

REVIEWS

Future Directions of Membrane Gas Separation Technology

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During the past 20 years, sales of membrane gas separation equipment have grown to become a \$150 million/year business. More than 90% of this business involves the separation of noncondensable gases: nitrogen from air; carbon dioxide from methane; and hydrogen from nitrogen, argon, or methane. However, a much larger potential market for membrane gas separation lies in separating mixtures containing condensable gases such as the C₃₊ hydrocarbons from methane or hydrogen, propylene from propane, and *n*-butane from isobutane. These applications require the development of new membranes and processes. In this review, the existing gas separation applications are surveyed, and the expected growth of these and potential new applications of gas separation membranes over the next 20 years are described. The improvements in gas separation technology needed to produce these changes in the membrane industry are also discussed.

Introduction

In 1980, Permea (now a division of Air Products) launched its hydrogen-separating Prism membrane.^{1,2} This was the first large industrial application of gas separation membranes. Since then, membrane-based gas separation has grown into a \$150 million/year business, and substantial growth in the near future is likely. In this review, current membrane gas separation applications are surveyed, and some predictions of likely future developments are made.

Membranes were known to have the potential to separate important gas mixtures long before 1980, but the technology to fabricate high-performance membranes and modules economically was lacking. The development of high-flux anisotropic membranes and large-surface-area membrane modules for reverse osmosis applications occurred in the late 1960s and early 1970s. Permea then adapted this technology to membrane gas separation. Its polysulfone hollow-fiber membrane was an immediate success, particularly for the separation and recovery of hydrogen from the purge gas streams of ammonia plants. Within a few years, Permea systems were installed in many such plants. This success encouraged other companies to advance their own technologies. By the mid-1980s, Cynara (now part of Natco), Separex (now part of UOP), and GMS (now part of Kvaerner) were using cellulose acetate membranes to remove carbon dioxide from natural gas.³ At about the same time, Generon (now part of MG) introduced a membrane system to separate nitrogen from air. These first air separation systems were based on poly(4-methyl-1-pentene) (TPX) membranes with an oxygen/nitrogen selectivity of about 4. These membranes were only competitive in a few niche areas requiring 95% nitrogen, but by 1990, Generon, Praxair, and Medal^{4,5} had all produced custom polymers with oxygen/

nitrogen selectivities of 6–8. Membranes made from these polymers could produce better than 99% nitrogen and offered a cost-competitive alternative to delivered liquid nitrogen for many small users. This application has grown to represent about one-third of new nitrogen production capacity; to date, 5000–10 000 nitrogen systems have been installed worldwide. Finally, membranes are also being used for a variety of small but growing applications, such as the dehydration of compressed air and the separation of hydrocarbons from nitrogen or air. A milestone chart summarizing the development of membrane gas separation technology is displayed in Figure 1.

A list of the principal gas separation applications and the approximate market size of each application is given in Table 1. These market estimates are based on the value of the new membrane equipment produced each year. In some areas, such as nitrogen-from-air separations, the equipment producers often install the systems on an own-and-operate basis, selling the nitrogen produced to the end user. The market for this service business is significantly larger than that for the equipment given in Table 1.

Current Membrane Technology

Gas Separation Membranes. Currently, only eight or nine polymer materials have been used to make at least 90% of the total installed gas separation membrane base. Several hundred new polymer materials have been reported in the past few years, and many have substantially higher permeabilities and selectivities than those listed in Table 1. Thus, it is surprising that so few are actually used to make industrial membranes. However, permeability and selectivity are only two of the criteria that must be met to produce a useful membrane; others include the ability to form stable, thin, low-cost membranes that can be packaged into high-surface-area modules.⁶

To obtain high permeation rates, the selective layer of gas separation membranes must be extremely thin.

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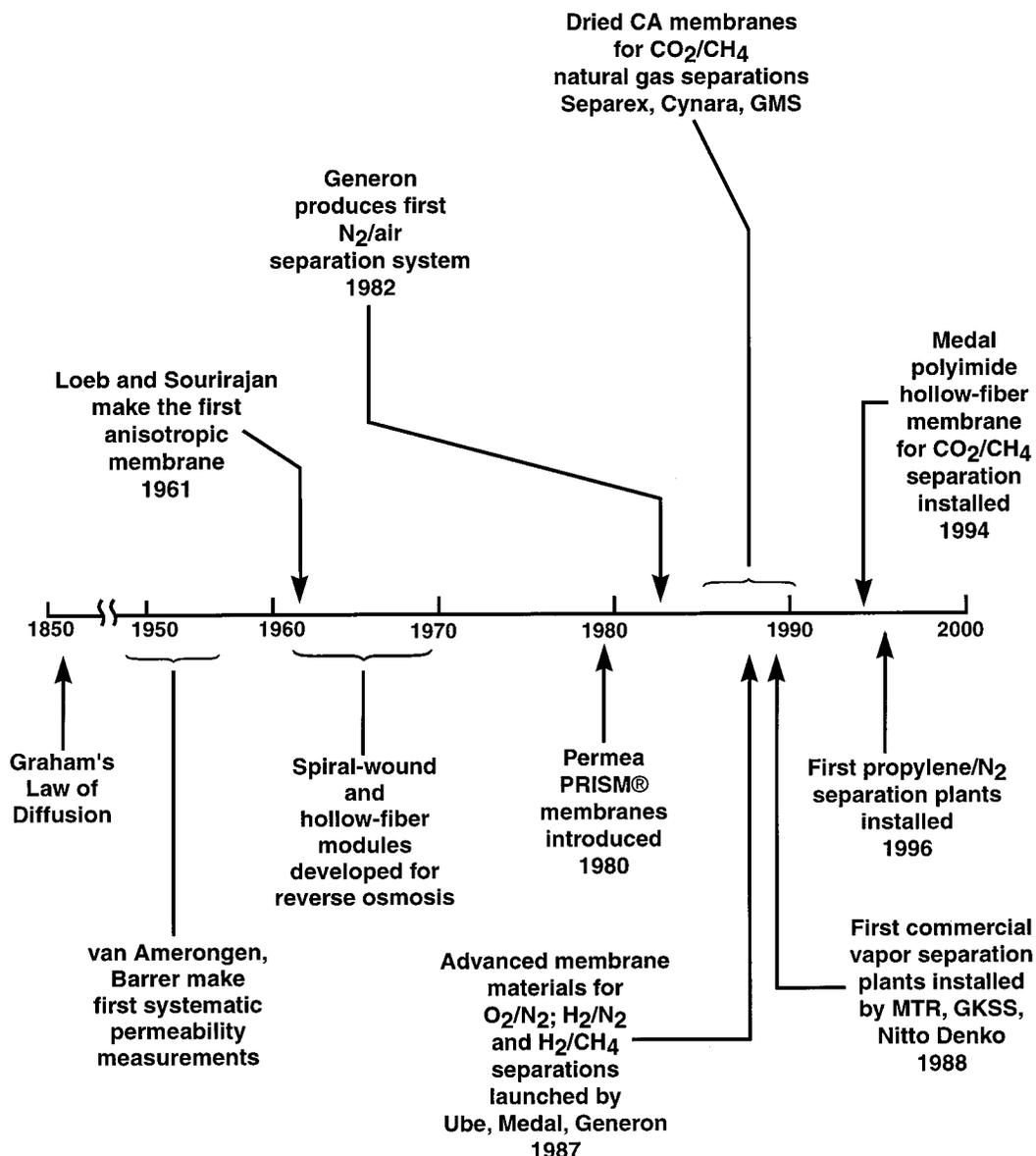


Figure 1. Milestones in the development of membrane gas separations.

Table 1. Principal Gas Separation Markets, Producers, and Membrane Systems (2000)

| company | principal markets/ estimated annual sales | principal membrane material used | module type |
|---|--|---|---|
| Permea (Air Products) Medal (Air Liquide) IMS (Praxair) Generon (MG) | large gas companies nitrogen/air (\$75 million/year) hydrogen separation (\$25 million/year) | polysulfone polyimide/polyaramide polyimide tetrabromo polycarbonate | hollow fiber |
| GMS (Kvaerner) Separex (UOP) Cynara (Natco) | mostly natural gas separations carbon dioxide/methane (\$30 million/year) | cellulose acetate | spiral-wound hollow fiber |
| Aquilo Parker-Hannifin Ube GKSS Licensees MTR | vapor/gas separation, air dehydration, other (\$20 million/year) | polyphenylene oxide polyimide silicone rubber | hollow fiber plate-and-frame spiral-wound |

Typical membranes have effective thicknesses of less than $0.5 \mu\text{m}$ and often less than $0.1 \mu\text{m}$. Many of these extremely thin membranes are made by a variant of the polymer phase separation process invented by Loeb and Sourirajan in the 1960s. These membranes have a thin, dense, nonporous skin layer that performs the separation, supported on a finely microporous substrate made from the same material that provides mechanical

strength.⁷ Membranes can be formed as flat sheets or as fine capillaries (hollow fibers) $50\text{--}500 \mu\text{m}$ in diameter. Figure 2a shows the structure of this type of membrane.

The method used to prepare anisotropic phase separation membranes limits the number of materials that can be formed into high-performance membranes. For this reason, membranes are increasingly formed as

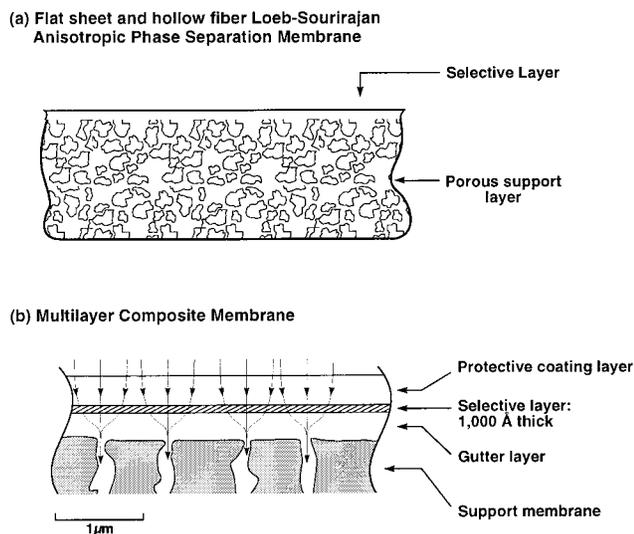


Figure 2. Gas separation membranes made by the Loeb–Sourirajan phase separation process or as composite membranes by a solution-coating procedure.⁷

composite structures of the type shown in Figure 2b. Composite membranes also contain less than 1 g of the selective polymer per square meter of the membrane, whereas anisotropic Loeb–Sourirajan membranes can use 40–60 g of the selective polymer per square meter of membrane. Increasingly, the new membrane applications require expensive, custom-made polymers for the selective layer. These polymers can cost \$10–20/g or more; therefore, they cannot be economically fabricated into Loeb–Sourirajan-type membranes.

Composite membranes consist of two or more layers of different materials. The support layer is made by the Loeb–Sourirajan procedure using a casting solution formulation such that the top skin layer is very finely microporous with pores in the 100–200 Å range. This layer performs no separation but is mechanically strong and chemically stable and can be made from a number of low-cost polymers. The selective layer can be coated directly onto the microporous support, but better membranes often result when an intermediate gutter layer made from a highly permeable, low-selectivity material is used. This gutter layer provides a smooth surface on which the ultrathin selective layer can be deposited. The gutter layer also serves to conduct the permeating gas to the pores of the microporous support. Finally, a 1- to 2- μm -thick protective layer of another highly permeable material might be deposited to protect the ultrathin selective membrane from chemical attack or mechanical abrasion.

Membrane Modules. As shown in Table 1, most of today's gas separation membranes are formed into hollow-fiber modules, with perhaps fewer than 20% being formed into spiral-wound modules. Schematics of these module types and some of the parameters that determine which type is employed for particular applications are shown in Figure 3.

Cost is, of course, always important, and low cost is a major advantage of hollow-fiber modules. Production costs are sensitive to volume, but in a hollow-fiber spinning plant operating on an around-the-clock basis, they are in the range \$2–5/m². This is much less than the production costs of equivalent spiral-wound modules, which are in the \$10–100/m² range. The module selling price will be 2–3 times higher than the produc-

tion cost, depending on the market. However, the importance of this cost advantage is often overstated. Gas separation plants, especially in refinery and petrochemical operations, require the membrane modules to be packaged in code-stamped steel pressure vessels fitted with expensive controls, valves, and instrumentation. Such plants also involve large compressors. The membrane module cost is often only 10–25% of the total cost. This means that significant reductions in membrane cost might not markedly change the cost of the complete plant.

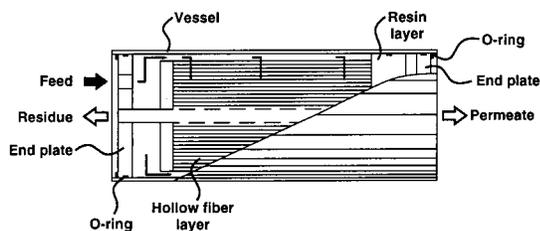
To date, two-thirds of the total gas separation market has involved the separation of nitrogen or water from air and of hydrogen from ammonia purge gas or syngas. These are clean gas streams, free of components that might foul or plasticize the membrane, so hollow-fiber modules function well. However, growing application areas for membranes are in natural gas treatment, refineries, and petrochemical plants, where the gas streams contain high levels of plasticizing, condensable vapors that degrade membrane performance. The gas might also contain suspended particulates or oil mist, which are easily trapped in stagnant areas of the module and lead to irreversible membrane fouling. The gas streams also vary in composition and flow. To address these issues, robust membrane systems able to handle changes and upsets are required. Significantly more careful and expensive pretreatment to avoid these problems is required in hollow-fiber membrane systems than in spiral-wound units. The balance between the benefits of low-cost hollow-fiber and more reliable spiral-wound modules is more even in these applications.

Current and Future Applications

Air Separation. Nitrogen. A simplified drawing of a nitrogen-from-air separation system is shown in Figure 4. The feed air is compressed to 8–10 atm with a low-cost screw compressor and then passed through a bore-side hollow-fiber module. The module operates in counter-flow mode. The first membranes used for nitrogen separation had an oxygen/nitrogen selectivity of about 4. As Figure 4 shows, these membranes can produce 95% nitrogen at a nitrogen recovery of about 50%; however, the principal market is for 99% nitrogen. At this concentration, membranes with a selectivity of 4 achieve only about 25% nitrogen recovery; the other 75% is lost with the permeate stream. The second generation of tailor-made membranes have selectivities of up to 8 and can generate a 99% nitrogen product at an overall nitrogen recovery of about 50%. The permeation rates of these membranes are lower than those of earlier low-selectivity membranes, but the cost of the extra membrane modules required to process the same volume of gas is more than offset by the reduced size of the compressor. In a membrane nitrogen-from-air plant, approximately two-thirds of the total component cost of a plant is associated with the air compressor; 20% or less is associated with the membrane modules. The energy used to power the compressor also represents the majority of the operating cost. It follows that reducing the size of the feed gas compressor is key to lowering the nitrogen production costs.

Improvements in membrane selectivity are now beginning to reach a point of diminishing returns, as illustrated by Figure 5. For example, a major improvement in membrane performance, such as increasing the oxygen/nitrogen selectivity from 8 to 12 (at the same

High-Pressure, Shell-Side Feed Hollow Fibers



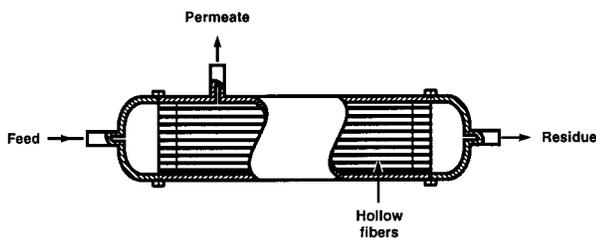
Features

- Cross-flow
- Feed gas needs very good pretreatment
- Good feed flow distribution
- Used by Medal, Cynara, others

Typical applications:

- H₂ recovery in refineries
- CO₂ removal from natural gas

Low-Pressure, Bore-Side Feed Hollow Fibers



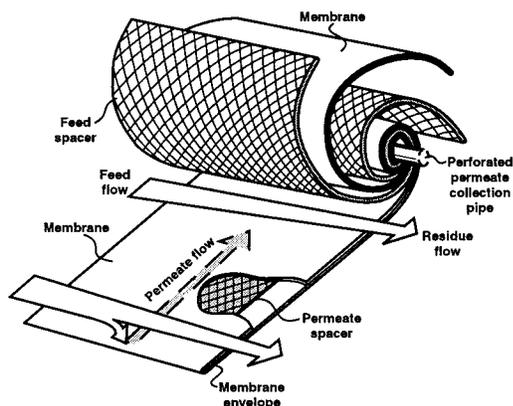
Features

- Counter-flow
- Fouling not usually a problem
- Used by Medal, Air Products, others

Typical applications:

- Nitrogen from air
- Dehydration of air

Spiral-Wound Modules



Features

- Cross-flow
- Fouling not usually a problem
- Wide range of membranes can be used
- Used by Separex, MTR

Typical applications:

- CO₂ removal from natural gas
- Vapor/gas separations

Figure 3. Principal gas separation membrane module configurations.

permeation rate), will reduce compressor size by about 20%. This might cut nitrogen production costs by 10–15%. In today's highly competitive market, such an improvement would be commercially significant for the company achieving the breakthrough, but it is unlikely to greatly expand the total market.

Oxygen. Unlike nitrogen production, the practicality of membrane-based oxygen production depends strongly on improvements in membrane performance. Various approaches to using membranes to separate oxygen from air have been investigated. All rely on selectively permeating oxygen and rejecting nitrogen. Because air already contains 80% nitrogen and because nitrogen remains on the residue side of the membrane, producing essentially pure nitrogen is comparatively easy. Producing oxygen is more difficult because some nitrogen always permeates with the oxygen, resulting in oxygen-enriched air rather than pure oxygen. The process was developed to the early commercial stage in the 1980s using silicone rubber and ethyl cellulose membranes, but the performance of these membranes was not good

enough to make the process competitive with other technologies.^{8–10}

A simplified flow schematic of a membrane separation process for producing oxygen-enriched air is shown in Figure 6a. Feed air containing 21% oxygen is passed across the surface of a membrane that preferentially permeates oxygen. In the schematic shown, the pressure differential across the membrane required to drive the process is maintained by drawing a vacuum on the permeate gas. The alternative is to compress the feed gas, but a few trial calculations show that this is never likely to be economical because of the quantity of electric power consumed.⁸ All of the feed air must be compressed, but only a small portion permeates the membrane as oxygen-enriched product. The power consumption of a vacuum pump on the permeate side of the membrane is one-half that of a feed compressor, because the only gas that needs to pass through the pump is the oxygen-enriched product. However, because the pressure difference across the membrane is less than 1 atm, vacuum operation requires a larger membrane

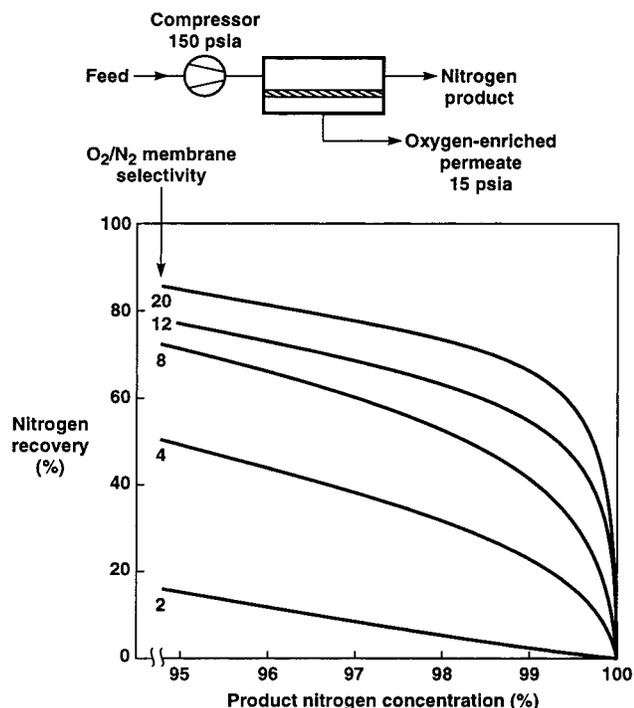


Figure 4. Nitrogen recovery as a function of product nitrogen concentration for membranes with selectivities between 2 and 20.

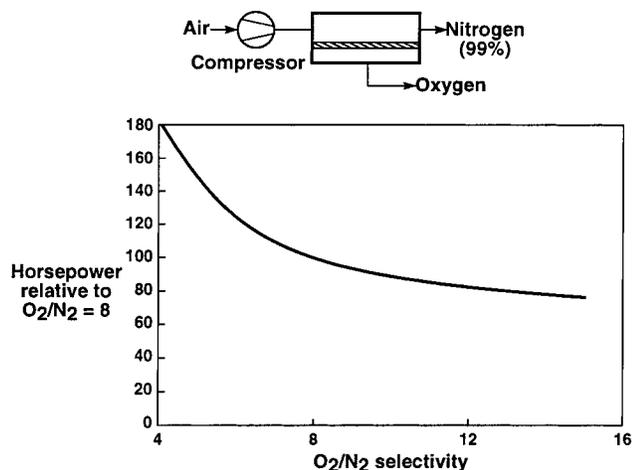
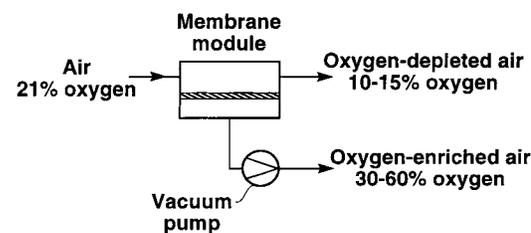


Figure 5. Effect of selectivity on the horsepower required for membrane systems producing equivalent amounts of 99% nitrogen from air (countercurrent flow, feed pressure 10 atm; permeate pressure 1 atm). Increasing the membrane selectivity from 4 to 8 reduces the compressor horsepower almost in one-half, but increasing the selectivity further has a much smaller effect.

area to produce the same flow of product gas. To make this operating mode economical, high-flux membranes and low-cost membrane modules are required.

Depending on the properties of the membrane and the pressure differential, a permeate gas containing 30–60% oxygen is produced. Oxygen-enriched air can be used in a number of processes, for example, in Claus plants and FCC catalyst regeneration in refineries or in improving the efficiency of high-temperature furnaces or cement kilns. However, most users require pure oxygen. Pure oxygen can be produced by adding a second separation stage, as shown in Figure 6b. Because the volume of gas sent to the second-stage separator is one-third to one-quarter of the volume entering the first-stage unit and because the gas is more concentrated, the second stage will be much smaller and lower-cost

(a) One-Stage Membrane Separation Process



(b) Two-Stage Separation Process

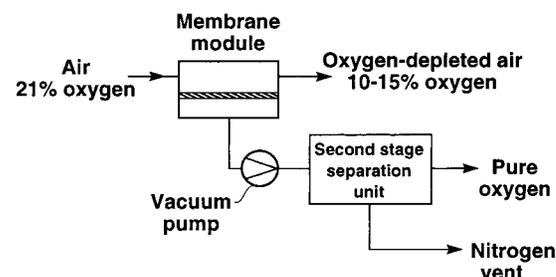


Figure 6. Membrane process flow schematics for the production of (a) oxygen-enriched air and (b) pure oxygen.

than would be the case if the same unit were operating on air. This second separation stage could be a vacuum swing adsorption system for small plants producing less than 200 tons/day of oxygen or a cryogenic fractionation system for plants producing more than 200 tons/day of oxygen.

To make membrane-produced oxygen costs competitive with current cryogenic technology, very good membranes will be required. Ideally, for this process, membranes that exhibit both high selectivity for oxygen over nitrogen (for good separation) and provide high transmembrane fluxes (to control costs) are needed. Robeson's well-known tradeoff curve (Figure 7) shows the strong inverse relationship between flux and selectivity.¹¹ Robeson's plot also shows a line linking the most permeable polymers at a particular selectivity. This line is called the upper bound, beyond which no better material is known. The movement of the upper bound between 1980 and 1991 shows the progress made from the times the first oxygen/nitrogen membranes were used and the designer polymers shown in Table 1 were synthesized. Development of improved membrane materials is a continuing topic of research, but movement of the upper bound has slowed considerably since 1991.

One way of circumventing the flux/selectivity tradeoff is by using facilitated-transport membranes. In these membranes, an oxygen-complexing carrier compound dissolved in a liquid membrane acts as a shuttle to selectively transport oxygen across the membrane.^{12,13} This process is illustrated in Figure 8. Figure 7 also shows some results obtained with liquid-facilitated-transport membranes based on a cobalt Schiff's base with the name Co(3-MeOsaltmen).¹² The spectacular permeability and selectivity of this type of membrane has maintained interest in facilitated transport despite the many problems, mostly related to poor chemical stability of the carriers and the evaporation, degradation, and other problems of the immobilized liquid membrane. The membranes shown in Figure 8 never functioned for more than a month. Nonetheless, this is an area of research where a breakthrough could lead to a significant commercial result.

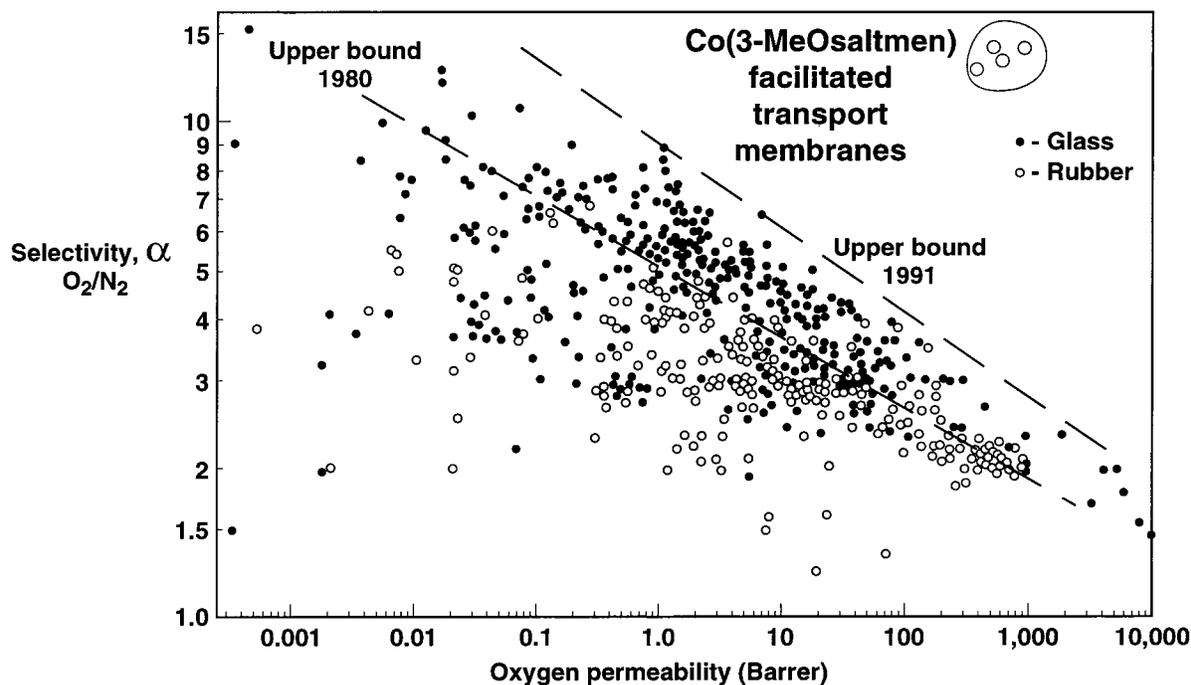


Figure 7. Oxygen/nitrogen selectivity as a function of oxygen permeability for all of the known membrane materials as of 1991. This plot by Robeson¹¹ illustrates the strong tradeoff between permeability and selectivity. The properties of some facilitated-transport membranes are also shown to illustrate the promise of this approach.

Facilitated transport

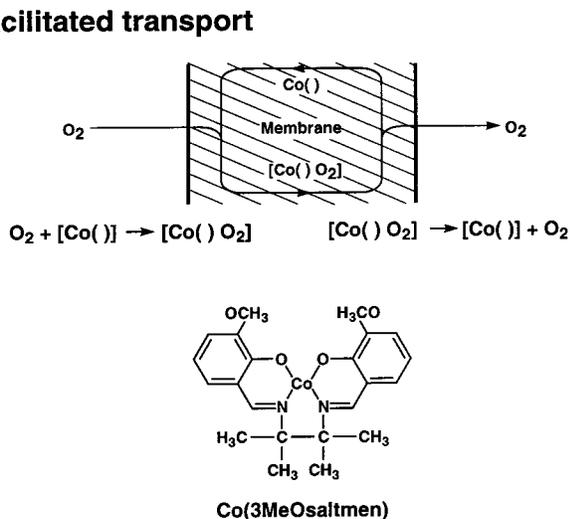


Figure 8. Schematic of a facilitated-transport membrane using the cobalt carrier Co(3-MeOsaltmen) [Co()] to transport oxygen across an immobilized liquid membrane.¹²

One promising approach to stabilizing liquid membranes, pioneered by Nishide and co-workers at Wasaga University, is to chemically bind the oxygen carrier to a polymer backbone, which is then used to form a dense polymer film containing no solvent.^{14–16} An example of this type of membrane based on poly(cobalt porphyrin) carriers is shown in Figure 9. Because the membranes contain no liquid solvent, they are more stable than liquid membranes and could potentially be formed into thin films in composite membrane form. Thus far, the selectivities and fluxes obtained with these membranes have been moderate.

Some years ago, Bhide and Stern calculated the membrane performance required to produce oxygen at a cost competitive to cryogenically produced oxygen at \$40–60/equivalent pure oxygen (EPO₂) ton.¹⁷ Their calculations were based on membranes with an installed

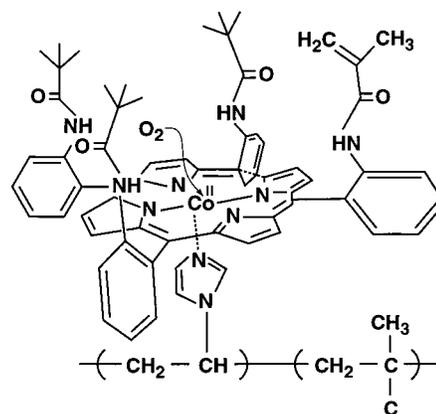


Figure 9. One of Nishide's polymeric oxygen carrier membrane materials.

cost of \$54/m² and a thin selective layer (1000 Å). The cost curves they produced are shown in Figure 10. The absolute values of these curves are sensitive to the cost assumptions made, and more optimistic numbers might be used today. However, the general form of the curves will not change. Also shown in Figure 10 is the position of the upper bound line taken from Robeson's plot. This figure shows that none of today's polymers can reach the \$40/EPO₂ ton target. It is also worth noting that the materials that come closest to this target are polymers with selectivities of 4–5 and very high permeabilities. Much academic research is aimed at producing very selective membranes, but such membranes have low permeabilities and are not likely to be optimum for this application. The figure also shows the potential of facilitated-transport membranes.

Hydrogen Separation. The first large-scale commercial application of membranes to gas separation was the separation of hydrogen from nitrogen, methane, and argon in ammonia purge gas streams—an ideal application for membranes. Hydrogen is highly permeable

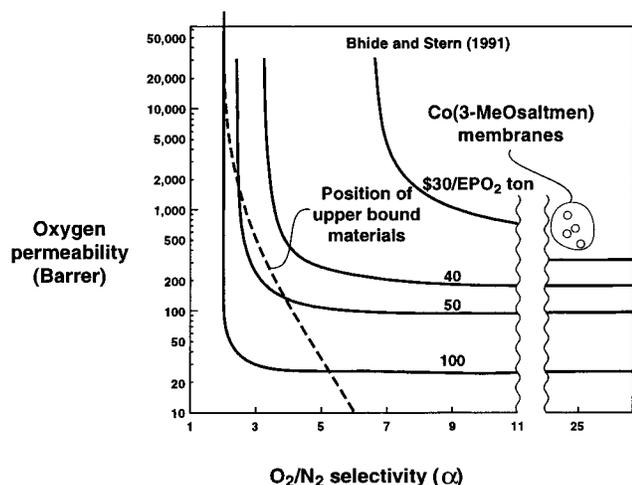


Figure 10. Bhide and Stern's estimate of the cost of producing oxygen as a function of membrane permeability and selectivity.¹⁷ In these calculations, oxygen costs are reported on an equivalent pure oxygen (EPO₂) basis. EPO₂ is defined as the amount of pure oxygen that must be mixed with normal air to obtain oxygen-enriched air at the specified concentration.

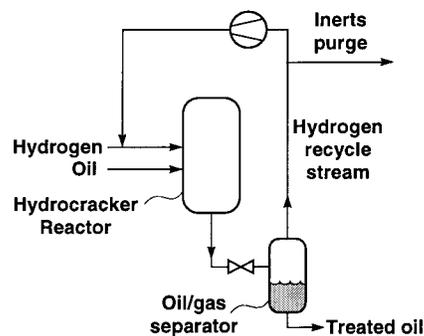
Table 2. Comparison of Chemical Feedstock and Fuel Values of Components of Refinery Gas Streams

| component | fuel value at \$2.00/MMBtu (c/lb) | chemical feedstock value (c/lb) | chemical feedstock value/fuel value |
|-----------|-----------------------------------|---------------------------------|-------------------------------------|
| methane | 4.3 | | |
| ethane | 4.1 | 4.2 | 1.0 |
| propane | 4.0 | | |
| butane | 3.9 | | |
| pentane | 3.9 | 7.0 | ~1.8 |
| hexane | 3.9 | | |
| ethylene | 4.1 | 15 | ~3.8 |
| propylene | 3.9 | | |
| hydrogen | 10.6 | 36 | ~3.4 |

compared to other gases, so selectivities and fluxes are high. Also, ammonia purge gas is delivered to the membrane at high pressure, and the hydrogen-rich permeate can be recirculated to the front of an existing feed gas compressor. Finally and most importantly, the gas is clean and free of condensable hydrocarbon vapors that might plasticize or foul the membrane. A similar application involving clean gas is hydrogen/carbon monoxide ratio adjustment in syngas plants. Several hundred hydrogen separation plants to treat these gas streams have been installed.

Another, even larger application of hydrogen-permeable membranes exists for hydrogen recovery in refineries. The demand for hydrogen in refineries is increasing because of increased environmental regulation and heavier crude. The cheapest sources of new hydrogen are refinery fuel gas streams, PSA tail gas, FCCU gas, and hydrocracker/hydrotreater off-gas. These gas streams contain 30–80% hydrogen mixed with light hydrocarbons (C₁–C₅). The opportunity represented by these streams is illustrated in Table 2, which compares the fuel and chemical feedstock values of the components. Methane and ethane have about the same value as fuel or as separated gas products, but the C₃₊ paraffins are 1.8 times more valuable if separated as LPG (liquid petroleum gas). Hydrogen and the olefins ethylene and propylene are more than 3 times more valuable if recovered rather than burned.

Current Process



Membrane Hydrogen Recovery

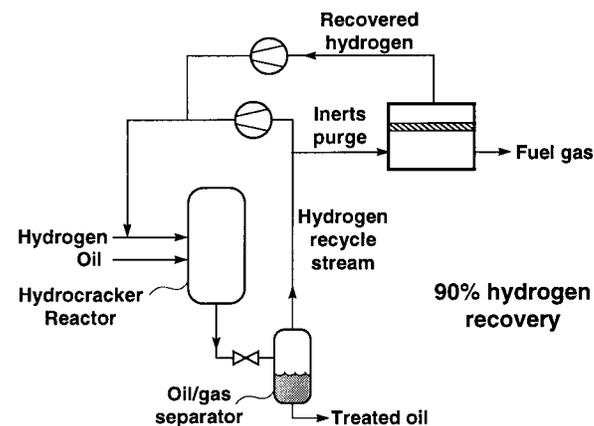


Figure 11. Use of hydrogen-permeable membranes to recover and recycle hydrogen from hydrotreater purge gas streams.

The problem that inhibits the application of membranes in refineries is poor reliability. Fouling, plasticization, and condensation of hydrocarbon vapors on the membrane surface are all serious issues. A typical application, illustrated in Figure 11, is the recovery and reuse of hydrogen from an oil hydrocracker purge gas.^{18,19} Hydrocrackers are used in refineries to break down high-molecular-weight components, to remove impurities, and to hydrogenate aromatics. Ideally, heavy oil is cracked to C₅₊ hydrocarbons, but inevitably some methane, ethane, and propane are produced as byproducts of the reaction. The oil/gas mixture from the hydrocracker is sent to a lower-pressure separator from which the C₅₊ product is removed. Unreacted hydrogen is recirculated back to the reactor. Methane, ethane, and propane accumulate in the recycle stream and must be removed as an inert purge. Typically, 3–4 mol of hydrogen are lost with every mol of light hydrocarbon purged from the reactor.

In principle, recovering hydrogen from the inert purge gas is an easy application for membranes. A simplified flow scheme for the treatment of a purge stream is shown in Figure 12. The feed gas, from a separator with a dew point of 31 °C, contains 75% hydrogen; 22% methane, ethane, and propane; and 3% C₄₊ hydrocarbons. As hydrogen is removed through the membrane, the remaining gas becomes enriched in hydrocarbons, and the dew point increases to 64 °C. To avoid condensation of hydrocarbons on the membrane the gas must, therefore, be heated to at least 64 °C. In practice, to provide a safety margin and to minimize plasticization of the membrane, the gas must be heated

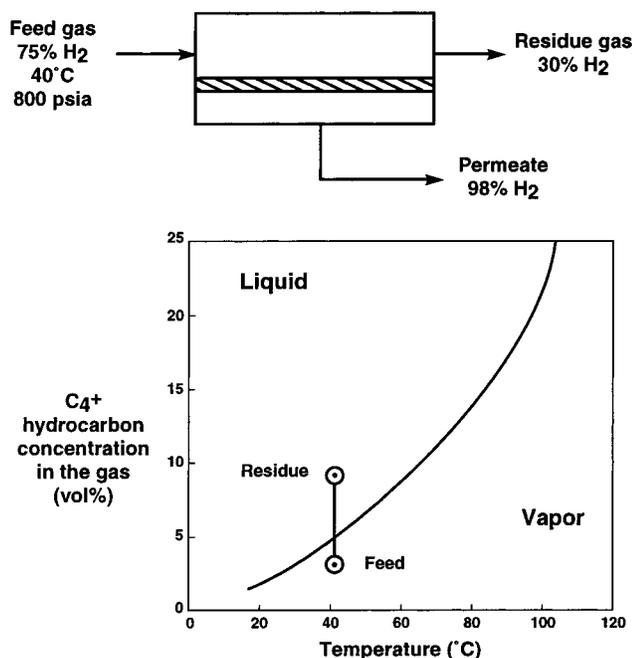


Figure 12. Illustration of the hydrocarbon condensation problem on the residue side of a hydrogen-permeable membrane. As hydrogen is removed from the pressurized feed, the gas becomes enriched in condensable hydrocarbons, and its dew point increases.

to 15–20 °C above the expected residue gas dew point. Thus, the example illustrated in Figure 12 implies that the gas must be heated to above 80 °C, at which temperature membrane and module performance can be adversely affected. Even heating the gas does not provide absolute membrane protection. Variations in gas composition are common in refinery applications, for example, when the gas source is a catalytic process from which off-gas content changes as the catalyst activity changes. More sudden changes occur when the feedstock to the upstream unit changes. The hydrocracker typically handles multiple streams from diverse sources; feed quality changes can be rapid and substantial as one or more streams are added or subtracted. At other times, process parameters, such as pressure and temperature, deviate from the normal operating range as a result of plant upsets or deliberate plant operator action to optimize a particular product. Any of these changes can bring the gas close to its dew point and cause membrane failure.

Although as many as 100 membrane plants have been installed in refineries, the market is far from saturated. There are 150 large U.S. refineries and an additional 300–400 in the rest of the world, as well as many small ones. Opportunities to place multiple hydrogen recovery units exist in all of these refineries, particularly if the operating margins and capital equipment budgets of refineries continue to increase from the very low levels of the past decade. However, the experience of operators with the plants installed to date has not been uniformly good, and the problems described above have led to shutdown and failure of a number of plants. This has inhibited more widespread adoption of the technology, but the opportunity is real. Developing new hydrogen-permeable membrane materials able to operate at high hydrocarbon partial pressures and at high temperatures is one approach. A second approach is to use better feed gas pretreatment to reduce the dew point of the feed gas to the hydrogen-permeable membrane. As these

problems are solved, this type of refinery application is likely to expand significantly.

Several authors have suggested the use of hydrogen separation membranes in large applications such as ethylene cracker cold trains.^{20–22} These are massive plants in which mixtures of hydrogen, methane, ethane, propylene, and other hydrocarbons are separated by low-temperature condensation followed by fractional distillation. A number of opportunities exist for membrane separation units in these plants. The first large opportunities are likely to be in debottlenecking processes, for example, using a membrane unit to perform an initial separation by removing hydrogen from the gas that is sent to the first-stage demethanizer column. This reduces the refrigeration load of the plant, and because the demethanizer can then operate at a higher temperature, avoids the need for special construction materials. A schematic of the process is shown in Figure 13.

A hydrogen-permeable membrane is used to produce 98% hydrogen from the gas to be fed to the low-temperature demethanizer. Hydrogen represents only a small weight fraction of this gas, but because its molecular weight is low, it can represent 20–30% or more by volume. Removing hydrogen prior to the demethanizer makes the gas much more condensable, reducing the refrigeration load as well as producing a valuable byproduct stream. Air Liquide has already installed the first unit of this type;²⁰ others might follow. This could become a very large application. Approximately 10 new crackers are built each year, and membrane units incorporated into these plants would be multimillion dollar installations.

The membranes used in the processes shown in Figures 11 and 13 are much more permeable to hydrogen than to the C₁–C₅ light hydrocarbons. This means that the hydrogen permeate stream is at lower pressure and must be recompressed before it can be reused. The cost of the permeate compressor is 2–3 times the cost of the membrane skid. One way to circumvent this problem is to use membranes that are more permeable to hydrocarbons than to hydrogen. A few materials with these properties are known, for example, some of the high-free-volume polyacetylene polymers such as poly(1-trimethyl-1-propyne) (PTMSP) and poly(4-methyl-2-pentyne) (PMP);^{23,24} the microporous absorbent carbon membranes developed by Air Products;^{25–27} and, perhaps surprisingly, silicone rubber.^{28,29} Because the hydrocarbon/hydrogen selectivity of these membranes is low, a fraction of the hydrogen is lost with the hydrocarbon-enriched permeate, and it is not economical to produce a very concentrated hydrogen-rich residue gas. Nonetheless, these deficits are offset by the elimination of an expensive permeate compressor.

A number of companies have worked on this approach, and some pilot plants have been installed. A typical application is the recovery of hydrogen from waste gas streams that would otherwise be used as fuel. The recovery of hydrogen and LPG from pressure swing adsorption (PSA) tail gas is illustrated in Figure 14, which shows a combined PSA/membrane process for treating a feed gas containing 90% hydrogen and 10% light hydrocarbons. The PSA unit fractionates the feed gas into an essentially pure hydrogen product and a low-pressure tail gas containing the hydrocarbon components and about 20% of the hydrogen in the original feed gas. Currently, this tail gas is usually used as fuel. In the process shown, the gas is compressed to 400 psia

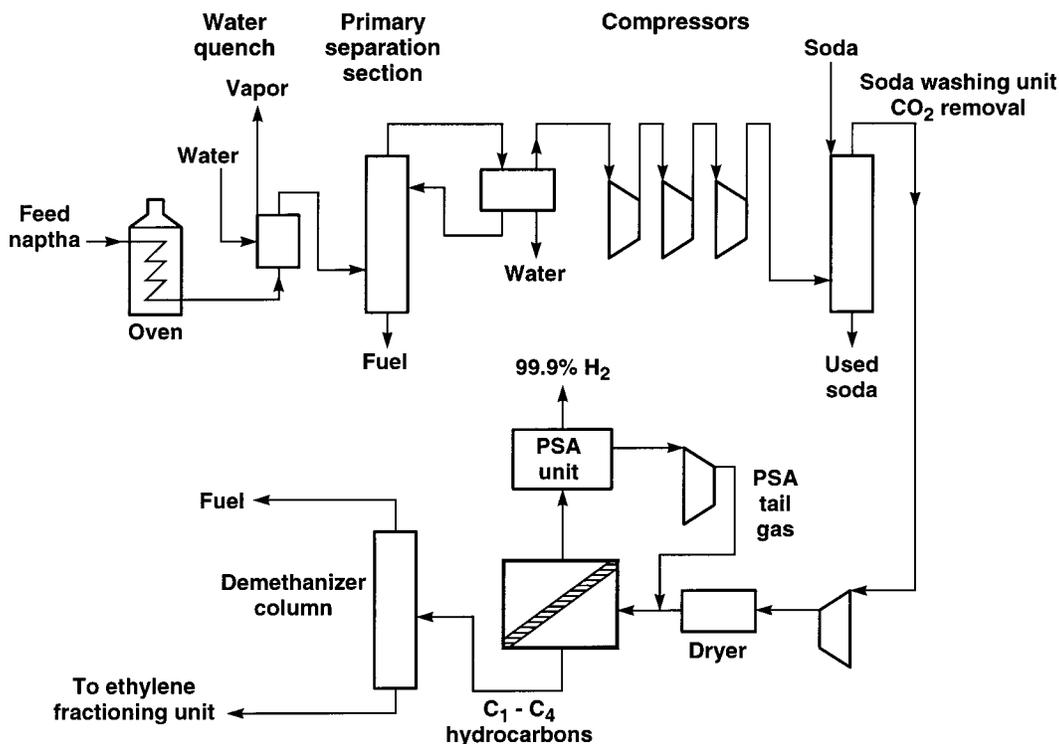


Figure 13. Use of hydrogen-permeable membranes to separate hydrogen from light hydrocarbons in a cracker before the gas is sent to the demethanizer column, the first step in the cracker cold train. By this means, the operating temperature of the first demethanizer column is raised significantly, resulting in operating and capital cost savings. A PSA unit is used to upgrade the hydrogen-rich gas from the membrane unit to 99.9% hydrogen and to recycle any ethylene that permeates the membrane.²⁰

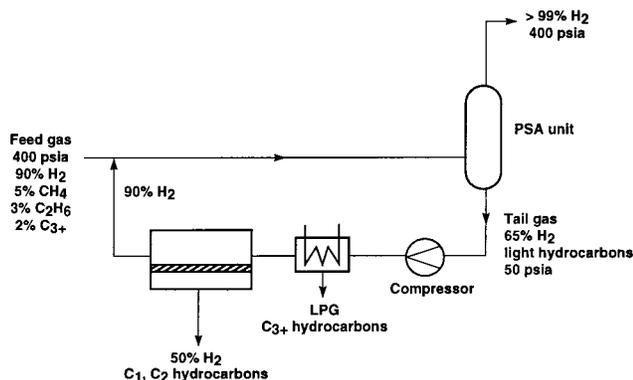


Figure 14. Combination of a hydrocarbon-permeable membrane with a PSA unit to increase the recovery of hydrogen from a refinery gas stream from 87 to 95%.²⁹

and cooled to remove a fraction of the C_{3+} hydrocarbons as a liquid condensate. The off-gas from the condenser is then passed through a silicone-rubber-based membrane unit that selectively permeates the remaining hydrocarbons. This step produces a 90% hydrogen residue stream that is recycled to the PSA step and a low-pressure permeate that can be sent to the refinery fuel gas stream. Thereby, more than half of the hydrogen formerly lost with the tail gas is recovered and recycled to the feed gas, increasing the overall hydrogen recovery of the process from 87 to 94%.²⁹

Natural Gas Separations. U.S. production of natural gas is about 20 trillion scf/year; total worldwide production is about 50 trillion scf/year. 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

Table 3. Composition Specifications for Natural Gas for Delivery to the U.S. National Pipeline Grid

| component | specification |
|--|---|
| carbon dioxide | <2% |
| water | <120 ppm |
| hydrogen sulfide | <4 ppm |
| C_{3+} content | 950–1050 Btu/scf dew point -20°C |
| total inert gases (N_2 , CO_2 , He, etc.) | <4% |

addition, the gas contains undesirable impurities: water, carbon dioxide, nitrogen, and hydrogen sulfide. Although the composition of raw gas varies widely, the composition of gas delivered to the pipeline is tightly controlled. Consequently, all natural gas requires some treatment, and about 20% requires extensive treatment, before delivery to the pipeline. Typical U.S. natural gas pipeline specifications are reported in Table 3. The opportunity for membranes lies in processing the gas to meet these specifications. The total worldwide market for new natural gas separation equipment is probably \$5 billion/year, making natural gas treatment by far the largest industrial gas separation application. Currently, membrane processes have less than 1% of this market, almost all for the removal of carbon dioxide.

Carbon Dioxide. About 17% of all domestic raw natural gas must be treated to remove carbon dioxide before it can be passed to the pipeline.³⁰ The technology most widely used is amine absorption, but amine plants suffer from a number of problems. First, capital costs are high. Second, operation of these plants is complex, usually requiring full-time supervision, and maintenance is expensive and labor-intensive. During the period 1980–1985, installation of membrane plants using carbon dioxide selective cellulose acetate membranes began,³ mainly at small gas processing plants (less than 5 million scfd). Amine systems are too

complex and expensive for these small producers. Currently, the market for membrane acid gas separation systems can be divided as follows:³¹ (1) Very small systems (less than 5 million scfd). 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 (5–40 million scfd). Two-stage membrane systems are used to reduce methane loss. In this gas flow range, amine and membrane systems compete—the choice depends on site-specific factors. (3) Medium to large systems (more than 40 million scfd). In general, membrane systems are too expensive to compete with amine plants in this range. However, a number of large membrane systems have been installed on offshore platforms, at carbon dioxide oilfield flood operations, or where site-specific factors particularly favor membranes.

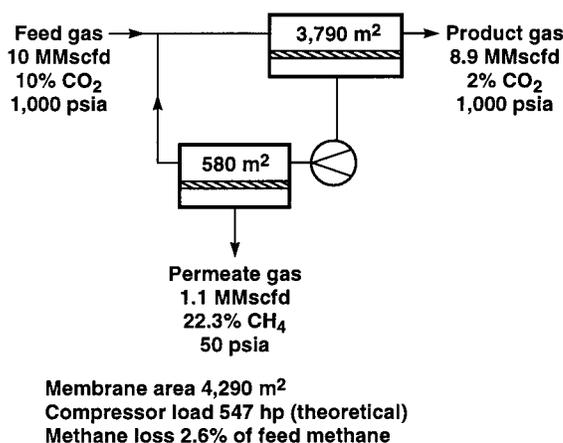
In principle, combinations of membrane systems to remove the bulk of the carbon dioxide and amine plants to act as polishing systems would be a low-cost alternative to amine plants. However, this approach has not been widely used, because the savings in capital cost are largely offset by the increased complexity of the plant, which now contains two separation processes.^{32,33} One exception has been in carbon dioxide flood-enhanced oil recovery projects, in which the composition and volume of the gas to be treated changes significantly over the project lifetime. The modular nature of membrane units allows easy retrofitting to existing amine plants so that the performance of the plant can be adjusted to meet the changing separation requirements. Also, the capital costs of the separation system can be spread more evenly over the project lifetime.

In summary, despite the advantages of a simple flow configuration and low-maintenance operation, membrane systems cannot compete with current amine systems for most carbon dioxide removal applications. The problem is the low selectivity and flux of current membranes. Cellulose acetate membranes have a carbon dioxide/methane selectivity of about 12–15 under normal operating conditions. This is significantly below the selectivity calculated from pure gas measurements and reflects the effect of membrane plasticization by carbon dioxide and heavier hydrocarbons. Despite this modest selectivity, cellulose acetate is only now being slowly replaced by polyimide and polyaramide membranes with selectivities of 20–25. The development of stable membranes with carbon dioxide/methane selectivities of 40 during operation would dramatically change the competitive position of membranes, as illustrated by the sample calculation given in Figure 15. The figure compares the performance of two-stage membrane systems designed to treat a 10-MMscfd gas stream containing 10 vol % of carbon dioxide using cellulose acetate membranes and a yet-to-be developed high-performance membrane.

The system shown in Figure 15a is fitted with good-quality cellulose acetate membranes, the current industry standard. The membrane selectivity for carbon dioxide over methane is about 15, and the carbon dioxide flux about $50 \times 10^{-6} \text{ cm}^3(\text{STP})/(\text{cm}^2 \text{ s cmHg})$. The second system is fitted with a yet-to-be developed membrane with a carbon dioxide/methane selectivity of 40 and a carbon dioxide flux of $100 \times 10^{-6} \text{ cm}^3(\text{STP})/(\text{cm}^2 \text{ s cmHg})$. The increased flux and selectivity have the following effects: (1) the membrane area is reduced by 40% (2540 m² versus 4290 m²), (2) the compressor

(a) Cellulose Acetate Membranes

CO₂ flux: $50 \times 10^{-6} \text{ cm}^3(\text{STP})/(\text{cm}^2 \text{ s cmHg})$
CO₂/CH₄ selectivity: 15



(b) High Performance Membranes

CO₂ flux: $100 \times 10^{-6} \text{ cm}^3(\text{STP})/(\text{cm}^2 \text{ s cmHg})$
CO₂/CH₄ selectivity: 40

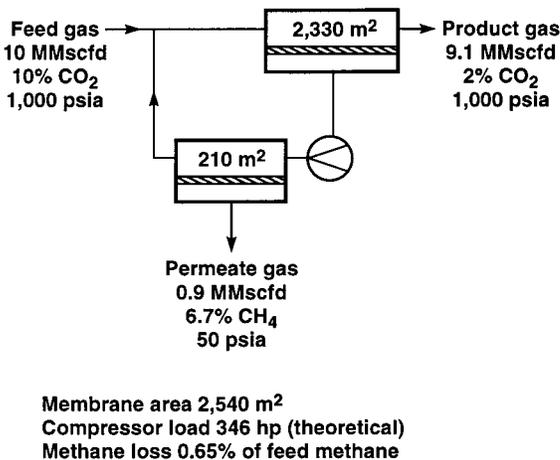


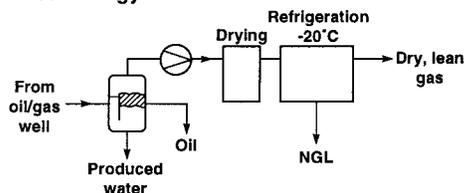
Figure 15. Comparison of system performance using (a) existing cellulose acetate membranes and (b) yet-to-be-developed high-performance membranes to treat a 10-MMscfd gas stream containing 10% carbon dioxide.

load is reduced by 35% (346 hp versus 547 hp), and (3) the methane loss in the permeate is reduced by 75% (0.65% of feed versus 2.6% of feed).

Numerous membrane materials with the target properties have been reported in the academic and patent literature. Unfortunately, most of these membranes do not maintain their properties when tested under real-world conditions. However, cellulose acetate is gradually being displaced by more selective membrane materials, and this trend is likely to continue. For this reason, the prospects for further growth in this application are good.

NGL Removal. Essentially all natural gas must be treated to lower the concentration of C₃₊ hydrocarbons in the gas. Raw gas is usually almost saturated with respect to these compounds, which will condense at cold spots in the pipeline. To avoid condensation, the dew point of the gas is usually lowered to about $-20 \text{ }^\circ\text{C}$

(a) Current Technology



(b) Membrane Technology

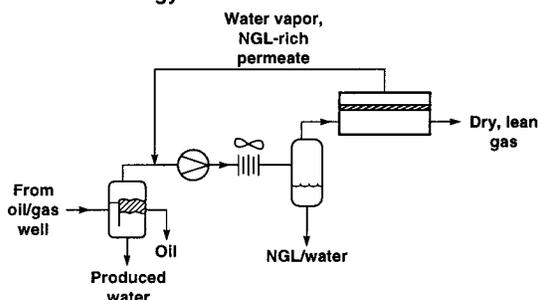


Figure 16. (a) Current conventional technology and (b) the membrane approach to the removal of water and heavy hydrocarbons from associated gas.

before delivery to the pipeline by the removal of propane, butane, and higher hydrocarbons.

A schematic representation of a conventional gas conditioning unit is shown in Figure 16a. The application is for associated gas, the low-pressure gas produced as a byproduct of oil production. The gas is usually compressed and dried by glycol absorption and then cooled to $-20\text{ }^{\circ}\text{C}$ in a propane refrigeration plant; dry, lean gas is produced.³⁴ The membrane process is shown in Figure 16b.³⁵ After compression and cooling to about $30\text{ }^{\circ}\text{C}$ by an air cooler, a portion of the water and C_3+ hydrocarbons is condensed and recovered. The off-gas from the condenser is then passed across the surface of a silicone rubber membrane that preferentially permeates condensable vapors such as C_3+ hydrocarbons and retains methane and ethane. Unlike the glassy membranes used in earlier applications, rubbery membranes

separate by virtue of permeant solubility in the membrane material rather than the permeant diffusion coefficient. A more detailed description of this transport mechanism is given elsewhere.³⁶ The heavy-hydrocarbons- and water-rich gas that permeates the membrane is recirculated to the front of the feed gas compressor. Water and C_3+ hydrocarbons are eventually removed as condensed liquids. This process is at the early commercial stage: A number of large trials have been performed, more are under way, and the first demonstration system has been installed. Judging from current performance data, the technology will be very competitive with propane refrigeration for flows up to 20–30 million scfd. At higher gas flows, economies of scale favor condensation by turbo expansion. Nonetheless, a healthy market should develop for these membrane systems over time because of their lower costs and simple flow schemes.

Natural Gas Dehydration. All natural gas must be dried before use. The current technology is glycol absorption; an estimated 42 000 glycol dehydration systems are operating in the United States.³⁷ This represents a significant opportunity for membrane technology. Water is a small, condensable compound, so many membranes have high water permeabilities and water/methane selectivities of several hundred. Because selectivities are so high, membranes have no technical problem in removing water from the feed gas. However, glycol dehydration is well accepted by the industry, and its cost is very low. To be competitive, the membrane system must minimize loss of methane with the permeate water. Some designs that have been considered are depicted in Figure 17. In the first design, shown in Figure 17a, a small one-stage membrane system removes 90% of the water in the feed, producing a permeate gas representing 4–5% of the initial gas flow. This methane loss cannot be reduced by making the membrane more selective because the process is completely pressure-ratio-limited. If the permeate gas could be used as a low-pressure fuel, this design would be economical. Unfortunately, most plants do not need this quantity of fuel gas, and the stream is too large to flare. A compressor could be used to recompress the

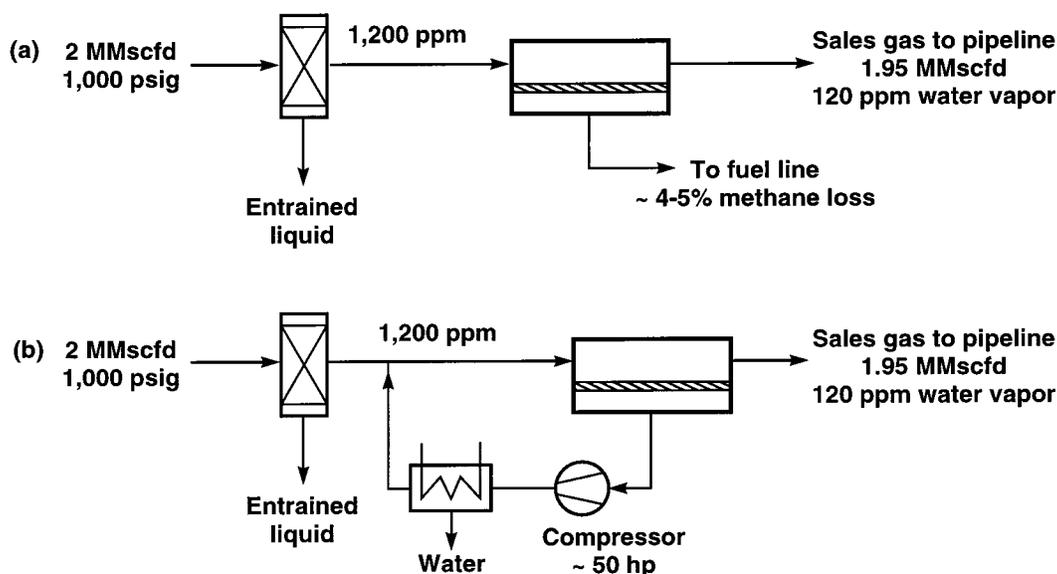


Figure 17. Two simple membrane processes for the removal of water from high-pressure natural gas. Water/methane membrane selectivities are very high (>200), so the separation achieved is completely pressure-ratio-limited.

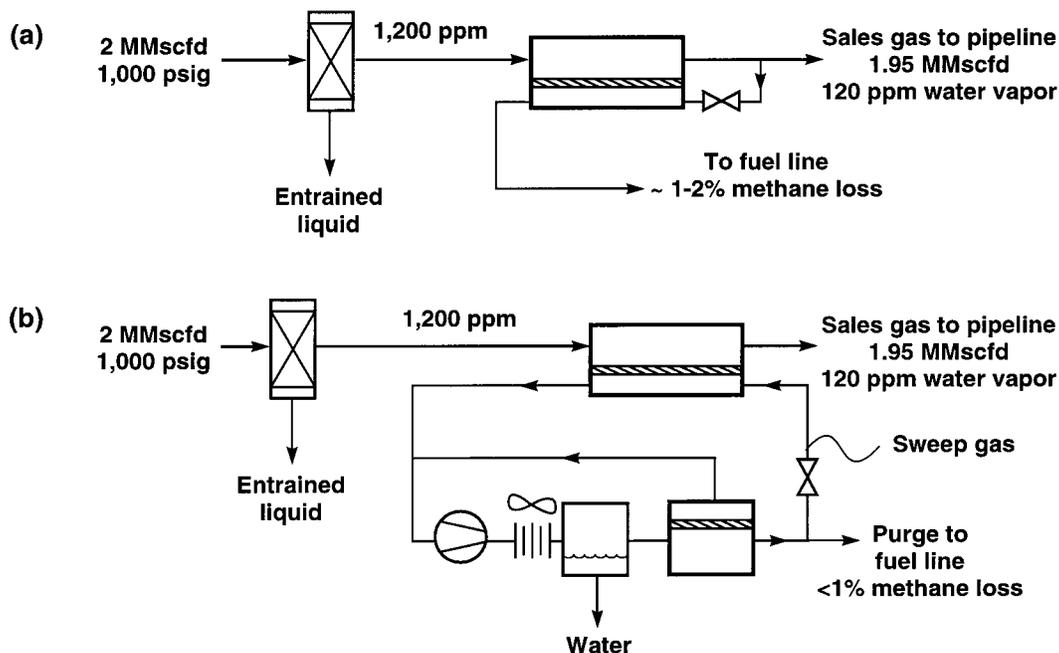


Figure 18. Use of countercurrent hollow-fiber modules to reduce methane loss in the drying of high-pressure natural gas.

permeate gas, as shown in Figure 17b, but the capital costs of the system would then more than double, and the process would only compete with glycol dehydration where glycol units are not well suited, for example, on offshore platforms.

The importance of the pressure ratio in the separation of gas mixtures can be illustrated by considering the separation of a gas mixture with component concentrations (mol %) n_{i_0} and n_{i_1} at a feed pressure of p_0 . A flow of component across the membrane can only occur if the partial pressure of component i on the feed side of the membrane, $n_{i_0}p_0$, is greater than the partial pressure of component i on the permeate side of the membrane, $n_{i_1}p_1$. That is

$$n_{i_0}p_0 > n_{i_1}p_1$$

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

$$\frac{n_{i_1}}{n_{i_0}} \leq \frac{p_1}{p_0}$$

This means that the separation achieved can never exceed the pressure ratio of p_1/p_0 , no matter how selective the membrane.

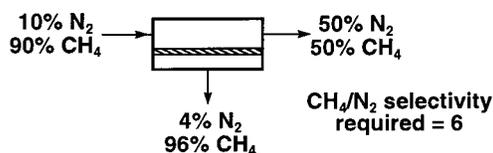
Hollow-fiber countercurrent-flow membrane modules of the type shown in Figure 3 are being developed by Air Products to minimize methane loss. For example, in the process illustrated in Figure 18a, a portion of the dried feed gas is used as a sweep on the permeate side of the membrane.^{38–40} Using a sweep gas reduces the membrane area and, more importantly, reduces methane loss to 1–2% of the feed gas. If a convenient place exists to send or use the gas, this process might be useful. An alternative design is to use a small, secondary methane drying loop to produce clean, dry methane to be used as a sweep gas, as shown in Figure 18b. In this design, methane loss is reduced to a fraction of 1%. However, the complexity of the system probably limits its application to relatively large dehydration plants.

Other designs are also being considered. The first plants have been installed, and this application will likely grow over the years, but it will do so slowly because of stiff price competition from glycol dehydration.

Nitrogen Removal. The natural gas pipeline specification for inert gases is less than 4%. On this basis, about 11% of known U.S. reserves (or about 16 trillion scf of gas) are subquality because of high nitrogen content. A further 6% (9 trillion scf) are subquality because of high nitrogen content plus high carbon dioxide and/or hydrogen sulfide content. Gas containing less than 10% nitrogen can generally be used by blending it with sufficient low-nitrogen-content gas for the product to meet the pipeline specification. However, blending is no longer feasible if the gas contains more than about 10% nitrogen, so much of this gas is not currently produced. This is particularly true if the carbon dioxide and hydrogen sulfide contents are also high. The value of the 10 trillion scf of shut-in gas containing 10–25% nitrogen is about \$30 billion.⁴¹ Because of the high value, several processes have been evaluated for the removal of nitrogen. Of these, only cryogenic technology has been used on a significant scale. To achieve economies of scale, cryogenic plants are typically very large, with a processing capacity of 100–500 MMscfd of gas. Most plants also produce helium and natural gas liquids (NGL); these coproducts contribute significantly to the overall economics. Nonetheless, cryogenic natural gas/nitrogen separation plants are marginally economical at best. No current technology can economically treat nitrogen-rich gas from smaller fields with flows in the 1–20 MMscfd range.

Membranes could be used to separate this mixture. The challenge is to develop membranes with the necessary nitrogen/methane separation characteristics. Either glassy polymers, usually nitrogen-permeable, or rubbery polymers, usually methane-permeable, could be used. Figure 19 compares trial calculations performed for methane-permeable and nitrogen-permeable membranes. The figure shows the calculated membrane selectivity required to separate a gas stream containing 10% nitrogen and 90% methane into two streams: one,

(a) Methane-permeable membrane



(b) Nitrogen-permeable membrane

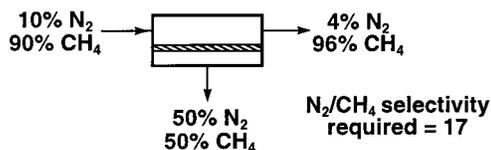


Figure 19. One-stage membrane separations of 10% nitrogen/90% methane feed gas to produce a 50% nitrogen/50% methane reject stream and a 4% nitrogen/96% methane product gas. This target can be achieved by (a) a methane-permeable membrane with a selectivity of 6, close to today's membranes, or (b) a nitrogen-permeable membrane with a selectivity of 17, far higher than that of the best membranes known.

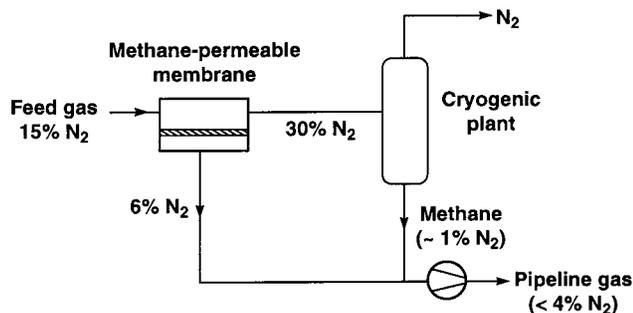


Figure 20. Combined membrane/cryogenic distillation plant for removal of nitrogen from natural gas.⁴²

containing 4% nitrogen, to be delivered to the pipeline and the other, containing 50% nitrogen, to be used as onsite fuel. The separation corresponds to 93% recovery of methane in the product gas stream, a very acceptable target for a nitrogen-removal process. A methane-permeable membrane with a methane/nitrogen selectivity of 6 can achieve the target separation. In contrast, a nitrogen-permeable membrane must have a methane/nitrogen selectivity of 17 to achieve the target separation. The best polymeric nitrogen-selective membrane currently known has a selectivity of 2–3, far below the value required. This is why the most developed membrane process uses methane-permeable membranes. This approach requires recompression of the permeate gas for delivery to the pipeline, but the cost is not high enough to significantly impact process economics.

Methane-permeable membranes can be used in stand-alone processes or in combination with a cryogenic plant to polish the gas. An example of a combined process is shown in Figure 20.⁴² The feed gas, containing 15% nitrogen, is separated by a methane-permeable membrane into two streams: a residue stream containing 30% nitrogen to be sent to the cryogenic plant and a permeate stream containing 6% nitrogen to be sent to the product gas stream. The membrane unit reduces the volume of the gas to be treated by the cryogenic unit by more than half. Simultaneously, the concentrations of water, C₃₊ hydrocarbons, and carbon dioxide are brought

to very low levels, because these components also preferentially permeate the membrane. Removal of these components prior to cryogenic condensation is required to avoid freezing in the plant. The savings produced by using a smaller, simpler cryogenic plant more than offset the cost of the membrane unit.

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,^{43,44} most installed plants use vapor-permeable membranes, often in conjunction with a second process such as condensation^{36,45} or absorption.^{46,47} The first plants, installed in the early 1990s, were used to recover gasoline 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 \$1–2 million/year.

One of the most successful petrochemical applications is illustrated in Figure 21: treatment of resin degassing vent gas in a polyolefin plant.^{48–50} 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.

The treatment of this vent gas with a membrane system is shown in Figure 21. The compressed vent gas from the resin degassing step is sent to a condenser, where a portion of the hydrocarbon vapors is removed as a liquid. The remaining uncondensed hydrocarbons and nitrogen are separated in the membrane unit, which produces a hydrocarbon-enriched permeate and a purified nitrogen stream (>98% nitrogen). This nitrogen is recycled to the resin degasser. The hydrocarbon-enriched permeate is recycled to the front of the compressor; the hydrocarbon liquid stream is upgraded in the monomer purification section of the plant and then recycled to the reactor.

Vapor/Vapor Separations. A final group of separations likely to develop into a major application area for membranes, if the appropriate membrane materials can be developed, is vapor/vapor separations, such as ethylene (bp –103.9 °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.

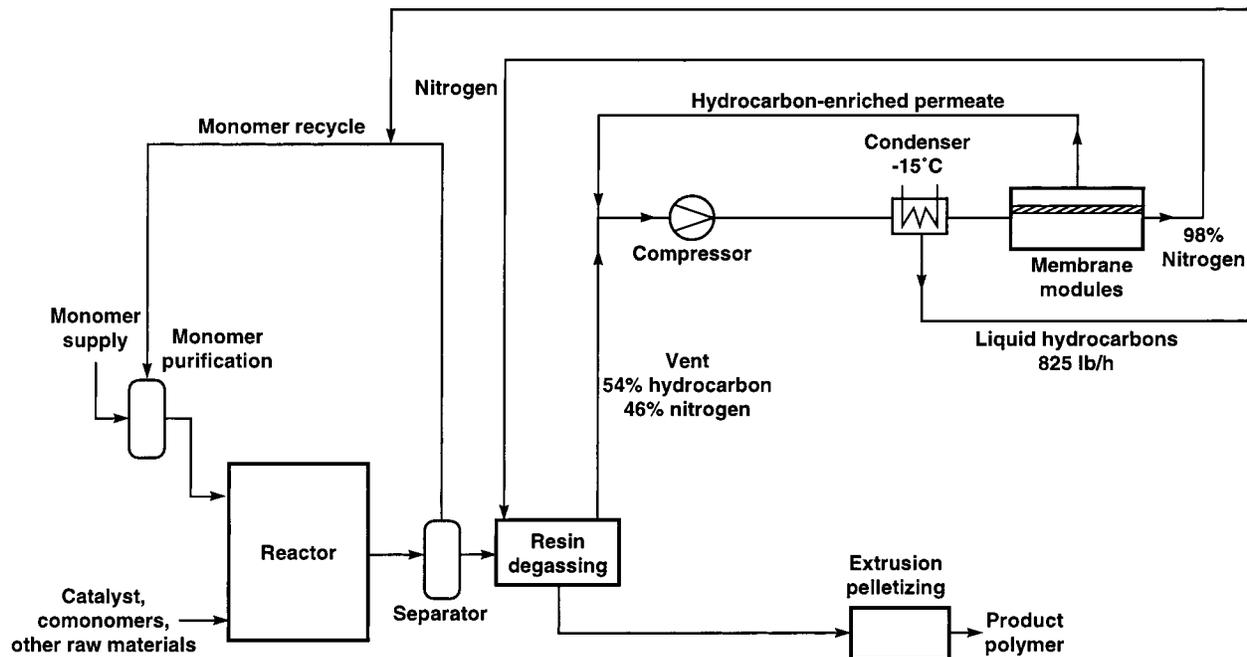


Figure 21. Membrane separation system applied to monomer recovery from a polyolefin resin degassing vent stream.

Several groups have measured the selectivities of polymeric membranes for these gas mixtures, particularly ethylene/ethane and propylene/propane mixtures.^{51–54} However, these 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 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 100–150 psig and a temperature sufficient to maintain the gas in the vapor phase; the permeate gas will be at a pressure of 10–20 psig. Under these operating conditions, plasticization and loss of selectivity occur with even the most rigid polymer membranes, so selectivities are usually low. Because of these problems, this application might be one for which the benefits of ceramic or carbon fiber membranes can justify their high cost. Caro et al. have recently reviewed the ceramic membrane literature.⁵⁵

Another approach is to use facilitated-transport membranes. This approach was taken to the small pilot-scale by Hughes and Steigelman at Standard Oil in the mid-1980s.⁵⁶ The work was eventually abandoned because of membrane stability problems. More recently, solid polymer electrolyte membranes have been reported to achieve good selectivities and to be stable in tests lasting more than a month.^{57,58} To form these membranes, the olefin carrier molecule, the silver salt AgBF_4 , is dissolved in a rubbery polymer; this solution is used to make a thin composite membrane. In such membranes the shuttle transport mechanism of carrier-facilitated membranes described earlier for liquid membranes seems less likely. Rather, the olefin molecules form a dynamic equilibrium with the relatively immobile AgBF_4 salt, rapidly moving off and onto the salt. When the membrane contains large amounts of dissolved silver salt, the salt molecules are only a few angstroms apart. Hopping from one silver ion to another becomes possible, and facilitation occurs. Some of the best permeation test results are shown in Figure 22. This type of membrane goes a long way toward solving the physical stability problems of facilitated transport.

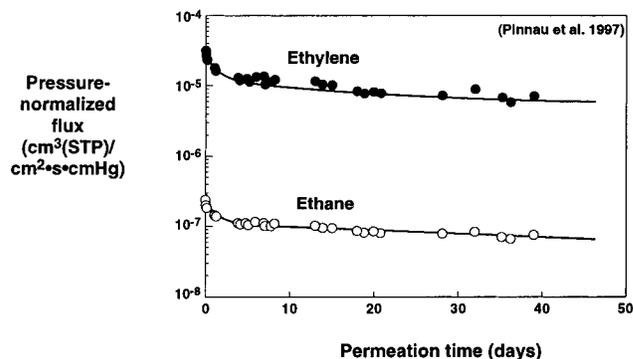


Figure 22. Permeation properties of solid polymer electrolyte membranes with a 50/50 ethylene/ethane mixture.⁵⁸

Chemical instability caused by degradation of the carrier ion remains a problem.

Olefin/paraffin separation is such an attractive target separation for membranes (although a challenging one), that the process is very likely to be developed to the commercial stage in the next few years. The first applications will probably be the treatment of relatively small gas streams such as propane vents in polypropylene plants. The process is illustrated in Figure 23a. In the polymerization step, propylene, catalyst, and other agents are mixed in a high-pressure reactor. The polypropylene product is transferred continuously to a low-pressure flash tank, where the residual monomer and other gases are released. These gases are compressed and recirculated to the reactor, and the polymer is removed for further downstream processing. A problem is buildup of propane in the process loop. The propane enters the process as an impurity in the feed gas, which typically contains 99% propylene and about 1% propane. Unreacted propane builds up in the reactor to concentrations of 20–30 vol %. Propane buildup is controlled by continuously removing a fraction of the flash-tank recycle stream as a purge, which is subsequently flared. The 2–3 mol of propylene monomer lost with every mol of propane purged represent 1–2% of the total feed to the plant and an annual value on the

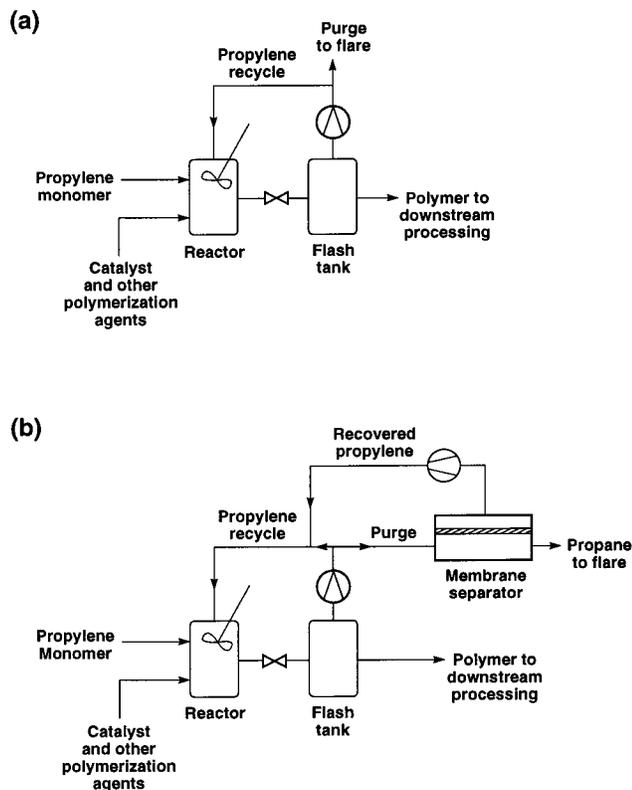


Figure 23. (a) Source of propylene/propane vent gas in a typical polypropylene plant and (b) use of a membrane system to recover and recycle the propylene to the reactor.

order of \$1 million per plant. The use of a membrane system to recover and recycle the propylene to the reactor is shown in Figure 23b. The membrane separation step produces a propylene stream that is recycled to the reactor, leaving a residual propane gas that is flared or used as fuel.⁵⁹ This system is an attractive first application because a membrane with a selectivity of 3–5 would be adequate for the process. If propylene/propane distillation columns are to be replaced by membranes, far more selective membranes will be required.

Other Gas Separations. Finally, there is the category *other*. Right now, this includes the production of small air dehydration modules (\$5–10 million/year) and the preparation of ultrapure hydrogen with palladium membranes for the electronics industry and for fuel cells (<\$5 million/year).

Another membrane application that could become a business is the use of ion-conducting membranes in membrane reactors. In the past 3 years, more than 70 U.S. patents have appeared on this topic, as well as many papers. The overall concept is to use ceramic membranes that conduct oxygen or hydrogen ions at high temperatures. Materials that can conduct both ions and electrons are called mixed-conducting matrixes. Several important early papers describing these materials were published by Teraoka et al. in the 1980s.^{60,61} Various complex metal oxide compositions, including some better known for their properties as superconductors, have mixed-conducting properties; recent efforts in the field focus on these materials. Examples are perovskites having the structure $\text{La}_x\text{A}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-z}$, where A is barium, strontium, or calcium; x and y are 0–1; and the value of z makes the overall material charge neutral. Passage of oxygen ions and electrons is

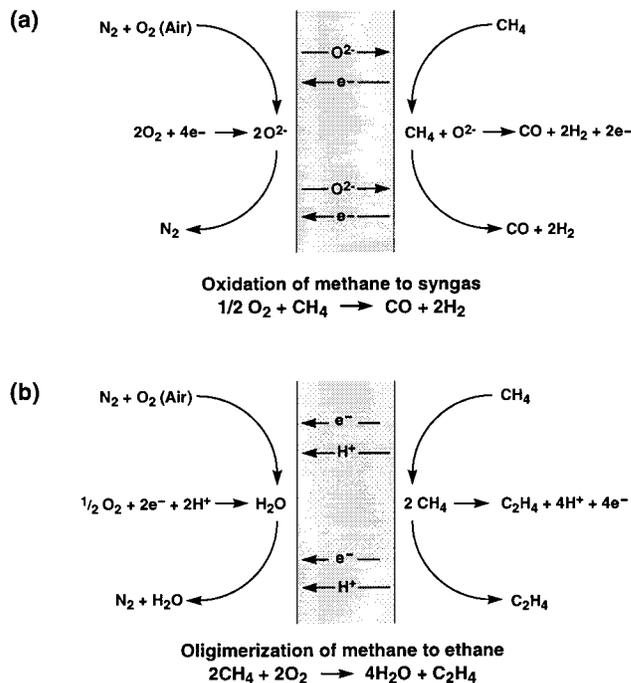


Figure 24. Use of ion-conducting ceramic membranes in a membrane reactor to produce (a) syngas ($\text{CO} + \text{H}_2$) and (b) ethylene.

related to the defect structure of these materials; at temperatures of 800–1000 °C, disks of these materials have shown extraordinary permeabilities to oxygen. Similar mixed-oxide membranes can also conduct protons.

Two large consortia, one headed by Air Products⁶² and the other by Praxair/BP,⁶³ are developing the membranes. At the appropriate operating temperatures of 800–1000 °C, the membranes are perfectly selective for oxygen over nitrogen, and oxygen permeabilities of 10 000 Barrer can be obtained. This means that, if the membrane thickness can be reduced to 1 μm , pressure-normalized fluxes of $10\,000 \times 10^6 \text{ cm}^3(\text{STP})/(\text{cm}^2 \text{ s cmHg})$ are possible. On this basis, for a plant to produce 1 MMscfh of oxygen, about 4000 m^2 of membrane tube area will be required—a large, but not inconceivably large, membrane area.

The most practical application and the principal driving force behind the development of these membranes are membrane reactor processes, such as the production of synthesis gas (syngas) by partial oxidation of methane or the oligomerization of methane to produce ethylene. Both processes are illustrated in Figure 24. In syngas production, oxygen ions diffusing through the membrane react with methane to form carbon monoxide and hydrogen. This gas can then be used without further separation to form methanol or other petrochemicals. In ethylene production, methane is catalytically reacted to produce ethylene and hydrogen. The hydrogen permeates the membrane and then reacts with the oxygen in air to produce water. This second reaction produces the energy necessary to heat the process. The membrane areas involved are not huge, but the technical challenges are substantial. Defect-free, anisotropic composite ceramic membranes that are 1–5 μm thick, able to operate continuously at 800–1000 °C, nonpoisoning, nonfouling, and low-cost are required—not impossible, but difficult. Conceptual designs of the type of reactor required are beginning to appear.

Table 4. Future Membrane Market

| separation | membrane market (\$ million, 2000 dollars) | | |
|-------------------|--|--------|---------|
| | 2000 | 2010 | 2020 |
| nitrogen from air | 75 | 100 | 125 |
| oxygen from air | <1 | 10 | 30 (?) |
| hydrogen | 25 | 60 | 100 |
| natural gas | 30 | 90 | 220 |
| vapor/nitrogen | 10 | 30 | 60 |
| vapor/vapor | 0 | 30 | 125 (?) |
| other | 10 | 30 (?) | 100 (?) |
| total | 150 | 350 | 760 |

The magnitude of the engineering task involved is indicated by the assumptions for the calculations:⁶⁴ a sealed vessel, containing 1000 1-in.-diameter tubes, each 31 ft long, coated inside with perovskite membrane, in which the tubes are 1.5 in. apart, with a lower preheated section of 6 ft, a central reaction section of 18 ft, and an upper cooling section of 7 ft. The construction of such a vessel is neither simple nor cheap. It has also been suggested that these materials, if developed, could be used to separate oxygen from air, but this seems a stretch.

Another topic of current interest is sequestration of carbon dioxide from power-plant flue gas.⁶⁵ This is not a membrane material problem. Membranes with carbon dioxide/nitrogen selectivities of 50 and high fluxes exist. The problem is the quantity of energy used to power the vacuum pumps or compressors for the separation, which can be a substantial fraction of the electric power generated by the plant. One approach to this problem would be to use one membrane unit to produce oxygen-enriched air to burn the fuel, followed by another membrane unit to remove carbon dioxide from the smaller, more concentrated flue gas. This is not quite as crazy as it seems. For example, imagine that 50% oxygen-enriched air can be produced by a membrane process at \$15/ton of oxygen. Compared with oil at about \$200/ton (\$35/barrel) and natural gas at \$150/ton (\$/1000 scfm), coal at \$50/ton is by far the cheapest fuel. However, the flue gas produced by burning coal is dirty, requiring treatment prior to discharge and producing significantly more carbon dioxide, a global warming gas, per Btu of useful power. Coal burned with 50% oxygen-enriched air produces one-third the volume of flue gas and increases the carbon dioxide content of the gas to the 40–50% range. The cost of the fuel is \$50/ton for the coal plus $3 \times \$15/\text{ton}$ for the oxygen-enriched air, for a total fuel cost of \$95/ton of coal burned. This cost is less than that of burning natural gas or oil with air. Sequestration of carbon dioxide from the reduced-volume, carbon dioxide-rich flue gas produced by this process is far more economical than carbon dioxide sequestration from the flue gas of a conventional coal- or natural-gas-fired plant. However, these and other similar processes will not occur unless the world is ready to accept significantly more expensive electric power, which does not seem likely.

Conclusions and Predictions

“Only fools make predictions—especially about the future.” Having headed this section with Sam Goldwyn’s warning, what are my predictions? They are given below as a series of bullet points and in Table 4. It is certain that some of these predictions will be wrong, some embarrassingly so. Those that disagree are welcome to send me their list, and we will compare in 2020.

- The membrane share of the nitrogen-from-air market will grow only slowly in the next 20 years. It is difficult to envisage any breakthroughs in membrane technology that will lead to a major change in the cost of membrane-produced nitrogen.

- The future growth of membrane gas separation technology will be in the refinery, petrochemical, and natural gas industries. Very large, untapped opportunities exist for membranes in all of these industries, and despite past failures, acceptance of membrane technology is increasing. It is worthwhile noting that this shift will result in a significant increase in the size of the average membrane plant, as illustrated below.

| application | typical plant size (MMscfd) |
|---------------------------------------|-----------------------------|
| nitrogen from air | 0.1–1.0 |
| hydrocarbon petrochemical plant vents | 0.5–5.0 |
| refinery hydrogen fuel gas streams | 5–50 |
| natural gas, ethylene cracker streams | 10–500 |

- As plant size increases, the enlargement of membrane modules becomes increasingly important. A recently installed large natural gas carbon dioxide separation plant used 2000 modules in 400 pressure vessels. The complexity, footprint, number of valves, and amount of instrumentation of this plant could have been significantly reduced if membrane modules 5 times larger than today’s industry standard were available.

- Success in the refinery/petrochemical/natural gas markets will require more robust membranes and modules than those used today. These new applications usually involve high partial pressures of hydrocarbons and other plasticizing gases. Membrane materials that maintain their useful properties in such environments are required. Membranes and modules able to operate at temperatures of 70–100 °C are also required. Spiral-wound modules, which allow a much wider range of membrane materials to be used than hollow fibers and which are also inherently more resistant to plasticization, are likely to be preferred in many of these applications.

- Custom-made, high-cost polymers will gradually displace off-the-shelf polymers such as cellulose acetate, polysulfone, and polyaramide as selective membrane materials. This, in turn, will mean that multilayer composite membranes will gradually displace simple Loeb–Sourirajan membranes.

- The production of oxygen from air will slowly become a significant membrane market. The first systems to be produced will likely be simple systems able to produce 0.1–1.0 million scfd of oxygen equivalent at concentrations of 30–50% oxygen. The competitive choice is delivered liquid or onsite pressure swing adsorption. The first systems will probably use polymer membranes with selectivities of 4–5. This is a low-pressure application, so the principal problem will be achieving sufficiently high fluxes; ultrathin membranes in composite hollow-fiber form are likely to be needed. However, even in 10 years, it is difficult to envisage this application growing into a major business, but as the base membrane technology improves, costs will decrease, and this market could grow. Because of the problems of carrier stability, facilitated transport is a long shot for this application.

- Recovery of hydrogen in refineries will become a significant growth area in the next decade. Hydrogen is in short supply in almost all refineries, and the

cheapest sources of new hydrogen are fuel gas and reactor off-gas containing 20–50% hydrogen. Existing hydrogen-permeable hollow-fiber membranes have the selectivities and fluxes required. The major problem is the low reliability of these membranes caused by fouling. The better design and pretreatment steps of today's membrane systems should resolve this problem.

If sufficiently selective hydrogen-rejecting, methane- and light-hydrocarbon-permeable membranes could be made (for example, membranes with methane/hydrogen selectivities of 3–4), a major new market would open up. With such membrane properties, the need to recompress the hydrogen permeate would be eliminated, and membrane system costs would be halved.

- Large opportunities for membranes in the separation of light hydrocarbon mixtures exist. The separation of propylene/propane gas mixtures from various reactor vent streams using simple polymeric composite membranes is likely to be developed first, perhaps as early as the next 2 or 3 years. Long-term, however, these applications will likely require membranes with higher selectivities than polymeric membranes are likely to achieve. The development of facilitated-transport membranes for olefin separation or ceramic membranes for hydrocarbon isomer separation could open up large new membrane markets. Unfortunately, today's membranes have a long way to go.

- Over the next, 10–20 years the use of membranes to separate natural gas mixtures could easily grow to become the largest single membrane gas separation application. Untreated natural gas is not a clean fluid, and it can contain oil mist, glycol, methanol, drilling fluids from earlier operations, and ultrafine iron sulfide particulates (formed by the reaction of hydrogen sulfide with iron pipes). These components must be removed for safe long-term operation of the membrane plant, particularly if hollow-fiber membranes are used. The need for good pretreatment was not appreciated by some of the early equipment producers, and a number of plants suffered module fouling problems. Modern plants have a substantial pretreatment train to avoid these problems, but this is costly. As more selective, fouling-resistant membranes are developed, this market will grow.

Current carbon dioxide/natural gas separating units use cellulose acetate membranes with a carbon dioxide/methane selectivity of 15. Replacement of these membranes by polyimides or polyamide with selectivities of 20–25 will certainly increase the membrane market share. If membranes with selectivities of 40 can be made commercially, membrane technology will replace most amine plants. Membrane materials with these selectivities have been reported in laboratory studies, so the issue is one of scale-up and commercialization.

NGL separation and dehydration of natural gas are two new applications of membranes just reaching the commercial stage. These applications are likely to grow significantly, particularly in applications such as offshore platforms and remote, small plants where membrane technology offers special advantages.

Finally, nitrogen removal from natural gas by membranes is at the field-test stage. If the technology is proved to be practical, this application will become very large indeed.

- It is difficult to foresee a great future for ceramic or carbon fiber membranes in noncondensable gas separation applications. These membranes are 10–100 times

more expensive than the equivalent polymeric membranes. This cost differential can be tolerated only in applications in which polymeric membranes completely fail to make the separation. However, in the high-temperature separation of hydrocarbon vapor/vapor mixtures, where the competition is distillation, these membranes might find a major use. The chemical and physical stability of the ceramic and carbon fiber membranes is a real advantage in this type of separation. Because the value of the components to be separated is high, the cost of the ceramic or carbon fiber membranes can be tolerated. Dehydration of alcohols in the vapor phase with ceramic membranes is already practiced, and other, similar applications are possible.⁶⁶

Ion-conducting membrane reactors are a special category of ceramic membranes and could become a very large application. It is difficult for an outsider to judge the likelihood of commercial success of these membranes, but the technical problems seem to be substantial.

- Finally, my prediction for the total membrane market is given in Table 4. By 2010, I expect the market to more than double to \$350 million and to double again by 2020 to \$760 million, an average growth rate of 7–8%/year. I also expect much of this growth to occur in new applications involving hydrocarbon vapors. Polymeric membranes will undoubtedly be used to separate some of these gas mixtures, but in the longer term, new membranes made from new materials such as ceramics, carbon fibers, or inorganic/polymeric hybrid mixed matrixes are likely to be required.

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