

## Gas Separation Membranes – Current Status

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### 1. Introduction

Membrane-based gas separation systems are now widely accepted and employed as unit operation in industrial gas, chemical, and allied industries. Following their successful commercialization in the late seventies to recover hydrogen from ammonia purge gas streams, membrane-based systems have gained acceptance in a wide variety of applications. Numerous systems are in operation today to: recover hydrogen from other purge gas and hydrocarbon streams; adjust the H<sub>2</sub>/CO ratio in syngas; remove CO<sub>2</sub> from natural gas; recover helium; dry gas streams; and separate air. Lower cost, ease of operation, operational flexibility and portability are a few of the reasons membrane-based systems are chosen over absorption and cryogenic-based separations in certain applications.

The world-wide annual installed gas handling capacity of membrane systems since 1977, when the first commercial installation was made, is given in Fig. 1. From a meager 5 million standard cubic feet per day(MMSCFD) of gas processed in 1977, installed capacity rose to an impressive 350-400 MMSCFD in the early nineties, thus reflecting customer confidence in this emerging technology. It is estimated that the current total worldwide installed capacity of gas separation systems using membranes is about 3500 MMSCFD. A breakdown of

the cumulative capacity for different gas separation applications(major applications) is given in Fig. 2. More than two-thirds of the total installed capacity is used for hydrogen separation in the various applications. Only 7% of the total installed capacity is for nitrogen separation. It is interesting that where-

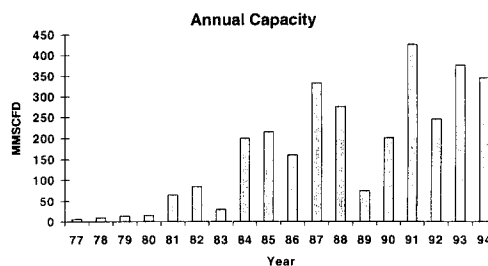


Fig. 1. Worldwide membrane annual capacity.

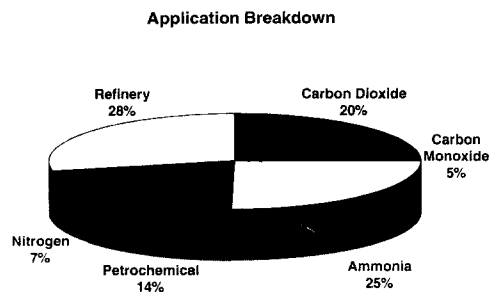


Fig. 2. Worldwide membrane cumulative capacity by industry.

**Table 1.** History of Gas Separation Membrane Commercialization

Year	Company	Membrane/Separation
1980	Monsanto(Permea)	Polysulfone Hollow Fiber H <sub>2</sub> , CO, CO <sub>2</sub> Separations
1982	Separex	Cellulose Triacetate Flat Sheet H <sub>2</sub> , CO <sub>2</sub> Separations
1984	Dow Chemicals	Polyolefin Hollow Fiber Air Separation
1986	Permea	Density Gradient Polysulfone Hollow Fiber Air Separation
1986	DuPont	Polyaramide Hollow Fiber H <sub>2</sub> Separation
1987	Innovative Membrane Systems	Thin Film Composite Hollow Fiber Air Separation
1988	Dow Chemicals	Tetrabromo Bisphenol Polycarbonate Hollow Fiber Air Separation
1989	Ube	Polyamide Hollow Fiber H <sub>2</sub> Separation
1991	Delair	Polyphenylene Oxide Fibers Air Separation

**Table 2.** Manufacturers of Gas Separation Membrane Systems

Company	Separations
Air Products(Permea)	N <sub>2</sub> , H <sub>2</sub> , H <sub>2</sub> O
Praxair(Innovative Membrane Systems)	N <sub>2</sub>
L'Air Liquide(Medal)	N <sub>2</sub> , H <sub>2</sub>
Generon	N <sub>2</sub>
Aquillo	N <sub>2</sub>
Cynara/Dow	CO <sub>2</sub>
Separex(UOP)	CO <sub>2</sub>
Ube	H <sub>2</sub>

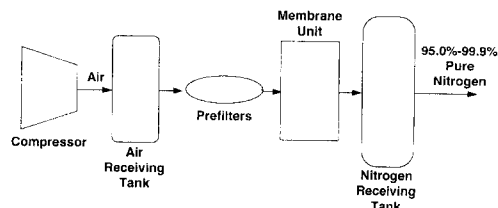
as nitrogen capacity is only 7% of the total, more than 50% of all the gas separation membranes produced are used in this application.

A brief history of the gas separation membrane commercialization is given in Table 1. Since the introduction of the first commercial gas separation system by Monsanto(Permea, Inc.) in the late seventies, several new players have entered in this area. Initial developments were made by major textile giants such as Monsanto, DuPont and Dow. However, due to the nature of the gas separation

business, this technology is now in the hands of major gas separation companies such as: Air Products; Praxair; and L'air Liquid. The current list of major gas separation system manufacturers and the intended applications is given in Table 2.

### The Membrane Separation System

A schematic of a typical membrane gas separation system is shown in Fig. 3. It consists of three major components: a means to provide feed gas at a given temperature and pressure; a means to

**Fig. 3.** Membrane gas separation system.

pretreat the feed gas to remove trace undesirable components (e. g. water, hydrocarbons, etc.); and a membrane separation module. The driving force for gas transport is the differential pressure across the membrane provided either by compressing the feed gas (which is the most common practice) or evacuating the permeate gas. The exact choice depends on the concentration and properties of the desired component in the feed and on the process economics.

A membrane system may consist of one or several membrane modules. These modules can be connected in a variety of fashions. When the modules are connected in parallel, the net performance is the sums of the performance of the individual modules. However, when modules are connected in series, i.e. two, three or more, a variety of possibilities exist to manipulate the various streams (feed, permeate and reject) from each of the modules to optimize the effectiveness of the modules and hence the performance of the system. Several such schemes have been taught and detailed information is available elsewhere [1].

To make membrane gas separation systems more efficient, versatile and acceptable, newer system controls and designs are being introduced. These designs exploit the fundamental characteristics of membrane modules such as: temperature; pressure and purity dependence on the productivity; and purity of the gases separated. Thus offering the customer turn-up and turn-down capability over the course of time and application. Competing gas separation technologies find it difficult to meet this unique feature of the membrane systems. Therefore, membrane systems, if 'intelligently' designed, offer a superior edge over other methods of gas separation.

### Membrane Selection Criteria

Criteria for selecting polymeric membranes for a given application are complex and generally include properties such as: permselectivity; mechanical in-

tegrity; and durability. Much of the literature deals with gas permeability and selectivity of the polymeric materials for a particular gas separation application. Information on the physical and chemical requirements of the membranes and membrane durability is missing, such information is either proprietary or is not available at all.

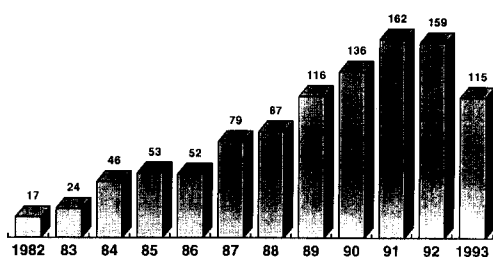
Most of the commercial gas separations are done at elevated pressure (10-200 bars) and at modest temperatures (20-80°C). Almost all the feed stocks contain trace contaminants such as: moisture; lower and middle aliphatic hydrocarbons; various organic solvents; ozone; and other undesired materials. These contaminants adversely affect the mechanical and permselective properties of the membranes by a variety of mechanisms. Also, all polymers age with time at ambient conditions, and the aging phenomenon can be aggravated at membrane use conditions.

In order to operate optimally, a membrane system must offer certain chemical and physical properties which are desired for a given application. The most important are: 1) mechanical strength to withstand static pressure, pressure fluctuations, resistance to creep and resistance to abrasion; 2) chemical resistance to be insensitive to the effect of a wide range of feed components and contaminants; and 3) thermal stability to maintain the basic properties over a reasonable range of temperatures. These membrane can be characterized by the various physical and chemical tests for selection of the most appropriate membrane for a given application [2].

### Membrane Technology Development

More than a century ago, Graham separated a mixture of gases using rubber membranes. Yet, membrane-based gas separation units were not commercially available until the early 1980's. The gap between discovery and commercialization was primarily due to low permeance and low selectivity of the earlier membranes, which made them uneconomical.

**Includes: Materials, Fabrication, and Applications**



**Fig. 4.** U. S. patents for membrane-based gas separation.

Over the last two decades, a flurry of activities was seen in all aspects of membrane gas separation technology, starting from the synthesis of novel polymers to the design of the systems. The intensity of activity which includes: the development of novel materials; fabrication methods and application is indicated by the number of United States patents is-

sued for membrane-based gas separation between 1982-92 and is shown in Fig. 4. From a meager seventeen US patents issued in 1982, patent activity grew to over 150 US patents per year during 1991-92. The country of origin for most of these patents is the United States with Japan being a country of origin for most of these patents is the United State with Japan being a distant second. The majority of the patents are due to the contribution of four major multi-national corporations, with Air Products/Permea in the leadership position.

A brief history of the major scientific discoveries in gas separation membranes is given in Table 3. It was recognized that for an economically successful gas separation membrane system, one not only needs highly selective polymer, but also a practical method to make high flux/high selective membranes and efficient gas separation modules. The discovery of asymmetric membrane fabrication technique by Loeb and Sourirajan[3] and the method of repairing the pinhole size defects in the thin skin of the

**Table 3.** History of Significant Scientific Discoveries in Gas Separation Membranes

Year			U. S. Patent #
1964	Loeb and Sourirajan	Asymmetric Membrane Formation	3,133,132
1972	Riley	Composite Membrane Formation	3,648,845
1975	Browall and Salemme	Multilayer Composite Laminate	3,874,986
1976	Browall	Surface Defect Coating on Laminate	3,980,456
1980	Henis and Tripodi	Multicomponent Membranes	4,230,463
1984	Coptan and Burchesky	Hollow Fiber Composite Membrane	4,467,001
1987	Langsam	Chemically Surface Treated Membranes	4,657,564
1987	Puri	Highly Permeable Coatings	4,968,470
1988	Hayes	UV Cross Linked Polyimide Membranes	4,717,393
1988	Peinemann and Pinnau	In-situ Multicomponent Membranes	4,746,333
1989	Sanders, Clark, Jensvold, Beck, Lipscomb and Coanu	Internal Separating Layer of Asymmetric Membrane(POWADIR)	4,772,392
1989	Kesting, Fritzsche, Murphy, Handermann, Cruse and Malon	Asymmetric Membranes Formed from Lewis Acid Lewis Base Complexes	4,871,494
1992	Exiner, Hayes and Manow	Integrally Skinned Asymmetric Composite Membranes	5,085,676
1992	Kusuki, Yoshinaga and Shimazaki	Integrally Skinned Asymmetric Composite Membranes	5,141,642

asymmetric membranes taught by Henis and Tripodi[4] alleviated the low flux problem. In combination of these and other modern membrane fabrication techniques membrane manufacturers today, make gas separation membranes with effective dense barrier layer thickness of 200-400Å[5]. The advanced polymeric materials, which offer superior permselective properties, are very expensive. To make commercially viable membranes from these polymers, several special membrane fabrication techniques have been proposed such as: Coplan et al.[6] used thin film coatings to make high performance membranes, which use much smaller amount of specialty polymer; Puri[7] and later Bixen et al. [8] has taught making high permeance coatings on microporous substrates to make thin film composite membranes. Recently, workers at Medal developed a method to make two layered membranes by co-extrusion[9]. All these efforts were directed to utilize more expensive specialty polymers in an efficient way to make membranes economically viable.

With the discovery of more efficient methods of making membranes, advances have also been made in the development of novel polymers especially suited for specific application. Understanding of the correlation between the polymer structure and its gas permselective properties has helped in custom design of the polymers. The so called upper bound line correlation's inverse relation between gas permeability and selectivity of the polymers for a given gas pair has been moved higher several times. Furthermore, in some instances it has been shown that within a given family of polymer, one may observe simultaneous increase of both selectivity and gas permeability[10]. Further advances in the molecular engineering and better understanding of the polymer area. A historic perspective of increase of permselective properties of polymers over the last two decades is given for O<sub>2</sub>/N<sub>2</sub> pair as an example in Table 4.

Simultaneously with the innovations of novel polymers and efficient membrane fabrication methods, the needs for the development of novel more ef-

**Table 4.** Progress of O<sub>2</sub>/N<sub>2</sub> Membrane Permselective Properties(25°C)

Year	Polymer	$\alpha_{O_2/N_2}$	PO <sub>2</sub> , Barrers
1982	4-methyl-1-pentene(TPX)	3.6	24.0
1985	Ethyl cellulose	3.4	15.0
1986	Polysulfone	6.0	1.2
1989	Polyphenylene oxide	4.0	16.0
1989	Halogen substituted polycarbonates	6.5	3.5
1996	Polyimides	6-9	4.0-0.1

ficient modules and system design were recognized. From the simple shell and tube heat exchanger type hollow fiber modules and plate and frame type filter designs for the flat sheet membrane, we today design efficient modules which are superior in their hydrodynamics and mass transfer performance. The hollow fiber bundles today are assembled mechanically, using more efficient designs. Flat sheet membranes are almost exclusively packaged in spiral wound bundles. The simple one pass systems of the early 1980's have now taken the shape of complex multi-module, multi-stream systems, which offer optimum separations of the given gas separation application. A superior membrane module design must be a very efficient mass transfer device. The module design should be such that all three gas streams (feed, reject, and permeate) are well distributed with little channeling and back mixing. The flow conditions should also offer minimum feed side pressure drop and pressure build-up on the permeate side. The flow of the feed stream should be counter current to the flow of the permeate stream in the module.

## Applications

### Nitrogen Production

The most prevalent methods used for nitrogen production are cryogenic distillation and pressure swing adsorption. It was about a decade ago when membranes entered in this arena and today have made a reasonable impact on the nitrogen genera-

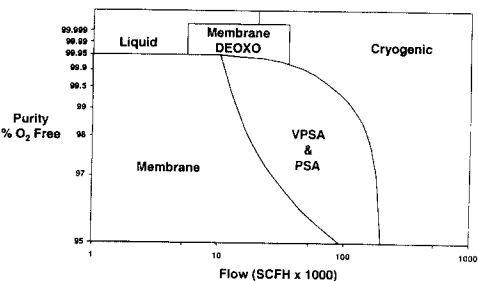


Fig. 5. Nitrogen generation technology map.

tion market. The nitrogen generation market breakdown by technology used is given in Fig. 5[1].

The major producers of nitrogen membrane system for both sale of gas and sale of equipment are: Air Products(Permea); L'air Liquide(Medal); Praxair; and Generon. Although some small players like Aquillo, AG Technology and others also have a small market niche. Due to their inherent advantage of having no moving parts and working totally unattended membrane systems are being accepted by more and more users. According to a recent report, the rate of growth and market penetration continues to be very high. For one company two-thirds growth and market penetration continues to be very high. For one company two-thirds of all new nitrogen capacity world wide in 1994 was based on membrane technology[11].

Simple single stage operation is preferred for nitrogen applications in most of the cases because of the low value of nitrogen product. However, higher purity nitrogen can be produced by the use of two- or more stage operations. The most common amongst the multi-stage operations is system consisting of two-stages with recycle of permeate from the second stage(which is richer in nitrogen than the feed air)[12].

Membranes today dominate the fraction of nitrogen market of those applications that are both small (less than 50 TPD) and low purity(0.5-5% O<sub>2</sub>). For nitrogen production capacity of up to 10 tons/day at 99% total inert purity, membrane separation

operations are the most economical. For high purity nitrogen generation, membrane separation system coupled with a catalytic oxygen trace removal or an adsorption system offers an economic way to make high purity(99.9% and 99.99%) nitrogen from air. Current and continual improvements in membrane and module efficiencies are paving the way for bigger(up to 50 tons/day) separation units to be economic in the near future.

The overall economics of a membrane system is dependent on two components: the capital cost and the operating cost. The operating cost is primarily due to the power cost and is determined by the product recovery and ultimately by the O<sub>2</sub>/N<sub>2</sub> selectivity of the membrane. Simply, the higher the O<sub>2</sub>/N<sub>2</sub> selectivity, the lower the cost of compression and higher the N<sub>2</sub> purity achievable. The productivity on the other hand, depends on the intrinsic gas permeability of the polymeric material and our ability to make a thin defect free barrier layer. The thinner the effective barrier layer of a given membrane is, the higher the productivity will be. To stay competitive in the future, membrane materials must offer an oxygen to nitrogen separation factor of 10 or more at the same or better oxygen permeability of today's polymers. Further, the membrane fabrication technology has to either become more cost effective or will have to provide total barrier layer thickness not in excess of a few hundred angstrom units.

For the larger membrane air separation systems, membranes will have to join forces with the pressure swing adsorption(PSA) processes based on activated carbon molecular sieves to make efficient separation units. Much work has been done in this area. An example of a membrane/PSA is given in Fig. 6. Other concepts of hybrid systems for optimum operations have also been proposed[13]. These included coupling membrane systems with both adsorption units as well as the cryogenic units. Although tempting, these hybrids as yet have not been commercially adopted.

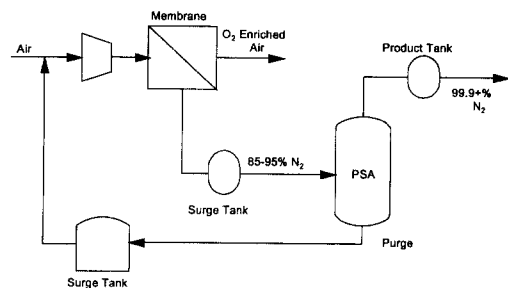


Fig. 6. Membrane/PSA hybrid process.

### Oxygen Production

Whereas nitrogen membrane separation has been a great success, oxygen separations using membranes is still under developed. Ironically, all the earlier membrane air separation work was directed towards production of oxygen enriched air; yet membrane processes for oxygen separation have not been able to meet the economic requirements thus far. There seems to be two major reasons for this, first, most of the industrial oxygen applications require purities higher than 90%, which are easily achieved by adsorption or cryogenic technologies but not by membranes. Secondly, polymeric membranes are most suited for production of oxygen enriched air (25-45%) usable in the combustion industry which is very sensitive to the energy costs. Fortunately, in recent years, abundant energy has been available at reasonable costs, making membrane oxygen separation uneconomical.

Today's limited application of membrane based oxygen generation systems operate either under feed compression or permeate compression mode, shown in Fig. 7. In the feed compression mode, the feed air is compressed at a high pressure and the enriched oxygen air is collected at a pressure slightly above the atmospheric pressure. This mode of operation is less energy efficient, because one has to compress the entire feed gas in which only 21% of the components are of interest. However, in this mode of operation, because of high differential pressure across the membrane, a lower membrane area,

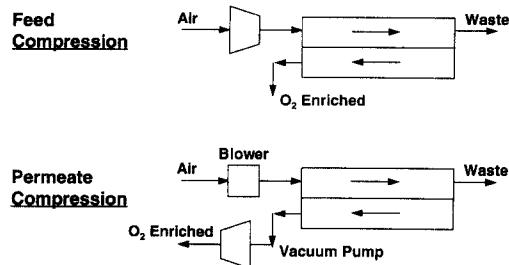


Fig. 7. Oxygen production systems.

and hence a smaller membrane module is needed. In the permeate compression mode, on the other hand, the feed air provided using a gas blower and the permeate is driven through the membrane by using vacuum on the permeate side. The sub-atmospheric pressure permeate is then compressed to the desired pressure. This mode of operation is highly energy efficient, but because of low differential pressures, requires a larger membrane area and therefore is more capital intensive. Both the feed compression and the permeate compression methods of separating oxygen are inferior to the adsorption separation processes using various zeolites. Innovative ways have to be devised to use membrane systems either self standing or in combination with other processes to make them more efficient.

Tomorrow's oxygen separation membranes will be attractive only if we can develop polymers with oxygen to nitrogen separation factors of two to three times that of silicone rubber (~4-6), and very high oxygen permeability (~250 Barrers). Making such materials offers a significant challenge for the polymer chemists.

### Hydrogen and Helium Recovery and Purification

A very attractive and challenging application of commercial interest is the separation of smaller molecules like hydrogen and helium from the lower hydrocarbons like methane, ethane, etc., and nitrogen. In fact, the first full size commercial application of polymeric membranes was the separation of hydrogen from the ammonia synthesis gas stream.

Today, the major membrane system suppliers for hydrogen application are Air Products(Permea), Linde(L'Air Liquide(Medal), Ube, and UOP(Separex). The membrane systems for a diverse list of applications are designed to optimize hydrogen recovery at a given acceptable rate of hydrocarbon loss from the feed. Although hydrogen separations in the various refinery streams are done very successfully, the field still requires membranes with better aromatic and aliphatic hydrocarbon resistance. Higher selectivity and productivity membranes will make this application still more attractive. However, one of the major drawbacks of the membrane technology in this application is that the product hydrogen stream is at a low pressure.

Hydrogen separation membranes operate both under external and internal both under external and internal challenging environments. This consists of high temperature, pressure, humidity, particulate matter, and excessive vibrations. Therefore, membranes in this application have to offer excellent thermal stability, chemical/solvent resistance, and mechanical strength under operating conditions. Membranes for this application are extensively tested in the laboratory and pilot plant prior to sale of full size units.

Generally, hydrogen separation membrane applications require higher operating pressures(1,000-2,000 psig) and temperature(60-250°F). The feed to the system may require pre-treatment such as liquid/mist knockout and coalescing to remove water, oil, and higher hydrocarbons. In some applications, a pre-treatment may also require the use of adsorption/absorption units to remove trace impurities such as mono- and diethanolamines (MEA/DEA), etc., which may be harmful to the membranes.

There are over eighty systems world-wide for hydrogen separation from ammonia plant purge gas. These plants operate typically at 1800-2000 psig with typical differential pressure across the membrane of 1500 psi. These units are large and handle 10-30 MMSFD. The module and system de-

sign for this application requires special membrane/module design considerations for high flow rates and elevated pressures. Adequate pressure/flow controls and alarms are installed for safety considerations.

#### Acid Gas Separations

Membranes are used in large commercial installations for the removal of carbon dioxide from methane at the well heads. In the production of merchant hydrogen, carbon dioxide which is a byproduct of the steam reforming and CO-shift conversion step, has to be removed from the hydrogen rich product gas. This is currently done using acid gas scrubbing solvents which require thermal energy for their regeneration. The polymeric membranes available today (cellulose acetate, polysulfone, etc.) have been used competitively in these applications.

The cellulose acetate polymer is the material of choice for major suppliers of CO<sub>2</sub> recovery membrane (Cynera, Separex, and Grace). The world's largest stand alone membrane separation system which processes 180 MMSCFD gas at 1350 psig in operation in Kadanwari in Pakistan. The design of this unit permits simultaneous reduction of CO<sub>2</sub> and H<sub>2</sub>S in natural gas from 12% to 3% and from 100ppm to 3 ppm, respectively. For some installations, hybrid systems[14] have been proposed which consist of a membrane system at the tail of an amine scrubbing system. These systems may offer advantage either to increase efficiency of the amine scrubbers or de-bottleneck various facilities.

For membranes to dominate in this application significant selectivity improvements of the membrane(50-100) at equivalent productivity are needed. Some of the polyimide membrane material recently developed[15] meet these requirements.

#### Dehydration Systems

One of the emerging application of the gas separation membranes is in the drying of air and natural gas. Bulk of the commercial air drying is done either by the use of refrigeration or the use of desic-



cants in pressure swing adsorption mode. The refrigeration process is unable to achieve very low dew points, therefore, for drying air to very low ( $-40^{\circ}\text{C}$ ) dew point, desiccant drying is used. Desiccant methods using adsorbent materials are cumbersome and require the use of a lot of movable parts and hence need high maintenance. However, their advantage is that for the same degree of drying, the air loss is almost half of most of the membrane drying systems available today.

The natural gas dehydration is done at higher pressures (1000 psig) and has a little less stringent drying requirements (dew point required is  $-20^{\circ}\text{C}$ ). The loss of the valuable component, methane, is very crucial in this application. The maximum tolerable loss of methane is 2-3%, which can be achieved by glycol absorption process. The disadvantage of the glycol process is that it generates aromatic hydrocarbons contaminated glycol waste material that requires expensive disposal methods. Also, due to its complexity, the glycol process has to be manned. The membrane processes on the other hand can be operated remotely, which is preferred in the unmanned operations like the oil and gas platforms. Unfortunately the current membranes are very inefficient and result in 5-10% methane loss.

In order for the dehydration membranes to be commercially successful we need to maintain or increase the existing water permeabilities, but at least quadruple the water to gas selectivity. It may be of interest to note that water permeability and selectivity of commercial polymers is two to three orders of magnitudes higher than most of the permanent gases. Therefore, to develop superior membrane dehydration systems, attention must be paid to the membrane and module development.

#### Future Perspectives

Commercialization of membrane gas separation's technology has a very short history. The first commercial size membrane gas separation system was put on stream in 1977 and today there are more than 10,000 commercial membrane systems in oper-

ation for the various gas separation applications. The gas separation business is currently valued at 85 million dollars in the United States and is growing at a rate of about 8% per year [16]. It is estimated that membrane gas separation business will grow to about \$500 million by year 2000 [17]. Thus, the short history of this technology has made major advances at a very rapid rate. The membrane gas separation technology is well accepted due to its simplicity, flexibility in scale-up, and low maintenance requirement. The fact is the operation of a membrane module is like 'operating a pipe'. There is a great potential for technological advances and opportunities for business growth. But the prerequisites of this growth are that we maintain of membrane system design simple, make them more reliable and continue to maintain low cost. Membrane technology will have to compete in all the arenas against the well-established separation technologies like distillation, adsorption, extraction, and absorption. The key to success is to routinely benchmark the capabilities of these technologies against the membrane technology. The world is only for the survival of the fittest!

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