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The Developing Technology of Gas Separating Membranes

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The ability to separate materials from each other economically is crucial and often limiting in large-scale chemical processes. Most existing petrochemical processes were developed during an extended period of cheap energy and a stable and plentiful basic feedstock supply. However, the increased cost of energy and raw materials since 1973 has made many existing processes less attractive and has created a need for new unit operations, and particularly new separation procedures, that are more compatible with current energy costs and feedstock supplies. In addition, new processes will have to be adaptable to future changes in energy and feedstock supplies and in manufacturing requirements.

Summary. The background of and commercial needs leading to the development of practical membrane systems for the separation of industrial gases are presented. The critical issues and fundamental technical limitations that delayed earlier development of such systems and the solutions of some of the major problems in the field are discussed. Particular attention is given to the methods by which high gas fluxes and high selectivities have been achieved in hollow fibers. The performance characteristics of various practical gas separation methods are compared, and the effects of parameters such as pressure and contaminant levels are illustrated with representative examples.

Separation systems based on membranes are particularly suited to these requirements. Recent developments in membrane technology have led to the commercialization of large-scale gas separation systems based on hollow fiber membranes which overcome many of the problems faced by earlier systems. These systems were initially developed for the separation of hydrogen from various gases, but are now used for other separations as well. They are expected to have a considerable impact on a number of petrochemical and refinery synthesis processes because they meet the need for resource conservation, flexibility, and reduced energy consumption.

Membrane separations is a dynamic and rapidly growing field. Annual sales of all membrane separation systems, which were almost nonexistent as recently as 1950, now exceed $1.0 billion. The study of membrane separations can be traced back to at least 1854 (*1*). Most research in the field was basic and quite fundamental until 1950, while most of the discoveries that have led to industrially useful membranes have taken place since that time.

The separation of gases by membranes is of particular interest not only because it is the most recent and rapidly growing segment of the industry, but also because it is in many ways one of the most technically challenging. In this article we review the development of membrane-based gas separation systems (particularly those used for H_2 separation) and illustrate some of their advantages.

Gas Separation Membranes

As applied to separations technology, the term membrane generally refers to a thin polymer barrier, or occasionally to a metal or liquid interface, between two substances. While they can be classified in many different ways (*2*, chapter 1) most practical membrane-based separation systems utilize polymer membranes in the form of flat sheets or hollow fibers that are nonuniform in structure (asymmetric) and are porous to some extent. In membranes used for filtration, pores extend throughout the membrane and the pore diameter determines the size of particles that may be filtered. Membranes used for such applications as reverse osmosis are relatively nonporous near the surface, but porous below the surface. Some membranes are composites consisting of two or more polymers in distinct layers. Here we discuss the development, properties, and potential of composite hollow fiber membranes, especially those used for gas separations.

The flux with which a gas a permeates a membrane is given by

$$Q_a = \frac{P_a A \Delta p_a}{l} \qquad (1)$$

where Q_a is the steady-state flux of the gas, P_a is the mean permeability coefficient, A is the membrane surface area, Δp is the partial pressure differential for the gas across the membrane, and l is the membrane thickness. Equation 1 is derived under the assumption of Fickian diffusion of a dissolved gas in an isotropic dense membrane of the polymer (*2*, chapter 2; *3*).

The selectivity or separation factor, α, for gas a over a second gas b in a mixture is given by

$$\alpha_b^a = \frac{P_a}{P_b} \qquad (2)$$

where P_a and P_b are the mean permeability coefficients for gases a and b. Inspection of Eq. 1 shows that where the partial pressure differentials for two gases in a mixture are the same, the selectivity will

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also be equal to the relative fluxes of the two gases across the same membrane.

Requirements for gas separation. Many improvements have had to be made in the state of the art since 1950 to develop a membrane system that would be useful for gas separations. Such a membrane system must meet the following major requirements:

1) It must exhibit a much higher gas flux (three to four orders of magnitude) than could be achieved by membrane systems at that time.

2) It must have a reasonably high selectivity (generally > 20, often > 40) for the gases to be separated.

3) It must function at very high pressures (2000 to 3000 pounds per square inch) and pressure differentials across the membrane (up to 2000 psi) for some applications.

4) It must maintain its properties and function in the presence of a variety of contaminants, at varying levels, and over a reasonable range of temperatures (for instance, between 0° and 100°C).

5) It must be compatible with large-scale modules, seals, and engineered systems that optimize the flow and distribution of gases to the membrane and remain stable in the necessary process environments.

Given such extensive requirements and the variety of existing separation methods applicable to gases (distillation, absorption, adsorption, and so on), one might well ask why membranes are needed. The potential operational advantages of membranes include energy efficiency, process flexibility, and utility in the presence of impurities. Another advantage is that membranes can discriminate between molecules on the basis of factors such as size, shape, polarity, and chemical interaction. As a result, they can be used to separate species that are often very difficult to separate by more conventional methods.

Critical Properties and Variables

Flux and selectivity. In order to achieve high flux and high selectivity, it was necessary to develop a system in which Q was large for one gas in a mixture and relatively small for at least one other gas in the mixture. This could be accomplished only by manipulating the four parameters P_a, A, Δp_a, and l in Eq. 1. However, while each of these parameters can be varied, there are problems associated with changing them that until very recently made the task of simultaneously achieving high flux rates and high selectivities an exceedingly difficult and challenging one.

Permeability. The coefficient P_a in Eq. 1 may be described as

$$P_a = S_a D_a \quad (3)$$

the product of the solubility coefficient, S_a, and diffusion coefficient, D_a, of molecule a in the polymer of interest. Transport of molecules across a membrane occurs by solution of the molecule in the membrane polymer at the high-pressure (or high-concentration) surface, diffusion of the molecule across the membrane, and desorption of the molecule at the low-concentration surface. The fact that permeability coefficients for most gases are orders of magnitude less than permeability coefficients for liquids in the same membranes (*4*) is one of the major reasons why it has been difficult to generate membranes with high gas fluxes. However, as shown in Table 1, the permeability coefficients for different gases and the selectivities for gas pairs vary widely. Many polymers are potentially very good separators in that they have high intrinsic selectivities for certain gas pairs. Many glassy polymers exhibit relatively high permeabilities for H_2, He, CO_2, NH_3, and H_2S (compared to other gases). The same polymers typically exhibit relatively low permeabilities for N_2, CO, methane, and ethane.

Glassy polymers, which ordinarily fall into the category of good engineering thermoplastics (high tensile strength and impact resistance), also typically have relatively high permeability coefficients for very small molecules such as H_2, due primarily to high diffusion coefficients (D_a in Eq. 3) for such gases. Polysulfone and polyphenylene oxide are examples of these polymers. They also have relatively high permeability coefficients for gases such as H_2S, CO_2, and NH_3, but this is because these gases have higher solubilities (S_a) than gases such as N_2 and CO in these polymers.

Rubbery polymers are often much more permeable to gases than glassy polymers, but selectivities tend to be lower. Gases such as methane are less permeable than H_2 or CO_2 in most glassy polymers but more permeable in some rubbery polymers, due principally to their greater relative solubility in rubbery polymers. In terms of the five criteria listed in the preceding section for useful gas separators, rubbery polymers have one major advantage, high permeability, but they also have a number of disadvantages. For example, they are not likely to be self-supporting and they are particularly susceptible to swelling. As a result, practical gas separation systems based on rubbery polymers have not yet been developed.

On the basis of selectivity, typical barrier polymers (*4*) such as polyacrylonitrile should make superb separators—for instance, α for $H_2/N_2 > 1000$ (Table 1). In fact, barrier polymers are often used as the substrate for plastic bottles because they limit gas permeation. This is because they are three to six orders of magnitude less permeable (depending on the gas studied) than engineering polymers such as polysulfone. Such low values of P make it difficult to achieve practical fluxes with barrier polymer membranes, and this limitation has not yet been overcome.

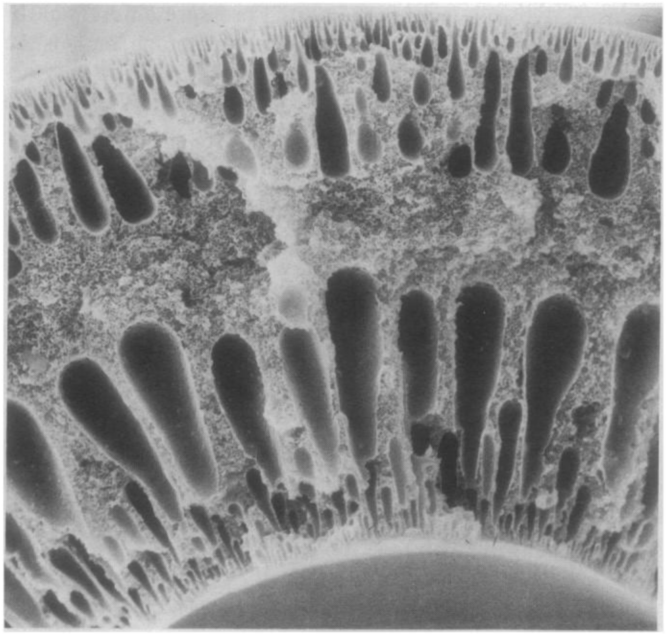

Fig. 1. Asymmetric hollow fiber. Fibers are typically spun from a water-miscible solvent into water.

Table 1. Hydrogen permeabilities and H_2/N_2 selectivities for various classes of polymers. See (*4*) for detailed values. The values given here are approximate and are intended to reflect general trends. Significant variations within classes can be found, and exceptions to the general trends exist.

Polymer	P_{H_2} ($\times 10^9$ cm^3 STP/ cm^2-sec-cmHg)	$\alpha_{N_2}^{H_2}$
Silicone rubbers	100 to 500	1.5 to 3.0
Hydrocarbon rubbers	50 to 300	2.0 to 4.0
Polyphenylene oxides	50 to 100	10 to 20
Substituted polysulfones	20 to 70	15 to 25
Polycarbonates, polysulfones	0.5 to 20	25 to 75
Polyesters, nylons	0.5 to 3.0	50 to 150
Acrylonitrile copolymers (high concentration acrylonitrile)	0.1 to 1.0	100 to > 1000

Table 1 contains only typical commercially available polymers, but new polymers with unique separating properties could be synthesized. Unfortunately, there are many problems associated with controlling the physical and separating properties of polymers in specialty synthesis, and such problems can be almost as great as those associated with making working membrane systems. Such problems would greatly complicate the development of a separation system with reproducible separating properties and environmental resistance. Consequently, commercial membrane separation systems have been based on generally available bulk polymers developed for other applications.

Membrane surface area. The need for high flux in a commercial membrane system can always be met by increasing surface area. However, this increases the size and cost of the system, but does not increase the value or total quantity of material being separated. At some point (which is specific for each application) use of additional surface area will make the system uneconomical.

Calculations made as early as 1950 (*1*, *5*) indicated that the use of polymers of even relatively high permeability in the form of dense membranes to separate gases would require millions of square feet of membrane surface to separate modest gas volumes. The need for so much surface area made the practical application of membranes to gas separation problems seem impossible.

Driving force. Permeation always requires a driving force, and for most gases this can be represented (as in Eq. 1) by the partial pressure differential across the membrane. Flux can always be increased by compressing the gas mixture and increasing Δp. However, compression consumes energy, and while adequate fluxes can theoretically be achieved by compressing the gas to high enough pressures, the increased cost of pressure vessels, compressors, and energy associated with the compression itself makes this approach generally unattractive. In addition, operating at higher pressure differentials requires much greater strength of the hollow fiber or membrane. Hence compression per se is not the general answer to the problem of low fluxes.

As the preceding discussion suggests, P, A, and Δp can be manipulated to increase fluxes, but practical and economic problems limit the degree to which they can be changed while still meeting the other requirements for a viable system. Indeed, it became evident after 1950 that some new approach was needed for improving membrane fluxes which would permit conventional polymers to be used while minimizing compression and surface area requirements.

Membrane thickness. As seen in Eq. 1, flux is inversely proportional to membrane thickness. It has been the manipulation to decrease the achievable thickness of membranes made from glassy polymers (polysulfone, cellulose acetate, and so on) that has made possible the production of high-flux systems that satisfy the demands of the chemical process industry.

Loeb and Sourirajan (*6*) made a major breakthrough in this area in 1960 that resulted in useful asymmetric membranes made of cellulose acetate. Membranes of this type are made by casting onto a glass plate thin sheets of polymer dissolved in a water-miscible solvent. After a short period the cast solution is immersed in water, and as water diffuses into the solution the polymer coagulates at a rate that is a complex function of the polymer and solvent properties. Such membranes are porous throughout, but invariably have a thin, relatively dense skin near one surface (Fig. 1) which generally occupies a very small fraction (0.1 to 1 percent) of the total membrane thickness. These membranes have proportionally higher fluxes than dense membranes of equivalent thickness because the effective separating layer (the dense skin region) is so small. It should be pointed out that such membranes are generally considered nonporous at the surface for reverse osmosis–type separations. However, they are found to have pores that are substantially larger than typical gas molecules (several angstroms), and as a result they make poor gas separators.

Methods have been developed over the years to permit the control of surface porosity on a smaller and smaller scale. This can be done by changing casting and coagulation conditions or by posttreatment of the membrane. For some uses (ultrafiltration and microfiltration) high surface porosity is necessary and useful. Other applications (liquid and especially gas separations) require much lower porosity in the membrane.

The same principles used for casting asymmetric membranes can be used to create asymmetric hollow fibers. Instead of being cast on a glass plate, the solution is pumped through a tube-in-orifice spinnerette (*7*), which is immersed in a water bath. A membrane or hollow fiber produced by any of these methods typically has a total wall thickness of 25 to 250 micrometers with a dense skin region (still porous to some degree) of 0.1 to 1.0 micrometer. The intrinsic permeation properties of the membrane should be independent of its form (flat sheet or hollow fiber).

Since the pioneering work of Loeb and Sourirajan, many workers have produced asymmetric membranes and hollow fibers from a variety of materials. Many of the practical ultrafiltration, microfiltration, and reverse osmosis systems currently available in flat sheet and hollow fiber form are based on such asymmetric membranes. Excellent reviews have been published on the applications, uses, and manufacturers of different types of commercial membranes and hollow fibers (*7*, *8*).

It is noteworthy that such membranes are all porous to some degree and, as shown in Fig. 2, a surface porosity as low as 10^{-6} percent is enough to prevent a membrane from effectively separating gases. When such a membrane is tested for gas separation, it will fail to separate and appear to be porous even though it may separate in a liquid medium as though it had no surface pores. If the skin of such a membrane were truly nonporous it would separate gases with the intrinsic polymer selectivity (P_a/P_b), but would have a flux two to four orders of magnitude higher than a dense membrane of the same total wall thickness. This is because most of the wall would have an open cellular porous structure, and only the very thin layer near the surface would be effecting the separation of the gas mixture.

Membrane porosity. One method (*9–12*) for overcoming the problem of surface porosity in asymmetric membranes is to coat the porous membrane with a material of relatively high permeability. The properties of such composite membranes are defined in terms of the relative resistance of their coating, substrate, and porous regions to gas flow. By appropriately matching the resistances of these three critical regions such a composite, called a resistance model or RM composite (*8*), can be made to approach the selectivity of an essentially defect-free asymmetric membrane composed of only the substrate polymer (Fig. 2), even though the porosity of the substrate can be quite high and can vary widely. At first glance such membranes appear to be similar to composites described below in that they consist of a dense polymer coating on a porous support. However, in RM composites it is the originally porous substrate that becomes the effective separating layer, not the coating layer as in conventional composites.

High fluxes and selectivities can be easily obtained for gases with this approach, and hollow fibers based on this principle are now used in commercially available systems (Prism separators) for the separation of gases such as H_2 and He from gases such as N_2, CO, and CH_4 (*13–16*). Similar fibers have been fully demonstrated and are being commercialized for the separation of CO_2 from various hydrocarbon gases. Some of the important commercial applications of such systems include H_2 recovery from purge gases in ammonia synthesis and in petrochemical and refinery processes utilizing H_2 as a reactant feedstock gas. Other uses include ratio adjustment of feed gases in petrochemical and refinery processes involving H_2, CO_2, CO, and CH_4, and recovery and recycle of CO_2 in enhanced oil recovery processes.

As stated above, there are other methods for reducing porosity in a membrane surface and other methods by which very thin membrane separating layers can be created. For example, a porous membrane can be treated by heat or by swelling agents after it is formed to close most or all of the pores in the surface. Such treatments tend to densify the separating layer and thus to decrease achievable fluxes, but the fibers that result from such treatments can separate gases. In some cases spinning or casting conditions can be found (particularly for cellulose acetate) which yield fibers or membranes with surface porosities low enough to permit some degree of separation (*17*). Again, such membranes will tend to have thicker separating layers and will in general have lower fluxes than RM composites in which the same polymer is the porous substrate. In addition, cellulosic polymers are particularly susceptible to many contaminants that may be present in gas streams. Nevertheless, modified cellulosics are being commercially tested by a number of companies for application in the recovery of CO_2 and other gases.

The most common approach to the development of high-flux membranes for gas separation has been to create composites in which the porous membranes act as supports for thin dense separating layers of a second polymer. Work of this type carried out by Ward *et al.* (*18*) involved the casting of ultrathin dense separating membranes on porous supports (*19*). A major problem in making such membranes is the delicate nature of the ultrathin skin, which is often less than 500 Å thick. Membranes of this type have been used in relatively small demonstration systems for O_2/N_2 and CO_2/CH_4 separation. However, it has proved difficult to control the properties of such membranes reproducibly, and this approach has not been pursued for the development of truly large-scale, high-pressure applications. Other factors limiting the applicability of such membranes are related to the inherent disadvantages (discussed below) of flat sheet membranes for any type of gas separation.

Workers in the field of membranes have come to recognize the difficulties and trade-offs involved in trying to achieve high fluxes, high selectivities, and acceptable environmental stability simultaneously. This problem has been particularly vexing for those working on gas separations because the small size and relatively low permeability of gas molecules place the greatest demands on the control and uniformity of fiber properties. However, it does appear that the RM composites used in Prism separators have made possible the broad utilization of membranes for gas separations. It is also likely that further developments will result in new membranes and systems based on RM composites and on other types of membranes which will be useful in many future applications.

Advantages of the hollow fiber form. In principle, it is possible to produce asymmetric hollow fibers and flat sheet membranes with equivalent properties. But there are significant practical differences between these two forms that affect their utility. Flat sheet membranes can be supported in stacks (*18*), or can be wound in spiral form into a tubular shell (*2*, chapter 15; *20*). In either case, the principal advantage of sheet membranes for gas separation is the relatively low pressure drop associated with gas flow on both the feed and permeate sides of the membrane.

Hollow fibers, on the other hand, have several distinct advantages for gas separation. Hollow fibers made of glassy polymers are excellent self-supporting structures in gas environments where high pressures and pressure differentials are required and where environmental contaminants that can weaken the polymer are present. Very high collapse pressures can be achieved (*13*) [$\Delta p > 2000$ pounds per square inch gauge (psig)] in such hollow fibers without the need to provide additional support. Flat or spiral wound sheets are not expected to be self-supporting, and high pressure drops across the membrane wall require strong (and generally more expensive) supports for the membrane.

Another advantage of hollow fibers is their very high surface-to-volume ratio. Regardless of module size, a hollow fiber system should contain 100 to 1000 times as much surface area as a stacked sheet system and 4 to 100 times as much surface area as a spiral wound system (*20*), depending on the size of the hollow fiber used. Thus, a hollow fiber system will generally have a significant advantage in performance on the basis of flux per unit system volume.

Perhaps the biggest potential disadvantage of hollow fibers as opposed to flat membranes is the fact that high gas fluxes and relatively small bore diameters (< 100 μm) can result in high pressure drops associated with gas flow through the fiber bore. These problems have been minimized by the development of spinning technology for the production of very strong large-bore (> 200 μm) fibers in which pressure drops are minimal (*15*).

Comparison of Membrane Systems with Other Separation Methods

Direct comparisons between different commercially accepted separation processes (for instance, membranes, adsorption, and distillation) are difficult to make. In fact, the specific characteristics of each unit operation can be advantageous or disadvantageous depending on specific needs and requirements. However, there are five major areas of difference among separation methods that are worth discussing because they show where each method is likely to be optimally used. These areas are (i) energy utilization, (ii) product purity, (iii) product pressure, (iv) effect of contaminants, and (v) flexibility and simplicity.

Distillation has always been the system of choice for the large-scale separation of materials (gases as well as liquids). Other separation methods have tended to be ignored in process designs unless for some specific reason it was known that distillation would not do the job. We limit our comparisons here to cryogenic distillation and membrane systems, because cryogenics has been the principal method by which industrial process gases such as H_2 have been separated in the past. However, there are other methods (for instance, pressure swing adsorption) applicable to specific gas separations.

Energy. The energy gained in mixing ideal or nearly ideal gases is usually quite small (just the heat of mixing). Separating such materials always requires the input of energy, and often the energy consumed in separating them is far greater than the energy gained in mixing them. In fact, the actual energy used in most large-scale separations is a complex function of plant design and how energy is utilized in all the related processes within the chemical complex (*21*). It is therefore difficult to assign a true energy cost to each process within the complex, and this is probably best done by determining the incremental fuel requirement for the entire complex associated with each process (*19*).

Both membranes and cryogenics can be highly energy-efficient if used correctly in large-scale processes. The separation of salt from seawater illustrates this (*22*). The energy gained in mixing sodium chloride with water is only ~ 0.7 kilocalorie per liter. Separating such a mixture by distillation, even with effective heat exchangers, typically consumes 75 to 150 kcal/liter. By comparison, purifying the same salt solution by reverse osmosis consumes only ~ 3 kcal/liter, and it appears that reverse osmosis is more energy-efficient than distillation. However, a meaningful comparison would be strongly dependent on the use of recovered energy from both processes as well as the cost and lifetime of the capital equipment required.

It is often possible to separate gases with membranes by using available pressures and pressure differentials with no additional input of energy. If compression is needed, a good rule is that the consumption of energy will not be excessive as long as the compression ratio is less than 2. However, it would be a mistake to assume that membrane separations are generally lower in energy consumption than cryogenics (desalination notwithstanding), and often the opposite is true. The key factor is usually the amount of compression and recycle used.

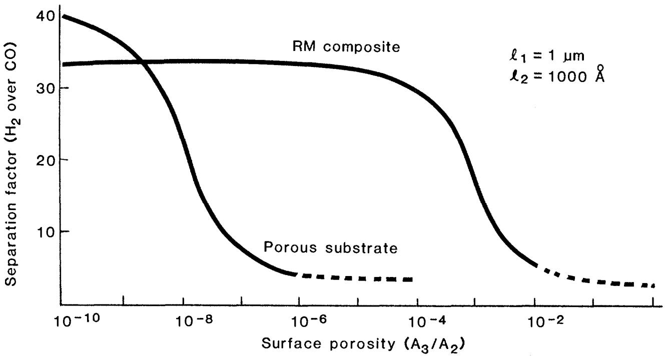

Fig. 2. Selectivity of polysulfone resistance model composite and a normal porous membrane versus surface porosity.

Product purity. Cryogenic systems can almost always produce relatively pure products. Synthesis gas (reformed methane) in large chemical complexes typically has a H_2/CO ratio of ~ 3/1. When such a stream is treated cryogenically, pure (> 99 percent) H_2 and CO streams can be easily obtained. Most of the energy consumed in such a cryogenic separation is used in the initial cooling of the gas stream. It costs relatively little (and consumes very little additional energy) to add more trays to the distillation column and produce the gas at high purity.

To produce high-purity H_2 from a membrane separation, the low-pressure H_2-enriched product would have to be recompressed and recycled or fed to another bank of separators (*23*). However, many large-scale hydrogen consuming processes do not require H_2 at purities greater than 90 to 95 percent. In some cases it is control of the H_2/CO ratio that is critical, and even if pure gases were available they would have to be mixed. The use of membranes to control gas composition can have significant advantages in such applications. Cases B, D, and F in Table 2 illustrate how a membrane separation can be used to produce two product streams of appropriate composition for different reactions.

A typical synthesis gas stream (here ~ 70 percent H_2) is fed to a hollow fiber separator unit. The high-pressure stream enriched in CO can be used for a reaction such as oxo-alcohol synthesis (*14*). The low-pressure H_2-rich stream can be used for various hydrogenation processes. It can be seen that the system is quite flexible in that the low-pressure H_2 product can be delivered at a variety of pressures depending on the needs of the various processes.

Table 3 illustrates the point that achievable product purity in a (single-pass) membrane system is directly related to the composition of the gas feed. Compare, for example, cases J, L, and O. Recovery of H_2 (that is, permeate H_2 as a fraction of the total H_2 present in the feed) in the high-purity stream is constant. The fiber surface areas are low and do not differ greatly. It is interesting to note here (case O) that even a 10 percent H_2 feed stream can be upgraded to a

Table 2. Effect of pressure differential (Δp) on product composition and recovery in a hollow fiber system. Fixed parameters of the system are $\alpha_{CO}^{H_2}$, 40 – membrane selectivity; feed composition, 70/30 (H_2/CO); and feed pressure, 400 psig.

Case	High-pressure (shell) product composition (H_2/CO, molar ratio)	Bore pressure (psig)	Δp (psi)	Low-pressure (bore) product composition (H_2/CO, molar ratio)	Percent recovery of H_2 in bore product	Relative fiber surface area*
A	5/95	50	350	87/13	98.5	23
B	55/45	50	350	96/4	50	4
C	24/76	150	250	90/10	90	23
D	55/45	150	250	96/4	50	6
E	68/32	150	250	97/3	10	1
F	55/45	250	150	90/10	56	23

*Actual surface areas will depend on total gas volume treated and fiber flux per unit area. Normalized surface areas may be considered as correction factors to be applied after fiber type (flux) and gas volume have been specified.

Table 3. Effect of changing variables on product composition and recovery in a hollow fiber system; $\alpha^{H_2}_{CO}$, = 40 − membrane selectivity.

Case	Feed composition (H_2/CO, molar ratio)	Shell feed and product pressure (psig)	Bore product pressure (psig)	Δp (psi)	Shell product composition (H_2/CO, molar ratio)	Bore product composition (H_2/CO, molar ratio)	Percent recovery of H_2 in bore product	Relative fiber surface area*
E	70/30	400	150	250	68/32	97/3	10	1
G	70/30	1500	150	1350	21/79	94/6	90	2.6
H	40/60	400	150	250	27/73	78/22	50	16
I	40/60	700	150	550	26/74	88/12	50	4
J	40/60	1500	150	1350	26/74	92/8	50	1
K	20/80	1500	150	1350	3/97	64/36	90	5
L	20/80	1500	150	1350	12/88	78/28	50	1
M	20/80	1500	150	1350	18/82	83/17	10	0.2
N	10/90	400	50	350	9/91	48/52	10	2
O	10/90	1500	150	1350	6/94	53/47	50	2
P	10/90	1500	150	1350	9/91	59/41	10	0.4

*Actual surface areas will depend on total gas volume treated and fiber flux per unit area. Normalized surface areas may be considered as correction factors to be applied after fiber type (flux) and gas volume have been specified.

reactable mixture if there is sufficient initial driving force (the feed pressure is 1500 psig). It should also be pointed out that H_2 purities in excess of 90 percent (compare cases C, D, and E in Table 2) can be achieved over a wide range of recoveries by changing surface area (analogous to changing the rate of feed flow past the fibers).

Product pressure. Most gas separation systems can function at high pressure. But as pressure increases so does the cost of piping and hardware, and small, simple separation systems like those based on hollow fibers are increasingly advantageous. In ammonia synthesis, hollow fibers now compete directly with cryogenics for the recovery of H_2 from purge gas at pressures as high as 2250 psig (*15*).

Since pressure is the driving force for membrane separations, the size of the system required to achieve a given gas throughput decreases as the pressure and pressure differential increase (see Tables 2 and 3). A comparison of cases A, C, and F (constant surface area) in Table 2 shows that a product stream containing 90 percent H_2 can be obtained at increasingly higher permeate pressures (lower driving force) at the expense of H_2 recovery.

Operation at high pressures can be an advantage in fiber systems as long as they can function under such conditions. For example, cases E and G in Table 3 show that much higher recovery of high-purity H_2 can be obtained at higher feed pressures. Regardless of the total pressure, it is the partial pressure of each gas that determines the flux of that gas in a membrane separation. Cases H, I, and J in Table 3 show that it requires far more surface area to recover 50 percent of the available H_2 at high purity with a 400-psig feed than with a 1500-psig feed; in fact, the achievable purity is higher at higher feed pressures. This is because the H_2 driving force (partial pressure differential) increases dramatically (from 50 to 100 psi in case H to about 450 psi in case J).

An interesting and useful feature of a fiber separation system is that there are actually two product streams. The low-pressure product, which comes from the bore, has been enriched in the high-permeability gas (H_2, CO_2, and so on) and is lower in both total and partial pressure than the feed gas for both gases. The high-pressure product, which comes from the shell, is at almost the same total pressure as the feed gas and enriched in the low-permeability gas. The low-permeability component in the shell product has, in fact, been compressed. For example, in case G the partial pressure of CO in the shell has been increased from 450 to almost 1200 psi.

As indicated by the discussion above, hollow fiber separation systems can be easily manipulated to accommodate changing composition, recovery, and pressure conditions in the feed and product streams. These characteristics should provide greater flexibility in process design and even challenge design engineers to devise new approaches to take advantage of the potential of such separators. Indeed, the importance of effective process design in the ultimate utilization of these systems can hardly be overemphasized [for instance, see chapter 13 in (*2*)].

Effect of contaminants. In any process or unit operation contaminants are of major importance. More energy can be consumed in removing contaminants that will destroy the effectiveness of the separation equipment than in carrying out the separation. Cryogenic systems are particularly sensitive and can be shut down by small quantities of water vapor or any other condensable material. As a result, streams must be carefully cleaned and dried before cryogenic treatment. For streams containing complex hydrocarbons this typically requires scrubbing, adsorption, and molecular sieve treatment before the cryogenic distillation step.

In many cases, hollow fiber systems are less sensitive to the presence of impurities. Even at very high pressures, Prism separators function in gas streams saturated with water vapor and scrubbing fluids such as diethanolamine. Such separators appear to function in the presence of almost any contaminant concentrations of 10^2 to 10^3 parts per million, and depending on the pressure differentials used, much higher concentrations of many materials can be tolerated.

Flexibility and simplicity. Perhaps the strongest advantages of fiber separators are compactness, flexibility, and simplicity. They have no moving parts and are mechanically no more likely to fail than a heat exchanger (to which they are analogous in many ways). They are typically modular (*13–16*), so that if a unit should fail in use it can be removed and replaced with little change in the overall process output. Indeed, if 25 percent of the units in a large-scale system were to fail, the product output would probably not change by more than 10 percent. The start-up and shutdown time of a fiber unit is also very short—usually not more than 1 or 2 hours (*15*). A related aspect of membrane-based separation systems is the ease with which changing capacity requirements can be met by adding modular units or switching existing units to other process applications.

New Uses and Applications

The first widely accepted commercial uses for fiber gas separators have been in H_2 recovery and composition control in petrochemical, refinery, and ammonia synthesis processes (*13–16*). However, several new applications have already been identified for existing hollow fiber systems, as well as for systems that remain to be developed. For instance, Dow and Monsanto are commercializing systems for the recovery of CO_2 in tertiary oil treatment. In this application CO_2 is pumped into old oil fields at great depths and pressures to lower the viscosity of residual oil and drive it to the surface. After a period of time, CO_2 begins to emerge with the hydrocarbon gases (casing head gas) typically recovered with the oil. To utilize these hydrocarbons and avoid losing the CO_2, which must be relatively pure to be effective in this application, the CO_2/hydrocarbon mixture must be separated. After separation, the CO_2 can be pumped back into the oil field and the purified hydrocarbons can be sold, mostly as natural gas.

Other potential applications of fiber separators include H_2 recovery in shale, tar sands, and coal conversion processes, which often involve high-pressure streams containing H_2 that must be treated in some fashion to recover the H_2. Utilizing the available high pressure (often $>$ 2000 psig) to produce 90+ percent H_2 for reuse in the process (essentially energy free) seems a natural application for fibers, and minimal pretreatment would be required.

Other commercially important gases that can be separated by membranes include O_2 and N_2 from air, and work is under way on this separation. Such separators would produce product streams enriched in O_2 or N_2 that could be used in combustion modification, medical applications, and nitrogen blanketing. Also of potential interest are hydrocarbon separations and the separation of gases such as CO, N_2, and CH_4 from each other. These gases tend to have low permeabilities in most glassy polymers and are therefore difficult to separate. New discoveries will be needed to make such separations practical with membranes, but the technology of membrane- and hollow fiber–based gas separation systems is still developing. It is difficult to say which separations and applications of membranes will prove most beneficial, but it is reasonable to project many new developments in both the membranes themselves and the process design of new applications in the next decade.

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