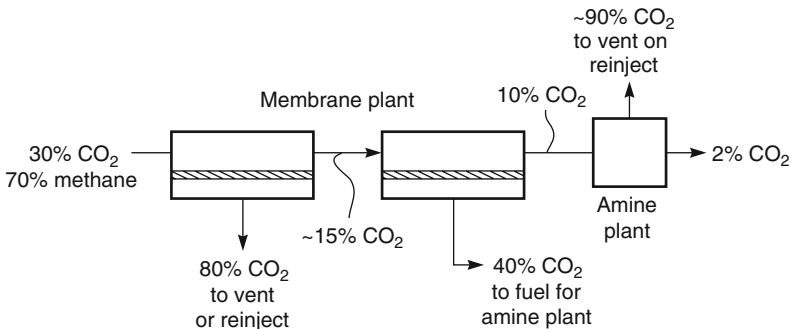


Figure 8.32 A typical membrane/amine plant for the treatment of associated natural gas produced in carbon dioxide/enhanced oil projects. The membrane permeate gas is often used as a fuel for the amine absorption plant

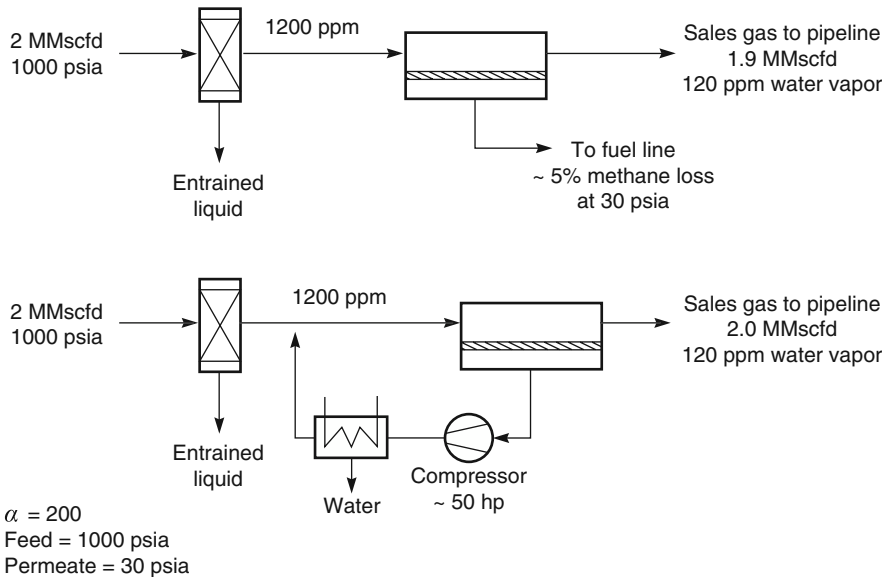


Figure 8.33 Two possible process designs for natural gas dehydration. Dehydration of natural gas is easily performed by membranes, but high cost often limits its scope to niche applications

that can choke valves. Currently, glycol dehydrators are widely used; approximately 50 000 units are in service in the United States. However, glycol dehydrators are not well suited for use on small gas streams or on offshore platforms, increasingly common sources of natural gas. In addition, these units coextract benzene, a known carcinogen and trace contaminant in natural gas, and release the benzene to the atmosphere. The Environmental Protection Agency (EPA) now requires large glycol units be fitted with benzene emission control systems.

Membrane processes offer an alternative approach to natural gas dehydration. Membranes with intrinsic selectivities for water from methane of more than 500 are easily obtained, but because of concentration polarization effects and membrane bypass, actual selectivities are typically about 200. Two possible process designs are shown in Figure 8.33. In the first design, a small one-stage system removes 90% of the water in the feed gas, producing a low-pressure permeate gas representing $\sim 5\%$ of the initial gas flow. The selectivity of the membrane (200) is much greater than the pressure ratio across the membrane (33), so this process is pressure ratio limited. If the permeate gas can be used as low-pressure fuel at the site, this design is economical and competitive with glycol dehydration, but normally the loss of methane to the permeate is too large to make this process economical. In the second design, the wet, low-pressure permeate gas is recompressed and cooled, so the water vapor condenses and is removed as liquid water. The natural gas that permeates the membrane is then recovered. However, if the permeate gas must be recompressed, as in the second design, the capital cost

of the system approximately doubles. Membranes are then only competitive in special situations where glycol dehydration is not possible.

8.5.4.2 Dew Point Adjustment, C_{3+} Recovery

Natural gas usually contains varying amounts of ethane, propane, butane, and higher hydrocarbons. The gas is often close to its saturation point with respect to some of these hydrocarbons, which means liquids will condense from the gas at cold spots in the pipeline transmission system. To avoid the problems caused by condensation of liquids, the dew point of US natural gas is lowered to about -20°C before delivery to the pipeline by removing portions of the propane and butane and higher hydrocarbons. For safety reasons, the Btu rating of the pipeline gas is also usually controlled within a narrow range, typically 950–1050 Btu per cubic foot. Because the Btu values of ethane, propane, and pentane are higher than that of methane, natural gas that contains significant amounts of these hydrocarbons may have an excessive Btu value, requiring their removal. Of equal importance, these higher hydrocarbons are generally more valuable as recovered liquids than as their fuel value in the natural gas stream. For all of these reasons, almost all natural gas is treated to control the C_{3+} hydrocarbon content.

The current technology used to separate the higher hydrocarbons from natural gas streams is condensation, shown schematically in Figure 8.34. The natural gas stream is cooled by refrigeration or expansion to between -20 and -40°C . The condensed liquids, which include the higher hydrocarbons and water, are separated from the gas streams and subjected to fractional distillation to recover the individual components. Because refrigeration is capital-intensive and uses large amounts of energy, there is interest in alternative techniques, such as membrane gas separation.

A flow diagram of a membrane system for C_{3+} liquids recovery is also shown in Figure 8.34. The natural gas is fed to modules containing a higher-hydrocarbon-selective membrane, which removes the higher hydrocarbons as the permeate stream. This stream is recompressed and cooled by a cold-water exchanger to condense higher hydrocarbons. The non-condensed bleed stream from the condenser will normally still contain more heavy hydrocarbons than the raw gas, so prior to returning the gas to the feed stream, the condenser bleed stream is passed through a second set of membrane modules. The permeate streams from the two sets of modules are combined, creating a recirculation loop around the condenser, which continuously concentrates the higher hydrocarbons [35].

Today's membranes, mostly silicone rubber-based, are insufficiently selective to be widely used to recover C_{3+} liquids from pipeline gas. However, these membranes have found an application in treating raw unprocessed gas often used as fuel at remote compressor stations. The unprocessed gas is rich in heavy hydrocarbons, resulting in engine knocking and frequent shutdowns. By removing the heavy hydrocarbons, the gas octane number is substantially improved at little cost [47].

8.5.4.3 Nitrogen Removal from Natural Gas

The US pipeline specification for natural gas requires the total inert content – predominantly nitrogen – to be less than 4%. Of known US natural gas reserves, 14% contain more than 4% nitrogen and, therefore, do not meet this specification. Many of these high-nitrogen gas streams can be diluted with low-nitrogen gas to meet the

Current Technology

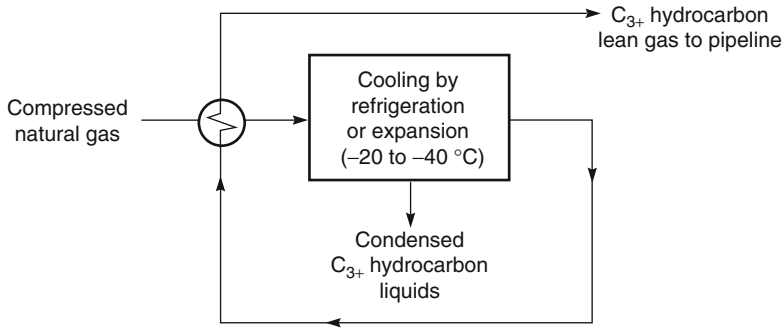
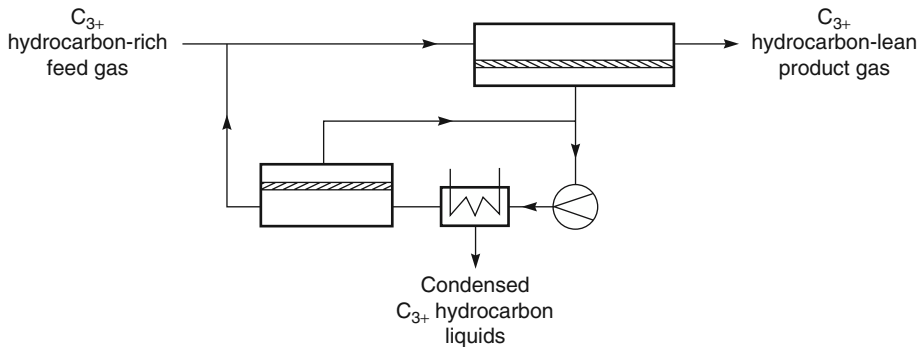
Membrane System Using C₃₊ Hydrocarbon-Selective Membranes

Figure 8.34 Recovery of C₃₊ hydrocarbons from natural gas

specification, but if dilution is not practical, a nitrogen removal unit must be installed. Cryogenic distillation is currently used to treat this gas. As of 1999, 26 cryogenic nitrogen removal plants were in operation in the United States. Cryogenic plants are most suited to large gas fields that can deliver 50–500 million scfd of gas for 10–20 years. These large gas flow rates allow the high capital cost of the cryogenic plant to be defrayed over a number of years. Many small gas wells are shut in for lack of suitable small-scale nitrogen separation technology. One technology that has been tried with some success is PSA using molecular sieves that preferentially adsorb nitrogen. Another technology is membrane separation [14]. Membranes that selectively permeate methane over nitrogen are available, but the selectivities for both types of membrane are low. For this reason, multistep or multistage systems are needed to process the gas. To date, most of the plants installed have used silicone rubber membranes that have a methane/nitrogen selectivity of 3.

A typical unit is illustrated in Figure 8.35 [14]. The operator was producing 12 MMscfd of gas that contained up to 16% nitrogen, which had a heating value of about 900 Btu/scf. The pipeline company was ready to accept the gas for dilution, provided the nitrogen

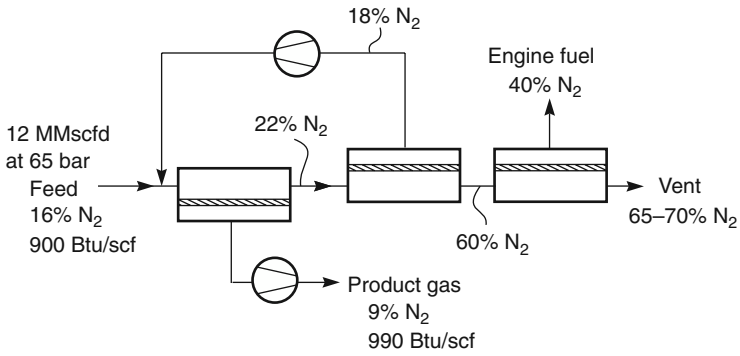


Figure 8.35 Flow diagram and a photograph of one of the two membrane skids at a 12 MMscfd membrane nitrogen removal plant installed on a high-nitrogen gas well in the Sacramento River Delta region of California

content was less than 10% and more importantly, that the gas heating value was more than 970 Btu/scf. To reach this target, the feed gas, at a pressure of 65 bar, was passed through three sets of modules in series. The permeate from the front set of modules was preferentially enriched in methane, ethane, and the C_{3+} hydrocarbons, and the nitrogen content was reduced to 9% nitrogen. These changes raised the heating value of the gas to 990 Btu/scf. This gas was compressed and sent to the pipeline. The residue gas from the first set of modules contained 22% nitrogen and was sent to a second membrane step, where it was concentrated to 60% nitrogen. The permeate from the second step contained 18% nitrogen and was recycled to mix with the feed gas. The second-step residue gas was sent to a third and final small membrane system to be fractionated. The permeate gas – containing 40% nitrogen – was used as fuel for the compressor engines.

The final residue contained 65–70% nitrogen and was essentially stripped of all C_{3+} hydrocarbons; it was vented.

Overall, this unit recovered 95% of the hydrocarbon values for delivery to the pipeline, 2% of the hydrocarbons were used as compressor fuel, and the final 3% were vented with the final residue nitrogen.

8.5.5 Vapor/Gas Separations

In the separation of vapor/gas mixtures, rubbery polymers, such as silicone rubber, can be used to permeate the more condensable vapor, or glassy polymers can be used to permeate the smaller gas. Although glassy, gas-permeable membranes have been proposed for a few applications, most installed plants use vapor-permeable membranes, often in conjunction with a second process such as condensation [31, 36] or absorption [55]. The first plants, installed in the early 1990s, were used to recover vapors from gasoline terminal vent gases or chlorofluorocarbon (CFC) vapors from the vents of industrial refrigeration plants. More recently, membranes have begun to be used to recover hydrocarbons and processing solvents from petrochemical plant purge gas. Some of these streams are quite large and discharge vapors with a recovery value of US\$2–5 million/year.

One of the most successful petrochemical applications is treatment of resin degassing vent gas in polyolefin plants [56, 57]. Olefin monomer, catalyst, solvents, and other co-reactants are fed at high pressure into the polymerization reactor. The polymer product (resin) is removed from the reactor and separated from excess monomer in a flash separation step. The recovered monomer is recycled to the reactor. Residual monomer is removed from the resin by stripping with nitrogen. The composition of this degassing vent stream varies greatly, but it usually contains 20–50% of mixed hydrocarbon monomers in nitrogen. The monomer content represents about 1% of the hydrocarbon feedstock entering the plant. This amount might seem small, but because polyolefin plants are large operations, the recovery value of the stream can be significant.

Several membrane designs can be used, but the most common is the hybrid process combining condensation and membrane separation, as shown in Figure 8.36 [58]. In this design, the compressed feed gas is sent to a condenser. On cooling of the feed gas,

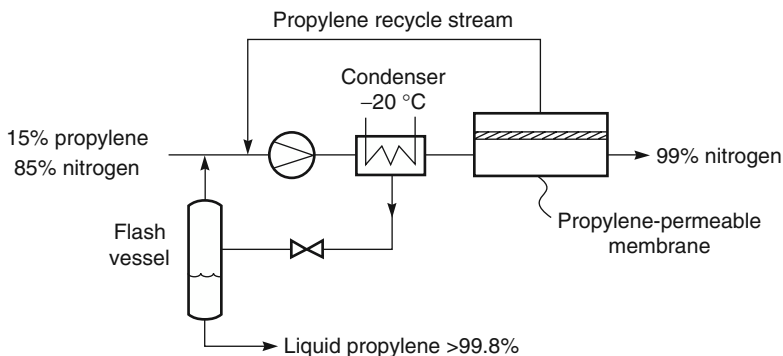


Figure 8.36 A hybrid compression–condenser–membrane process to recover propylene from a propylene/nitrogen mixture. Silicone rubber propylene-selective membranes are used

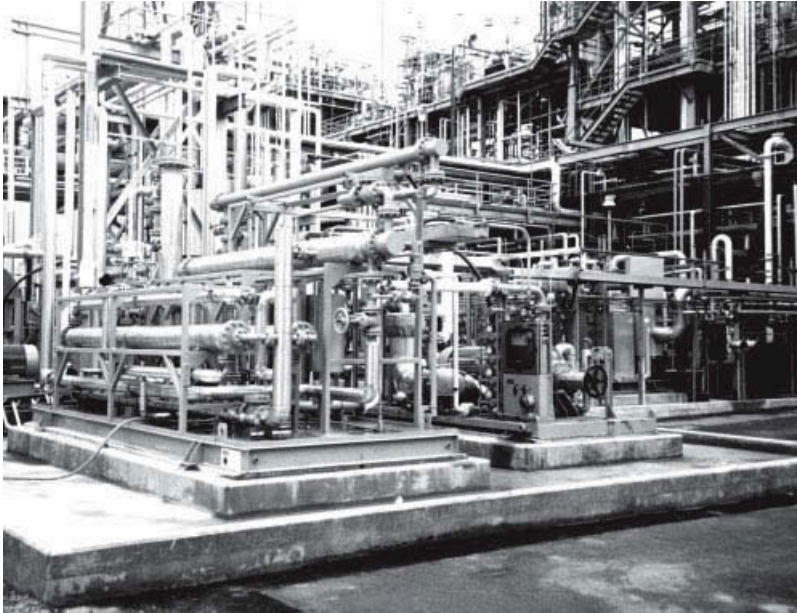


Figure 8.37 Photograph of a membrane unit used to recover nitrogen and propylene from a polypropylene plant vent gas

a portion of the propylene content is removed as a condensed liquid. The remaining, uncondensed propylene is removed by the membrane separation system to produce a 99% nitrogen stream. The permeate gas is recycled to the incoming feed gas from the purge bin.

Because the gas sent to the membrane stage is cooled, the solubility of propylene in the membrane is enhanced, and the selectivity of the membrane unit is increased. The propylene condensate contains some dissolved nitrogen so the liquid is flashed at low pressure to remove this gas, producing a better than 99.5% pure hydrocarbon product. A photograph of a propylene/nitrogen vent gas treatment system is shown in Figure 8.37.

8.5.6 Dehydration of Air

Another application of vapor/gas separation membranes is dehydration of compressed air. The competitive processes are condensation or solid desiccants, both of which are established, low-cost technologies. Membranes with water/air selectivities of more than 200 are used. The problem inhibiting their application is the loss of compressed feed air through the membrane. Compressed air is typically supplied at about 7 atm (105 psi), and the membrane permeate is at 1 atm, so the pressure ratio across the membrane is about 7. Because air dehydration membranes have a selectivity of more than 200, these membranes are completely pressure-ratio-limited. Based on Equation 8.10, this means that the permeate gas cannot be more than seven times more concentrated than the feed. The result is that a significant fraction of the feed gas must permeate the membrane to

carry away the permeate water vapor. Typically, 15–20% of the pressurized feed gas permeates the membrane, which affects the productivity of the compressor significantly. Counter-flow sweep designs of the type discussed in Chapter 4 are widely used to reduce permeant loss. Membrane air dehydration systems have found a significant market, especially for small gas streams where the reliability and simplicity of the membrane design compared to adsorbents or cooling is particularly attractive.

8.5.7 Carbon Dioxide/Hydrogen and Carbon Dioxide/Nitrogen Separations

The emergence of global warming as a significant environmental problem is likely to change the way the world produces and uses energy in the next decades [59]. The costs involved in solving the problem are huge, and so significant amounts of money are being spent looking for lower-cost solutions. A number of these solutions could involve membranes.

One of the most direct ways of addressing the problem is to separate and sequester the carbon dioxide (CO_2) produced in the production of electricity. Power production at electrical power plants is responsible for 35–40% of global CO_2 emissions. In addition, power stations are an attractive target for carbon capture, because they are large point sources of CO_2 emissions; there are about 5000 large power plants around the world. The amount of CO_2 emitted depends on the plant size and fuel feed, but an average (500 MW_e) coal-fired power plant will emit about 10 000 tons of CO_2 per day. Separating the CO_2 from these emissions and then compressing the gas to high pressure (80–100 bar) and injecting it deep underground would go a long way to mitigating the global warming problem.

Two membrane methods under development to separate CO_2 produced during power production are shown in Figure 8.38. A world-scale coal power plant (illustrated in Figure 8.38a) has a relatively straightforward flow scheme. Coal is burned with air in a boiler to make high-pressure steam, which is then sent to a steam turbine to make power. The flue gas from the boiler (at low pressure; a few inches of water above atmospheric pressure), is sent through an electrostatic precipitator to remove particulates, scrubbed to remove sulfur dioxide (SO_2) in a flue gas desulfurization unit, and then emitted directly to the atmosphere. Removal of CO_2 from the flue gas, although being considered, is not currently practiced. Amine absorption is the most commonly considered technology to separate the CO_2 , but would double the cost of the electricity produced. Membranes could be used, and a number of materials have the required CO_2/N_2 selectivities. However, for this application, extremely high permeance membranes will be needed. With the highest permeance membranes now known, plant membrane areas will be in the 1–2 million m^2 range per power plant – as large as the largest reverse osmosis plants. Possible membrane process designs are described by Merkel *et al.* [60] and Favre [61].

The Integrated Gasification Combined Cycle (IGCC) process flow scheme shown in Figure 8.38b is significantly more complex. Typically, an air separation plant is first used to produce oxygen, which together with water is then used to gasify coal at high pressure and temperature. The syngas produced (CO and H_2) is contaminated with carbon dioxide, nitrogen, methane, argon, hydrogen sulfide, particulates, and tars. The gas is quenched and scrubbed to eliminate tar and particulates. If CO_2 capture is to be used at an IGCC

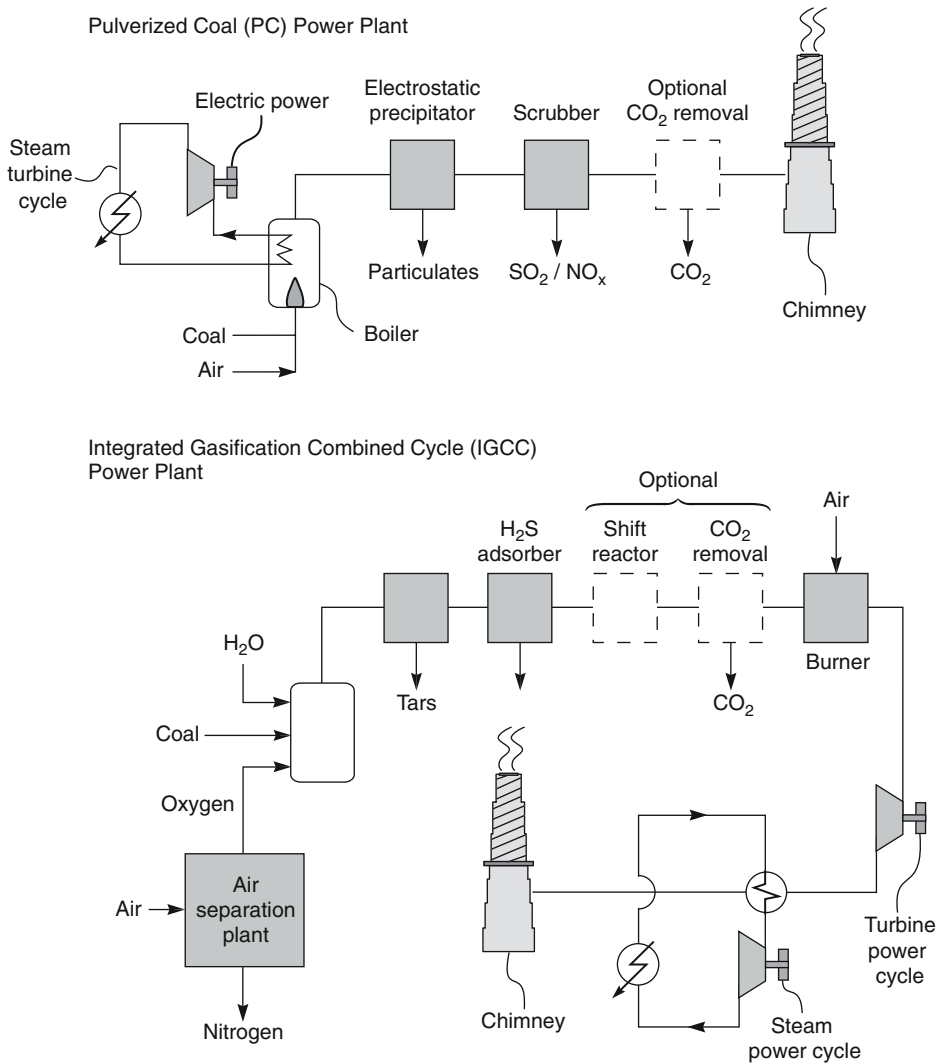


Figure 8.38 Comparison of pulverized coal (PC) and Integrated Gasification Combined Cycle (IGCC) electric power plants

plant, the syngas will be reacted with steam in a shift reactor to produce more hydrogen by the reaction:



Sulfur compounds, and optionally CO₂, are then removed by a low-temperature absorption process. The high-pressure hydrogen is then burned with air and the hot

high-pressure gas product is used to drive a gas turbine and make electricity. The hot turbine exhaust is used to produce steam that makes additional electricity in a steam turbine. The cooled gas is vented to the atmosphere. An IGCC plant has an overall heat to electric power efficiency of about 45%, significantly better than the 35% efficiency of a conventional subcritical pulverized coal power plant. However, today this advantage is more than offset by the higher capital cost of an IGCC plant. The result is that without CO₂ capture, the electric power produced at an IGCC plant is expected to be 25% more expensive than electricity produced in subcritical pulverized coal power plants.

The real benefit of IGCC technology kicks in if a cost is placed on CO₂ emissions. This is because CO₂ removal from high-pressure, high-concentration gasification streams will be significantly less costly than CO₂ removal from conventional pulverized coal power plants. The reason for the lower cost of CO₂ removal from an IGCC plant is apparent from Figure 8.38. In a conventional coal power plant, CO₂ has to be separated from a dilute (13% CO₂) and atmospheric pressure (<1.05 bar) gas stream. The gas to be separated in an IGCC plant contains about 40–50% CO₂ and is at a much higher pressure and concentration. The gas leaving the shift reactor is usually at a pressure of ~50 bar and contains about 56% hydrogen, 40% CO₂, and 4% carbon monoxide, nitrogen, methane, argon, hydrogen sulfide. Separation of CO₂ from this gas stream is far easier and lower cost than separation from flue gas. Currently, absorption of the CO₂ in chilled methanol or ethylene glycol would be used for CO₂ capture (the Rectisol® or Selexol™ processes), but hydrogen- or CO₂-permeable membranes are being developed for this application and are likely to be significantly lower cost and be less energy intensive [62].

8.5.8 Vapor/Vapor Separations

A final group of separations likely to develop into a major application area for membranes is vapor/vapor separations, such as ethylene (bp -93.9°C) from ethane (bp -88.9°C), propylene (bp -47.2°C) from propane (bp -42.8°C), and *n*-butane (bp -0.6°C) from isobutane (bp -10°C). These close-boiling mixtures are separated on a very large scale in the synthesis of ethylene and propylene, the two largest-volume organic chemical feedstocks, and in the synthesis of isobutane in refineries to produce high-octane gasoline. Because the mixtures are close-boiling, large towers and high reflux ratios are required to achieve good separations.

If membranes are to be used for these separations, highly selective materials must be developed. Several groups have measured the selectivities of polymeric membranes for ethylene/ethane and propylene/propane mixtures. Burns and Koros have reviewed these results [63]. Much of the literature data should be treated with caution. Some authors report selectivities based on the ratio of the permeabilities of the pure gases; others use a hard vacuum or a sweep gas on the permeate side of the membrane. Both procedures produce unrealistically high selectivities. In an industrial plant, the feed gas will be at 8–10 bar and a temperature sufficient to maintain the gas in the vapor phase; the permeate gas will be at a pressure of 1–2 bar. Under these operating conditions, plasticization and loss of selectivity occur with even the most rigid polymer membranes, so selectivities are usually much lower than the ratio of pure gas permeabilities suggests. Because of these problems, this application might be one for which the benefits of ceramic or carbon

membranes can justify their high cost. Caro *et al.* have reviewed the ceramic membrane literature [21].

8.6 Conclusions and Future Directions

The application of membranes to gas separation problems has grown rapidly since the installation of the first industrial plants in the early 1980s. The current status of membrane gas separation processes is summarized in Table 8.7, in which the processes are divided into three groups. The first group consists of the *established processes*: nitrogen production from air, hydrogen recovery, natural gas processing, treatment of petrochemical purge gas, and air drying. These processes represent more than 90% of the current gas separation membrane market. All have been used on a large commercial scale for 10 years, and dramatic improvements in membrane selectivity, flux, and process designs have been made during that time. For example, today's hollow fine fiber nitrogen production module generates more than 10 times the amount of nitrogen, with better quality and lower energy consumption, than the modules produced in the early 1980s. For most of these applications, the technology has reached a point at which, barring a completely unexpected breakthrough, further changes in productivity are likely to be the result of a number of small incremental changes. The one exception is the removal of carbon dioxide from natural gas. Membranes still have a small market share. Development of more selective membranes (not an impossible dream) could improve the competitiveness of the membrane process for this application substantially.

Developing processes are the second group of applications. These include recovery of light hydrocarbons from refinery and petrochemical plant purge gases, and separation of C_{3+} hydrocarbons, hydrogen sulfide, nitrogen, and water from natural gas. All of these processes are performed on a commercial scale. Significant expansion in these applications, driven by the development of better membranes and process designs, is occurring.

The "*to be developed*" membrane processes represent the future expansion of gas separation technology. The production of oxygen-enriched air is a large potential application for membranes. The market size depends completely on the properties of the membranes that can be produced. Improvements in flux by a factor of 2 at current oxygen/nitrogen selectivities would probably produce a limited membrane market; improvements by a factor of 5–10 would make the use of oxygen-enriched air in natural gas combustion processes attractive. In the latter case, the market could be very large indeed. The separation of carbon dioxide from nitrogen at electric power plants or from hydrogen in coal gasification plants are two environmental applications linked to global warming. A large research effort is underway to develop membrane and other separation technologies for these applications. If governments decide that carbon dioxide separation and sequestration will be carried out, this application could be huge. The final application listed in Table 8.7 is the separation of organic vapor mixtures (for example, propylene/propane mixtures) using membranes in competition, or perhaps in combination, with distillation. Ten years ago, plants for these separations seemed to be just around the corner. Today, they do not look so near. Membranes that retain their properties at high temperature and

Table 8.7 *Status of membrane gas separation processes*

Process	Application	Comments
Established Processes		
Oxygen/nitrogen	Nitrogen from air	Processes are all well developed. Only incremental improvements in performance and market share expected
Hydrogen/methane; hydrogen/nitrogen; hydrogen/carbon monoxide	Hydrogen recovery; ammonia plants and refineries	
Water/air	Drying compressed air	
Light hydrocarbons from nitrogen or hydrogen	Reactor purge gas, petrochemical process streams, refinery waste gas	Application is expanding
Carbon dioxide/methane	Carbon dioxide from natural gas	Many plants installed, but better membranes could change economics significantly and increase market share
Developing Processes		
VOC/air	Air pollution control applications	Several applications being developed; for example, gasoline stations and terminals, but high costs inhibit growth
C ₃₊ hydrocarbons/methane	NGL recovery from natural gas	Processes used for fuel gas conditioning, but NGL recovery requires better economics
Hydrogen sulfide, water/methane	Natural gas treatment	Niche applications, difficult for membranes to compete with existing technology for large flows
To-Be-Developed Processes		
Oxygen/nitrogen	Oxygen-enriched air	Requires better membranes to become commercial. Size of ultimate market will depend on properties of membranes developed. Could be large
Carbon dioxide/nitrogen	Carbon dioxide capture and sequestration	Potential application is enormous and technically feasible, but requires government regulation of CO ₂ emissions
Carbon dioxide/hydrogen	Hydrogen production in refineries and IGCC plants	Could be big, but also depends on adoption of government regulations for CO ₂ recovery
Organic vapor mixtures	Separation of organic mixtures in refineries and petrochemical plants	Requires better membranes and modules. Potential size of application is large

in the presence of high concentrations of organic vapors are required. This may be a separation for which ceramic membranes finally find an application. Overall, the outlook for growth in the use of membrane gas separation technology is bright.

References

1. Graham, T. (1866) On the adsorption and dialytic separation of gases by colloid septa. *Philos. Mag.*, **32**, 401.
2. Barrer, R.M. (1951) *Diffusion In and Through Solids*, Cambridge University Press, London.
3. van Amerongen, G.J. (1950) Influence of structure of elastomers on their permeability to gases. *J. Appl. Polym. Sci.*, **5**, 307.
4. Stern, S.A. (1966) Industrial applications of membrane processes: the separation of gas mixtures, *Membrane Processes for Industry, Proceedings of the Symposium*, Southern Research Institute, Birmingham, AL, pp. 196 –217.
5. Meares, P. (1954) Diffusion of gases through polyvinyl acetate. *J. Am. Chem. Soc.*, **76**, 3415.
6. Henis, J.M.S. and Tripodi, M.K. (1980) A novel approach to gas separation using composite hollow fiber membranes. *Sep. Sci. Technol.*, **15**, 1059.
7. MacLean, D.L., Bollinger, W.A., King, D.E., and Narayan, R.S. (1986) Gas separation design with membranes, in *Recent Developments in Separation Science* (eds N.N. Li and J.M. Calo), CRC Press, Boca Raton, FL, p. 9.
8. Gruen, F. (1947) Diffusionmessungen an kautschuk (Diffusion in rubber). *Experimenta*, **3**, 490.
9. van Amerongen, G.J. (1946) The permeability of different rubbers to gases and its relation to diffusivity and solubility. *J. Appl. Phys.*, **17**, 972.
10. Behling, R.D., Ohlroge, K., Peinemann, K.V., and Kyburz, E. (1989) The separation of hydrocarbons from waste vapor streams, in *Membrane Separations in Chemical Engineering*, AIChE Symposium Series Number 272, Vol. **85** (eds A.E. Fouda, J.D. Hazlett, T. Matsuura, and J. Johnson), AIChE, New York, p. 68.
11. Robeson, L.M. (1991) Correlation of separation factor versus permeability for polymeric membranes. *J. Membr. Sci.*, **62**, 165.
12. Stern, S.A. (1994) Polymers for gas separation: the next decade. *J. Membr. Sci.*, **94**, 1.
13. Robeson, L.M. (2008) The upper bound revisited. *J. Membr. Sci.*, **320**, 390.
14. Lokhandwala, K.A., Pinnau, I., He, Z., Amo, K.D., DaCosta, A.R., Wijmans, J.G. and Baker, R.W. (2010) Membrane separation of nitrogen from natural gas: a case study from membrane synthesis to commercial deployment. *J. Membr. Sci.*, **346**, 270.
15. Freeman, B.D. (1999) Basis of permeability/selectivity tradeoff relations in polymeric gas separation membranes. *Macromolecules*, **32** (2), 375.
16. Lee, S.Y., Minhas, B.S., and Donohue, M.D. (1988) Effect of gas composition and pressure on permeation through cellulose acetate membranes, in *New Membrane Materials and Processes for Separation*, AIChE Symposium Series Number 261, Vol. **84** (eds K.K. Sirkar and D.R. Lloyd), AIChE, New York, p. 93.

17. Merten, U. and Gantzel, P.K. (1968) Method and apparatus for gas separation by diffusion. US Patent 3,415,038, Dec. 1968.
18. Henis, J.M.S. and Tripodi, M.K. (1980) Multicomponent membranes for gas separations. US Patent 4,230,436, Oct. 1980.
19. Alefeld, G. and Völkl, J. (eds) (1978) *Hydrogen in Metals I: Basic Properties*, Springer-Verlag, Berlin.
20. Philpott, J.E. (1985) Hydrogen diffusion technology, commercial applications of palladium membrane. *Platinum Met. Rev.*, **29**, 12.
21. Caro, J., Noack, M., Kolsch, P., and Schäfer, R. (2000) Zeolite membranes: state of their development and perspective. *Microporous Mesoporous Mater.*, **38**, 3.
22. Brinker, J., Tsai, C.Y., and Lu, Y. (2003) Inorganic dual-layer microporous supported membranes. US Patent 6,536,604, Mar. 2003.
23. Kondo, M., Komori, M., Kita, H., and Okamoto, K. (1997) Tubular-type pervaporation module with zeolite NaA membrane. *J. Membr. Sci.*, **133**, 133.
24. Castricum, H.L., Kreiter, R., van Veen, H.M., Blank, D.H.A., Vente, J.F. and ten Elshof, J.E. (2008) High-performance hybrid pervaporation membranes with superior hydrothermal and acid stability. *J. Membr. Sci.*, **324**, 111.
25. Koresh, J.E. and Soffer, A. (1983) Molecular sieve carbon selective membrane. *Sep. Sci. Technol.*, **18**, 723.
26. Kim, Y.K., Park, H.B., and Lee, Y.M. (2005) Gas separation properties of carbon molecular sieve membranes derived from polyimide/polyvinylpyrrolidone blends: effect of the molecular weight of polyvinylpyrrolidone. *J. Membr. Sci.*, **251**, 159.
27. Park, H.B., Kim, Y.K., Lee, J.M., Lee, S.Y. and Lee, Y.M. (2004) Relationship between chemical structure of aromatic polyimides and gas permeation properties of their carbon molecular sieve membranes. *J. Membr. Sci.*, **229**, 117.
28. Williams, P.J. and Koros, W.J. (2008) Gas separation by carbon membranes, in *Advanced Membrane Technology and Applications* (eds N.N. Li, A.G. Fane, W.S.W. Ho, and T. Matsuura), John Wiley & Sons, Inc., Hoboken, NJ, pp. 599–631.
29. Yoshino, M., Nakamura, S., Kita, H., Okamoto, K.-i., Tanihara, N. and Kusuki, Y. (2003) Olefin/paraffin separation performance of carbonized membranes derived from an asymmetric hollow fiber membrane of 6FDA/BPDA-DDBT. *J. Membr. Sci.*, **215**, 169.
30. Tanihara, N., Shimazaki, H., Hirayama, Y., Nakanishi, S., Yoshinaga, T. and Kusuki, Y. (1999) Gas permeation properties of asymmetric carbon hollow fiber membranes prepared from asymmetric polyimide hollow fiber. *J. Membr. Sci.*, **160**, 179.
31. Baker, R.W. and Wijmans, J.G. (1994) Membrane separation of organic vapors from gas streams, in *Polymeric Gas Separation Membranes* (eds D.R. Paul and Y.P. Yampolskii), CRC Press, Boca Raton, FL, pp. 353–398.
32. Weller, S. and Steiner, W.A. (1950) Fractional permeation through membranes. *Chem. Eng. Prog.*, **46**, 585.
33. Coker, D.T., Freeman, B.D., and Fleming, G.K. (1998) Modeling multicomponent gas separation using hollow fiber membrane contactors. *AIChE J.*, **44** (6), 1289.
34. Stern, S.A. and Wang, S.C. (1978) Countercurrent and cocurrent gas separation in a permeation stage: comparison of computation methods. *J. Membr. Sci.*, **4**, 141.

35. Baker, R.W. and Wijmans, J.G. (1993) Two-stage membrane process and apparatus. US Patents 5,256,295 and 5,256,296, Oct. 1993.
36. Wijmans, J.G. (1992) Process for removing condensable components from gas streams. US Patents 5,199,962, April 1993 and 5,089,033, Feb. 1992.
37. Hwang, S.T. and Thorman, J.M. (1980) The continuous membrane column. *AIChE J.*, **26** (4), 558.
38. Paul, D.R. and Yampolskii, Y.P. (eds) (1994) *Polymeric Gas Separation Membranes*, CRC Press, Boca Raton, FL.
39. Koros, W.J. and Fleming, G.K. (1993) Membrane based gas separation. *J. Membr. Sci.*, **83**, 1.
40. Baker, R.W. (2002) Future directions of membrane gas separation technology. *Ind. Eng. Chem. Res.*, **41**, 1393.
41. Bollinger, W.A., MacLean, D.L., and Narayan, R.S. (1982) Separation systems for oil refining and production. *Chem. Eng. Prog.*, **78**, 27.
42. Henis, J.M.S. (1994) Commercial and practical aspects of gas separation membranes, in *Polymeric Gas Separation Membranes* (eds D.R. Paul and Y.P. Yampolskii), CRC Press, Boca Raton, FL, pp. 441–530.
43. Prasad, R., Shaner, R.L., and Doshi, K.J. (1994) Comparison of membranes with other gas separation technologies, in *Polymeric Gas Separation Membranes* (eds D.R. Paul and Y.P. Yampolskii), CRC Press, Boca Raton, FL, pp. 531–614.
44. Prasad, R., Notaro, F., and Thompson, D.R. (1994) Evolution of membranes in commercial air separation. *J. Membr. Sci.*, **94**, 225.
45. Bhide, B.O. and Stern, S.A. (1991) A new evaluation of membrane processes for the oxygen-enrichment of air. *J. Membr. Sci.*, **62**, 87.
46. Spillman, R.W. (1989) Economics of gas separation by membranes. *Chem. Eng. Prog.*, **85**, 41.
47. Baker, R.W. and Lokhandwala, K.A. (2008) Natural gas processing with membranes: an overview. *Ind. Eng. Chem. Res.*, **47**, 2109.
48. White, L.S. (2010) Evolution of natural gas treatment with membrane systems, in *Membrane Gas Separation* (eds Y. Yampolskii and B.D. Freeman), John Wiley & Sons, Ltd, Chichester, pp. 313–332.
49. Schell, W.J., Wensley, C.G., Chen, M.S.K., Venugopal, K.G., Miller, B.D. and Stuart, J.A. (1989) Recent advances in cellulosic membranes for gas separation and pervaporation. *Gas. Sep. Purif.*, **3**, 162.
50. Chatterjee, G., Houde, A.A., and Stern, S.A. (1997) Poly(urethane) and poly(ether urethane urea) membranes with high H₂S/CH₄ selectivity. *J. Membr. Sci.*, **135**, 99.
51. Lokhandwala, K.A., Baker, R.W., and Amo, K.D. (1995) Sour gas treatment process. US Patent 5,407,467, April 1995.
52. Dortmund, D. and Doshi, K. (2002) Recent developments in CO₂ removal membrane technology, *Proceedings of the Laurance Reid Gas Conditioning Conference*, University of Oklahoma, Norman, OK, p. 22.
53. Parro, D. (1985) Membrane carbon dioxide separation. *Energy Prog.*, **5**, 51.
54. Hamaker, R.J. (1991) Evolution of a gas separation membrane, 1983–1990, in *Effective Industrial Membrane Processes* (ed. M.K. Turner), Elsevier, New York, pp. 337–344.

55. Ohlrogge, K., Wind, J., and Behling, R.D. (1995) Off gas purification by means of membrane vapor separation systems. *Sep. Sci. Technol.*, **30**, 1625.
56. Baker, R.W. and Jacobs, M.L. (1996) Improve monomer recovery from polyolefin resin degassing. *Hydrocarbon Process*, **75**, 49.
57. Baker, R.W., Lokhandwala, K.A., Jacobs, M.L., and Gottschlich, D.E. (2000) Recover feedstock and product from reactor vent streams. *Chem. Eng. Prog.*, **96**, 51.
58. Baker, R.W., Wijmans, J.G., and Kaschemekat, J. (1998) The design of membrane vapor-gas separation systems. *J. Membr. Sci.*, **151**, 55.
59. Pacala, S. and Socolow, R. (2004) Stabilization wedges: solving the climate problem for the next 50 years with current technologies. *Science*, **305**, 968.
60. Merkel, T.C., Lin, H., Wei, X., and Baker, R.W. (2010) Power plant post-combustion carbon dioxide capture: an opportunity for membranes. *J. Membr. Sci.*, **359**, 126.
61. Favre, E. (2007) Carbon dioxide recovery from post-combustion processes: can gas permeation membranes compete with absorption? *J. Membr. Sci.*, **294**, 50.
62. Merkel, T.C., Zhou, M., and Baker, R.W. (2012) Carbon dioxide capture with membranes at an IGCC power plant. *J. Membr. Sci.*, **389**, 441.
63. Burns, R.L. and Koros, W.J. (2003) Defining the challenges for C₃H₆/C₃H₈ separation using polymeric membranes. *J. Membr. Sci.*, **211**, 299.