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Natural Gas Processing with Membranes: An Overview

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Every year, the world uses close to 100 trillion scf (standard cubic feet) of natural gas. All of this gas requires treatment before it enters the pipeline, making natural gas processing by far the largest market for industrial gas separation processes and equipment. Of this huge market, membranes have less than a 5% share, but this is changing; membrane-based removal of natural gas contaminants is growing faster than any other segment of the membrane gas separation business. This paper gives an overview of the membrane technology in current use for natural gas treatment and outlines the future prospects.

1. Introduction

Raw natural gas varies substantially in composition from source to source. Methane is always the major component, typically 75%−90% of the total, but 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, such as water, carbon dioxide, nitrogen, and hydrogen sulfide. Although the composition of raw gas varies widely, the composition of gas delivered to commercial pipeline grids is tightly controlled. Typical U.S. natural gas pipeline specifications are shown in Table 1.

To meet pipeline specifications, all natural gas requires some treatment (if only to remove water), and ∼20% requires extensive treatment, before delivery to the pipeline.[1] The opportunity for membranes lies in processing raw gas to meet these specifications.

Processing of natural gas is, by far, the largest industrial gas separation application. The U.S. consumption of natural gas is ∼22 trillion scf/yr; total worldwide consumption is ∼95 trillion scf/yr. (Throughout this paper, "scf" is used to represent standard cubic feet.) This consumption drives a worldwide market for new natural gas separation equipment of ∼$5 billion per year. Currently, membrane processes have <5% of this market, almost all of which is applied toward the removal of carbon dioxide.

The principal current suppliers of membrane natural gas separation systems are listed in Table 2.

Membrane technology competes most directly against absorption for carbon dioxide removal.[2] A typical absorption process is illustrated in Figure 1. Two towers are used. In the first tower, the feed gas, usually at high pressure, and an absorbent liquid flow countercurrent to each other. The absorbent liquid that contains the absorbed component (carbon dioxide, water, or heavy hydrocarbon) is removed from the bottom of the tower. The liquid is then heated and sent to a low-pressure stripper tower. The combination of heat and lower pressure liberates the sorbed component, which leaves the stripper tower as a low-

Table 1. Composition Specifications for Natural Gas Delivery to the U.S. National Pipeline Grid[1]

component	specification	Range in U.S. Well Compositions	
		% of total U.S. gas	component content
CO$_2$	<2%	72%	<1%
		18%	1−3%
		7%	3−10%
		3%	>10%
total		100%	
water	<120 ppm		800−1200 ppm
H$_2$S	<4 ppm	76%	<4 ppm
		11%	4−1000 ppm
		4%	1000−10000 ppm
		8%	>10000 ppm
total		100%	
C$_{3+}$ content	950−1050 Btu/scf; dew point: < −20 °C		
total inert gases (N$_2$, He)	<4%	14%	>4%

pressure overhead gas. The regenerated absorbent liquid is then recycled to the first tower. Heat exchangers are used to minimize the cost of heating the absorber fluid.

Absorber-stripper units represent a proven, well-accepted technology in the gas processing industry, and no gas processing plant designer will be fired for recommending the installation of one of these units. Having said this, the high-pressure absorber tower in particular is an expensive, large, thick-walled, heavy vessel. The size of such a tower is proportional to the mass of the material to be absorbed. In natural gas dehydration, only a few hundred parts per million (abbreviated hereafter as ppm) of water must be removed; consequently, these systems are relatively compact and low in cost. On the other hand, the removal of carbon dioxide from natural gas may require 10%−20% of the gas to be removed, which means large amounts of absorbent fluid must be used in large towers. Carbon dioxide absorber-strippers are also relatively high-maintenance units. The need to heat and cool the recirculating fluids requires careful, well-monitored operating procedures. Furthermore,

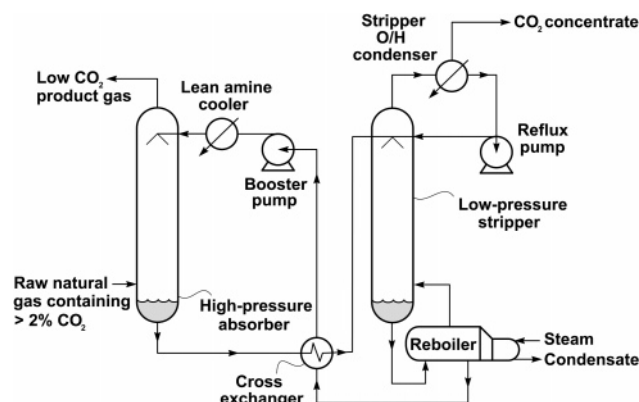* To whom correspondence should be addressed. E-mail address: kaaeid@mtrinc.com.

Figure 1. Typical natural gas absorber-stripper treatment process using amine absorbents to remove carbon dioxide. Similar processes use triethylene glycol for water removal and lean oil for heavy hydrocarbon removal.
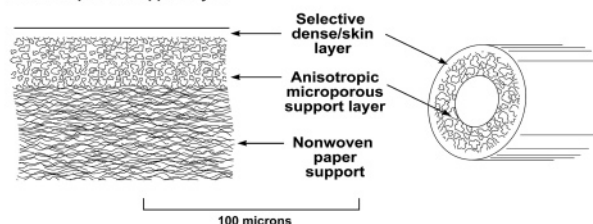
corrosion is a critical maintenance issue. Amines are the most common sorbents for carbon dioxide, and the degradation of amines leads to corrosive mixtures that can destroy the system within a few days if left unchecked. Constant monitoring of the amine absorbent chemistry is needed. The need for regular maintenance and good operator care hinders the use of amine absorber-strippers in remote locations.

Membrane companies first broke into the natural gas processing industry in the 1980s, offering systems for carbon dioxide removal in competition with amine absorption. Membranes could gain a foothold in locations where the operational issues previously mentioned are especially problematic. The first membrane systems to separate carbon dioxide from natural gas were introduced by Grace Membrane Systems (a division of W.R. Grace), Separex (now part of UOP), and Cynara (now part of Natco). These companies used anisotropic cellulose acetate membrane that was produced using the Loeb−Sourirajan technique.[3−5] Cellulose acetate membranes are still widely used. In the last 10 years, they have begun to be challenged by newer membranes, such as the polyimide membranes (made by Medal a division of Air Liquide)[6] and perfluoropolymer membranes (made by ABB/MTR).[7−9]

1.1. Membrane Production Trends Making Membrane Separations More Competitive. Current membranes used for natural gas separation applications are produced as hollow fibers or flat sheets packaged as spiral-wound modules. Hollow-fiber modules allow large areas of membrane to be packaged into compact membrane modules. This advantage proved decisive in the choice of membranes for the separation of nitrogen from air, which was an early large-scale membrane gas separation process. Nitrogen production from air uses relatively low-permeability membrane materials to process a clean, non-plasticizing gas (air) at low pressures (generally <10 bar). Essentially all membrane nitrogen-from-air separation systems use hollow-fiber modules. Natural gas streams, in contrast, contain multiple components, some of which (water, carbon dioxide, C_{4+} hydrocarbons, aromatics) degrade and plasticize the membrane. Natural gas streams may also contain entrained oil mist, fine particles, and hydrocarbon vapors that can easily
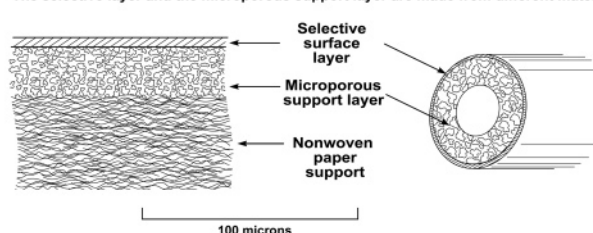

Figure 2. Structure of membranes used in membrane gas separation processes: (a) anisotropic Loeb−Sourirajan membranes and (b) composite membranes.

collect on the membrane surface. In addition, the gas is typically treated at relatively high pressures of 30−60 bar. Under these conditions, the generally higher permeances of flat sheet membranes formed as spiral-wound modules can compensate for their higher cost (on a $/(m^2 membrane) basis), compared to hollow-fiber modules. Currently, both types of membrane modules (spiral and hollow-fiber) are produced, by different companies, and no clear winner has emerged.

One trend that has emerged in commercial gas separation membranes is a move to composite membranes, in which a base anisotropic membrane is used as a highly porous support (to provide the mechanical strength required), and a thin layer of permselective material (typically 0.2−1.0 μm thick) is deposited onto the support to perform the separation. Hollow-fiber membranes and flat sheet membranes can be made in this composite membrane form. Composite membranes, as shown in Figure 2b, offer two key advantages over the conventional Loeb−Sourirajan anisotropic membrane (shown in Figure 2a). In Loeb−Sourirajan membranes, the porous support layer that provides mechanical strength and the relatively dense surface layer that performs the separation are formed at the same time from the same material. This limits the number of materials that can be used to make the membrane. It also means the separation properties are often compromised to make membranes with sufficient mechanical strength.

Composite membranes consist of a microporous support layer coated with one or more thin layers of a different polymer that performs the separation. Because the separation function and the mechanical support function are separated, each can be optimized separately, and the polymer best suited for each

Table 2. Principal Suppliers of Membrane Natural Gas Separation Systems

company	principal natural gas separation	membrane module type	membrane material
Medal (Air Liquide)	CO_2	hollow fiber	polyimide
W.R. Grace	CO_2	spiral-wound	cellulose acetate
Separex (UOP)	CO_2	spiral-wound	cellulose acetate
Cynara (Natco)	CO_2	hollow fiber	cellulose acetate
ABB/MTR	CO_2, N_2, C_{3+} hydrocarbons	spiral-wound	perfluoro polymers silicone rubber
Permea (Air Products)	Water	hollow fiber	polysulfone

Table 3. Typical Costs for Membranes, Membranes in 8-In.-Diameter Spiral-Wound Modules, and Module Skids[a]

	Typical Cost ($/m² of membrane)	
type of unit	gas separation (steel vessels and components)	reverse osmosis (fiberglass vessels, plastic components)
membrane	20	5
membrane in spiral-wound module form	100	10–15
membrane modules in a skid	500	30–50

[a] Hollow-fiber reverse osmosis skids are normally less expensive on a per-square-meter-of-membrane basis; however, lower permeances offset much of this advantage.

function can be used. Composite membranes allow high-cost polymer materials to be used economically in the separating layers. Tailor-made polymers with good separating properties often cost as much as $1000/kg–$10000/kg to synthesize. A Loeb–Sourirajan membrane generally uses ~50 g of polymer/(m² membrane), so the material cost of membrane made from these high-cost polymers is in the $50/m²–500/m² range. Composite membranes generally use a dense layer of polymer only 0.2–0.5 μm thick, so less than one gram of polymer/m² of the high performance material is needed for a comparable separation. The cost of this polymer is much more affordable, at $1/m²–10/m². The microporous support membrane for most natural gas applications can be made from conventional low-cost materials.

A second emerging trend in commercial membrane separations is a move to larger membrane modules. Natural gas separations operate with high-pressure flammable gases that must be contained in code-stamped heavy steel vessels. The impact of the cost of these vessels, flanges, valves, and pipes on the system capital cost is illustrated in Table 3. Costs of module skids purchased for ultrafiltration/reverse osmosis applications are lower by a factor of 5–10. This difference reflects the higher production volumes and lower costs of the plastic components and fiberglass housings that can be used in water treatment processes.

Table 3 shows that the cost of membranes used in gas separation processes is a small fraction of the final membrane skid cost. High skid costs arise because of the many pressure vessels, pipes, flanges, and valves that are required. One way to reduce membrane skid cost is to increase the permeance of the membranes, allowing a smaller membrane area to be used to treat the same volume of gas. All membrane manufacturers pursue this approach. Increasing the feed gas pressure also reduces the membrane area required, and, hence, skid size, but at the expense of larger compressors (higher capital cost) and increased energy consumption (higher operating cost). A third approach is to develop larger membrane modules and new skid designs. Currently, most modules, both spiral-wound or hollow-fiber, are designed to fit in 8-in.-diameter housings. However, 12-in.-diameter spiral-wound modules are now being installed in some units, and some hollow-fiber module producers are also beginning to introduce very large modules, as shown in Figure 3.[10] These developments, combined with the use of lower-cost module skids,[11] are likely to significantly reduce the cost of future membrane systems and increase their long-term competitiveness.

2. Permeation Theory

The factors that affect polymer membrane permeance and selectivity have been discussed in detail in several review articles[12–15] and will only be briefly reviewed here.

Figure 3. Photograph showing the development of hollow-fiber membrane modules at Cynara, from the first 5-in. modules of the 1980s to the 30-in. diameter behemoths currently being introduced.[10] Photo courtesy of Cynara Company (now part of NATCO Group, Inc.).

Gas transport through dense polymer membranes is governed by the expression

$$j_i = \frac{D_i K_i (p_{i_o} - p_{i_\ell})}{\ell} \qquad (1)$$

where J_ℓ is the volume (molar) flux (expressed in terms of cm³(STP) of component i/(cm² s)), ℓ the membrane thickness, p_{i_o} the partial pressure of component i on the feed side, and p_{i_ℓ} the partial pressure of component i on the permeate side. The diffusion coefficient (D_i) is an indication of the mobility of the individual molecules in the membrane material, and the gas sorption coefficient (K_i, with units of cm³(STP) of component i per cm³ of polymer per unit pressure) is an indication of the number of molecules dissolved in the membrane material. The product $D_i K_i$ can be written as P_i, which is called the membrane permeability; this is a measure of the membrane's ability to permeate gas.

The best measure of a membrane's ability to separate two gases i and j is the ratio of their permeabilities, $\alpha_{i/j}$; this parameter is called the membrane selectivity, and it can be written as

$$\alpha_{i/j} = \frac{P_i}{P_j} = \frac{[D_i/D_j]}{[K_i/K_j]} \qquad (2)$$

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, which indicates the relative motion of individual molecules of the two components i and j. The mobility selectivity is proportional to the ratio of the molecular size of the two permeants. The ratio K_i/K_j is the ratio of the sorption coefficients, which indicates the relative concentration of the components i and j in the membrane material. The sorption of a component increases with condensability of the component; therefore, the sorption selectivity is proportional to the relative condensability of components i and j.
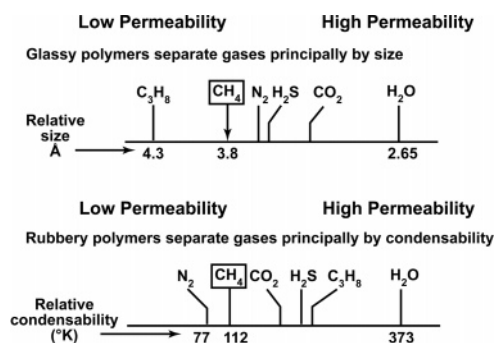
Figure 4. Depiction showing the relative size (kinetic diameter) and condensability (boiling point) of the principal components of natural gas. Glassy membranes generally separate using differences in size; rubbery membranes separate using differences in condensability.

In polymer materials, diffusion coefficients decrease as the molecular size increases, because large molecules interact with more segments of the polymer chain than do small molecules. Hence, the mobility selectivity D_i/D_j always favors the permeation of small molecules (such as water (kinetic diameter of 2.65 Å) and carbon dioxide (kinetic diameter of 3.30 Å)) over larger ones (such as methane (kinetic diameter of 3.80 Å)).

The sorption coefficient of gases in a polymer is a measure of the energy required for the gas to be sorbed by the polymer, and it generally increases as the condensability increases. Hence, the sorption selectivity K_i/K_j favors absorption of the more-condensable gas. Methane (which has a boiling point of 113 K) is less condensable than almost all of the other components in natural gas, so the sorption selectivity usually favors permeation of the nonmethane components.

The sorption selectivity term K_i/K_j for a particular gas pair is relatively constant for all amorphous polymers, but the magnitude of the diffusion selectivity term D_i/D_j is very dependent on the nature of the polymer and, in particular, whether the polymer is above or below its glass-transition temperature. Below the glass-transition temperature, the polymer chains are essentially fixed; the polymer is a rigid, tough, glassy material and the effect of differences in size of the permeating gases on their relative mobility is large. If the polymer is above its glass transition temperature, motion of the polymer chains is possible. The polymer is then rubbery and elastic and the effect of molecular size of the permeating gases on relative mobility is reduced. In extreme cases, if the polymer is plasticized by a low-molecular-weight component that facilitates motion of the polymer chains, the mobility selectivity term can be quite small, and for similarly sized permeating molecules, the ratio D_i/D_j can approach unity. It follows that changing the membrane material chemistry to obtain the optimum mobility selectivity term is the most widely used method for tailoring membrane materials and performance.

The molecular size and condensability of the principal components in natural gas, relative to methane, are shown graphically in Figure 4. Water is small and condensable; therefore, it is easily separated from methane by both rubbery and glassy polymers. Rubbery and glassy polymers can also separate carbon dioxide and hydrogen sulfide from natural gas. However, in practice, carbon dioxide is best separated by glassy polymer membranes (maximizing size selectivity) whereas hydrogen sulfide, which is larger and more condensable than carbon dioxide, is best-separated by rubbery polymer membranes (maximizing sorption selectivity). Nitrogen can be separated from methane by glassy polymers, but the difference in size is small, so the separations achieved are small. Alternatively, rubbery polymers can be used to permeate methane over

Table 4. Current Commercial Membrane Materials and Selectivities for Separation of Impurities from Natural Gas

component to be permeated	category of preferred polymer material	typical polymer used	typical selectivities over methane (%)[a]
CO_2	glassy	cellulose acetate, polyimide, perfluoro polymer	10−20
H_2S	rubbery	ether−amide block co-polymer	20−30
N_2	glassy	perfluoropolymer	2−3
	rubbery	silicone rubber	0.3
water	rubbery or glassy	many	>200
C_{3+} hydrocarbons	rubbery	silicone rubber	5−20

[a] Selectivities are typical of those measured with high-pressure natural gas.

nitrogen. These membranes minimize size selectivity and maximize sorption selectivity, and, therefore, they are methane-permeable; but again, the selectivity is small. Finally, propane and other hydrocarbons, because of their condensability, are best-separated from methane with rubbery sorption-selective membranes.

Table 4 shows typical membrane materials and the selectivities that can be obtained with good-quality membranes. These selectivities may seem low, compared to values commonly found in the literature. This difference occurs because the literature values are usually the ratios of the pure gas permeabilities. Selectivities measured with high-pressure gas mixtures, especially natural gas mixtures that contain plasticizing components such as water, BTEX aromatics (benzene, toluene, ethylbenzene, and xylene), and other heavy hydrocarbons are usually significantly lower. The values given in Table 4 are selectivities that might be reasonably expected by current commercial membranes operating on "real" gas streams.

3. Applications

3.1. Carbon Dioxide Removal. Carbon dioxide is a common contaminant of natural gas and must be removed to a level of <8% (usually <2%) to minimize corrosion of the pipeline. Until the introduction of membrane technology, the standard removal technique was amine absorption.[2] Amine absorption technology achieves almost complete removal of carbon dioxide. Generally, ~1% of the methane in the gas being treated is lost with the amine plant's carbon dioxide vent gas stream, and another 1%−4% of the methane is used as fuel to heat the reboiler of the amine stripper, so the total hydrocarbon losses are in the range of 2%−5%. Early membrane plants had difficulty in meeting this low hydrocarbon loss target. Better membranes and improved process designs have since improved the competitiveness of membranes.

The size of the absorbent recirculation rate, reboiler stripping tower, pumps, and heat exchangers of an amine plant all increase in proportion to the mass of carbon dioxide to be removed, and they are relatively independent of the volume of gas to be treated. Only the high-pressure absorption tower increases in proportion to the volume of gas to be treated. Overall, this means an amine plant that is designed to treat 20 million scfd (scfd = standard cubic feet per day) of gas that contains 5% carbon dioxide would be only slightly more costly than an amine plant designed to treat 5 million scfd of gas that contains 20% carbon dioxide. Membrane plants, on the other hand, are able to treat high-concentration gas streams much more efficiently than low-
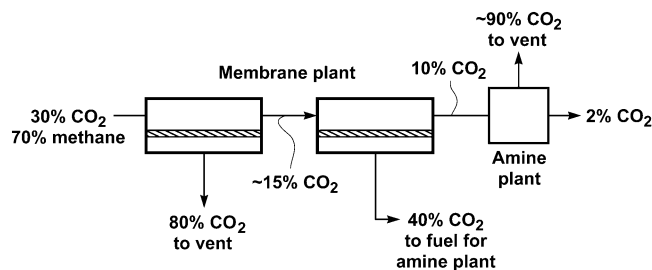
Figure 5. Typical membrane/amine hybrid plant for the treatment of associated natural gas produced in carbon dioxide/enhanced oil projects; a portion of the membrane plant's permeate gas is usually used as a fuel for the amine absorption plant.
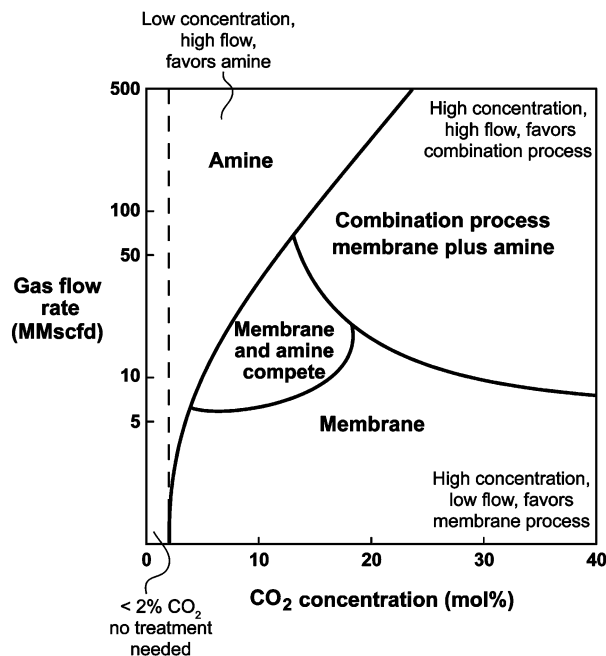

Figure 6. Schematic plot illustrating the effect of gas flow rate and carbon dioxide concentration in the gas on the choice of carbon dioxide removal technology. This figure should be used with care, as site-specific issues can produce very different results.

Figure 7. Photographs showing CO_2 membrane separation plants. Top photograph shows a 9 million scfd membrane plant designed to bring 6% CO_2 gas to 2%; the plant is compact enough to be moved when the gas field is exhausted after a few years of operation (UOP/cellulose acetate membranes/spiral-wound modules; photo courtesy of UOP LLC). Bottom photograph shows the world's largest membrane CO_2 removal plant; this is a 500 million scfd unit that is designed to bring 5.7% CO_2 gas to 2% (UOP/cellulose acetate membranes/spiral-wound modules).

concentration gas streams. A membrane plant designed to treat 5 million scfd of gas that contains 20% carbon dioxide would be less than half the size of a membrane plant designed to treat 20 million scfd of gas that contains 5% carbon dioxide. It follows that membrane plants are preferred for high-concentration gas streams and amine plants are preferred for relatively low-concentration gas streams. Membrane plants, because of their simple flow schemes, are also generally preferred when processing small gas flows. Membrane plants processing <20 million scfd of gas are usually designed for unattended operation. Amine plants are more complex and require careful, well-monitored operating procedures, so that unattended operation is generally less practical.

In principle, the combination of membranes for bulk removal of the carbon dioxide from natural gas with amine units as polishing systems offers a low-cost alternative to all-amine or all-membrane plants. However, this approach is limited to large plants where the overall savings in capital cost are large enough to offset the increased complexity of the plant, which now contains two separation processes.[10,16] Hybrid plants have also been used in carbon dioxide flood-enhanced oil recovery projects in which carbon dioxide is injected into an oil formation to reduce 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. Approximately 5% of U.S. oil is produced this way.[17] In these projects, the composition and volume of the gas changes significantly over the lifetime of the project. The modular nature of membrane units lends itself to easy retrofitting of 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. A block diagram of a membrane/amine plant is shown in Figure 5. In this design, the membrane unit removes two-thirds of the carbon dioxide, and the amine plant removes the remainder. A portion of the permeate gas from the membrane unit is used as fuel for the amine plant; the remainder is vented or reinjected. The combined plant is significantly less expensive than an all-amine or all-membrane plant.

A schematic plot that illustrates the effect of gas flow rate and carbon dioxide composition on the choice of separation processes is shown in Figure 6. Similar figures with different numbers have appeared in the literature. Many site-specific issues can change these plots. Membrane systems, for example, are strongly favored in offshore platforms that produce an increasing fraction of natural gas. An amine plant producer might draw a different figure. The range of size and complexity of membrane carbon dioxide separating plants is illustrated in Figure 7.

3.1.1. Membranes Used. As shown previously in Table 4, current membrane carbon dioxide separation plants use a

very limited number of membrane materials, of which cellulose acetate is probably the most common. This result surprises many researchers who point to literature data that show the
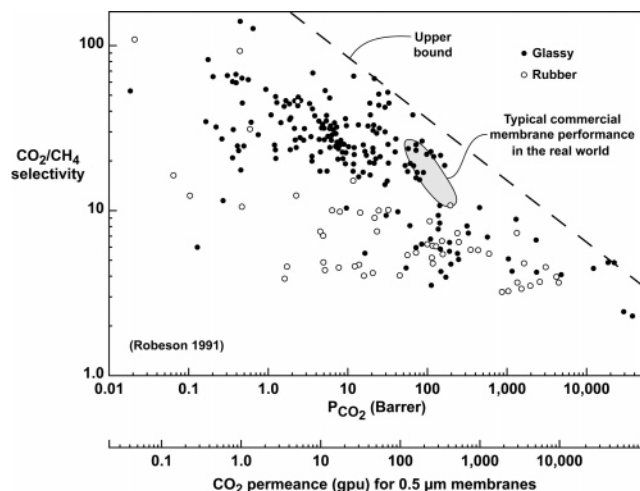
Figure 8. Robeson plot of CO_2/CH_4 selectivity versus membrane permeability (permeance);[18] the points shown are based on low-pressure pure-gas measurements. For comparison, the performance of commercial membranes when used to separate carbon dioxide from high-pressure natural gas is shown on the same figure.

Figure 9. Graph showing that the difference between selectivities calculated from pure gas measurements and selectivities measured with gas mixtures can be large. The graph was constructed using data from Donohue et al.[19] for carbon dioxide/methane with cellulose acetate films.

availability of much-better membrane materials. A widely used method of comparing the performance of various membrane materials is the selectivity/permeance plot popularized by Robeson and shown in Figure 8.[18] This plot shows the selectivity for CO_2/CH_4 obtained from the ratio of pure-gas permeabilities plotted against carbon dioxide permeability for all the membrane materials then reported. The line that links the most-selective polymers at a particular carbon dioxide permeability is called the "upper bound", beyond which no material is currently known. The performance of today's commercial membranes, when used with high-pressure natural gas, is also shown on this Robeson plot. Generally, commercial membranes that are in use have half the selectivity of the best upper bound materials. This difference reflects the effect of water, carbon dioxide, and heavy hydrocarbons present in the gas on the membrane selectivity, as estimated from the ratio of pure-gas permeances.

3.1.2. Membrane Plasticization. The difference between pure-gas membrane selectivity and the selectivity measured with high-pressure natural gas is due to membrane plasticization, which is a phenomenon that is well-known to industrial membrane system producers.[19−23] The most important plasticizing component in natural gas is carbon dioxide. At the high pressures of natural gas operations, membrane materials absorb 30−50 cm³(STP) of CO_2/(cm³ polymer). This is equivalent to 5−10 wt % of carbon dioxide in the polymer; not surprisingly, the membrane materials become plasticized. The absorbed carbon dioxide swells and dilates the polymer, increasing the mobility of the polymer chains. One consequence is a sharp drop in the polymer glass-transition temperature (T_g); another is a decrease in the mobility (size) term in the selectivity equation (eq 2). Some old, but representative, results on the plasticization of cellulose acetate membranes are shown in Figure 9.[19] Cellulose acetate has a low-pressure pure-gas (CO_2/ CH_4) selectivity of ∼40. At higher pressures, the pure-gas selectivity (the ratio of pure-gas permeability) increases sharply, because the permeability of pure carbon dioxide increases as the pressure increases, but the pure-gas methane permeability is relatively constant. When the same membranes are tested with CO_2/CH_4 mixtures, the membrane performance is quite different. The mixed-gas membrane selectivity decreases as the pressure increases, because the membrane absorbs carbon dioxide, which
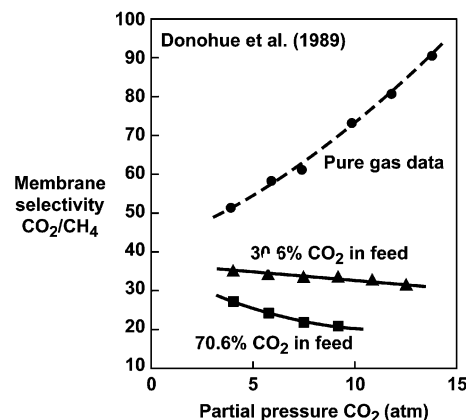
plasticizes the membrane, increasing the methane permeability far above its pure-gas value.

The mixed-gas data shown in Figure 9 are limited to simple CO_2/CH_4 mixtures; however, natural gas also contains water, and 1%−5% heavy hydrocarbons. These hydrocarbons are also absorbed by the membrane and often have as large a plasticization effect on membrane permeances as carbon dioxide. The BTEX aromatics present in most natural gas at concentrations of 200−1000 ppm are particularly troublesome. At this concentration, the BTEX aromatics can reduce membrane selectivity by 30%−50%.[24] The overall result of plasticization is to reduce the membrane selectivity far below the pure-gas values. The magnitude of the effect is dependent on the gas composition and pressure, and it is also related to the material used. Rubbery polymers are less affected than glassy polymers. The 6-FDA polyimides, which are a widely studied class of polymers that often have very high pure-gas selectivities, are particularly susceptible to plasticization.[25] It follows from the aforementioned discussion that it is the membrane's gas permeance and selectivity at the expected operating conditions (mixed gas, high pressure) that determines its suitability for practical applications.

Several strategies have been used to overcome membrane plasticization. Pretreatment to remove aromatics and other heavy hydrocarbons from the gas is widely used (described below). Crosslinking the membrane material often increases the membrane selectivity and makes the membranes more resistant to plasticization.[23,25] However, fabricating cross-linked polymers into thin membranes is not straightforward. Another strategy is to use polymers such as the Teflon-like perfluoro polymers, which are inherently resistant to plasticization by absorbed hydrocarbons,[7−9] as the membrane selective layer.

In addition to plasticization, another problem with the glassy materials used to make CO_2-selective membranes is physical aging. The glassy polymers used in CO_2-selective membranes are in a nonequilibrium state and, over time, the polymer chains can slowly relax into a preferred higher-density−lower-permeability form.[26] This type of aging effect can reduce membrane permeabilities significantly over the average 2−5-year life of a membrane used in natural gas service.

3.1.3. Membrane Pretreatment. Pretreatment of natural gas feed streams to control the fouling, plasticization, and condensation of hydrocarbons on the membranes is required for all membrane systems. Oil mist and particulates must always be removed, but for CO_2 removal systems, treatment of the gas to control condensation of liquids on the membrane or excessive plasticization of the membrane is also required.
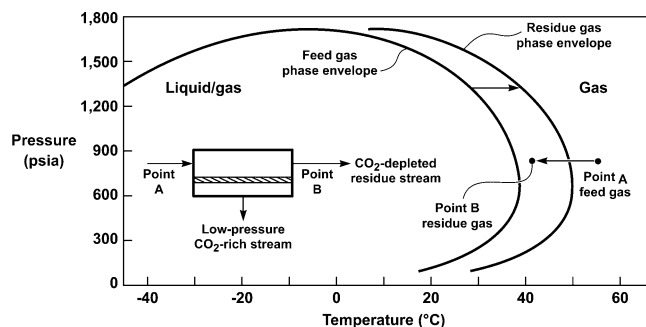
Figure 10. Graph showing the change in the phase envelope of CO_2-containing natural gas during processing of the gas by a CO_2-selective membrane.

Figure 11. Natural gas pretreatment trains used in front of carbon dioxide membrane separation systems.[4]

The problem of liquid condensation on the membrane surface is illustrated in Figure 10. This figure shows two natural gas-phase envelope curves. These curves are calculated by computer process simulators, using equations of state that have been derived to predict the condensation point of complex natural-gas mixtures. At high temperatures, the natural-gas mixture exists as a single phase. However, when the gas is cooled, heavy hydrocarbons in the gas will reach their saturation values and condensation will occur. The dew point is the temperature at which condensation just begins and the gas enters the two-phase region of the phase envelope. The dew-point temperature is dependent on the pressure and the concentration of heavy hydrocarbons in the gas mixture. In the example calculation shown in Figure 10, the feed gas (A) is at 55 °C and 850 psia, comfortably above the dew point of the feed, which is ~35 °C.

When the gas is processed by a membrane, carbon dioxide and some methane is removed in the permeate. Because membranes are relatively impermeable to heavier hydrocarbons, these components are retained and concentrated in the residue gas. This increase in heavy hydrocarbon concentration in the gas causes the phase envelope to shift to higher temperatures, as shown in Figure 10. The dew point of the residue gas (B) is increased to ~50 °C. A dew point of 50 °C is still below the temperature of the feed gas, but Joule−Thompson cooling, because of expansion of the carbon dioxide permeating the membrane, cools the residue gas to 10− 15 °C below the feed gas. In the example shown, the combination of Joule−Thompson cooling and increased heavy hydrocarbon levels in the residue gas is sufficient to bring the gas into the two-phase region of the phase envelope. Condensation of hydrocarbon liquids at the residue end of the membrane train would then likely occur. Condensation of this type will damage most membrane modules.

A solution to the condensation problem previously described is to heat the feed gas sufficiently so that the residue gas, even when cooled by Joule−Thompson expansion, does not enter the phase envelope. In the example shown, condensation would be avoided if the feed gas were heated to 65 °C. However, these high temperatures reduce the selectivity of the membrane. A second solution is to remove some of the most condensable components in the gas to change the shape of the phase envelope before sending the gas to the membrane unit. This could be done using glycol absorption (to remove water), in combination with cooling and condensation (to remove C_{4+} hydrocarbons). Temperature swing adsorption is also used to remove small amounts of C_{12+} hydrocarbons in the gas with carbon or silica bed adsorbents.[16] In practice, feed gas heating and some form of hydrocarbon removal technique are often used together.

Two possible pretreatment trains for a carbon dioxide membrane separation plant are illustrated in Figure 11.[4] The amount of pretreatment is dependent on the membranes used
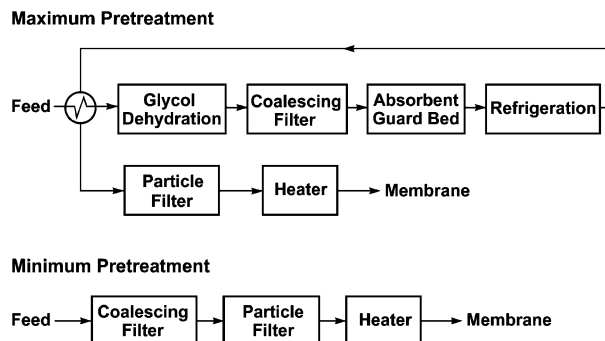
and the nature of the gas to be treated. Cellulose acetate membranes, for example, are particularly sensitive to water and, therefore, glycol dehydration followed by silica bed drying would be used for most streams.

In Figure 11, 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 byproduct 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.

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.

3.1.4. System Design. The design of a membrane carbon dioxide removal system will be dependent on the following factors:

(i) The selectivity and permeances of the membranes used

(ii) The carbon dioxide concentration of the gas and the separation required (for other components in the gas)

(iii) The value of the gas (in the United States, the current (2007) price of gas is $6−$7 per 1000 scf. In Nigeria, which is far from being as well-developed a gas market, the gas price may be as low as $0.50 per 1000 scf, if the gas can be used at all)

(iv) The location of the plant (on an offshore platform, the weight, footprint, and simplicity of operation are critical; onshore, total cost is more significant)

Block diagrams of two typical carbon dioxide removal plants that treat natural gas with low CO_2 concentration are illustrated in Figure 12. Both plants are designed to treat 10 million scfd of gas that contains 10% carbon dioxide. One-stage plants, which are simple, contain no rotating equipment, and require minimal maintenance, are preferred for very 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. For gas wells that produce <1 MMscfd, one-stage membrane units, with their low capital and operating costs, may make sense economically. As the natural gas stream increases in size, the methane loss from a one-stage system and the resultant loss in revenue soon make the choice of a one-stage system unattractive. Usually, the permeate gas is recompressed and passed through a second membrane stage. This second stage reduces the methane loss to a few percent, which is comparable to amine plant losses.
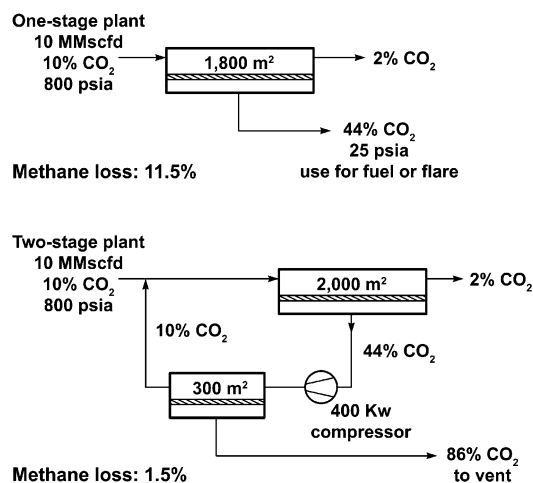
Figure 12. Flow scheme of one-stage and two-stage membrane separation plants to remove CO_2 from natural gas (P/l_{CO_2} = 100 gpu; P/l_{CH_4} = 5 gpu). Because the one-stage design has no moving parts, it is very competitive with other technologies, especially if there is a use for the low-pressure 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 significantly reduced.
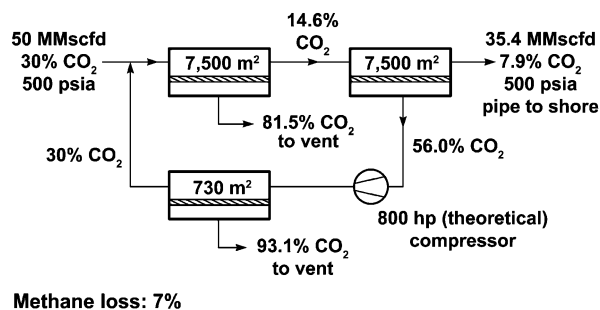

Figure 13. Flow design of a combination two-stage and one-stage membrane system to remove CO_2 from high CO_2 concentration gas on an offshore platform. The CO_2 concentration is reduced to ~8%, which is low enough to allow pipelining to shore.

The type of process design that might be used to treat a high-concentration gas on an offshore platform in the Far East is shown in Figure 13. The design combines a one-stage and a two-stage system. The 50 million scfd of feed gas that contains 30% CO_2 is sent, after pretreatment, to two sets of membrane modules. The first set of modules reduces the CO_2 concentration from 30% CO_2 to 15% CO_2, producing a permeate stream that contains 82% CO_2. This permeate gas is vented or reinjected. The second set of modules reduces the carbon dioxide concentration in the residue gas from 15% CO_2 to 8% CO_2. This is the product gas that is piped to shore. The permeate from this set of modules contains 56% CO_2; it contains too much hydrocarbon to be vented, so it is compressed and passed through a second membrane stage to produce a second-stage permeate that contains 93% CO_2 that can be vented. The second-stage residue that contains 30% CO_2 is recycled to the front of the system.

The product gas from the combined system contains 8% carbon dioxide. This is well above the U.S. gas pipeline specification, but is low enough to control the corrosion of dry gas, and it allows the gas to be piped to shore, where the remaining carbon dioxide can be removed. The process design shown in Figure 13 loses ~7% of the hydrocarbons with the carbon dioxide streams. This methane loss could be reduced by increasing the size of the second-stage compressor and membrane unit to treat some of the first-stage permeate. Installing this larger equipment would be worthwhile at most

onshore plants, and its installation could reduce methane loss to 3%−4%. However, offshore, the increase in weight, footprint, power consumption, and other cost-of-plant factors, may not be offset by the value of extra gas recovered.

Amine absorption-stripper technology still has the bulk of the carbon dioxide natural gas treatment market. However, in some niche applications, such as offshore platforms treating high-carbon dioxide, membranes are already preferred. As membrane permeance and selectivity increase, membranes are beginning to compete in more mainstream applications.

3.2. Separation of C_{3+} Hydrocarbons. Natural gas usually contains propane, butane, and other higher hydrocarbons, and often the gas is close to saturation, with respect to these components. There are several reasons to control the concentration of these heavy hydrocarbons in the gas. For example, at many remote natural gas production sites, only raw, untreated gas is available to drive field compressor engines or power-generating turbines. High levels of heavy hydrocarbons in the gas cause pre-detonations and coking problems in these engines. Removal of the heavy hydrocarbons is needed to use the gas as fuel. At other locations, large amounts of gas are produced as a byproduct of oil production. Often, this gas cannot be transported easily to users. This "associated gas" is then usually compressed to high pressure and reinjected into the oil formation. The heavy hydrocarbon content of these gases, although only a small volume fraction of the gas, may represent one-third of the mass of the gas. Separation of the heavy hydrocarbons from the gas, followed by mixing of the heavies with the liquid oil, increases the amount of transportable hydrocarbon liquids produced. Finally, to avoid problems caused by condensation of liquids, the dew point of U.S. natural gas is often reduced to −20 °C before delivery to the interstate pipeline. This means removing portions of the propane, butane, and higher hydrocarbons from the gas.

The current technology to separate heavy hydrocarbons from natural gas is cooling and condensation, or lean oil absorption. The condensed heavy hydrocarbons separated from the gas stream are then subjected to fractional distillation to recover the individual components. Because refrigeration is costly and uses large amounts of energy, there is interest in alternative techniques such as membrane gas separation.

The competitiveness of membrane systems in this application is sensitive to the selectivity of the membrane for propane, butane, and other hydrocarbons. These selectivities, in turn, are dependent on the pressure and composition of the gas being processed.[27,28] Currently, silicone rubber membranes with a typical mixed-gas propane/methane selectivity of 3−5 and a butane/methane selectivity of 5−10 are used.[29,30] Other more-selective materials have been reported; however, they are not used in industrial systems.[31,32]

Engine fuel gas conditioning is currently the most widely used application of membranes for heavy hydrocarbon separations.[33] A flow diagram and a photograph of a recently installed fuel gas conditioning unit (FGCU) are shown in Figure 14. At this site, the gas to be treated was being used to power a field compressor gas engine. The gas was very rich, resulting in engine knocking and frequent shutdowns. A portion of the high-pressure gas (at 450 psia) was diverted from the pipeline and passed across the surface of a membrane that selectively permeates the heavier components of the gas. Methane and ethane are retained by the membrane; propane, butane, C_{5+} hydrocarbons, and the BTEX aromatics all permeate preferentially. The performance of the unit is shown in Table 5. The membrane selectivity increases as the size and condensability
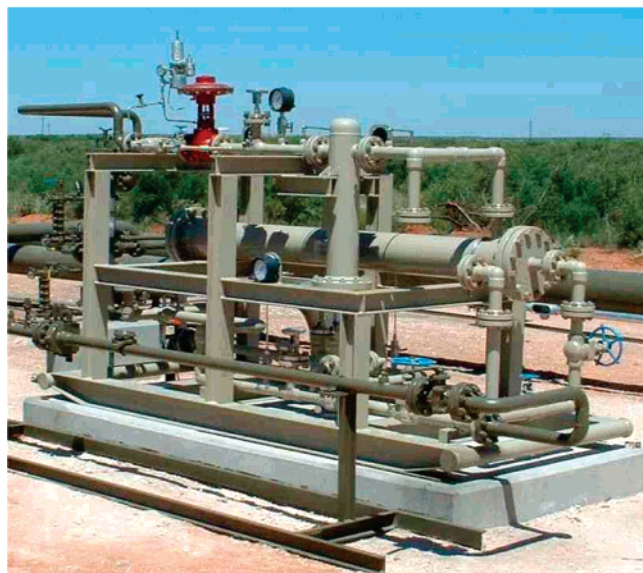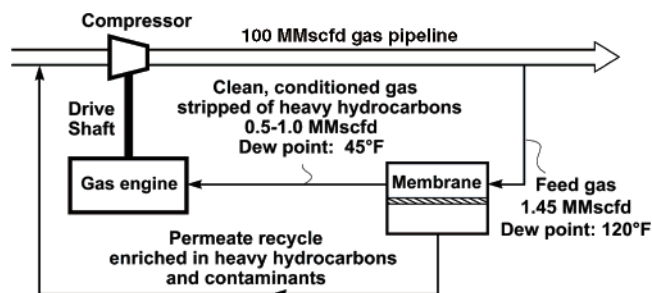
Figure 14. Block diagram (top) and photograph (bottom) of a membrane fuel gas conditioning unit (FGCU) used for a field gas compressor engine (MTR/silicone rubber membranes/spiral-wound modules). The membrane modules are contained in the horizontal pressure vessels, and the unit produces 0.5−1.0 MMscfd of clean gas.

Table 5. Performance Data for a Remote Site FGCU Removing C$_{3+}$ Components from a Natural Gas Stream[a]

| | Gas Composition (mol %) | |
component	feed gas	conditioned fuel gas
propane	4.6	1.5
isobutane	2.0	0.5
n-butane	1.5	0.3
pentanes	1.7	0.3
hexane	1.1	0.1
C$_6+$	0.9	0.1
balance methane and ethane		
total C$_{3+}$ hydrocarbons	11.8	2.8
methane number	16	71

[a] Data taken from ref 33.

of each hydrocarbon in the stream increase, so the C$_{5+}$ hydrocarbons with a selectivity of >20, are almost completely removed. In this particular application, the concentration of the C$_{3+}$ hydrocarbons is reduced from 11.8% to 2.8%. The gas methane number (which is a measure similar to the octane number of gasoline) increased from 16, which denotes a very poor fuel, to 71, which denotes an excellent fuel.

The relative volume flows of the conditioned gas and the permeate recycle gas are dependent on the separation required. Generally, the streams will be approximately equal in size, in which case installation of the membrane unit will require ~2%−4% of the pipeline gas to be diverted from the pipeline and through the gas conditioning unit. The process as shown uses no new rotating equipment and, therefore, is ideal for remote locations where maintenance is difficult.
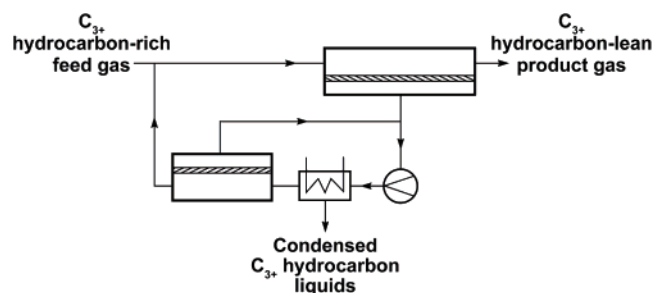

Figure 15. Flow scheme (top) and photograph (bottom) of a membrane dew point control unit (MTR/silicone rubber membranes/spiral-wound modules).

The type of membrane system used to treat associated gas or control the dew point of pipeline gas is shown in Figure 15. High-pressure feed gas is sent to modules that contain a higher-hydrocarbon-selective membrane, which removes the higher hydrocarbons as the permeate stream. This stream is recompressed and cooled by a fan-cooled heat exchanger to condense higher hydrocarbons. The noncondensed 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. The higher hydrocarbons are continuously concentrated until their condensation point is reached and they are removed as hydrocarbon liquids.[34] The system shown in Figure 15 reduced the dew point of the feed gas by 25 °C. In these systems, the cost of the compressor, visible in the right-hand side of the photograph in Figure 15, is often larger (sometimes significantly larger) than the cost of the membrane unit. Higher selectivity membranes would help in this application, even if the membrane permeance were lower. Unfortunately, no membrane that is significantly more selective than silicone rubber has yet been found for higher hydrocarbon separations.

3.3. Nitrogen Removal. Approximately 14% of U.S. natural gas contains >4% nitrogen, which is the U.S. pipeline specification for this contaminant. Many of these high-nitrogen gas streams can be diluted with low-nitrogen gas to meet pipeline specifications. If dilution is not practical, a nitrogen removal unit must be installed. Cryogenic distillation is the only nitrogen removal process used on a large scale to date. As of 1999, 26 nitrogen-removal cryogenic plants were in operation in the United States.[35] Cryogenic plants are most suited to large gas
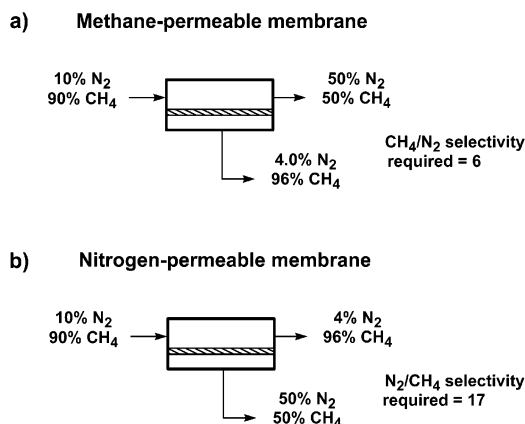
a) **Methane-permeable membrane**

b) **Nitrogen-permeable membrane**

Figure 16. One-stage membrane separations of a 10% N_2/90% CH_4 feed gas to produce a 50% N_2/50% CH_4 reject stream and a 4% N_2/96% CH_4 product gas. This target can be achieved using (a) a CH_4-permeable membrane with a selectivity of 6 or (b) an N_2-permeable membrane with a selectivity of 17, which is far greater than that of the best membranes known.

fields that can deliver 50−500 million scfd of gas for 10−20 years. These large fields allow the high capital cost of the cryogenic plant to be defrayed over several years. Many small nitrogen-contaminated gas wells are shut in for lack of suitable small-scale nitrogen separation technology. One new technology that has been attempted is pressure swing adsorption (PSA), using molecular sieves that adsorb nitrogen.[36,37] Another technology is membrane separation.

The nitrogen molecule is smaller than methane, so the diffusion selectivity term in eq 2 always favors the permeation of nitrogen. However, methane is more condensable than nitrogen, so the sorption selectivity term in eq 2 always favors the permeation of methane. Because the two terms are opposed, membranes can be made that selectively permeate nitrogen (maximum selectivity of nitrogen over methane ($\alpha_{N_2/CH_4} \approx 2.5$)), or that selectively permeate methane (maximum selectivity of methane over nitrogen ($\alpha_{CH_4/N_2} \approx 3-4$)).

The ability of nitrogen- and methane-selective membranes to perform a target separation are compared in Figure 16. In this comparison, a single-stage membrane unit is used to process a gas stream contaminated with 10% nitrogen into a product gas that contains 4% nitrogen and a waste gas that contains 50% nitrogen (the latter of which is to be vented. Single-stage membrane units would rarely be used for these separations; however, they do provide a good example for the difference between the two types of membranes. A membrane unit able to perform this separation would recover ∼93% of the hydrocarbons in the gas stream, which is sufficient for most small producers. The simulation was run iteratively, increasing the membrane selectivity by small increments until the membrane can just perform the separation required. In a single-stage process (rarely used), methane-permeable membrane with a methane/nitrogen selectivity of 6 can achieve the target separation. A selectivity of 6 is within striking distance of today's most methane/nitrogen selective membranes (which have a selectivity of 3−4).[38] In contrast, a nitrogen-permeable membrane must have a nitrogen/methane selectivity of 17 to achieve the same separation. The best nitrogen-selective membrane currently known has a nitrogen selectivity of 2.5, which is far below the value required; this is why methane-permeable membranes are used for this separation. Even so, multistep or multistage systems are required in almost all applications.[38,39] In some applications, a combination of these two membranes proves to be the best solution.
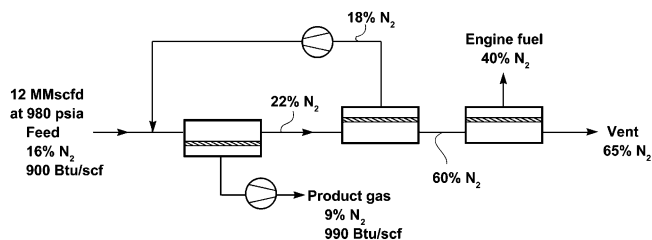

Figure 17. Flow diagram of a 12 MMscfd membrane N_2 removal plant installed on a high-N_2 gas well in the Sacramento River Delta region of California.

The design of a two-step nitrogen separation plant that was installed in a Sacramento River Delta gas field in California is shown in Figure 17. The feed gas contained 16% nitrogen. The heating value of the gas was 900 Btu/scf. The pipeline would accept gas for dilution with low-nitrogen gas if the heating value was increased to 990 Btu. To reach this target, the feed gas, at a pressure of 980 psia, 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%. These changes increased the heating value of the gas to 990 Btu/scf. This gas was compressed and sent to the pipeline. The residue gas that contained 22% nitrogen 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 residue gas from this unit was then sent to a final small module to be further fractionated. This module's permeate gas, which contained 40% nitrogen, was used as fuel for the compressor engines. The final residue contained 65%−70% nitrogen, and it was essentially stripped of all C_{3+} hydrocarbons and was vented.

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 separated nitrogen. This system allowed 12 million scfd of gas with an annual value of approximately $20 million to be produced. On this basis, the system had a payback time of just a few months.

3.4. Water Removal. The removal of water from natural gas is an extremely common operation and is usually performed close to the wellhead to avoid hydrate formation and corrosion in the gas gathering system. By far, the most widely used technology is absorption of water with diethylene or triethylene glycol.[40] Approximately 40 000 absorber−stripper units are in operation at gas wellheads in the United States; there are many more in use around the world.[41] The water content of high-pressure, water-saturated gas is usually ∼1000 ppm, and the objective of the glycol absorption gas dryers is to bring this concentration to ∼100 ppm, which would be sufficient to prevent condensation, hydrate formation, and corrosion in the pipeline. Because the mass of water removed by the dryer is small, glycol absorbers are much smaller than carbon dioxide amine absorbers. A typical system that is designed to dry 10 million scfd of gas can be purchased for $100 000 and is fully automated for unattended operation, using pneumatic controls and valves and pumps. The operating costs are only a few cents per 1000 scf of gas treated.

The low cost and wide industry acceptance of glycol dehydration systems has proved to be a stiff barrier to membrane competition. However, a few membrane dehydration systems have been built. Producing competitive membrane dehydration systems for natural gas treatment is not a membrane material performance problem. Membranes widely used to remove water from air could be used; these membranes have good water
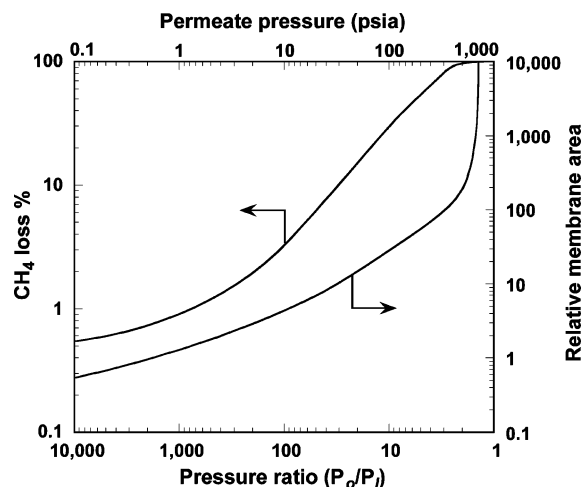
Figure 18. Effect of permeate pressure on the efficiency of a membrane natural gas dehydration system. (Conditions: feed concentration, $n_{H_2O_o} = 1000$ ppm; residue concentration, $n_{H_2O_l} = 100$ ppm; H_2O/CH_4 membrane selectivity, 500; feed pressure, 1000 psia.) Both CH_4 loss and required membrane area decrease as the pressure ratio increases (or as the permeate pressure decreases).

Figure 19. Membrane system designs for dehydration of natural gas (H_2O/CH_4 selectivity = 500; P/l_{H_2O} = 2,000 gpu): (a) dehydration using a recycle compressor and (b) dehydration using a permeate sweep gas.

permeances and water/methane selectivities of ≥500. The problem is a loss of methane, with the water vapor permeating the membrane. Membrane units used to dry air also lose a fraction of the high-pressure air to the permeate. In air dehydration, this loss of air to the permeate is inconsequential; with natural gas, a loss of even 1% of the feed gas makes the process noncompetitive.

The reason these very high selectivity membranes lose methane to the permeate gas is due to pressure ratio limits on membrane performance. The importance of pressure ratio in the separation of gas mixtures can be illustrated by considering the separation of a gas mixture with water concentration of $n_{H_2O_o}$ at a feed pressure p_o. A flow of water across the membrane can only occur if the partial pressure of water on the feed side of the membrane ($n_{H_2O_o}p_o$) is greater than the partial pressure of water on the permeate side of the membrane ($n_{H_2O_l}p_l$); that is,

$$n_{H_2O_o}p_o \geq n_{H_2O_l}p_l \qquad (3)$$

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

$$\frac{p_o}{p_l} \geq \frac{n_{H_2O_l}}{n_{H_2O_o}} \qquad (4)$$

That is, the separation achieved is always smaller than the pressure ratio p_o/p_l, no matter how selective the membrane.

The effect of pressure ratio on system performance with high selectivity membranes is illustrated in Figure 18. A membrane with a water/methane selectivity of 500 is used to remove water from high-pressure natural gas. With this high selectivity membrane, the membrane area required to perform the separation, and the amount of methane lost with the permeate gas decreases sharply as the permeate pressure is reduced (increasing the pressure ratio). Clearly, operating at low permeate pressures is beneficial. Nonetheless, even at a permeate pressure of 15 psia (atmospheric pressure), ~5% of the feed gas methane is lost with the permeate gas. This is too much gas to be useful as onsite low-pressure fuel; therefore, the bulk of the lost gas must be vented or flared. The loss of this much gas makes the process noncompetitive.
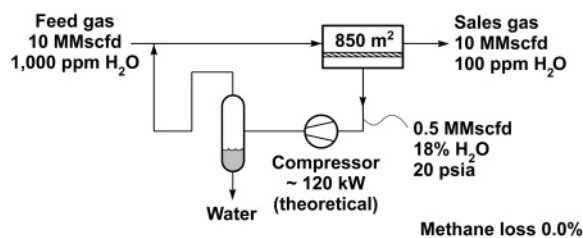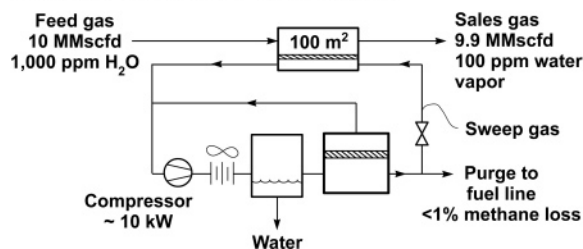
One way to reduce the methane loss to an acceptable level is to use a small vacuum pump to reduce the pressure of the permeate gas to 1−2 psia.[42,43] The membrane system then becomes small and the methane loss decreases to <1%. The cost of such a membrane-vacuum system could be competitive with glycol dehydration, and in offshore applications, the small footprint and low weight would be attractive. A membrane system would have approximately one-fifth the weight and footprint of a glycol absorption plant. However, the potential hazard posed by air leaks contaminating the permeate gas has to date made operators reluctant to send the gas to the plant fuel line, so the gas must be vented or flared, and even a methane loss of <1% normally is not economically acceptable.

Another solution to this problem, shown in Figure 19a, is to operate the membrane system at a permeate pressure close to atmospheric pressure and then recompress the permeate gas. Compressing the gas would cause almost all of the water vapor to condense and the remaining gas could be sent back to the high-pressure feed. The problem with this system is cost of the permeate compressor. This cost is larger than the cost of the membrane system, so this approach is not appealing.

Yet another process design, which was developed by Air Products and used in a few systems, is shown in Figure 19b.[44,45] In this process, a sweep gas of dry methane is passed across the permeate side of the membrane. The sweep gas increases the effective pressure ratio for water transport and reduces methane loss to ~1%. The wet sweep gas−permeate mixture leaving the membrane unit is sent to a small secondary methane drying loop, which produces clean dry methane to be recirculated. The complexity of the system and the need for a small compressor has limited use to a few offshore applications. Because of all the problems previously outlined, membrane technology is still struggling to break into the natural gas dehydration market.

3.5. Other Membrane Applications. The separations of carbon dioxide, heavy hydrocarbons, nitrogen, and water are the principal applications of membrane technology in the natural gas processing industry. At least one membrane plant to separate helium from natural gas has been installed. However, most of the world's helium is produced as a byproduct of cryogenic units that remove nitrogen from natural gas, so it is unlikely

that more than a few membrane plants will be installed in the near future for this application. Membrane systems have also been suggested as an alternative to amine absorption for the separation of H_2S from natural gas. Membranes with good H_2S/CH_4 selectivities and high permeances have been made,[33] so membranes could be useful as part of a hybrid membrane-plus-absorption process to process gas that contains high levels of H_2S. However, the complexity of this type of combination process is only justified for relatively large gas streams, which are limited in number.

4. Conclusions

The use of membranes to process natural gas is a rapidly growing area of technology. More than 20 large ($>$100 million scfd) carbon dioxide membrane removal plants have now been built, as well as many smaller systems. Membranes are the technology of choice for carbon dioxide removal systems on offshore platforms, and they are beginning to compete head-to-head with amine systems at onshore plants. As the technology matures, it seems likely that the membrane market share for carbon dioxide separations will grow from the present low level, especially for gases that have high carbon dioxide contents (20% or higher). Cellulose acetate, which was the first material developed for carbon dioxide separation applications, is still the industry standard, but alternatives are now commercially available. Over time, these new materials will increase the competitiveness of membranes in the realm of carbon dioxide/natural gas separations.

Another growing application is the removal of heavy hydrocarbons. Thus far, the most important use of membranes has been in small (0.2−2.0 million scfd) streams to produce clean gas for field engines and turbines. This application is growing, but a much larger market exists for units to recover heavy hydrocarbons as natural gas liquids from associated gas streams produced on offshore platforms or at remote wells. These streams are large and not uncommon, and the value of the liquids recovered by the membrane process can lead to short payback times. The development of better, more-selective membranes would accelerate the development of these applications.

Nitrogen removal with membranes has also experienced development over the past two years. Membranes offer a modest separation selectivity of methane from nitrogen; however, the separation is difficult using any other technology, so membranes are still the low-cost solution in these applications. Most U.S. high-nitrogen gas can be brought to specification by blending it with sufficient quantities of low-nitrogen gas. When dilution is possible, it is very difficult for membranes, or any other technology, to compete. However, site-specific issues can arise requiring a membrane nitrogen removal unit, so this application will likely grow, although it may be significant in the U.S. market only.

The dehydration of natural gas, which is a very common natural gas treatment process, has proved disappointing as an application for membrane technology. A handful of systems that are based on membranes and process designs developed for air dehydration have been installed; however, current membrane technology cannot compete with glycol absorption, except in a few offshore operations where size and weight considerations favor a membrane solution. Therefore, the dehydration of natural gas with membranes is likely to remain a niche application. The issue is not the availability of good membranes, but rather the pressure ratio needed to allow the membrane to be used.

In summary, membrane-based removal of natural gas contaminants is the most rapidly growing segment of the membrane gas separation industry, especially in applications for the separation of carbon dioxide, nitrogen, and heavy hydrocarbons. Improvements in polymer performance, membrane structure, module fabrication, and process design have all contributed to increasing the potential range of applications for membranes in natural gas treatment. Membranes now give natural gas producers an additional tool for upgrading the quality of the gas streams that they can deliver to the natural gas market.

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