GAS SEPARATION BY MEMBRANES: TECHNOLOGY AND BUSINESS ASSESSMENT

by

SORAB R. VATCHA

B. Tech., Indian Institute of Technology, Bombay
(1969)

SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS OF THE
DEGREE OF

MASTER OF SCIENCE

IN THE MANAGEMENT OF TECHNOLOGY

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

June 1985

Signature of Author ____________________
Department of Chemical Engineering
May 17, 1985

Certified by ____________________
Kay Tamaribuchi
Thesis Supervisor

Certified by ____________________
Raymond F. Baddour
Thesis Supervisor

Accepted by ____________________
William M. Deen
Chairman, Departmental Committee on Graduate Students

GAS SEPARATION BY MEMBRANES:
TECHNOLOGY AND BUSINESS ASSESSMENT

by

SORAB R. VATCHA

Submitted to the Department of Chemical Engineering
on May 17, 1985 in partial fulfillment of the
requirements for the Degree of Master of Science in the
Management of Technology

ABSTRACT

The separation of gases by membranes on a commercial scale has grown rapidly, from a handful of units a decade ago to over one hundred units worldwide by the end of 1985. This market is expected to grow at an average annual rate of 12% over the next 15 years, from its present base of about $60 million/year. The technology-push and market-pull incentives for this industry's past, present and future growth are discussed.

Membrane separation technology can replace or augment alternative gas separation technologies such as cryogenic distillation, absorption in a liquid, and adsorption on a solid. The four major applications at present and probably over the next decade are: acid gas removal from hydrocarbon streams and flue gases; hydrogen recovery in oil refineries and chemical plants; air separation; and dehydration. Monsanto is the industry leader by a wide margin, with about 89% of the 1985 worldwide installed capacity.

The technology and economics are analyzed at five levels: the membrane material; element; module or stage; the separation system; and the entire process plant. There are complex trade-offs among the key system variables, such as membrane permeability and selectivity. Selectivity generally has greater economic value than permeability, although both are desirable.

Facilitated transport, a significant advancement already demonstrated on a small scale, will probably be in commercial use by 1990. Promising directions for future R&D, and strategies for success in the membrane separation business, are recommended.

Thesis Supervisors: Dr. Kay Tamaribuchi
Associate Director, Industrial Liaison Program

Dr. Raymond F. Baddour
Professor of Chemical Engineering

ACKNOWLEDGEMENT

I am grateful to Dr. Kay Tamaribuchi and Professor Raymond F. Baddour, who jointly supervised this thesis.

Many people from various organizations provided useful information. I thank all of them, but I cannot acknowledge them individually.

My parents deserve special thanks for their encouragement and understanding.

I also thank Ms. Lynne Sheinfeld for typing this document.

TABLE OF CONTENTS

1. INTRODUCTION

The use of membranes for gas separation on a commercial scale has grown rapidly during the past decade. The number of commercial units, their capacities, and the number of different applications have all increased. Over 30 organizations, including corporations, universities, nonprofit institutions and Government agencies, are participating in and shaping a dynamic new industry based on gas separation by membranes. The historical evolution, the current status and the future prospects of this industry, and of the related markets and technologies, form the main subjects of this thesis.

A membrane-based separation process is often just one of several separation processes that would be technically feasible for a particular application. Membrane-based processes may not only replace, but may also synergistically augment, other separation processes. A new process will displace existing processes only in the applications where it has a relative economic advantage. Therefore, the salient aspects of the broad field of separation technology are covered in this chapter.

The vital importance of separation technology in general, and gas separation in particular, throughout the energy and process industries, is indicated in Section 1.1. This section also presents three useful taxonomies of separation technology.

The four leading commercial processes for gas separation are described and compared in Section 1.2. These are cryogenic distillation, absorption in a liquid, adsorption on a solid, and selective membrane permeation. The latter's commercial applications, at present and expected in the future, are discussed in Section 1.3.

Although the commercial use of membranes for gas separation is relatively recent, scientific inquiries, discoveries and inventions were being made in this field for over one century. The historical evolution of the technology is outlined in Section 2.1, divided into the periods 1700-1940, 1941-1960, 1961-1970 and 1971-1985. Because of the long lead times from scientific discovery to commercial use, the recent scientific activity provides insights into the nature and timing of future commercial technology.

A selective review of the literature, with emphasis on recent works, is given in Section 2.2.

The separative action of a selective membrane is based on the differences in the rates of permeation of different species through the membrane under identical conditions. The theory of the transport of gases through membranes, including the dependence of the permeability and selectivity on the membrane's structure and on the state variables, are discussed with illustrative data in Section 2.3.

The key properties of various membrane materials, the methods of fabrication of membrane elements, and criteria for selecting membranes are discussed in Section 2.4.

The process engineering aspects of membrane separation systems are covered in Chapter 3. The trade-offs among the key variables are discussed. Economic comparisons of membrane-based and other gas separation processes, and of different membranes in the same application, are presented in Section 3.4. The continuous membrane column described in Section 3.3 is a technical success that has not become a commercial success.

The present size and projected future growth rates of the membrane gas separation market are estimated in Section 4.1. The key contributors to this industry are from the private sector (Section 4.2), the public sector (Section 4.3) and the academic and nonprofit sector (Section 4.4).

Strategies for success in this industry were inferred from a retrospective case study of Du Pont and Monsanto. Du Pont pioneered the development and commercial use of hollow-fiber membranes for gas separation in the 1960's. It withdrew from the market in the 1970's, and is now re-entering this market. Monsanto entered the market in the late 1970's, and is now the worldwide market leader by a wide margin.

The principal conclusions of this thesis, and recommended directions for future R&D in the field of membrane separations, are summarized in Chapter 5.

1.1 Separation Technology: Significance and Structure

The need for separation and purification occurs throughout the energy and process industries. These include oil and gas production, petroleum refining, synthetic fuels, petrochemicals, commodity and specialty chemicals, food and beverage processing, pharmaceuticals, metallurgical processing, combustion for generating heat and/or power, nuclear fuel preparation, pollution control and waste disposal.

Separation equipment accounts for 50-90% of the capital investment in petroleum refining and petrochemical facilities (King, 1980). In the process industries as a whole, 40-70% of the capital costs and the operating costs, and up to 80% of the energy consumption, are for separation (Membranes Simplify Catalytic Reactions, 1980; Zanetti, 1984).

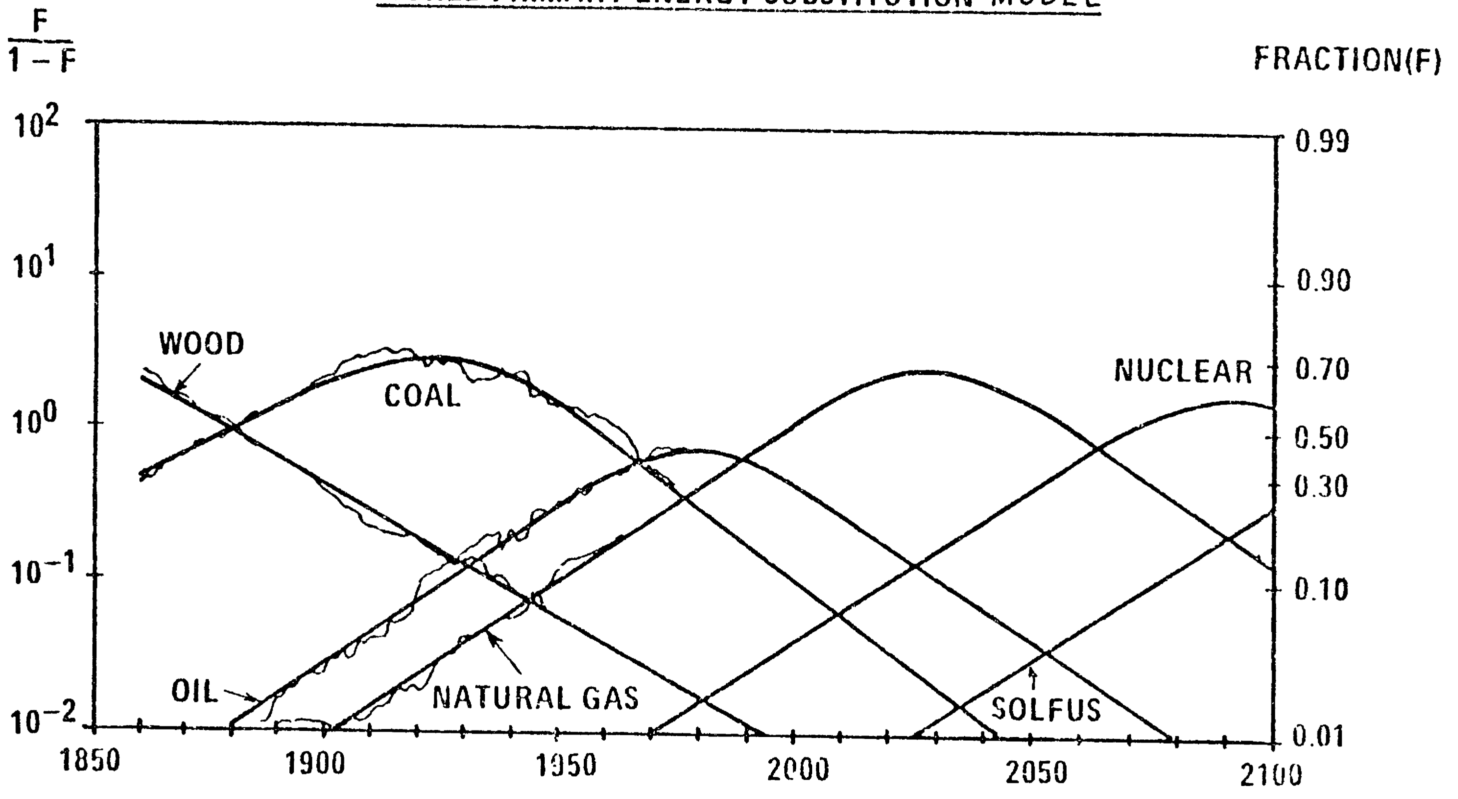
The enrichment of uranium-235 by gaseous diffusion was the key to the Manhattan Project and to the subsequent nuclear industry. This is a very difficult and hence expensive separation because the two isotopes are so similar in their properties, and because the concentration of uranium-235 in the raw material is so low -- around 0.7% (King, 1980). This was the first large-scale use of gas separation by permeation through a microporous solid medium.

Separation technology will play a critical role in the solutions to major societal problems such as environmental pollution, resource depletion and malnutrition. New high-technology industries depend heavily on separation technology, e.g. ultra-pure chemicals in electronic component manufacturing, life support in spacecraft, and product recovery in biotechnology. Thus, separation technology has great economic, strategic and societal significance, and its impact is pervasive throughout industry.

The historical patterns of the world's energy consumption since 1860 are shown in Fig. 1.1. The data are fitted to a simple yet accurate substitution model, developed at the International Institute for Applied Systems Analysis (IIASA). The assumptions and methodology of this model are discussed by Marchetti (1982). As the energy mix evolves to higher H/C ratios, methane or natural gas will become the dominant fuel after the year 2000, according to this model.

Figure 1.1

WORLD PRIMARY ENERGY SUBSTITUTION MODEL



IIASA Version 14.10.1982

Source: Marchetti (1982)

As the world's fossil fuel resources of high grade get gradually depleted (Fig. 1.2), the remaining resources of lower grade will require greater inputs of hydrogen to upgrade them (Fig. 1.3). Hydroprocessing of hydrocarbons increases their H/C ratio and removes undesirable elements such as sulfur, nitrogen and metals. These trends imply growth in gas separation facilities.

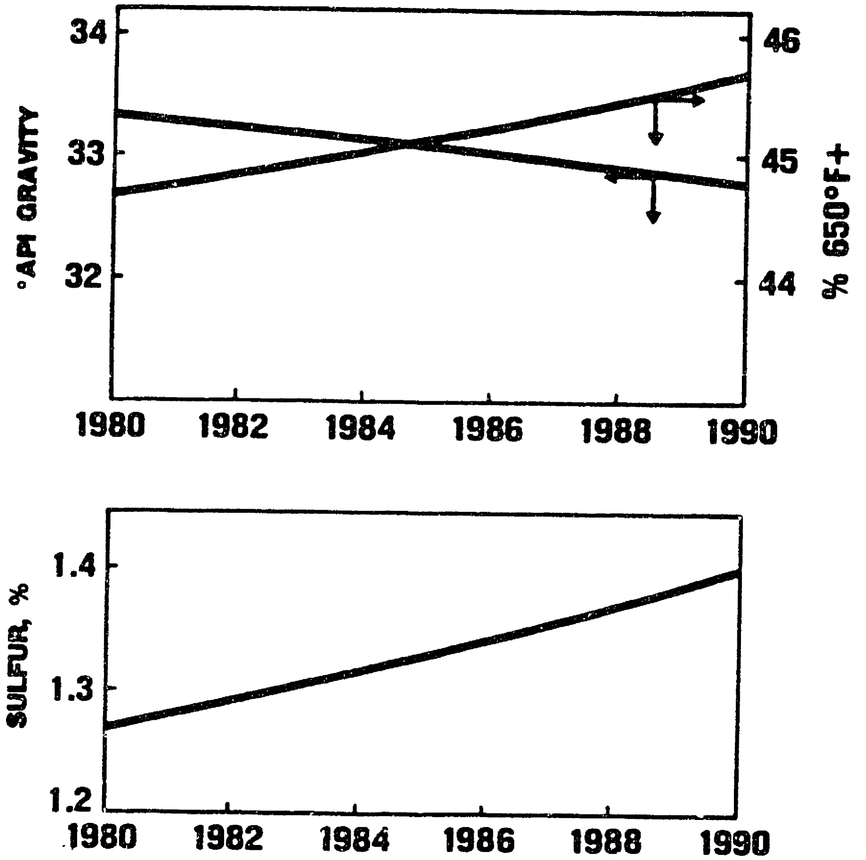
Conventional energy sources are being supplemented with unconventional sources, such as methane from landfills and coal deposits, as well as enhanced oil recovery (EOR). Synthetic fuels from coal, oil shale or tar sands have not materialized in the U.S., nor has the hydrogen-based economy, despite extensive R&D. If and when they emerge after a few decades, they will require massive investments in gas separation equipment and systems. For example, 10-20% of the capital cost of a synthetic fuels plant would be for oxygen generation; and 0.5 to 1 ton of oxygen is consumed per ton of coal (Synfuels Market..., 1980; Gasification Units..., 1980). In coal gasification plants, methane and carbon dioxide are produced in roughly equal amounts, and have to be separated and purified for sale (SNG Process..., 1982).

Some of the world's natural resources of low grade have remained unexploited because the necessary separations would have been uneconomical. For example, there are large reserves of very sour natural gas containing 15-90% hydrogen sulfide (Hyne, 1982). Some natural gas contains significant amounts of carbon dioxide, as high as 85% when enhanced oil recovery (EOR) by CO_2 flooding is practiced. Advances in gas separation technology are enabling the economical exploitation of such resources that were heretofore marginal or uneconomical.

The use of oxygen-enriched air or nearly pure oxygen instead of atmospheric air can be technically advantageous in many applications. These include combustion of fuels, incineration of wastes, sewage treatment, metallurgical processing, gasification, aerobic fermentation, various oxidation processes in the manufacture of chemicals, pulp and paper, and controlled-atmosphere food packaging (Chowdhury and Lewald, 1984). Yet the cost of producing oxygen has often been the limiting factor in its use. The separation of air into its constituents

FIGURE 1.2

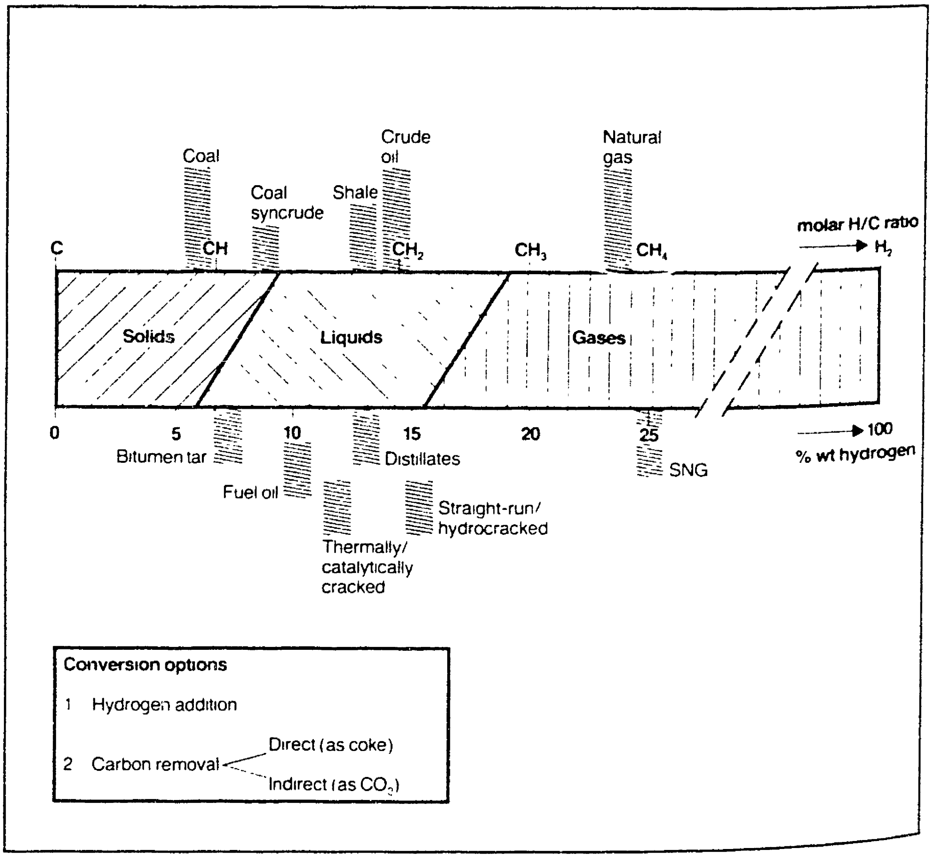
WORLD CRUDE OIL ANTICIPATED QUALITY TRENDS



Source: Eckhouse, Conser and Meier (1982)

Fig. 1.3

THE ELEMENTAL COMPOSITION SPECTRUM OF HYDROCARBON RESOURCES AND FUELS



Source: The Petroleum Handbook (1983)

is relatively difficult because oxygen and nitrogen are quite close in their molecular weights and boiling points, and also because there are many trace constituents in air. Advances in air separation technology would enable more widespread and economical use of oxygen and nitrogen in many industrial applications.

Gas separation technology's great leverage in its effect on many other significant technologies provides strong economic incentives for R&D leading to innovation.

A separation process converts a feed stream into two or more product streams that differ in composition from the feed stream and from one another. There are numerous separation processes available based on various physicochemical concepts, usually the difference in some key property such as phase, density, boiling point, solubility, permeability, etc. Even for a specific application, there are usually several applicable separation processes, so the selection would be based on economic and other considerations.

A relatively new technology, such as membrane-based gas separation, does not completely displace the existing alternative technologies (just as the automobile has not completely displaced the bicycle). The new technology gradually gains market share from the competing technologies only in those specific niches in which it has a clear competitive advantage.

For example, membrane air separators are now being commercially used on board ships and offshore oil platforms, for producing dry nitrogen of 95-99% purity. In such applications, the system should be compact, lightweight, energy-efficient, very reliable, require low maintenance, and should be economical on a small scale. Membranes have strong technical and economic advantages over competing air separation systems for meeting the specific needs of this market niche (Membranes Vie for On-Site Nitrogen Output, 1985).

Separation technologies can be competitive as well as complementary. Different separation processes may sometimes be combined in a given application, where they operate synergistically. For example, in the separation of carbon dioxide from hydrocarbons in EOR applications, a membrane-based separation system in combination with a conventional distillation or absorption system may prove more economical than either system alone (Parro, 1984; Schendel, 1984). Thus, membrane gas separation technology should be evaluated on a stand-alone basis as well as in combination with other gas separation technologies for any particular application. Also, the possibility of simultaneous chemical conversion and product separation in the same process step should not be overlooked (Shinnar and Feng, 1985).

The task of selecting and specifying the optimal separation system for a given application is complex yet important, because:

- Separation costs usually dominate the total production costs.
- More than one type of separation process is usually available for most applications.
- Combinations of different separation processes should be considered, to exploit synergistic effects.
- The optimal sequencing or cascading of the multiple separation units has also to be determined, especially for multicomponent, multiproduct separations.

A systematic description and classification of separation technologies is useful for these purposes.

One 3-way classification scheme is (King, 1980):

- Mechanical or heterogeneous feed
  v. Diffusional or homogeneous feed
  (see Fig. 1.4 for a more detailed breakdown).
- Equilibration or partitioning
  v. Rate-governed or nonpartitioning.
- Energy separating agent (ESA)
  v. Mass separating agent (MSA).

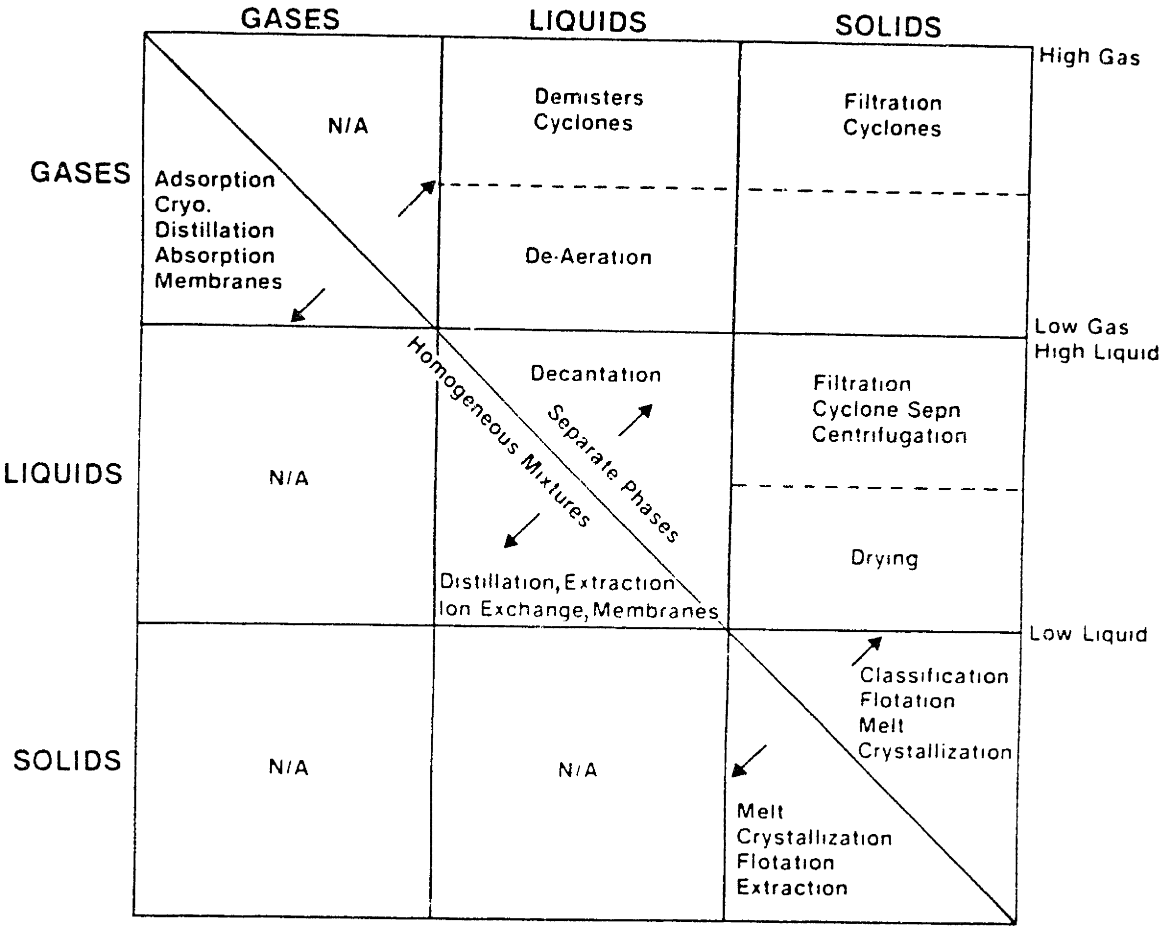
More than one separating agent may be used simultaneously in one process. The separation of gases by selective permeation through membranes would be classified as diffusional, rate-governed, having an ESA (pressure gradient) and MSA (membrane).

Another more complex 3-way classification scheme is (Lee *et al.*, 1977):

- Morphology of the process.
- Mechanism (driving force) of the separation.

Fig. 1.4

CLASSIFICATION OF SEPARATIONS BY PHASES INVOLVED



Source: Proc. First GRI Gas Separations Workshop, Denver, Oct. 1981.

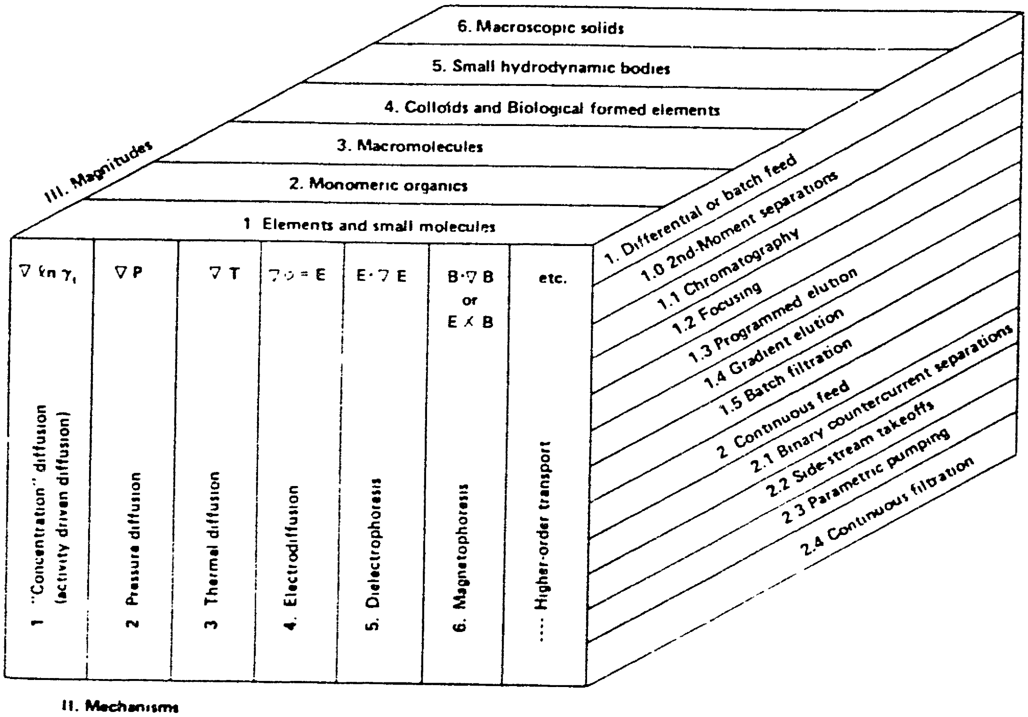


Fig. 1.5

A THREE-WAY CLASSIFICATION SCHEME FOR SEPARATION TECHNOLOGY

Source: Lee, Lightfoot, Reis and Waissbluth (1977)

- Magnitude of the molecules or particles being processed.

Separation by selective gas permeation would be classified under this scheme as having Morphology No. 2.1, Mechanism No. 1 and Magnitude Nos. 1 and 2 (Fig. 1.5).

A third classification scheme is: Bulk removal v. Purification. In bulk removal, the key component is in fairly high concentrations in the feed, and the purities of the product streams are moderate (up to 98%). In purification, the key component is in fairly low concentrations in the feed, and the purities of the product streams are high (over 98%). This classification scheme is based on the inherent tradeoff between recovery and purity in any separation scheme. Further discussion of this tradeoff is given in Chapter 3.

Such classification schemes provide some understanding of the essential characteristics of various separation processes and their relative advantages. Guidelines for screening, evaluating and optimizing separation processes for particular applications are given by Mix (1984), King (1980) and Seader (1982).

1.2 Gas Separation Technology: A Comparative Survey

The major commercial processes for separating gases are listed below in chronological order of first commercial use:

- Cryogenic distillation
- Absorption in a liquid
- Adsorption on a solid
- Selective membrane permeation

Their key principles and features are briefly reviewed, to provide a common framework in which to compare them. Other processes such as reversible chemical reactions (or thermochemical cycles), chromatography, pressure diffusion (gas centrifuging), thermal diffusion and sweep diffusion are used to a very limited extent in specialized applications, so will not be discussed further. The reader is referred to Perry's Handbook (1984) and other literature sources for further information on these less common or unconventional means of separation.

Cryogenic Distillation

Cryogenic distillation consists of liquefying the feed gas, distilling it in one or more columns, and (optionally) vaporizing the products. The first commercial use of cryogenic distillation was by Linde in 1902 for air separation. Nowadays, cryogenic distillation is used extensively for making or purifying oxygen, nitrogen, hydrogen, helium, natural gas liquids (NGL), and olefinic petrochemicals. The refrigeration required to achieve cryogenic conditions can be accomplished by:

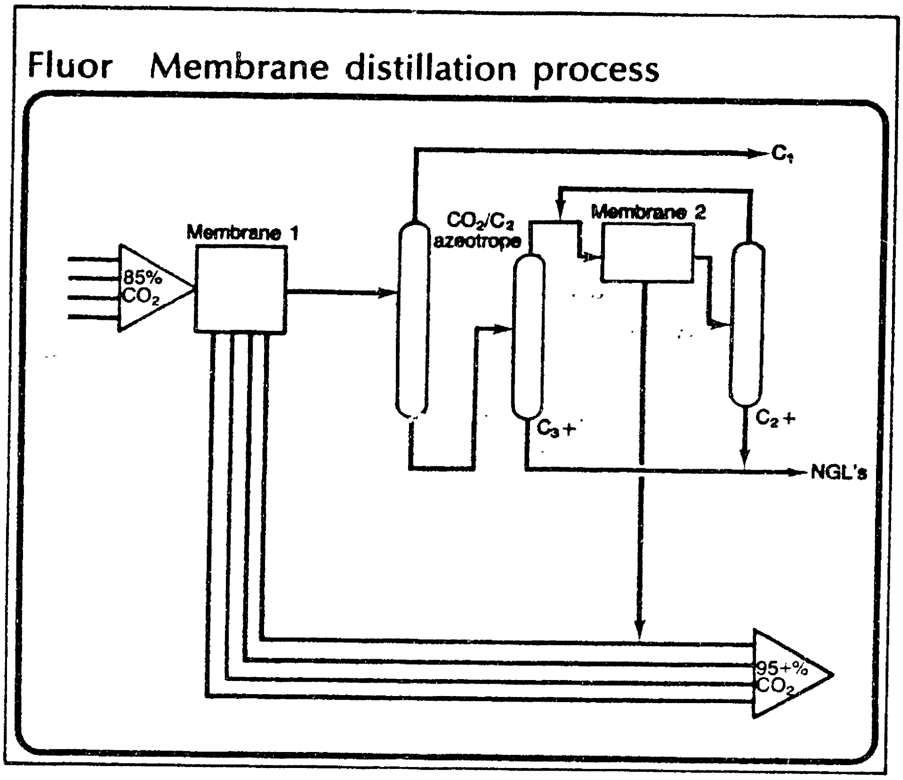
- Evaporation of a liquid
- Joule-Thomson expansion
- Gas expansion in a work-producing engine (such as a turboexpander)

Despite extensive use of "cold box" equipment, the thermodynamic efficiency of cryogenic distillation is rather low. For example, in the case of air separation, the thermodynamic efficiency is about 4% for the Linde single column system and about 15-20% for most modern plants (Perry's Handbook, 1984, pp. 4-89 to 4-91 and 12-53 to 12-55). Energy costs make up 60-70% of the total production costs of such plants (Scharle and Wilson, 1980).

Removal of certain impurities in the feed gas may require extra processing at the front end of the cryogenic plant. The formation of azeotropes by the feed constituents at the conditions of distillation would limit the achievable product purities. In the separation of carbon dioxide from light hydrocarbons, the formation of azeotropes or a solid carbon dioxide phase is possible (Schendel, 1984; Holmes, Ryan, Price and Styring, 1982). The carbon dioxide/ethane azeotropes have compositions of roughly 65/35%. So extractive or azeotropic distillation is required. The Ryan/Holmes process uses part of the recovered NGL stream as the extracting agent, but requires 3 or 4 columns as well as pretreating and sulfur recovery facilities.

A process that advantageously combines membranes and cryogenic distillation has been developed and patented by Fluor (Schendel, 1984; Schendel and Seymour, 1985). In this process (Fig. 1.6), one membrane system at the upstream end recovers a 95% pure CO_2 permeate stream from the feed containing 85% CO_2. The retentate stream from this

Fig. 1.6



Source: Schendel and Seymour (1985)

system goes to a cryogenic distillation system. Another membrane system separates the azeotropic stream, thereby avoiding the need for azeotropic or extractive distillation. Note how membrane separation technology combines synergistically with cryogenic distillation technology in this application.

The refrigeration required for achieving and maintaining cryogenic temperatures is generally an expensive utility (Mix, 1984; Steinmeyer, 1984). The largest modern refrigeration systems have efficiencies of around 40% of the Carnot efficiency, and these actual efficiencies have generally not increased during the past decade (Perry's Handbook, 1984, p. 12-53).

In cryogenic air separation plants, special precautions must be taken against potentially explosive conditions arising from contact between oxygen and hydrocarbon impurities. Atmospheric pollutants and compressor lubricating oils are potential sources of flammable impurities. A detailed discussion of this subject, including a flow sheet of a cryogenic air separation plant, is given by Wilson (1982).

Cryogenic gas separation processes are energy-intensive and capital-intensive. They exhibit efficiencies of scale and economies of scale. They are generally best suited to large-scale applications, for bulk removal at steady throughputs. The possible occurrence of azeotropes, solid phases, or impurities in the feed requires special processing equipment that increases complexity and cost.

Absorption in a Liquid

The separation of gases by absorption in a liquid solvent is based on the differences in solubilities of the various feed components in the liquid. The solvent is regenerated by heating, flashing or steam stripping, and recirculated. This process is widely used for the removal of acidic gases, such as carbon dioxide and hydrogen sulfide, from natural gas, synthesis gas, landfill gas, etc. (Table 1.1). The recovery of carbon dioxide from boiler flue gases by this technique has recently been commercialized (Pauley, Simiskey and Haigh, 1984).

Gas absorption is a mature technology that is about 50 years old. Scores of different commercial processes, employing various

TABLE 1.1

Major Industrial Processes that Need Gas Treating

Process	Acid gases to treating	Common cleanup targets (% acid gas)
Hydrogen manufacture	CO_2	$<0.1\%$ CO_2
Petroleum desulfurization	$CO_2 + H_2S + COS$	10 ppm H_2S
Coal liquefaction		
Chemicals		
Ammonia manufacture	CO_2	<16 ppm $CO_2 + CO$
(H_2/N_2 mixture)	$CO_2 + H_2S + COS$	0.01 ppm H_2S
Natural gas purification		
Pipeline gas	H_2S, CO_2, COS, RSH, etc.	<4 ppm H_2S; $<1\%$ CO_2
LNG feedstock		1–2 ppm H_2S; <50 ppm CO_2
Syn gas for chemicals (H_2/CO)		<500 ppm CO_2; <0.01 ppm H_2S
Coal gasification		
SNG (high Btu gas)	CO_2, H_2S, COS	500 ppm CO_2; 0.01 ppm H_2S
Intermediate Btu gas		
Low Btu gas		100 ppm H_2S
Oil desulfurization	H_2S	100 ppm H_2S
Refinery fuel gas treating	H_2S, CO_2, COS	100 ppm H_2S
Ethylene manufacture	H_2S, CO_2	~1 ppm H_2S, 1 ppm CO_2
(steam cracker gas treating)		
Flue gas desulfurization	SO_2	90% removal
Utilities (electric)		
Refineries, etc.		

Source: Astarita, Savage and Bisio (1983) solvents and operating conditions, are used in thousands of commercial installations. The processes may be classified as follows:

- Physical solvent (e.g., methanol)
- Chemical solvent
    - Organic (e.g., alkanolamines)
    - Inorganic (e.g., potassium carbonate)
- Hybrid or dual solvent

Generally, the physical solvents provide greater capacity (or loading) but lower selectivity; the chemical solvents provide greater selectivity at lower capacity. Chemical solvents are better suited for reducing feed impurities to very low levels (Table 1.1). However, problems of foaming, corrosion, toxicity, insufficient selectivity, and solvent losses are sometimes encountered. These processes are quite energy-intensive, because of the energy consumed for feed compression, product compression, solvent circulation and solvent regeneration.

Membrane processes are being used in combination with absorption processes in EOR applications (Fig. 1.7). In particular, the combination of membranes upstream and chemical solvent absorption downstream can provide capacity characteristics comparable to physical solvent absorption without the hydrocarbon losses associated with the latter (Schendel and Seymour, 1985).

Thus, membrane technology competes with, but also complements, absorption technology. A more detailed discussion of the latter would be beyond the scope of this document. For additional information, see Astarita, Savage and Bisio (1983), Fayed (1983), Newman (1985) and Chem. Eng. Progress (Oct. 1984) which is a special issue on treating acid and sour gas. The annual Gas Conditioning Conferences organized by the University of Oklahoma are also useful sources of information.

Adsorption on a Solid

The separation of gases by adsorption is based on the selective adsorption of the various feed components on the solid adsorbent. The most common adsorbents are molecular sieves, whose pore sizes can be tailored to adsorb certain molecules selectively according

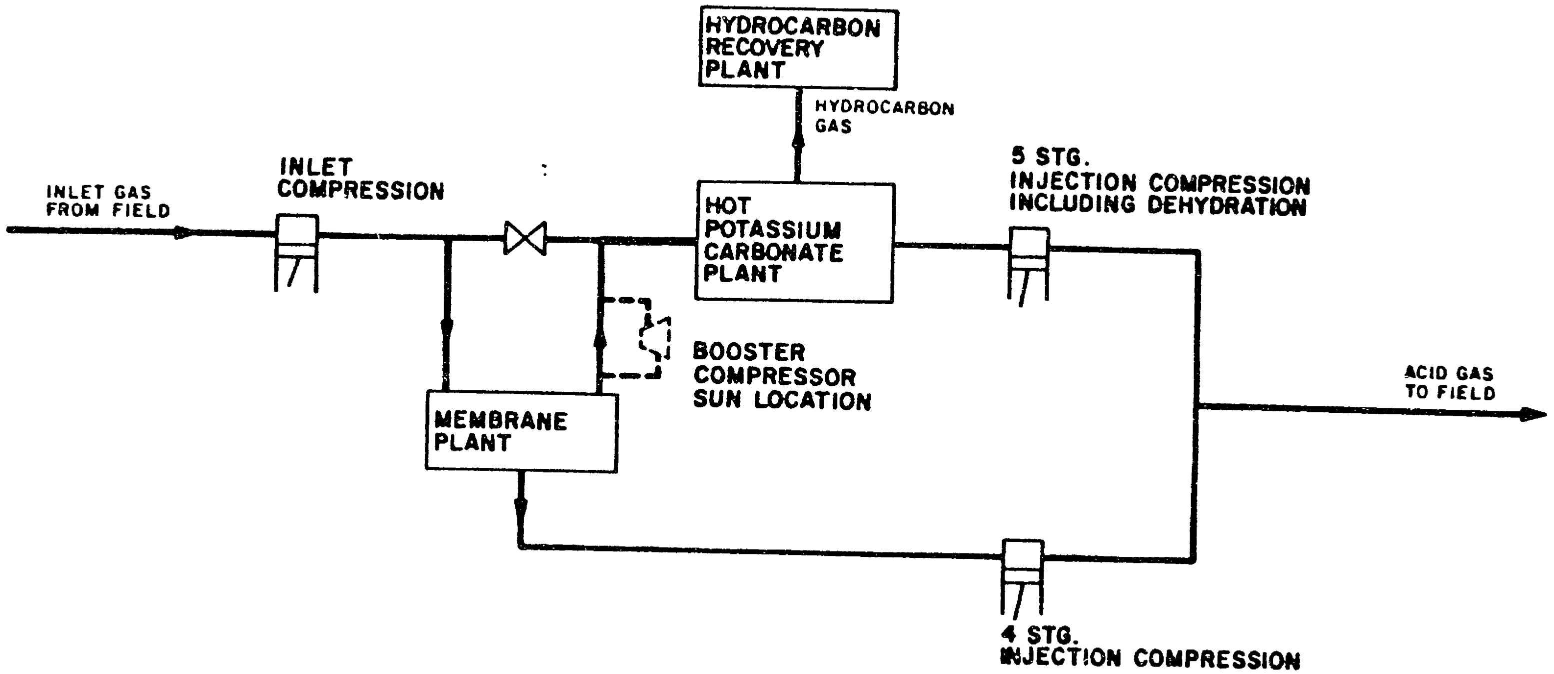


FIGURE I.7

SACROC CO_2 REMOVAL FACILITIES

to their size and shape. The process operates in a cyclic regenerative manner, that is, some beds are adsorbing while other beds are desorbing. Desorption can be effected by heating, reducing the pressure, purging with an inert gas, or some combination thereof.

The process was developed by Union Carbide and first commercialized in 1966. It is now sold under the trade name "Polybed PSA" (PSA for Pressure Swing Adsorption). There are several hundreds of such units now in commercial operation. They are used for hydrogen recovery, acid gas removal, dehydration, air separation, and the separation of hydrocarbon isomers. Performance can sometimes be enhanced by parametric pumping.

Such processes are generally competitive on a medium scale, when very high purities are desired, and/or when separation by distillation would be impractical. In the manufacture of 90 wt % oxygen from air, the PSA process consumes about 27% more energy than the cryogenic process (Mix, 1984). Adsorption processes are generally quite simple, rugged and reliable, and exhibit weak economies of scale due to their modularity. In these respects, they fall between membrane processes and the other processes discussed above.

For further information on the separation of gases by adsorption, see Chi and Cummings (1978), Frank (1980), Mix (1984) and the numerous references cited therein.

Selective Membrane Permeation

The separation of gases by membranes is based on the principle that different components of the feed stream permeate through the membrane at different rates. Unlike the aforementioned equilibration processes, membrane separations are rate-governed processes. The driving force for transport through the membrane is the gradient of chemical potential of each species. In the case of gases, this is closely approximated by the gradient of partial pressure across the membrane.

There are two product streams from one membrane permeation module. The permeate stream, on the low pressure side of the membrane, is enriched in the more permeable component(s). The retentate or residue stream, on the high pressure side, is enriched in the less permeable component(s). A sweep gas could optionally be introduced on the low pressure side, but the resulting dilution of the permeate may be unacceptable.

Since the extent of separation achievable in a single membrane unit, no matter how large, is limited, cascading in multiple stages with or without recycle is commonly practiced (Fig. 1.8). Cascading imparts great flexibility to membrane systems, with respect to changes in the flow rates or compositions of the feed and product streams. However, the costs of compression and piping in multistage cascades can be comparable to, or even greater than, the costs of the membrane modules themselves (Section 3.4; Schell, 1983, 1985).

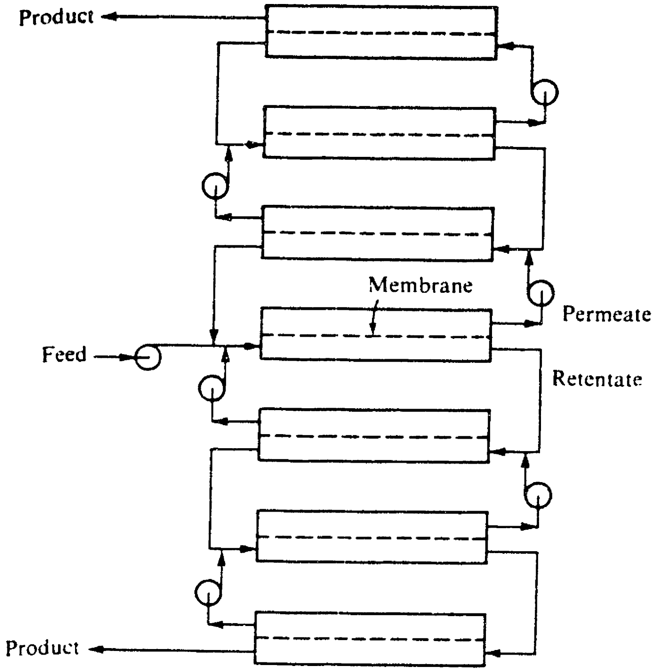
Membrane-based gas separation technology is the most recent of the major gas separation technologies. Although a few units were placed in service during the late 1960's, this technology was not fully commercialized until the late 1970's, when Monsanto offered its Prism product on the market.

Membrane systems have many advantageous characteristics. They are very simple, rugged and reliable, with few moving parts, hence they are easy to maintain, operate, start up and shut down. Their modular structure imparts considerable flexibility with respect to variations in the feed composition, throughput, or operating conditions. They are compact and light in weight. They can be shop-fabricated and skid-mounted, thus enabling rapid delivery and installation. Pilot plants mounted on truck trailers can be easily transported from one site to another.

The membrane elements can be replaced in the field, without shutting down the entire plant in the case of multiple units. Polymeric membranes have demonstrated useful lives of 3-6 years, depending on the type of service. The systems can be easily upgraded as new improved membranes become available.

Membrane systems operate at near ambient temperature. About the only energy required is for compression, and this varies widely by the type of application. Membrane systems are safe and nontoxic. The commonly used polymeric membranes block the passage of bacteria

Fig. 1.8



Multistage membrane separation process.

Source: King (1980)

and particulates, so the permeate is extremely clean. This property is useful in biological, medical and life support applications.

Membrane systems are relatively easy to scale up from pilot plant data to commercial designs, with the aid of computer simulation models. Good agreement between predicted and actual operating data has been reported.

Membrane systems' weak economies of scale beyond the scale of a single module is advantageous in small-scale applications (Section 3.4).

The pressure drop between the feed and retentate streams is low, typically 5-10 psi per module. So the only significant source of resistance to gas flow is the membrane element itself.

Water vapor permeates most polymeric membranes more rapidly than the permanent gases and organic gases. So some dehydration occurs along with the primary separation. This feature is advantageous when the retentate product must be dry (e.g. pipeline-grade natural gas), and/or when the permeate product must be humidified (e.g. oxygen-enriched air for respiration).

Membrane systems also have some drawbacks. Since high pressure drops are necessary for achieving economical throughputs, the feed streams to each unit in a cascade generally require compression (Fig. 1.8). The continuous membrane column does not require multiple compressors, but this does not necessarily make it more economical than cascades (Section 3.3).

A suitable membrane, with the requisite combination of selectivity, permeability, durability and other desirable properties, may not always be available for a particular application. Certain species may interact adversely with the membrane and hence may be unacceptable in the feed. Since condensation in the membrane module must be avoided, the feed stream's dewpoint must be well below the operating temperature, allowing for the cooling effect resulting from the irreversible expansion of the gas across the membrane. Thus, some feed pretreatment is often required, but this is also generally the case for other separation processes.

Polymeric membranes are limited in the temperatures they can withstand. This is disadvantageous if the feed gas has to be cooled for separation, and if one or more of the product streams have to be heated. Ceramic or metallic membranes can be used in high temperature applications, but they are less favorable than polymeric membranes in other respects.

Membrane separations are generally better suited for bulk removal rather than for purification to a high degree, i.e. to the parts-per-million impurity levels that are required in some applications (Table 1.1).

Perhaps the greatest disadvantage of membrane technology is its novelty. Its installed capacity, its data base of commercial operation, the number of products and vendors in the market, and the number of engineers with expertise in the subject, are much smaller than for the older, well established technologies. This creates a perception of high risk that any new entrant in a competitive market faces and has to overcome.

1.3 Commercial Applications of Membrane Gas Separation

The essential characteristics, strengths and weaknesses of the four major gas separation technologies discussed above suggest the conditions under which membranes are likely to be competitive. These conditions, listed in Table 1.2, delineate the application niches for which membrane separation should be evaluated, per se and in combination with other separation technologies.

Applications for which membrane gas separation is currently feasible, and for which it is expected to become feasible in the future, are listed in Table 1.3. Membranes are currently being used commercially for gas separation in ammonia plants, chemical plants, oil refineries, natural gas processing plants, CO_2-EOR facilities, biogas (landfill gas), air separation plants, and in medical oxygen enrichment devices.

The largest commercial application of membrane gas separation to date has been for the separation of hydrogen in ammonia plants, chemical plants and in oil refineries. Hydrogen separation was also the first commercial application of Monsanto's Prism separation system. The high permeability of hydrogen relative to the other gases was the main reason why membrane gas separation became economically competitive in these applications.

The largest future application of membrane separation after 1990 will most probably be for acid gas removal from hydrocarbon streams and flue gases (Table 1.1). This is because of the expected growth of natural gas, unconventional gas, synthetic fuels, enhanced oil recovery, and the abatement of emissions that contribute to 'acid rain" (Section 1.1).

The dehydration of gases and vapors is another significant future application of membranes. The use of membranes in an energy-efficient drying process is described by Akin, King et al. (1984). Monsanto offers a commercial Prism system that makes anhydrous (99.5%) ethanol from a 90% aqueous ethanol solution (Monsanto Tests Separators for Dehydration, 1985). Such a process may be simpler and more efficient than the conventional azeotropic or extractive distillation.

This chapter provided a framework for positioning membrane technology relative to other separation technologies, and for identifying applications that match its characteristics.

Table 1.2

CONDITIONS FAVORABLE FOR THE APPLICATION OF MEMBRANES

1. When a membrane material having the necessary selectivity, permeability, durability and other appropriate characteristics is commercially available.

2. For small to medium scale applications, in which compactness, portability and light weight are desirable.

3. For bulk removal or composition adjustment rather than for final purification to high purity products.

4. When high reliability, simplicity of operation, safety and low maintenance are essential, as in remote, unattended installations and medical systems.

5. When the feed stream is available at a high pressure and moderate temperature.

6. When the composition and/or flow rate of the feed is variable.

7. When a high partial pressure difference for the component(s) desired in the permeate stream can be maintained.

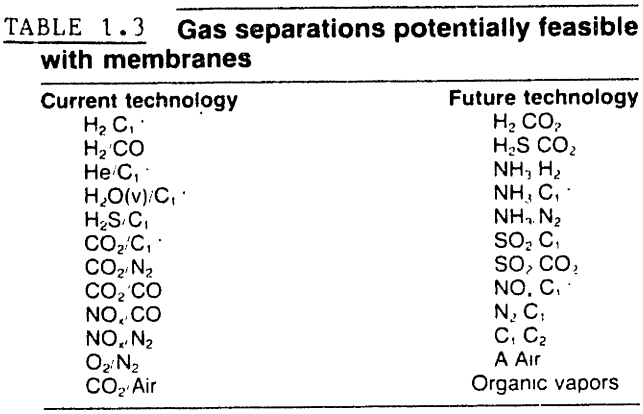


TABLE 1.3 **Gas separations potentially feasible with membranes**

Current technology	**Future technology**
H_2/C_1^+	H_2/CO_2
H_2/CO	H_2S/CO_2
He/C_1^+	NH_3/H_2
$H_2O(v)/C_1^+$	NH_3/C_1^+
H_2S/C_1	NH_3/N_2
CO_2/C_1^+	SO_2/C_1
CO_2/N_2	SO_2/CO_2
CO_2/CO	NO_x/C_1^+
NO_x/CO	N_2/C_1
NO_x/N_2	C_1/C_2
O_2/N_2	A/Air
CO_2/Air	Organic vapors

Source: Schell (1983)

Note: Include H_2/N_2 under current technology.

2. MEMBRANE TECHNOLOGY

2.1 Progress in Membrane Technology

Key trends and milestones of past progress and innovation in membrane science and technology are outlined chronologically in this section. This information is relevant to the prognostication of future technological trends in this field. The six principal membrane-based separation processes are shown in Fig. 2.1.

1700-1940

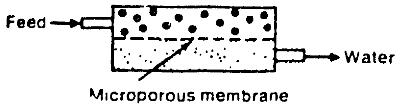
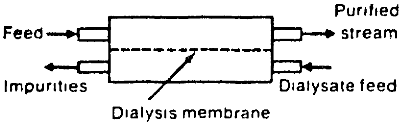
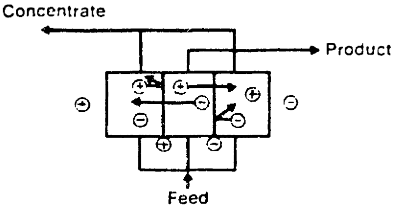
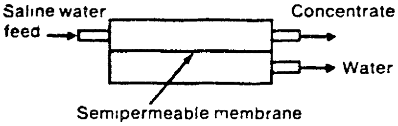
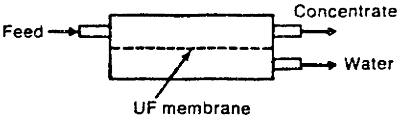
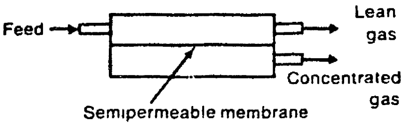
The earliest known experiments on membranes were carried out in Europe during the 18th century, on membranes of animal origin. The phenomena of dialysis, osmosis and gas permeability across membranes of natural rubber, animal organs and collodion, were systematically studied during the 19th century. The permeation rates of ten different gases through rubber balloons were reported by Mitchell (1831), a lecturer at the Philadelphia Medical Institute. These rates spanned a 100-fold range. Large differences in permeation rates form the basis of a viable separation process. Fick's law, Graham's law, Darcy's law, Henry's law, and the solution-diffusion model of mass transport, which together form the foundation of modern theories of mass transport in membranes, had been formulated and published by 1880.

The first patent on the separation of gases by membrane permeation was issued in Germany to Margis (1881). It described a method for making rubber membranes, and an apparatus for enriching air to 40%, 60%, 80%, and 95% oxygen in the first, second, third and fourth stages, respectively.

The first two U.S. patents on the separation of gases by membrane permeation were issued to Herzog (1884a and 1884b). The first patent describes an apparatus for making oxygen or oxygen-enriched air in a series of chambers containing colloid or rubber membranes. The second patent describes the use of oxygen-enriched air together with a hydrocarbon, to make illuminating gas. The earliest inventors recognized the need for multiple stages to achieve high degrees of separation of air.

Fig. 2.1

Membrane separation processes

Process/Concept	Materials passed	Driving force	Material retained
Microfiltration  	Water and dissolved species	Pressure difference, typically 10 psi	Suspended material (silica, bacteria, etc.). Variable particle-size cutoffs
Dialysis  	Ions and low-molecular-weight organics (urea, etc.)	Concentration difference	Dissolved and suspended material with molecular weight > 1000
Electrodialysis  	Ions	Voltage, typically 1 to 2V/cell pair	All nonionic and macromolecular species
Reverse osmosis  	Water	Pressure difference, typically 100 to 800 psi	Virtually all suspended and dissolved material
Ultrafiltration  	Water and salts	Pressure difference, typically 10 to 100 psi	Biologicals, colloids, and macromolecules. Variable molecular weight cutoffs
Gas separation  	Gases and vapors	Pressure difference, 1 to 100 atm	Membrane-impermeable gases and vapors

Source: Fox (1982)

Considerable data on the permeabilities of various fluids through membranes of various materials, including the effects of temperature and pressure, had been accumulated by 1940. Experiments involving microfiltration, ultrafiltration, reverse osmosis, electrodialysis and hemodialysis, mostly on cellulose membranes, had been performed by 1940. Membranes were being used in the laboratory, but not on a large scale, up to 1940.

1941-1960

The first large-scale system for separating gases by membranes was the gaseous diffusion plant for separating the isotopes of uranium, as part of the Manhattan Project during World War II. Porous sintered metal membranes were used in a cascade of about 3,000 stages with high recycle rates, to accomplish this very difficult and expensive separation. This Government-owned wartime project was not subject to the same economic criteria as a peacetime commercial venture. It was the source of significant theoretical developments in the design and optimization of membrane cascades with recycle, although the information was kept classified for several years.

The 1950's marked an important turning point, from the era of membrane science to the era of membrane science and technology. The emergence of synthetic polymers, whose properties could be controlled according to the method of formulation, greatly increased the number and variety of candidate membrane materials. The formation of small companies specializing in membrane-based products and services marked the beginning of the membrane industry. For example, the Millipore Filter Co. was founded in 1954 (it adopted its present name of Millipore Corp. in 1966).

Mathematical models for designing membrane systems for gas separation, and for determining the effects of gas flow pattern on system performance, were derived and applied in the classic papers by Weller and Steiner (1950a, 1950b). They worked out designs for air separation, helium recovery from natural gas, and hydrogen recovery from coke-oven gas and petroleum refinery gases. Membrane technology was not competitive with the alternative commercial technologies for these applications at that time. The requisite membrane surface area and the energy consumption were prohibitively large. For example, a plant to make 120,000 SCFH oxygen-enriched air using a 0.001 inch thick ethyl cellulose membrane, and a feed/product pressure ratio of 8, would have had the following design (Stern, 1966):

Product Purity (% O_2)	32.6	91.1
No. of Stages	1	5
Membrane Area (10^7 ft^2)	1.15	13.3
Power (MW)	0.41	4.8

In those days, polymeric membranes were available only in sheet or film form, and membrane modules were of the plate-and-frame configuration. The membrane areas required, as calculated above, are a few orders of magnitude greater than the area of a football field. Scientific and technical breakthroughs, not mere incremental improvements, were needed to make membrane separation technology competitive. Fortunately, the needed breakthroughs were not long in coming.

Cellulose acetate (CA) membranes for the desalination of seawater by reverse osmosis (RO) had been developed by Reid and Breton at the University of Florida, and by Mahon of Dow Chemical Co., during the 1950's. The asymmetric CA membranes developed at UCLA by Loeb and Sourirajan (1960, 1963, 1964, 1965) represented a breakthrough. Such membranes exhibited high flux, high selectivity, and the ability to withstand high pressures, in an unprecedented combination. This technology was the basis of the RO industry, which now exceeds $100 million/year (Lonsdale, 1982b).

1961-1970

The next breakthrough occurred in the 1960's, when Du Pont and Dow Chemical developed hollow fiber polymeric membranes. Hollow fibers provide surface area/module volume ratios one or two orders of magnitude greater than the previous conventional membrane modules. A module typically contains millions of these hair-thin fibers, whose wall thicknesses are comparable to their internal diameters, so they can withstand high pressures and high pressure differentials without collapsing or bursting (Paul and Morel, 1981).

Another configuration, the spiral-wound membrane module, was invented by the General Atomic Co. and patented in 1968. The hollow-fiber and the spiral-wound configurations have remained the dominant commercial designs for membrane equipment until the present time.

A few commercial-scale gas separation plants were placed in service during the late 1960's and early 1970's. Du Pont built two plants using hollow fibers of homogeneous Dacron polyester membranes. One was for recovering hydrogen from refinery gases, and the other was for recovering 85-90% pure CO from a 50/50 H_2/CO feed. Du Pont later developed asymmetric, aromatic polyamide (Aramid) membranes which were far superior to the homogeneous Dacron membranes for gas separation (Hoehn, 1985). Union Carbide operated a small plant to recover helium from natural gas at Shiprock, New Mexico. This natural gas contained 5-6% helium and 87% nitrogen, which is a rare composition. An asymmetric cellulose acetate membrane in flat sheet form was used (Kammermeyer, 1976).

Hydrogen recovery by means of palladium-silver alloy membranes was commercially practiced by Union Carbide and the Humble Oil & Refining Co. (now part of Exxon Corp.) in their petrochemical facilities. Such metallic membranes are highly selective for hydrogen, so a permeate product of over 99% hydrogen purity can be achieved in a single stage. However, such membranes require operation at high temperatures (over 300°C) and high feed pressures (500-600 psi). Their permeabilities for hydrogen are lower than modern polymeric membranes and they cannot be fabricated in configurations of very high surface area per unit module volume. Furthermore, palladium-silver alloys are expensive, and are subject to contamination by carbon monoxide, hydrogen sulfide, ethylene, etc. (Kammermeyer, 1976). Thus, metallic membranes are not competitive with modern polymeric membranes in most situations.

The status of the membrane industry and technology around 1968 was summarized by Pattison (1968).

Research and development related to all aspects of membrane science and technology continued at a rapid pace throughout the 1960's. Novel concepts such as pervaporation, liquid membranes, facilitated transport, and the continuous membrane column were conceived and developed. In pervaporation, the feed is in the liquid phase, and the permeate is in the vapor phase (Sanders and Choo, 1960). The incentive was for pervaporation to substitute for distillation in separating close-boiling or azeotropic mixtures.

Liquid membranes are of two types: supported or immobilized liquid membranes (ILM), and emulsion or liquid surfactant membranes (ELM). The former (ILM) was developed at General Electric, and the latter (ELM) was developed at Exxon Research and Engineering. Both these efforts were terminated in 1978 and 1980 respectively, although R&D continues elsewhere (Parkinson, 1983; Flynn and Way, 1982).

In facilitated transport, the membrane plays an active rather than passive role, by reversibly forming chemical complexes with the species desired in the permeate. In principle, facilitated transport should provide a very favorable combination of high permeability and high selectivity. Potential applications in hydrometallurgy, waste water treatment, air separation, and acid gas removal (CO_2, H_2S and SO_2) have been extensively investigated.

A significant novel membrane module configuration, invented around 1960, is described in a patent issued to Pfefferle (1964). It is a continuous membrane column, consisting of an enriching section and a stripping section, with a compressor and provision for reflux. In principle, it could effect a separation comparable to a cascade of conventional membrane modules, yet it is much simpler. This concept was later developed and refined by researchers at the Universities of Iowa, Cincinnati and Dortmund (W. Germany).

None of these four novel and promising concepts -- pervaporation, liquid membranes, facilitated transport, and the continuous membrane column -- has yet been implemented commercially, even after 15-25 years of research and development.

1971-1985

During this latest period, membrane-based separation became an established, commercially proven process. It formed the basis of an entire new industry, consisting of dozens of large and small companies, engaged in R&D, manufacturing, business/market research, consulting, etc. all related to membranes. Several universities established research programs or centers specializing in membrane related topics.

The rapidly growing body of information on the subject of membranes was being disseminated by means of specialized journals, newsletters, books and conferences.

The emergence of a full-fledged membrane-based industry was a result of both endogenous and exogenous factors. The latter are discussed first. The energy crisis, with its sharp increase in the cost of energy and raw materials, spurred the search for more energy-efficient processes, enhanced oil recovery, synthetic fuels, nonfossil energy sources, etc. Compliance with more stringent environmental regulations required improved pollution control, water purification, waste treatment and resource recovery technologies. The high-technology industries based on electronics, biotechnology and health care, advanced rapidly and posed challenging separation problems. The U.S. chemical industry shifted its emphasis from commodity products to specialty products and services. Meanwhile, the OPEC nations invested heavily in large petrochemical and desalination facilities as they built up their economic infrastructure. All these major trends are expected to continue for at least the next decade. They created a "market-pull" demand for improved separation technology, in which membranes played a prominent role.

The main endogenous factor was the "technology-push" arising from the stepped-up R&D activity in the disciplines underlying membrane technology, especially in polymer science. Technical milestones in the development of membranes for gas separation since 1970 are listed in Table 2.1. The development of thin-film composite (TFC) membranes by Monsanto, UOP and GE represented another breakthrough in this field. These were implemented commercially in the late 1970's in a variety of applications.

Table 2.1 Milestones in membrane development for gas separation

Year	Inventor	Invention	Main Improvement
1970	Gantzel and Merten	freeze-dried, asymmetric CA membranes	high N_2 permeation rate of $3.1x10^{-6}$ 1) at a He/N_2 selectivity of 34
1975	Schell	solvent-dried, asymmetric CA blend membranes	higher N_2 permeation rate of $4.8x10^{-6}$ 1) at a He/N_2 selectivity of 68
1976	Ward et al.	TFC membranes made of silicone/ polycarbonate block copolymers	extremely high N_2 permeation rate of $8.6x10^{-2}$ 1) at a low O_2/N_2 selectivity of 2.3
1979	Henis and Tripodi	asymmetric polysulfone hollow fibers coated with silicone rubber	high H_2/CO selectivity of 33 with a low-cost module system

1) $\bar{P}/\ell$, $cm^3(STP)/cm^2$-s-cmHg; to obtain $m^3(STP)/m^2$-s-MPa multiply by 7.501.

Source: Finken (1985)

Another endogenous factor was the operating experience gained from the first generation of commercial membrane-based gas separation plants that were installed in the late 1960's and early 1970's. These early installations were essentially in-house demonstration plants, used to prove feasibility. They facilitated the sale of the next generation of systems, starting in the late 1970's, to various customers who would buy only a reliable, field-proven system.

Thus, both market-pull and technology-push factors have contributed to the establishment of a distinct high-technology industry centered on membrane technology.

The time lag from scientific discovery or invention to commercial implementation in this field has been of the order of decades, up to about one century. Perhaps this time lag will shorten as the pace of advancement quickens. Reduction of this time lag in the innovation cycle should be an objective of high priority for industrial, academic and governmental organizations concerned with membrane technology.

2.2 Literature Review

The literature pertaining to membrane technology is very extensive, partly because it spans two centuries, and partly because of the wide range of applications, disciplines, and organizations involved. The emphasis of this review is on the recent literature (since 1970) relating to gas separations, in the English language.

"Membrane Gas Separation" is a bibliography published and regularly updated by the National Technical Information Service (NTIS) in three versions, based on the NTIS, DOE, and Engineering Index databases, which can also be searched on line.

The books by Hwang and Kammermeyer (1975), Meares (1976), Sourirajan (1977) and Cooper (1982), cover all aspects of membrane science and technology, including gas separation. Historical reviews of the field are given by Edwards (1971, 1972), Michaels (1976), Stannett (1978), and Lonsdale (1982b).

Current reviews of membrane separation technology are written by Stannett *et al.* (1979), Paul and Morel (1981), Strathmann (1981), Lonsdale (1982a, 1982b), Flynn and Way (1982), Hwang and Kammermeyer

(1982), Rain (1983) and Leeper et al. (1984). Reviews dealing exclusively with membrane technology for gas separation are written by Matson, Lopez and Quinn (1983), Kulkarni et al. (1983), Schell (1983, 1985), Henis and Tripodi (1983), Egli et al. (1984) and Saltonstall (1985).

There are numerous publications covering the more theoretical aspects of transport across membranes, relationships between the preparation methods, structures and properties of membranes, and compilations of permeability data. See for example, Crank and Park (1968), Hopfenberg (1974), Stern and Frisch (1981), Frisch and Stern (1983), Pusch and Walch (1982a, 1982b) and Lloyd (1985).

Business and market information on the membrane industry has been reported by Pattison (1968), Fox (1982), Hughey (1983), Crull (1983, 1984), Parkinson (1984), Brooks (1985a,b), and Saltonstall (1985), as well as the publications listed in Table 2.2.

Membrane-related papers have appeared in many journals, due to the interdisciplinary nature of the subject as well as the international scope of the R&D activities. "Desalination," the "Journal of Membrane Science," and "Membrane and Separation Technology News" are specialized journals devoted to the subject.

There have also been many conferences and symposia on the themes of gas separation technology and/or membrane separation technology. The U.S. Department of Energy (DOE) holds annual Membrane Technology R&D Workshops at which its contractor organizations report on their current projects. The latest workshop was held at Clemson, SC in October, 1984. Annual Membrane Conferences are organized by Business Communications Co., a business and market consulting firm that also publishes several membrane-related items (see Table 2.2). The following proceedings of recent American Chemical Society (ACS) symposia are good sources of current information:

- Synthetic Membranes (2 volumes), 1981
- Industrial Gas Separations, 1983
- Materials Science of Synthetic Membranes, 1985.

Other pertinent conferences held regularly are:

- The International Gas Research Conferences (annual).

- The Gas Conditioning Conferences (annual).
- The Gas Processors Association's Annual Conventions and Regional Conventions.
- The Gas Research Institute's Gas Separation Workshops.

Patents constitute a rich source of technical information spanning over one century, especially on membrane materials, membrane fabrication methods, module designs, system designs, permeability measurement apparatus and data, and performance data in specific applications. Patents are also useful for strategic competitive analysis of firms in the membrane industry.

Most of the pertinent patents are in the following classes:

U.S. Patent Classes:

- 55-16: Processes of gas separation by gas diffusion into a solid barrier.
- 55-158: Barrier for selective diffusion of gases.

International Patent Classes:

- B01D 13/00: Processes of separation employing semipermeable membranes.
- B01D 13/04: Special methods for the production of semipermeable membranes.
- B01D 53/22: Separation of gases or vapors by diffusion, or recovering vapors of volatile solvents from gases by diffusion.

Convenient compilations of patents, indexed for retrieval by multiple keys, are contained in some publications listed in Table 2.2.

Table 2.2

BUSINESS/MARKET/PATENT REPORTS RELATED TO GAS SEPARATION BY MEMBRANES

	Title	Publisher
1.	Business Opportunities in Membrane Separations (1984; Quarterly, Client Private Reports)	SRI International Menlo Park CA 94025
2.	Business Opportunities in Membrane Technology (1982)	Battelle Columbus Laboratories Columbus OH 43201
3.	Emerging Membrane Separation Technologies (1984)	International Resource Development Inc. Norwalk CT 06855
4.	Hollow Fibers: Manufacture and Application (1981) Membrane and Ultrafiltration Technology: Developments Since 1981 (1984)	Noyes Data Corp. Park Ridge NJ 06855
5.	Industrial Membrane Systems, 1982-1990 (1982)	T.A. Sheets Co. Cleveland Heights OH 44118
6.	Membrane & Separation Technology Directory (1985) Membrane & Separation Technology News (Monthly) Membrane Conference Proceedings (Annually) Membrane Technology Patent Sourcebook (1983) Membranes in Separations and as Supports (1983)	Business Communications Co. (BCC) Stamford CT 06906
7.	Membrane Separation Processes (Annually)	Lexington Data Inc. Ashland MA 01721

2.3 Transport of Gases Through Membranes

The transport of gases through membranes is a complex phenomenon that depends on:

- The properties of all the gases present.
- The membrane's composition, structure and dimensions.
- The operating conditions.

The differences in permeation rates of two or more components through the membrane form the basis of the separation. The transport of a molecule from the upstream side to the downstream side can be modeled in many cases as a sequence of five steps:

1. Diffusion from the bulk of the feed stream to the upstream surface of the membrane.
2. Sorption or solution of the gas molecule into the membrane phase.
3. Diffusion of the molecule within the membrane to the downstream surface.
4. Desorption from the downstream membrane surface into the gas phase.
5. Diffusion from the downstream membrane surface into the bulk of the permeate stream.

The net overall rate of transport at steady state is the rate of the slowest or rate-limiting step, since these steps are in series. The third step is generally rate limiting, and concentration polarization is insignificant in gas separation (MacLean, Stookey and Metzger, 1983). In facilitated transport, however, steps (2) through (4) are speeded up considerably by a reversible chemical reaction.

The five-step solution-diffusion model is a simple, classical model that was first proposed by Graham in 1866. It adequately describes the permeation of simple gases above their critical temperatures through homogeneous, nonporous films of rubbery polymers. More complex models are needed for other cases.

Many common transport phenomena are modeled by equations of the form:

$$\text{Flux} = (\text{Driving Force})/(\text{Resistance}) \tag{2.3.1}$$

Fick's law of diffusion, Fourier's law of heat conduction, and Ohm's law of electricity are well known equations of this form. For transport mechanisms involving multiple steps, the overall resistance is a simple combination of the individual resistances in series and/or in parallel. This concept was successfully applied by Monsanto researchers in the development of their Resistance Model (RM) composite membranes (Henis and Tripodi, 1981, 1982).

The driving force for transport across a membrane is the net gradient of chemical potential. For gas transport through polymeric membranes, this is well approximated by the gradient of partial pressure across the membrane. However, for gas transport through metallic membranes by atomic diffusion, the gradient of the square root of partial pressure is the driving force (Kammermeyer, 1976).

The resistance depends on the transport mechanism. The dominant mechanism is determined by the relative dimensions of the mean free path (λ) of the gas molecules and the mean pore radius (r_p) of the membrane. The permeability coefficient is the reciprocal of the resistance. The net flux is the algebraic sum of the flux contributions by the various transport mechanisms, although in practice one mechanism is usually dominant. The transport equations for the various mechanisms are summarized in Table 2.3.

The mean free paths of the common light gases at ambient conditions are in the range 0.05-0.15 microns. Numerical data on mean free paths are given by Sourirajan (1977, Chap. 26).

According to the solution-diffusion model, the permeability of a component is the product of its diffusivity and its solubility:

$$P_i = D_i S_i \tag{2.3.2}$$

D_i and S_i are each assumed to depend only on temperature, and not on the partial pressures of component i or the other components. Since diffusivity increases with temperature, while solubility decreases

Table 2.3

MECHANISMS OF MEMBRANE TRANSPORT

Transport Mechanism	Condition	Membrane Type	Transport Equation for Steady State Flux	Selectivity for Separation	Comments
Viscous flow	$r_p >> \lambda$	Porous	$q = (\frac{\varepsilon r_p^2}{8\mu})(\frac{p_1 - p_2}{\ell})$	$\alpha_{ij} \approx 1$	Darcy's law for volumetric flux. Essentially no selectivity.
Knudsen diffusion	$r_p \approx \lambda$	Microporous	$N_i = \frac{8\varepsilon r_p}{3(2\pi RTM_i)^{1/2}}(\frac{p_{i1} - p_{i2}}{\ell})$	$\alpha_{ij} = \sqrt{\frac{M_j}{M_i}}$	Knudsen law for molar flux. Selectivity depends only on molecular weights of the gases.
Solution and molecular diffusion	$r_p << \lambda$	Nonporous	$N_i = P_i(\frac{p_{i1} - p_{i2}}{\ell})$	$\alpha_{ij} = \frac{P_i}{P_j} = \frac{D_i S_i}{D_j S_j}$	Selectivity depends on the properties of the gases and the membrane. More complex models are needed in some cases.
Dissociation and atomic diffusion	$r_p << \lambda$	Metallic	$N_i = P_i(\frac{p_{i1}^{1/2} - p_{i2}^{1/2}}{\ell})$	$\alpha_{ij} = \frac{P_i}{P_j}$	Transport of diatomic gases through metallic membranes by dissociation and atomic diffusion.

with temperature, both in Arrhenius law form, the permeability's dependence on temperature may be positive or negative according to which effect predominates (Perry's Handbook, 1984, p. 17-15):

$$D_i = D_{io}\exp\left[-\frac{E_{Di}}{RT}\right] \tag{2.3.3}$$

$$S_i = S_{io}\exp\left[-\frac{\Delta H_{si}}{RT}\right] \tag{2.3.4}$$

$$P_i = P_{io}\exp\left[-\frac{E_{pi}}{RT}\right] \tag{2.3.5}$$

where

$$P_{io} = D_{io}S_{io} \tag{2.3.6}$$

and

$$E_{pi} = E_{Di} + \Delta H_{si} \tag{2.3.7}$$

Thus, according to this model, for a given gas and membrane material:

- A plot of log (permeability) v. 1/T, or log (permeability) v. log (vapor pressure of a reference substance), should be linear (Othmer and Frohlich, 1955).
- Permeability should be independent of the other components and all the operating variables except temperature.
- Permeability should equal the product of diffusivity and solubility.

The solution-diffusion model has been found to correlate a considerable amount of permeability data, especially for simple gases above their critical temperatures permeating through homogeneous, nonporous films of rubbery polymers. Advantages of this model are:

- It is simple, having just two parameters, P_{io} and E_{pi}.
- If D_i and S_i have been measured separately, P_i can be readily obtained as their product. It is sometimes impractical to

measure P_i directly by experiment.

The permeability of hydrogen through various polymers as a function of temperature is shown in Fig. 2.2. The permeability values span a range of six orders of magnitude, from Silastic 500-1 at the low end to polyvinyl alcohol (PVA) at the high end. The temperature sensitivies also vary widely being lowest for polystyrene and highest for PVA and Saran 925. Since the lines in this Arrhenius plot are straight, the solution-diffusion model appears to describe adequately these data for hydrogen permeability in the temperature range 0-50°C.

It is also of interest to consider data on the permeabilities of several gases through the same membrane. Permeation data for nitrogen, hydrogen, sulfur dioxide and carbon dioxide, through a membrane of polyvinylidene fluoride (Kynar) containing 18 wt % sulfolene, reported by Zavaleta and McCandless (1976), are shown in Figs. 2.3-2.6.

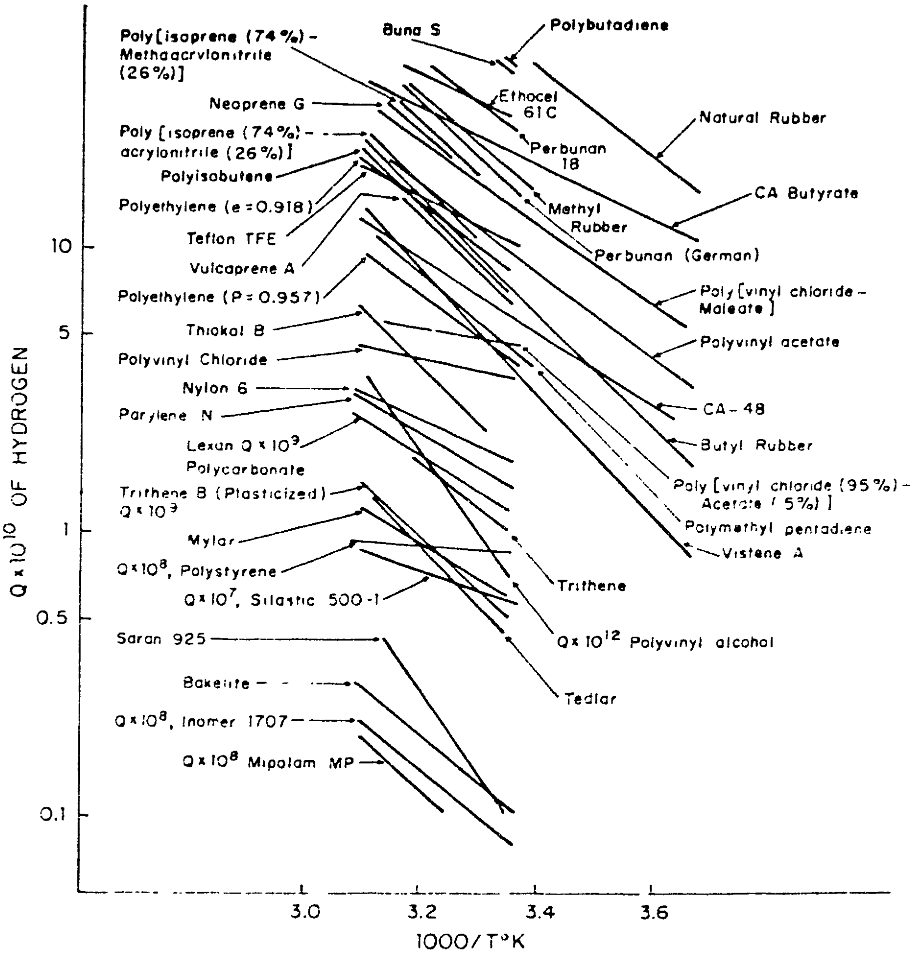
The permeability of nitrogen is independent of pressure drop, and has an Arrhenius dependence on temperature (Figs. 2.3, 2.4). The permeability of hydrogen increases linearly with pressure but the effect of pressure is not strong (Fig. 2.5). The permeability exhibits Arrhenius temperature dependence (Fig. 2.6). The permeability of sulfur dioxide increases steeply with pressure (Fig. 2.7), and decreases with temperature, in a non-Arrhenius manner (Fig. 2.8). For carbon dioxide, the permeability increases strongly with pressure (Fig. 2.9) and it may increase or decrease with temperature, depending on the pressure (Fig. 2.10). Also, nitrogen and hydrogen are much less permeable than sulfur dioxide and carbon dioxide.

For this particular membrane, nitrogen behaves ideally, hydrogen behaves nearly ideally, sulfur dioxide behaves nonideally, and carbon dioxide behaves highly nonideally. The latter two substances interact strongly with the membrane. Thus, the simple solution-diffusion model summarized by equations (2.3 - 2.7) can adequately predict the transport behavior of nitrogen and hydrogen, but not sulfur dioxide and carbon dioxide, under this set of conditions. For additional data and explanations of these phenomena, see the paper by Zavaleta and McCandless (1976), and other publications by the latter author.

The solution-diffusion model has a limited range of applicability.

Fig. 2.2

HYDROGEN PERMEABILITIES THROUGH VARIOUS POLYMERIC MEMBRANES



Source: Hwang and Kammermeyer (1982)

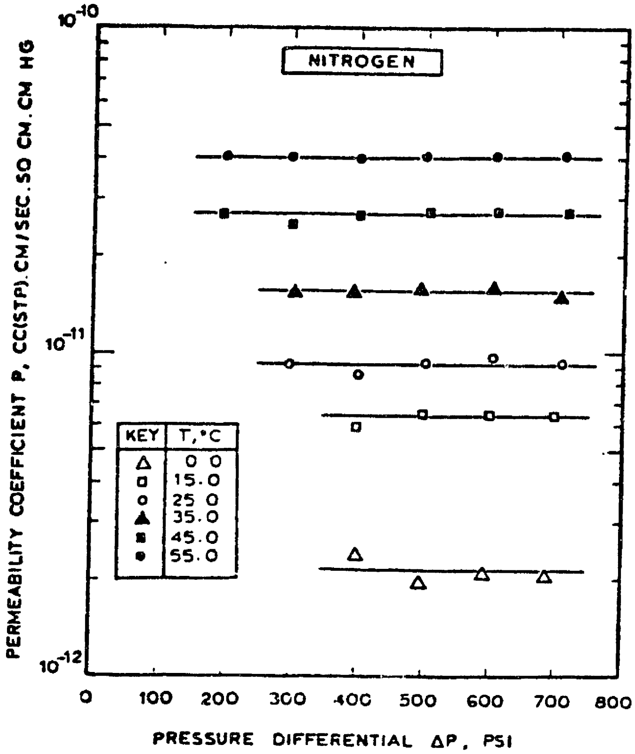


Fig. 2.3 Permeability coefficient vs. pressure differential for nitrogen.

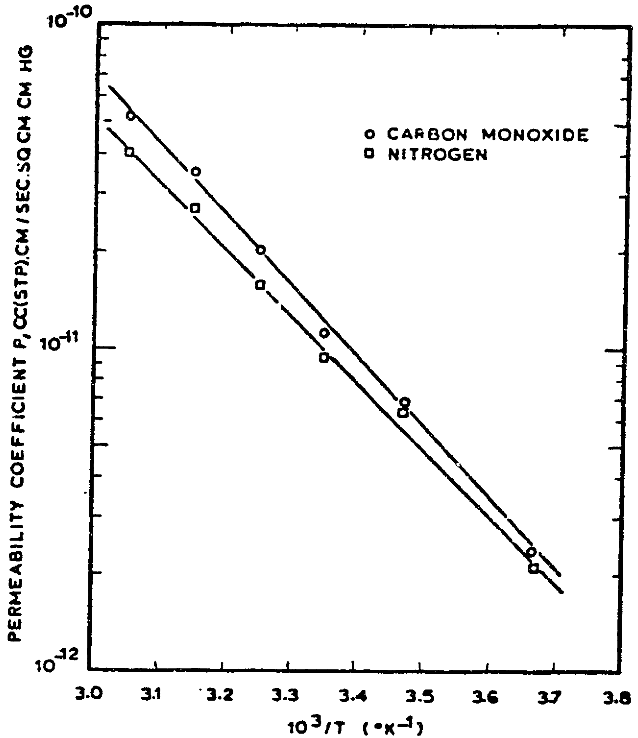


Fig. 2.4 Permeability coefficient vs. $10^3/T$ for carbon monoxide and nitrogen.

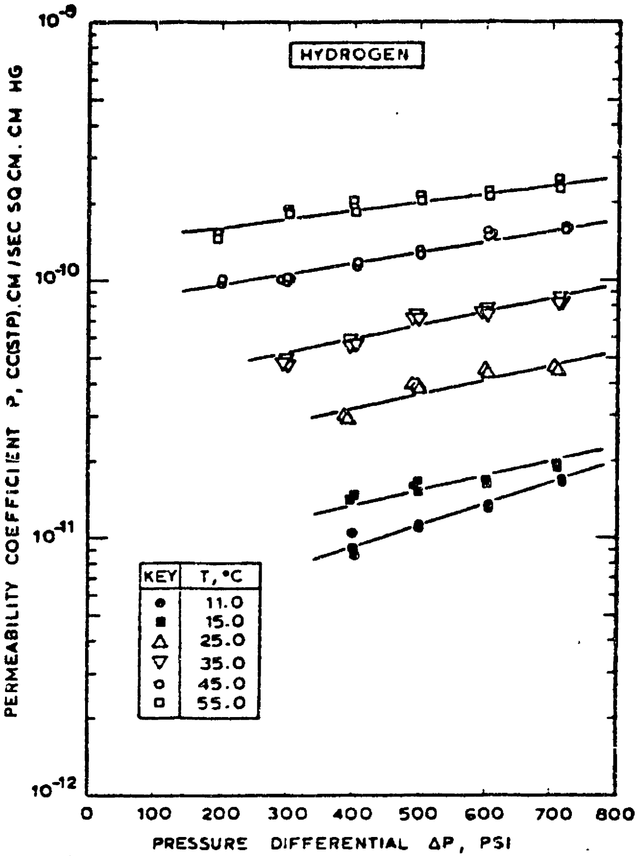


Fig. 2.5

Permeability coefficient vs. pressure differential for hydrogen.

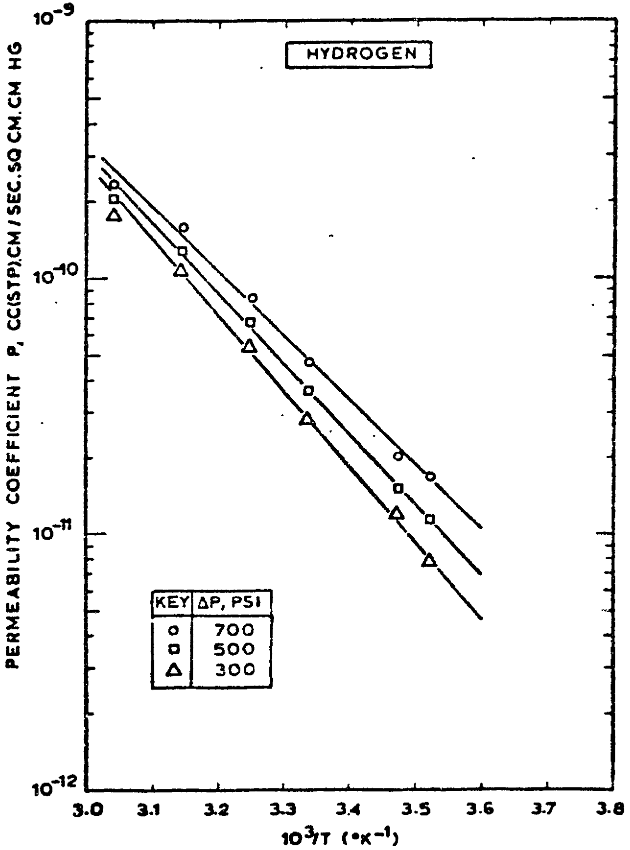


Fig. 2.6

Permeability coefficient vs. $10^3/T$ for hydrogen.

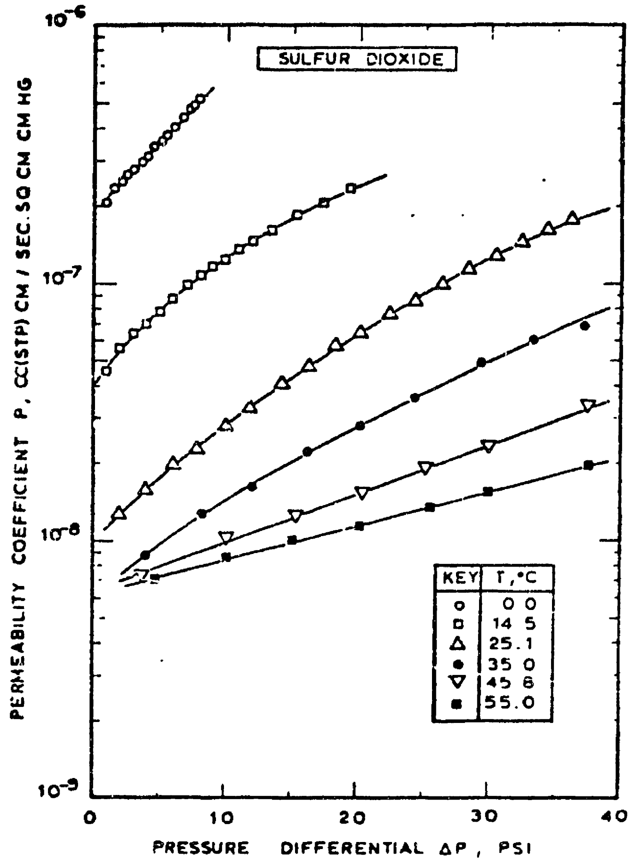


Fig. 2.7

Permeability coefficient vs. pressure differential for sulfur dioxide.

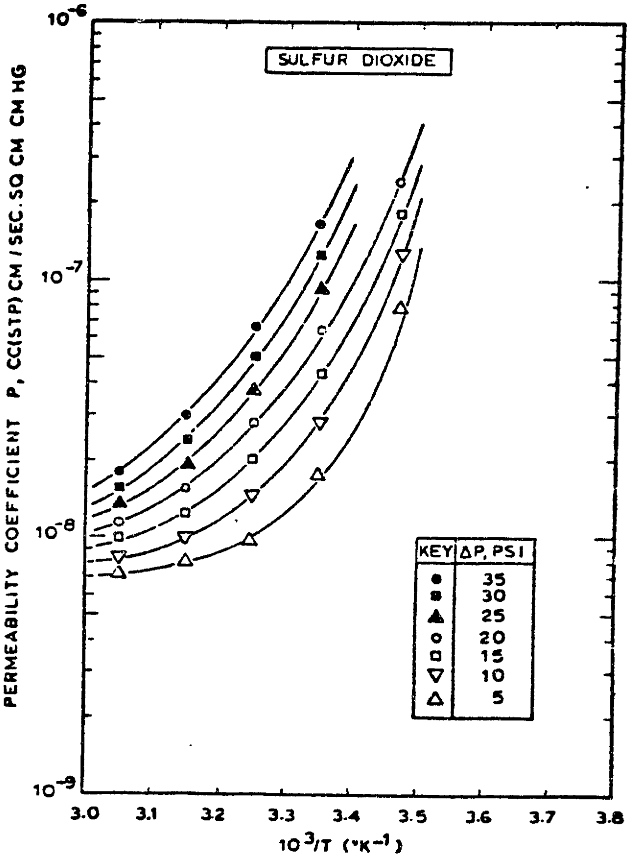


Fig. 2.8

Permeability coefficient vs. $10^3/T$ for sulfur dioxide.

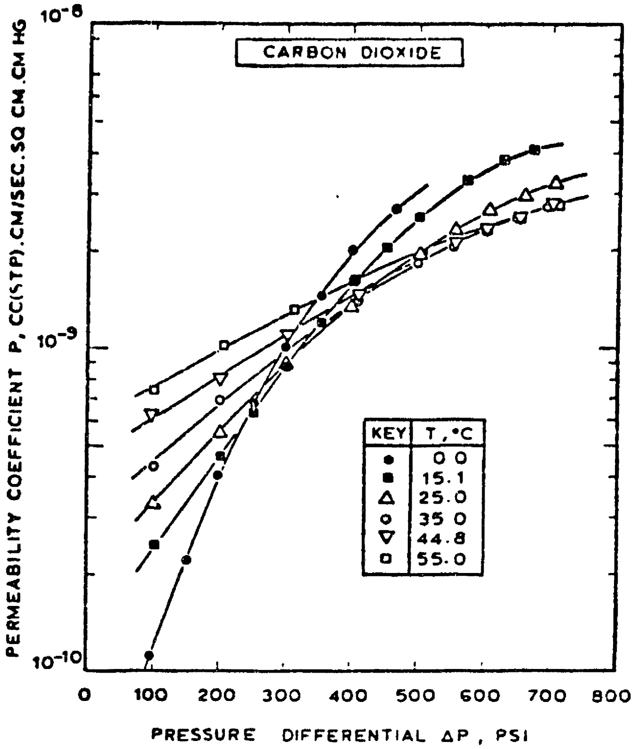


Fig. 2.9 Permeability coefficient vs. pressure differential for carbon dioxide.

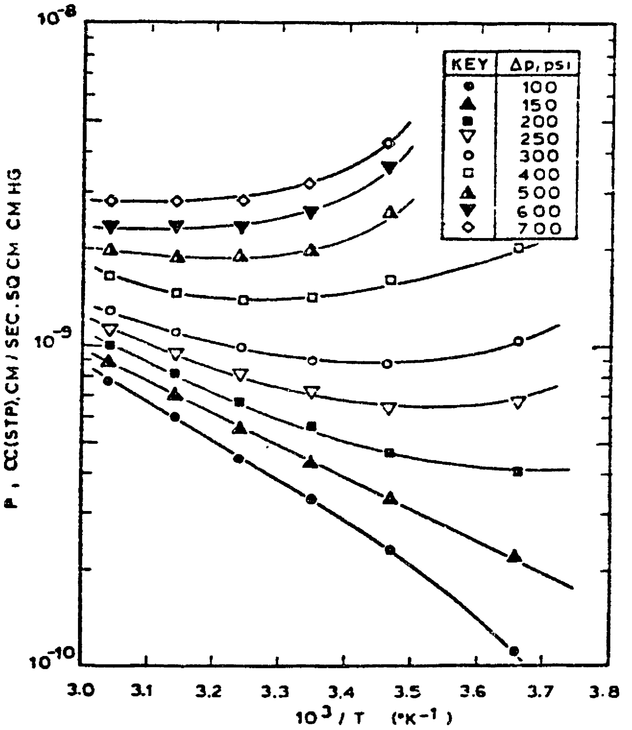


Fig. 2.10 Permeability coefficient vs. $10^3/T$ for carbon dioxide.

Other more complex models are needed to explain and correlate permeation data when the solution-diffusion model does not apply.

The "concentration-dependent" model is an extension of the classical solution-diffusion model that allows the diffusivity and solubility coefficients to depend on concentration as well as temperature. Thus, in one such model,

$$P_i = D_i S_i \tag{2.3.2}$$

$$D_i = D_{io}[1 + f_D(c)]\exp\left[-\frac{E_{Di}}{RT}\right] \tag{2.3.8}$$

$$S_i = S_{io}[1 + f_s(c)]\exp\left[-\frac{\Delta H_{si}}{RT}\right] \tag{2.3.9}$$

This model reduces to the solution-diffusion model as the limiting case as the functions $f_D(c)$ and $f_s(c)$ tend to zero.

Another concentration-dependent model is based on the relationship (Perry's Handbook, 1984, p. 17-15):

$$P_i = P'_{io}e^{Ap_i} \tag{2.3.10}$$

where the parameter A may be positive or negative. Then the flux of component i is given by:

$$N_i = \frac{P'_{io}}{A\ell}(e^{Ap_{i1}} - e^{Ap_{i2}}) \tag{2.3.11}$$

The permeation behavior depends strongly on whether the polymer is in the rubbery state ($T>T_g$) or in the glassy state ($T<T_g$). Polymers in the rubbery state generally exhibit higher permeabilities but lower selectivities than those in the glassy state (Stannett <u>et al.</u>, 1979). Data on the glass transition temperatures (T_g) of various natural and synthetic polymers are reported in the Polymer Handbook (Brandrup, Immergut and McDowell, 1975). Because of these strong structural effects, different transport models have been used for rubbery and glassy polymers.

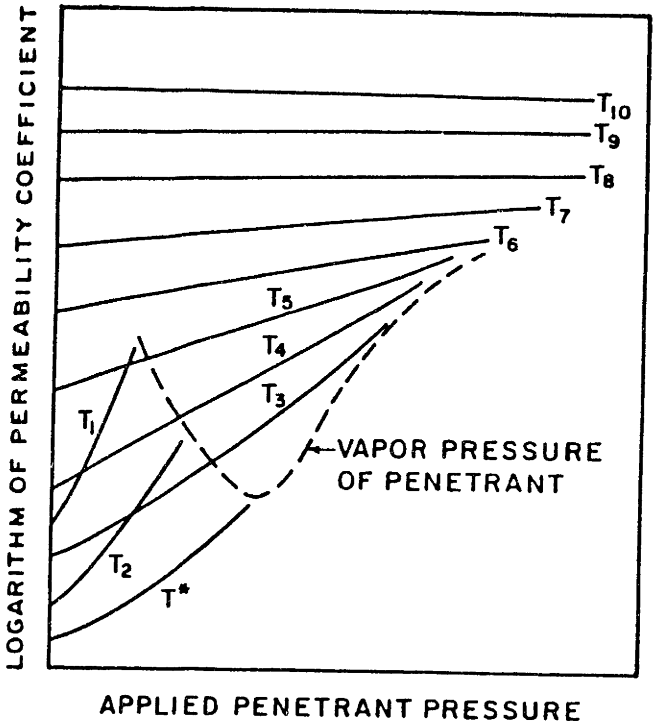
Experimental data on the permeability of gases through rubbery polymers show the general pattern depicted in Fig. 2.11. In this figure, the temperature increases from T_1 to T_{10}. Below temperature T^*, the permeability increases with temperature, at a constant pressure. Hence, at a given pressure, the permeability is minimum at T^*. The pressure dependence of permeability is nonnegative, being greatest at low temperatures and small or nil at high temperatures. The behavior also depends on whether the gas is above or below its critical temperature, T_c. The permeation behavior of rubbery polymers has been explained by the "free volume" model (Stern and Frisch, 1981; Matson, Lopez and Quinn, 1983; Stern, Mauze and Sampat, 1984).

Experimental data on the permeability of gases through glassy polymers show a different pattern. For example, the permeability of carbon dioxide decreases with pressure initially, then levels out to become independent of pressure; except that its permeability in cellulose acetate increases monotonically with pressure (Fig. 2.12). The positive pressure dependence of the permeability is because carbon dioxide plasticizes the cellulose acetate, thereby making it more rubber-like and increasing its diffusivity.

The "dual-mode sorption" model has been used to correlate and explain the permeability data for glassy polymers. The model's basic premise is that the sorption occurs by two independent but additive modes -- a Henry's law mode and a Langmuir law mode. The two diffusion coefficients have different but constant values, that is, they are not concentration-dependent. This model adequately correlates data for carbon dioxide and light hydrocarbons through glassy polymers. It reduces to the solution-diffusion model as the limiting case as the Langmuir term tends to zero. Further details on the dual-mode sorption model are given by Vieth, Howell and Hsieh (1976), Stannett et al. (1979), Matson, Lopez and Quinn (1983), Chern et al. (1983) and Chern et al. (1985).

Fig. 2.11

Generalized dependence of mean permeability coefficients on pressure and temperature.



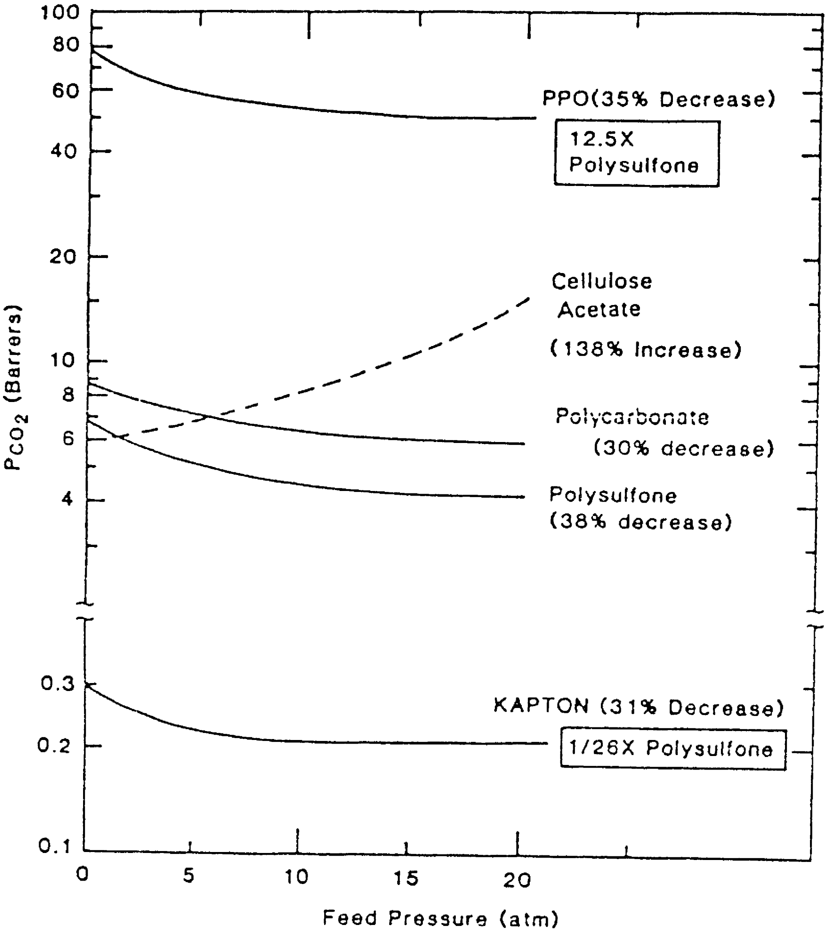


Fig. 2.12 Pressure dependence of CO_2 permeability in a variety of glassy polymers at 35 °C.

Source: Chern, Koros, Hopfenberg and Stannett (1985)

The transport models discussed above originated in the 1950's. They have been refined and extended over the years, but they are still inadequate in some cases and some of their basic assumptions are not supported by recent experimental evidence.

A generalized transport model that combines the free-volume and dual-mode sorption concepts, and is applicable to both rubbery and glassy polymers, was formulated by Stern, Mauze and Sampat (1984).

The molecular diffusion model of Pace and Datyner, and the "gas-polymer-matrix" model of Raucher and Sefcik are more advanced contemporary models. They are both discussed by Raucher and Sefcik (1983).

The state of the art of interpreting and explaining the phenomena of gas transport through membranes will undoubtedly continue to advance in the future. It would be highly desirable to be able predict the permeabilities of a gas-solid system from the other known properties of the gases, the solid, and the operating conditions. A reliable, universal theory of permeation would save considerable expense and time needed for gathering experimental data, and it would facilitate the design and selection of membranes for specific applications. Despite great progress over the past thirty years, no such universal theory of permeation exists today.

Many different correlations have been reported between the permeabilities (or the diffusivities and solubilities individually) of gases and other physical properties. For example, a plot of log (diffusivity) vs. log (molecular weight) for various gases is roughly linear for a given polymer. The slopes are -3 to -2 for rubbery polymers, and -6 to -5 for glassy polymers (Lonsdale, 1982a). Correlations of log (diffusivity) vs. van der Waals volume and kinetic diameter, and of log (solubility) vs. critical temperature, were presented by Chern et al. (1985).

Correlations of the transport properties of common gases with their boiling points were reported by Stannett (1978) and by Andrews (1984).

The permeability of a component in the presence of other gases, sometimes known as pseudo-permeability, is usually greater than its permeability as a pure component, at the same partial pressures and temperature. Components having high solubilities in the polymer, such as polar gases, tend to have a strong positive effect on the permeabilities of other components (MacLean, Stookey and Metzger, 1983; Stern Mauze and Sampat, 1984). This synergistic effect in multicomponent permeation tends to suppress selectivity in gas separation. It is generally attributed to plasticization of the polymer. However, in the absence of plasticization and at low concentrations, the effect may be opposite (Chern et al., 1983).

The variation of gas permeability with the properties of solid polymer can be qualitatively characterized as follows. Permeability generally increases with increasing plasticizer content (Zavaleta and McCandless, 1976), and with increasing moisture content. Permeability generally decreases with increasing density, crystallinity, crosslinking, molecular orientation and filler content (Hwang and Kammermeyer, 1975, Table 5.3; Yasuda and Stannett, 1975).

The trends in selectivities and permeabilities are generally in opposite directions, as illustrated by the data for air separation in Fig. 2.13, and the data compiled by Stern (1966).

The permeability of a composite or multilayered membrane can be estimated from the permeabilities of the individual layers by the "resistance model" method. Thus, when permeability is independent of concentration, the overall permeability P_n of n layers in series, each of permeability P_i and thickness ℓ_i, is given by:

$$P_n = \ell_n / \sum_{i=1}^{n} (\ell_i / P_i) \qquad (2.3.12)$$

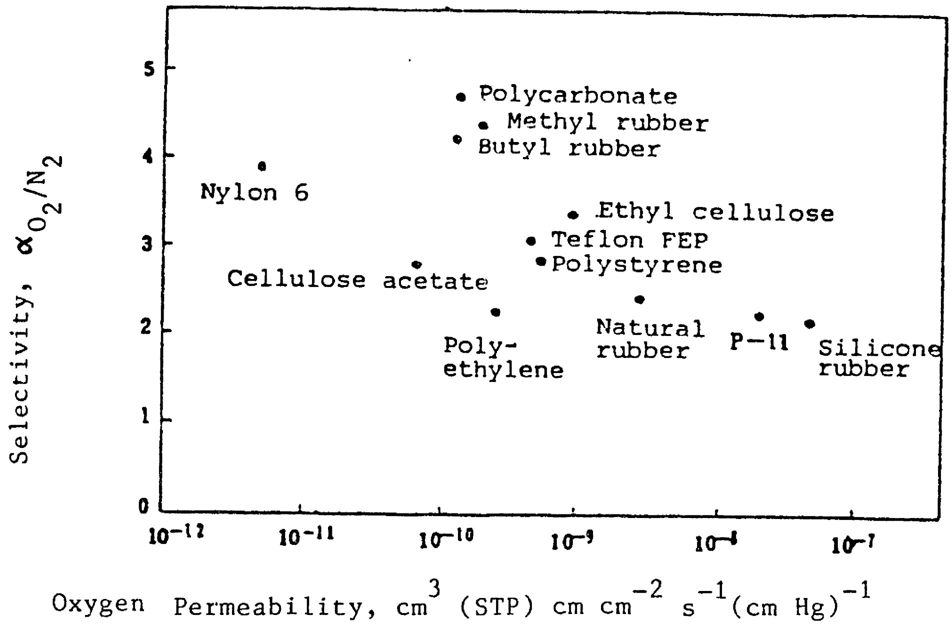
where

$$\ell_n = \sum_{i=1}^{n} \ell_i \qquad (2.3.13)$$

The resistance model concept was successfully applied by Monsanto in the design of membranes for their Prism separation systems (Henis and Tripodi, 1980a,b, 1981 and 1982). More complex models of transport

Fig. 2.13

SELECTIVITY vs. PERMEABILITY IN AIR SEPARATION



Source: Ito (1983)

through asymmetric membranes were developed by Sirkar (1977, 1978).

The effective permeability in facilitated transport may be expressed as:

$$P_i = D_i S_i (1+F_i) \qquad (2.3.14)$$

where F_i is the facilitation factor, which depends on the species concentrations and other parameters (Matson, Lopez and Quinn, 1983).

The transport of multiple gaseous components through permeable membranes is a highly complex phenomenon. Several theories and models have been developed to help explain and correlate observed permeability data, but their ranges of application and predictive capabilities are limited. Progress towards more general and accurate models and theories of permeation will continue to be made in the future.

2.4 Membrane Elements: Properties and Selection Criteria

The membrane itself is the heart of any membrane-based separation process. So the most appropriate membrane for a particular application must be selected from among many candidates. Such selection requires data on membrane properties, criteria for evaluation, and an understanding of the constraints and tradeoffs involved.

The principal criteria for selecting and evaluating membranes are listed in Table 2.4. This table also serves as a partial checklist for R&D opportunities and objectives, in roughly descending order of priority. The tradeoffs between items 1(a) and 1(b), 2(b) and 3(a), 3(b) and 3(c), are examples of the complex tradeoffs inherent in this technology.

Membrane elements may be classified by their materials of construction, phase, structure, method of fabrication, and their geometry (Table 2.5). However, candidate membranes for commercial gas separation belong in just a few of these categories, as indicated in Table 2.5.

Table 2.4

CRITERIA FOR MEMBRANE SELECTION AND EVALUATION

1. Permeation Characteristics:
   - (a) High selectivity or separation factor
   - (b) High permeability for the component(s) desired in the permeate product stream

2. Durability and Stability:
   - (a) Long service life (at least 5 years)
   - (b) Mechanical strength to withstand high pressure differentials, and also vibration
   - (c) Resistance to high temperatures
   - (d) Chemical resistance to the main components and contaminants (including water vapor or condensate) in the feed stream
   - (e) No excessive plasticization, swelling, cracking or leaking

3. Geometry and Fabrication:
   - (a) Low thickness
   - (b) High surface area per unit volume, e.g. spiral-wound or hollow-fiber form
   - (c) Easy to fabricate, with high reproducibility and low scrap rate
   - (d) Easy to service and replace in the field

4. Low Manufacturing Cost

5. Versatility and Standardization:

   If the same or similar membranes can be used in several different applications, then the benefits of standardization and economies of scale can be exploited.

Table 2.5

CLASSIFICATION OF MEMBRANE ELEMENTS

1. Material
   - Inorganic

     - Ceramic
     - Metallic*
     - Other
   - Organic, Solid Polymeric*
     - Cellulosic
     - Noncellulosic

     or

     - Natural
     - Synthetic
   - Biological
   - Other

2. Phase and Structure
   - Solid
     - Microporous
     - Homogeneous (isotropic)
     - Asymmetric (anisotropic)*
     - Composite*
   - Liquid
     - Immobilized (liquid-solid)*
     - Emulsion (liquid-liquid)
   - Gas, Immobilized (gas-solid)

3. Method of Fabrication (for Solid Polymeric Membranes Only)
   - Phase inversion*
   - Interfacial polymerization*
   - Ultrathin film*
   - Dynamic formation
   - Plasma polymerization

4. Geometric Configuration
   - Tubular
   - Plate-and-frame
   - Septum
   - Spiral-wound*
   - Hollow-fiber*

---

*categories significant for commercial gas separation

Membrane Materials

Cellulosic polymers such as various cellulose acetates, and noncellulosic polymers such as polysulfones, polyamides, polyimides, polycarbonates, polyolefins, silicone rubbers, and composites thereof, have been or are being used commercially for gas separation. The permeances and selectivities of six common gases in four asymmetric membranes are given in Table 2.6. The permeance is the ratio of permeability to membrane thickness (P/ℓ). The physical and mechanical properties of cellulose acetates and polysulfones are given in Table 2.7.

The permeation rates of helium and hydrogen are one or two orders of magnitude greater than those of methane and nitrogen. The silicone-based composite membrane has higher permeances than the other membranes for all the gases, but the differences are much greater for the slower permeating gases. Its selectivities are much lower and vary over a smaller range than those of the other membranes.

Cellulosic materials are generally limited to moderate temperatures. Cellulose acetate has a glass transition temperature of 115°C but it undergoes a higher-order transition at 60°C, which limits its operating temperature to 40-50°C (Wensley and Jakabhazy, 1984). Cellulose acetate is highly permeable to water vapor, so it is well suited to dehydration applications such as in processing natural gas to pipeline specifications (maximum 7 lb $H_2O/10^6$ SCF). Asymmetric cellulose acetate membranes show selectivities for H_2O/CH_4 of about 500 (Schell and Houston, 1982a), and for H_2O/Air of 430-670 (Akin, King <u>et al.</u>, 1984). The effects of possible hydrolysis or plasticization by components in the feed stream must be considered. Carbon dioxide tends to plasticize cellulose acetate, as noted earlier (Section 2.3, Fig. 2.12). Cellulose acetate membranes can be readily manufactured, with reproducible properties, at moderate cost. Further data on cellulose acetate membranes are given by Gantzel and Merten (1970), Pusch and Tanioka (1983), and Finken (1985).

Polysulfones can operate at higher temperatures (up to 150°C) and can withstand higher pressures than cellulose acetate membranes (Table 2.7). Prism membranes, whose base material is polysulfone,

Table 2.6

PERMEANCES AND SELECTIVITIES FOR SEVERAL COMMON GASES AND MEMBRANES

Gases	Cellulose Acetate	Polysulfone	Polyimide	Silicone Composite
Permeance at 22°C, P/ℓ, 10^6 cm^3 (STP) cm^{-2} s^{-1} (cm Hg)$^{-1}$				
He	296	185	189	362
H_2	237	144	100	289
CO_2	85.2	74	18.5	260
O_2	17.0	13.7	5.79	145
CH_4	3.11	2.96	0.56	145
N_2	3.11	1.96	0.67	46.3
Selectivity at 22°C, $\alpha_{ij} = P_i/P_j$				
H_2/CH_4	76	49	180	2.0
H_2/N_2	76	73	150	6.2
O_2/N_2	5.5	7.0	8.7	3.1
CO_2/CH_4	27.4	25.0	33.3	1.8

Source: Mazur, Jakabhazy and Mendia (1984)

Table 2.7 **Comparison of polymer properties**

Physical Properties	**Cellulose acetates**	**Polysulfones**
Melting Temperature, °C		
T_m (crystalline)	230–300	
T_g (amorphous)		190–230
Heat Distortion Temperature, °C	49–98	181
Coef. of linear thermal expansion, 10^{-6} in/in/°C	110–170	52–56
Thermal conductivity, 10^{-4} cal-cm/sec-cm^2 – °C	4–8	2.8–4.4
Specific gravity	1.28–1.34	1.24–1.37
Water absorption, %	1.7–7.0	0.22–0.43
Mechanical Properties		
Tensile strength at break, psi	5,000–9,000	
Tensile yield strength, psi		10,200
Elongation at break, %	6–70	50–100
Flexural strength, psi	6,000–10,000	15,400–18,600
Flexural modulus, 10^{-5} psi	1.2–1.4	3.9

Table 2.8 **Chemical species encountered by PRISM™ separators**

Applications qualified	**Chemical species present**												
	H_2	N_2	O_2	CH_4	CO	CO_2	H_2S	H_2O	Methanol	Alkanes	Aromatics	Olefins	NH_3
Hydrogen Separations													
Ammonia synthesis purge	x	x		x				x					x
Ammonia synthesis gas	x	x		x				x					
Catalytic reformer offgas	x			x						x	x		
Catalytic cracker purge	x	x	x	x	x	x	x	x		x	x	x	x
Hydrocracker purge	x			x			x	x		x	x		x
Hydrotreater purge	x			x			x	x		x	x		
Toluene hydrodealkylation purge	x			x				x		x	x		
Methanol synthesis purge	x			x	x	x		x	x				
Oxo-alcohol synthesis gas	x				x								
Carbon monoxide recovery	x			x	x								
Hydrogenator purge	x			x									
Steam-methane reformer gas	x			x	x	x		x					
PSA purge	x			x						x			
Carbon Dioxide Separation													
CO_2 from EOR Flood				x		x				x			
Sour natural gas				x		x	x			x			
Landfill gas		x	x	x		x		x					
Digester gas		x				x		x					
Miscellaneous													
Air enrichment		x	x					x					
Nitrogen inerting gas		x	x					x					
Helium recovery		x		x									

Source: MacLean, Stookey and Metzger (1983) are quite resistant to many chemicals (Table 2.8). Polysulfones make rugged, versatile membranes for many applications.

Polyimide membranes have exceptionally high selectivities for many applications (Table 2.6), they can tolerate temperatures up to 90°C, and they are also resistant to many chemicals (Wensley and Jakabhazy, 1984). The preparation and properties of polyimide membranes are also described by Makino et al. (1983).

Even within one chemical class of polymers, differences in the molecular structures and the functional groups can substantially affect their permeation characteristics. A specific example is given in Table 2.9. Structure-permeability relationships are reviewed by Pusch and Walch (1982a).

The foregoing discussion and the data in Tables 2.4-2.9 elaborated upon the following points:

- The choice of membrane material has a significant impact on all aspects of the separation.
- Permeabilities and selectivities for various gas-membrane systems vary widely.
- There are complex trade-offs among the various factors to be evaulated in selecting the best membrane for a particular application.

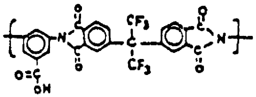
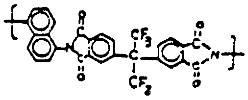
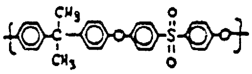
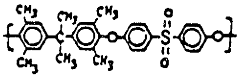
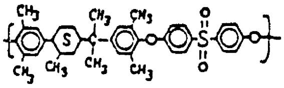
Structures and Methods of Fabrication

The method of fabrication of a membrane has a strong effect on its properties and performance. The technical breakthroughs and advances that led to the commercialization of membrane-based gas separations occurred largely in membrane structures and fabrication methods (Section 2.1, Table 2.1). A great deal of the R&D effort in membrane technology is therefore directed to the formulation and fabrication of membranes. Fabricability in commercial quantities with high reproducibility and at low cost is an important criterion in membrane selection (Table 2.4). The isotropic, anisotropic and thin film composite structures are shown in Fig. 2.14.

Existing fabrication methods may be classified into the five

Table 2.9

EFFECTS OF MOLECULAR STRUCTURE ON THE PERMEATION PROPERTIES OF POLYMERS

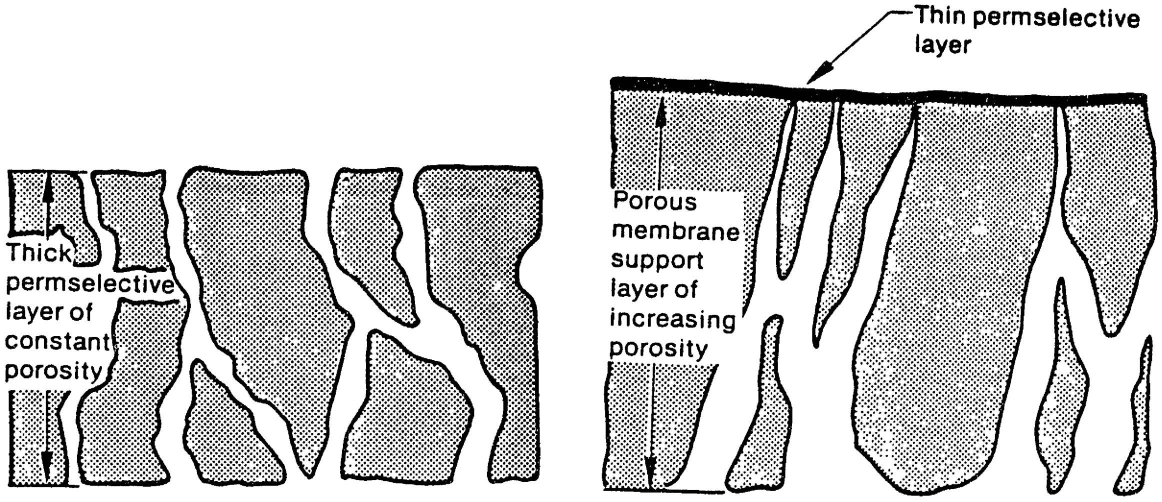
POLYMER	STRUCTURE	P_{H_2}	$\frac{P_{H_2}}{P_{CH_4}}$	P_{CO_2}	$\frac{P_{CO_2}}{P_{CH_4}}$
A		32	427	-	-
B		76	112	-	-
POLYSULFONE		12	78	4.4	28
C		-	-	21	68
D		-	-	65	24

A and B: Polyimides
C and D: Polysulfones

Source: Chern, Koros, Hopfenberg and Stannett (1985)

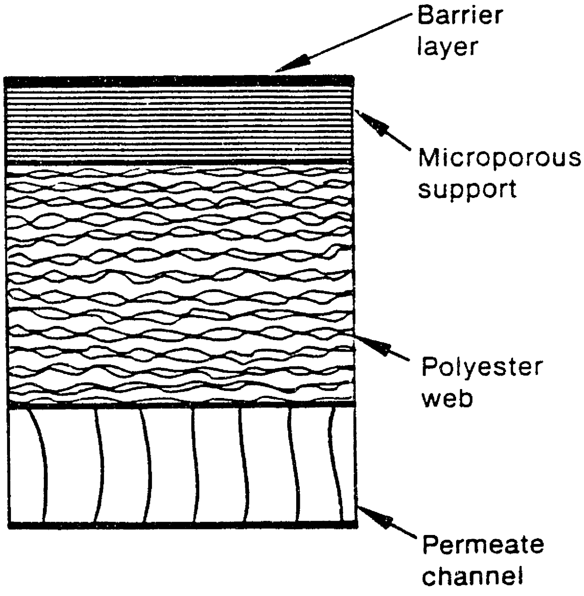
Fig. 2.14

MEMBRANE STRUCTURES



(a) Isotropic membrane

(b) Anisotropic membrane



(c) Thin film composite membrane

Source: Leeper *et al*. (1984)

categories listed in Table 2.5. Within these categories, a great variety of fabrication techniques, including surface modification techniques, have been reported in the literature. Much of this information is disclosed in patents, and some of it is kept a trade secret. For a more detailed treatment of this subject, see Sourirajan (1977), Turbak (1981), Pusch and Walch (1982b), Torrey (1984), Leeper et al. (1984), Lloyd (1985), and Kesting (1985).

Geometric Configurations

Membrane elements can be fabricated in five different geometric configurations, which are listed below in ascending order of packing density (surface area per unit volume, m^2/m^3):

Tubular	150-300
Plate-and-Frame	200-400
Septum	600
Spiral-Wound	300-900
Hollow-Fiber	9,000-30,000

The tubular configuration consists of a bundle of parallel tubes in a cylindrical shell, resembling a shell-and-tube heat exchanger. This configuration is resistant to fouling and the tubes can be cleaned in situ when necessary. Therefore, it is used in desalination and in processing liquids that are viscous and/or contain suspended solids. It may be used for gas separation by inorganic membranes (Kammermeyer, 1976) that could not be fabricated in the other forms. But it would generally be uneconomical for gas separation by polymeric membranes because of its low packing density.

In the plate-and-frame configuration, the membrane is in the form of flat parallel sheets, separated by spacers. It is used commercially in electrodialysis but not for gas separtaion, where it would be uneconomical although technically feasible. An example of a plate-and-frame membrane system for gas separation was given by Steiner and Weller (1952).

The septum configuration consists of a tightly packed stack of membrane sheets and intermediate spacers, enclosed in a pressure vessel.

It was developed at Union Carbide in the 1960's (Stern, 1966), but it is not commercially competitive for gas separation at the present time.

In the spiral-wound configuration, layers of membrane sheets and porous channel spacers are wound around a central perforated hollow tube. One or more such units, typically up to six, are enclosed in a cylindrical pressure vessel. The feed enters at one end and flows axially through the annular channels. The retentate is withdrawn at the opposite end, while the permeate is withdrawn at one end of the central tube (Figs. 2.15-2.17).

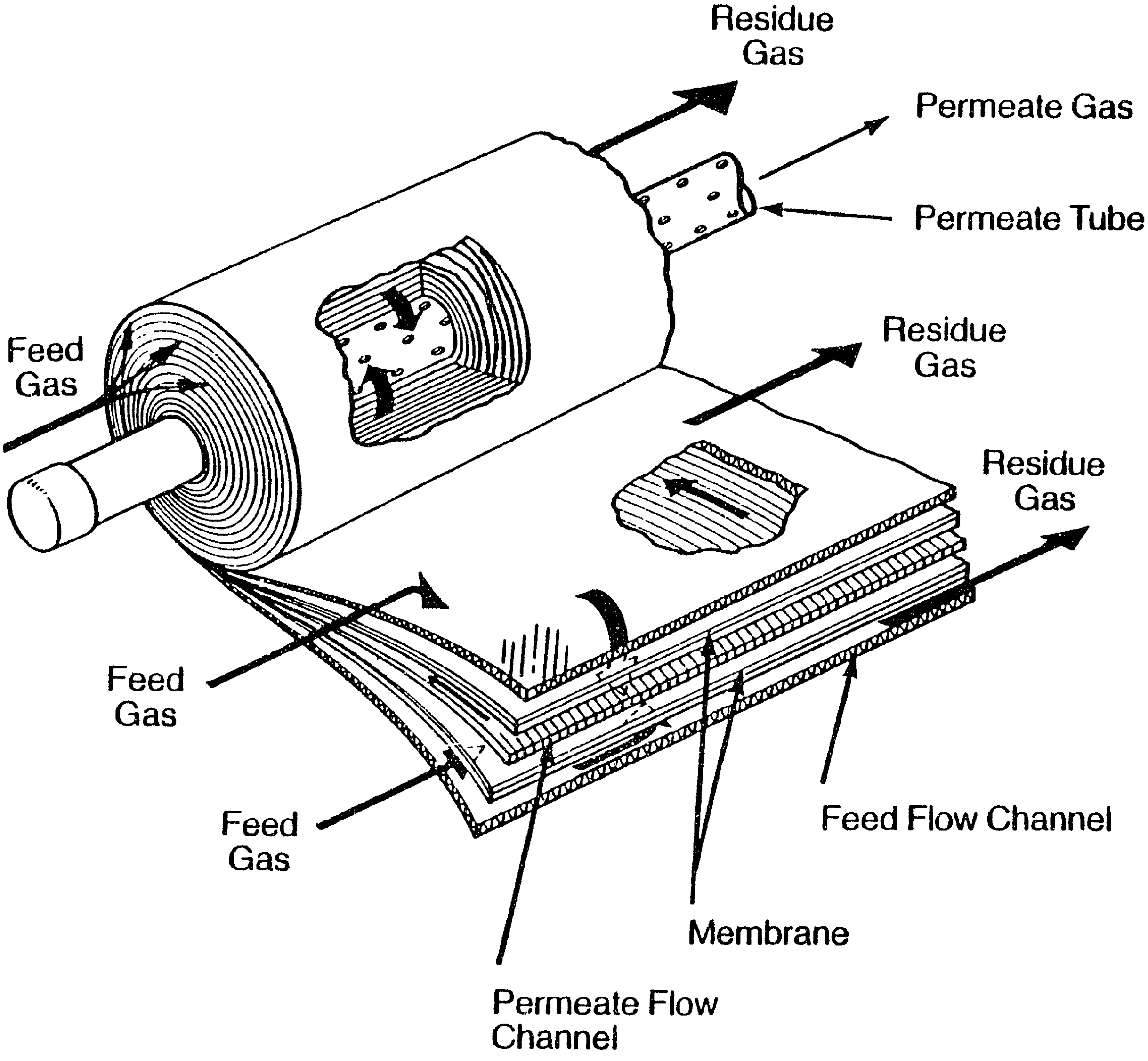
Spiral-wound membrane elements are commercially used for several membrane-based separations, including gas separation. The concept was invented during the mid-1960's at the General Atomic Co., whose membrane business was later acquired by UOP and continues as the UOP Fluid Systems Division. Spiral-wound membranes account for about half of the worldwide RO desalination capacity (Lonsdale, 1982b). So it represents a well proven technology, by virtue of the size of its installed base and its two decades of experience in various service environments. Additional information on spiral-wound membrane elements is given by Schell and Houston (1982a,b), Mazur and Chan (1982), Mazur, Jakabhazy and Mendia (1984), and by the vendors of these products.

The hollow-fiber configuration generally provides the highest packing densities and flux densities among the leading alternative membrane element designs. A hollow-fiber membrane module consists of a bundle of millions of fibers, joined in epoxy resin tubesheets and mounted in a pressure vessel. The fibers' wall thickness and internal diameter are of comparable dimensions, around 20-50 microns, so they can withstand high pressures and pressure differentials without collapsing or bursting. In asymmetric hollow fibers, the dense layer may be on the inside or on the outside. The feed can be introduced on the shell side or the bore side, the former being more common.

Hollow fiber membranes are fabricated by an extrusion process that requires high precision equipment, specialized expertise and good quality control. Commercial hollow-fiber membrane systems are made and sold by Dow Chemical, Du Pont and Monsanto, who have had

Fig. 2.15

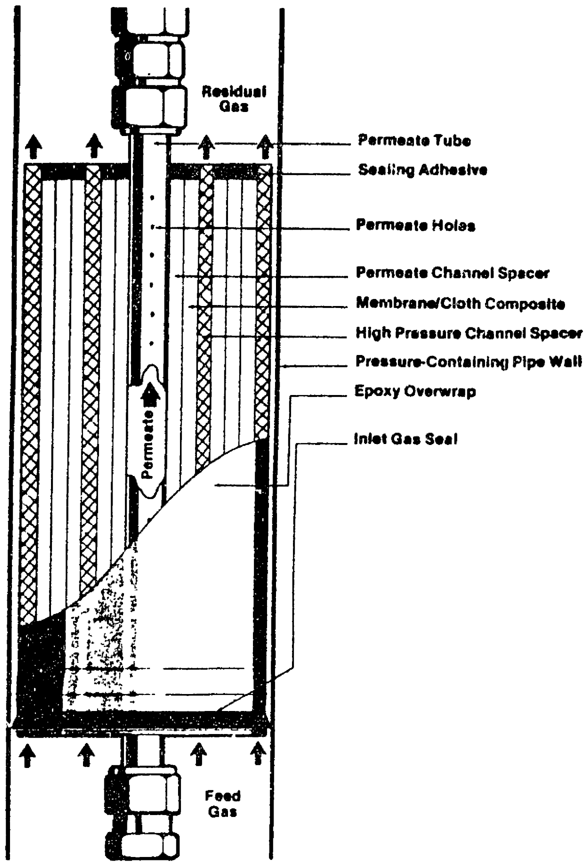
SPIRAL WOUND ELEMENT



Source: Mazur, Jakabhazy and Mendia (1984)

Fig. 2.16

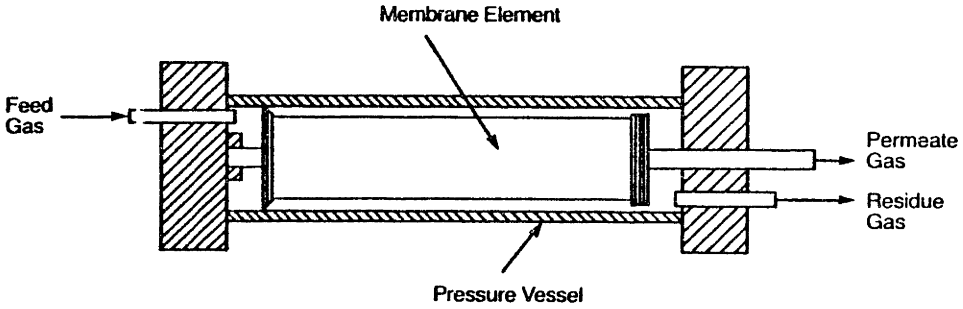
SPIRAL-WOUND ELEMENT



Source: Schell and Houston (1982b)

Fig. 2.17

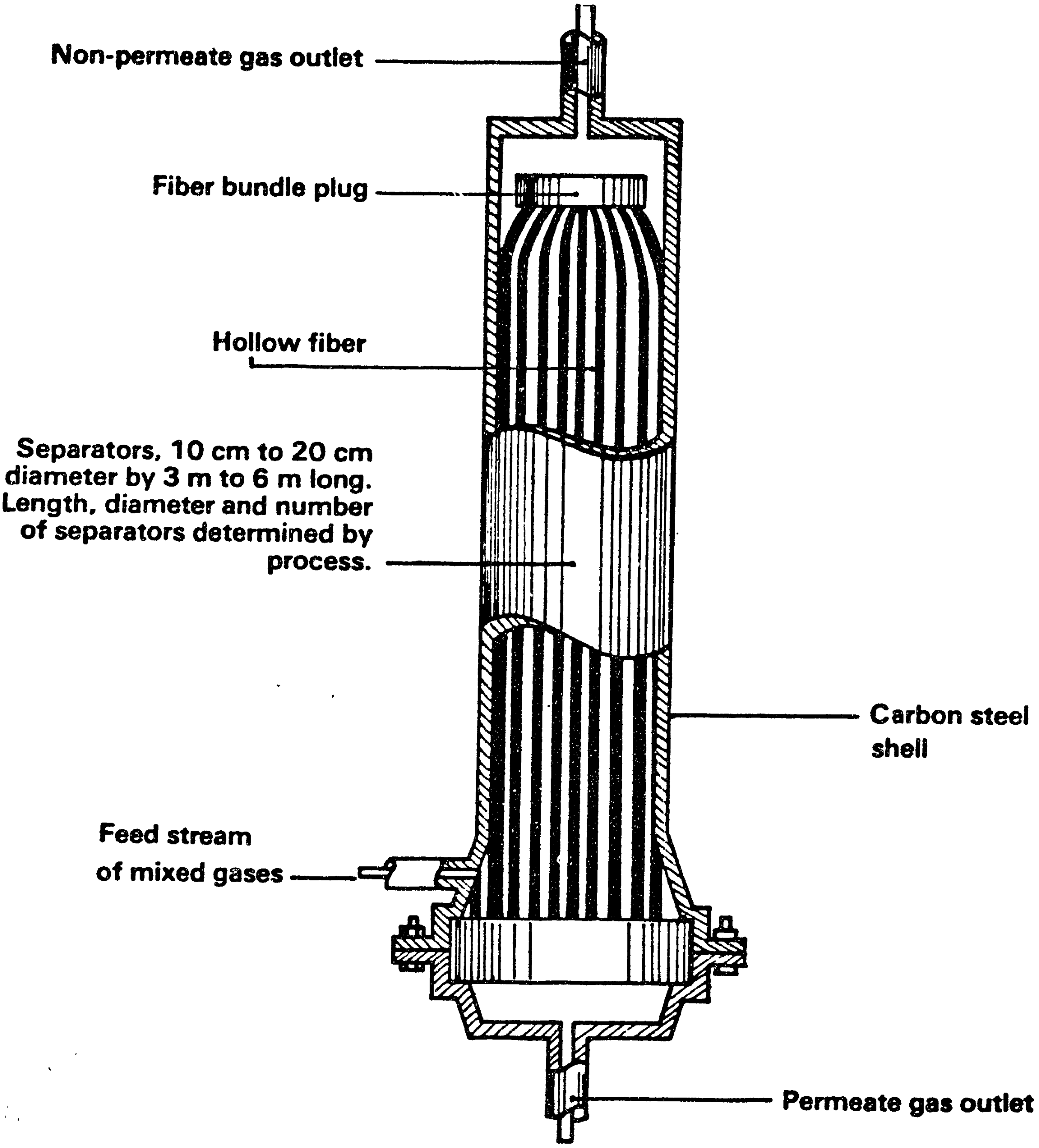
SPIRAL-WOUND MODULE



Source: Mazur and Chan (1982)

Fig. 2.18

MONSANTO PRISM HOLLOW-FIBER MODULE



Source: Van Gelder (1982)

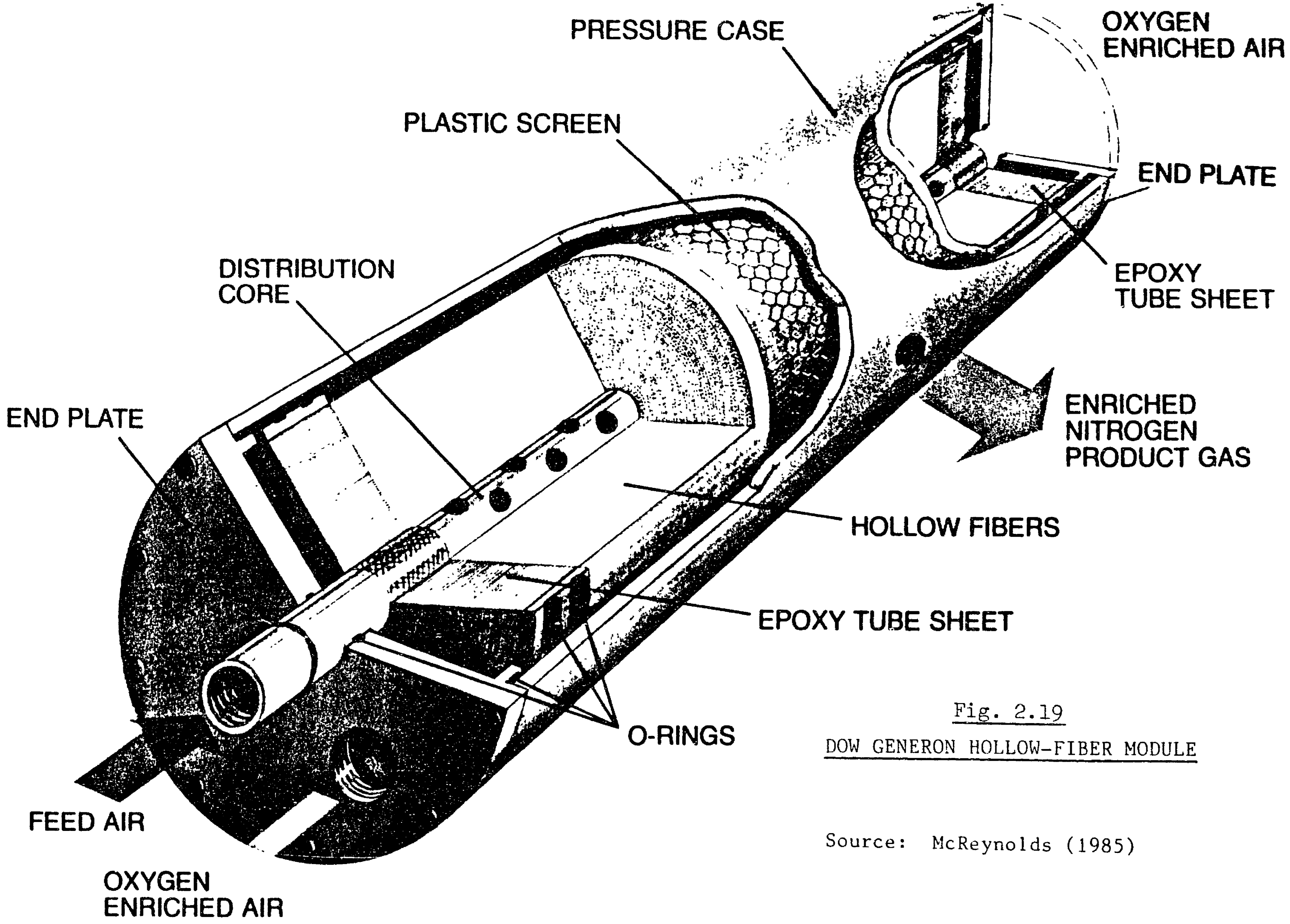


Fig. 2.19

DOW GENERON HOLLOW-FIBER MODULE

Source: McReynolds (1985)

decades of fiber manufacturing experience.

Monsanto's PRISM (Fig. 2.18) and Dow's GENERON (Fig. 2.19) and Cynara are the leading commercial hollow-fiber membrane systems for gas separation. Du Pont had offered its Permasep hollow-fiber membrane systems for gas separation in the early 1970's, but then withdrew from the gas separation market. Du Pont is preparing to re-enter the gas separation market with a new line of products this year.

The hollow-fiber configuration is the dominant one for gas separation and for clean liquid separations. It is the configuration of choice for any membrane material that can be fabricated in this form. The spiral-wound configuration would generally be the next best choice, for materials that cannot be fabricated as hollow fibers.

Further information on hollow-fiber membrane products and technology is given by Gardner, Crane and Hannan (1977), Sourirajan (1977), Cabasso (1980), Scott (1981), Rosenzweig (1981), Lloyd (1985), McReynolds (1985), and by the vendors of these products.

Stability and Service Life

In designing and specifying a membrane separation system, allowance must be made for the gradual decay of system performance over time. The nature and dynamics of such decay depend upon the type of membrane, the feed composition, and the operating conditions, including startups, shutdowns, and upsets.

The decline over time of the permeation rate of carbon dioxide in two commercial cellulose acetate spiral-wound membranes is shown in Fig. 2.20. The permeability declines roughly exponentially with time, according to the following expression (Mazur and Chan, 1982):

$$P_2 = P_1(t_2/t_1)^{-m} \qquad (2.3.15)$$

The time intervals between membrane element replacement must be determined on an economic basis, by comparing the costs of such replacement with the benefits of better performance. The economic service life of polymeric membranes averages about 3-6 years.

Another source of performance decline is gas leakage due to defective seals or broken hollow fibers. Leakage increases the permeation rates of all components in the feed, thereby reducing the selectivity of the separation. The effects of leakage on the performance of hollow-fiber membrane systems were simulated on a computer by Antonson _et al._ (1977).

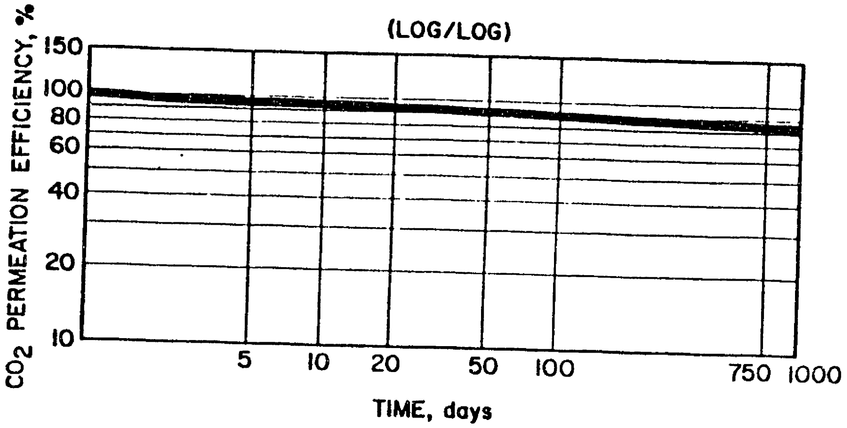
Important goals of R&D should be:

- To develop an improved understanding of the factors and mechanisms underlying membrane aging and leakage, under various operating conditions.
- To increase the durability and the economic service lives of membranes, especially under severe operating conditions.

Fig. 2.20

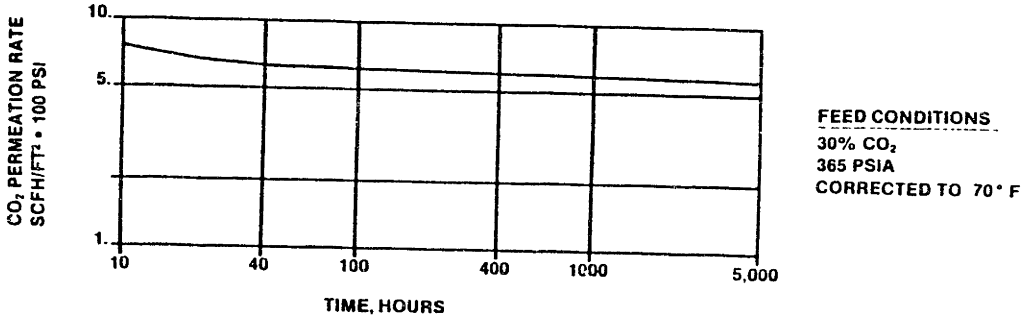
TIME DECAY OF THE PERFORMANCE OF CELLULOSE ACETATE MEMBRANES

(a) Envirogenics Spiral-Wound Membrane



Source: Coady and Davis (1982)

(b) Separex Spiral-Wound Membrane



Source: Schell and Houston (1982b)

3. MEMBRANE SYSTEMS AND ECONOMICS

A complete membrane-based separation system can be analyzed at five levels:

- The membrane material
- The membrane element
- The membrane module
- The membrane system
- The entire process plant that includes one or more membrane separation systems

There are trade-offs to be considered and choices to be made among alternatives at each level. Therefore, there are very many variables and configurations to be analyzed at the system or plant level, at which the optimization must be performed.

Membrane materials, elements, and the geometric aspects of modules were covered in the previous chapter. The process engineering and economic aspects of membrane modules and systems are covered in this chapter. Analysis at the total plant level is specific to the particular plant being analyzed.

3.1 Membrane Modules

A membrane module is a self-contained separation device that can accept a feed stream and produce two output streams of different compositions. Modules are the building blocks or stages of a multistage membrane system, along with the required compressors, piping, valves, filters, heat exchangers, instrumentation and control equipment.

The flux of component i across a small section of a nonporous membrane by the solution-diffusion mechanism is given by (Table 2.3):

$$N_i = \frac{Q_i}{A} = P_i \left[\frac{p_{i1} - p_{i2}}{\ell} \right] \qquad (3.1.1)$$

Since the pressure gradient varies along the flow path, and since the permeability may also vary, equation (3.1.1) has to be expressed in differential form and integrated along the flow path, to give either the total permeate flow rate Q_{iT} or the total area A_T:

$$Q_{iT} = \int_0^{A_T} \frac{P_i}{\ell} (p_{i1} - p_{i2}) dA \tag{3.1.2}$$

$$A_T = \int_0^{Q_{iT}} \frac{\ell}{P_i(p_{i1} - p_{i2})} dQ_i \tag{3.1.3}$$

The above mass transfer equations have to be solved together with the mass balance equations for each component, and the momentum transfer equations relating the pressure drop and the flow rate along the high pressure and low pressure sides of the membrane.

A rigorous solution to the system of equations describing a membrane module is most often obtained by a numerical finite element procedure executed on a computer. Analytical solutions have also been obtained for the separation of binary gas mixtures in each of the four idealized flow patterns shown in Fig. 3.1. Analytical solutions for the limiting cases of no mixing (Fig. 3.1c) and perfect mixing (Fig. 3.1d) were derived by Weller and Steiner (1950a,b). The remaining ideal cases of countercurrent flow (Fig. 3.1a) and cocurrent flow (Fig. 3.1b) were worked out analytically and numerically by Boucif, Majumdar and Sirkar (1984). An analytical solution for the separation of binary gas mixtures in cross flow was given by Saltonstall, Lawrence and Niu (1983). The extension of the Weller-Steiner models to multicomponent feeds was derived by Brubaker and Kammermeyer (1954). Other recent models have allowed for the elastic deformation of the hollow fibers or capillaries under pressure, for the variation of permeability with the operating conditions (Blaisdell and Kammermeyer, 1972, 1973; Antonson _et al._, 1977), for a nonpermeable component in the feed, and/or for a sweep gas (Pan and Habgood, 1974).

Antonson _et al._ (1977) analyzed six flow patterns for the separation of binary gases in hollow fibers: cocurrent, countercurrent and cross flow, each with shell-side feed and tube-side feed. They recommended countercurrent flow with tube-side feed as the best flow pattern, at least for the H_2-CH_4 mixture under their assumed conditions. However, the commercial hollow-fiber membrane modules use shell-side feed (Figs. 2.18 and 2.19), so it must be superior under most practical conditions.

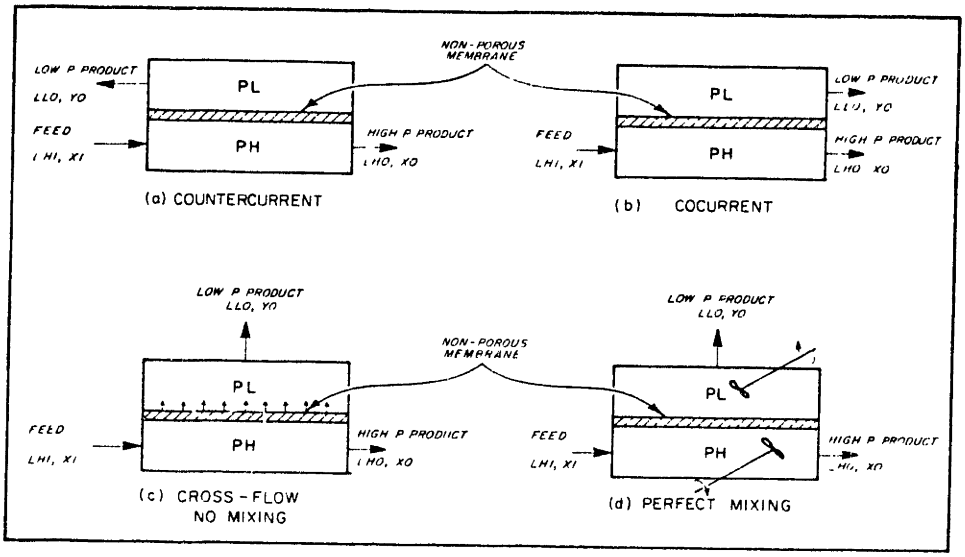
McCandless (1984a,b) analyzed by computer simulation the case of air separation for each of the four ideal flow patterns shown in Fig. 3.1. The extent of separation passes through a maximum with increasing stage cut, and it decreases in the sequence: countercurrent flow, cross flow, cocurrent flow, and perfect mixing (Fig. 3.2).

McCandless (1984a,b) also explains why the extent of separation, first proposed by Rony (1968), is the most meaningful technical figure of merit for comparing and evaluating separation processes. Most authors have used only product purity, recovery or separation factors as figures of merit, while ignoring throughput. The inherent tradeoff between throughput and product purity or recovery should be incorporated in a proper figure of merit. Ultimately of course, economic criteria should be used for commercial designs, but these involve many more variables and assumptions, and the results are specific to a particular application. On the other hand, the extent of separation is a mathematical function of only the flow rates and compositions of the streams entering and leaving the separation process. It provides a useful and meaningful index for comparing separation processes, or different conditions in the same process, on a consistent basis.

The effects of the flow pattern on the separation are much less pronounced for high-flux asymmetric membranes than for homogeneous membranes. The microporous layer gives rise to cross flow across the dense active layer, regardless of the direction of gas flow in the bulk of the feed and permeate streams (Pan, 1983). For this reason, much of the earlier computer simulation work does not apply to most modern commercial membrane modules that contain asymmetric membranes.

The tradeoff between product purity and recovery is illustrated by the data in Fig. 3.3. These data are for the separation of CO_2 from light hydrocarbons, typical of the gas from a CO_2-EOR operation.

Fig. 3.1



Ideal permeation stages for different flow patterns.

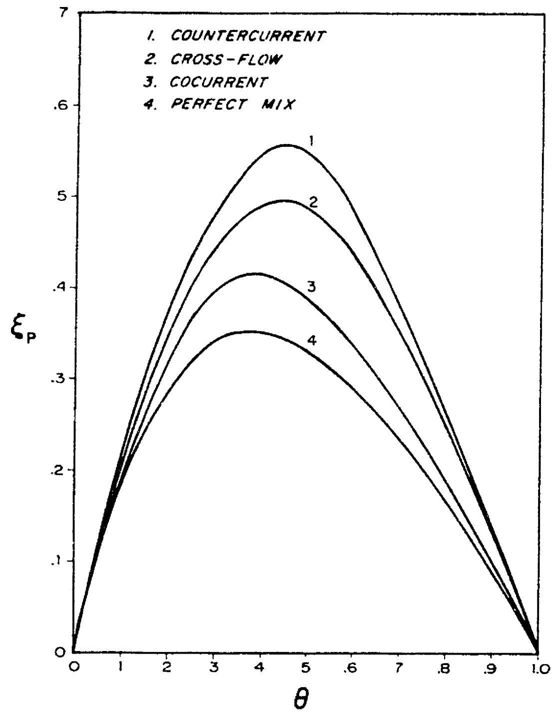
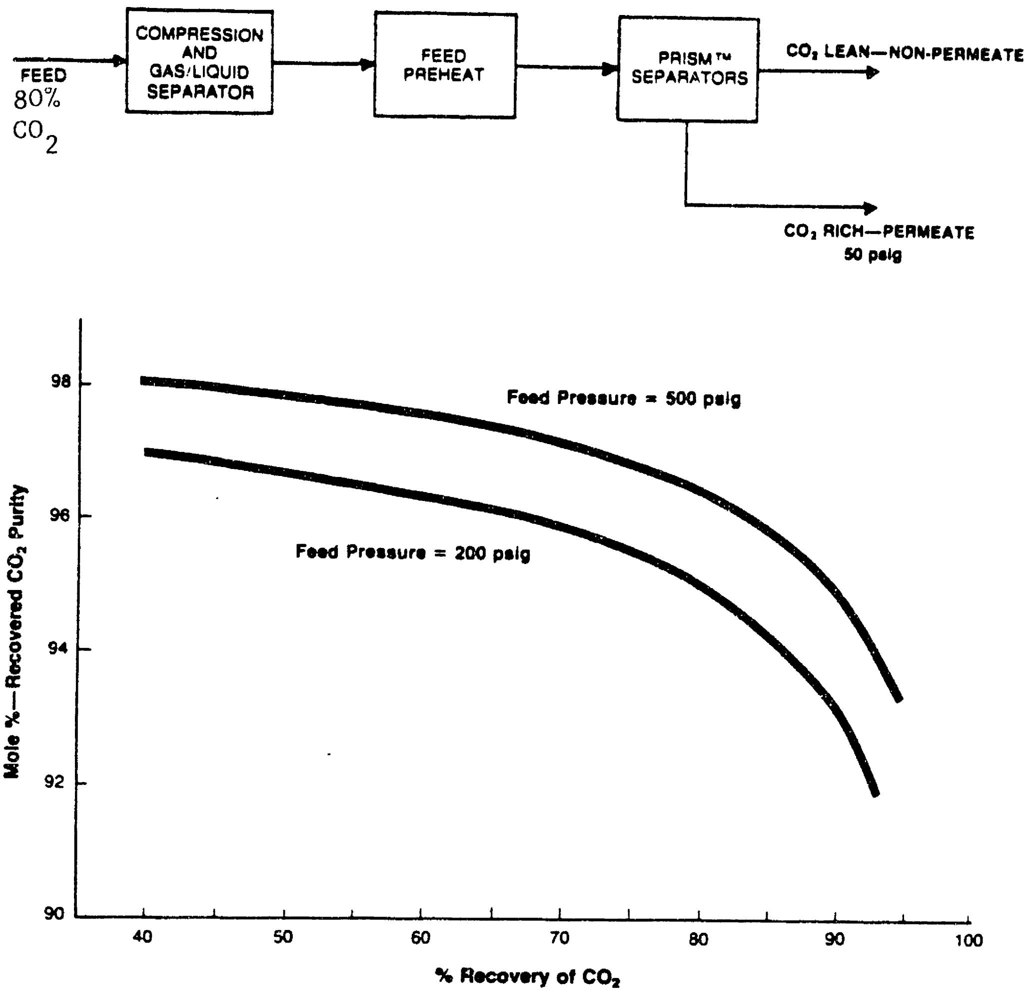


Fig. 3.2 **Extent of separation as a function of stage cut.**

Source: McCandless (1984b)

Fig. 3.3

PRODUCT PURITY vs. RECOVERY IN A SINGLE-STAGE SYSTEM



Source: Bollinger, MacLean and Narayan (1982)

Increasing the feed pressure would increase both recovery and purity, but would also increase the cost. Further discussion of the relationships among the key process variables is given by Schell and Houston (1982a).

For a given feed composition and flow rate in a binary membrane separation, the product purity can be increased by increasing the permeability ratio ($\alpha_{12} = P_1/P_2$) and/or the pressure ratio ($\phi = p_1/p_2$). In the limit as the pressure ratio tends to infinity, the separation factor (α_0) tends to the permeability ratio. In the notation of Fig. 3.1:

$$\underset{\phi\to\infty}{\text{Lt.}} \quad \alpha_0 \equiv \frac{YO(1-XO)}{XO(1-YO)} \longrightarrow \alpha_{12} \equiv \frac{P_1}{P_2} \qquad (3.1.4)$$

The important consequence of this result is that the product purity attainable in a single membrane module (or stage) is limited. To achieve higher purities than the limiting values, recycle and/or cascading would be required.

3.2 Recycling and Cascading

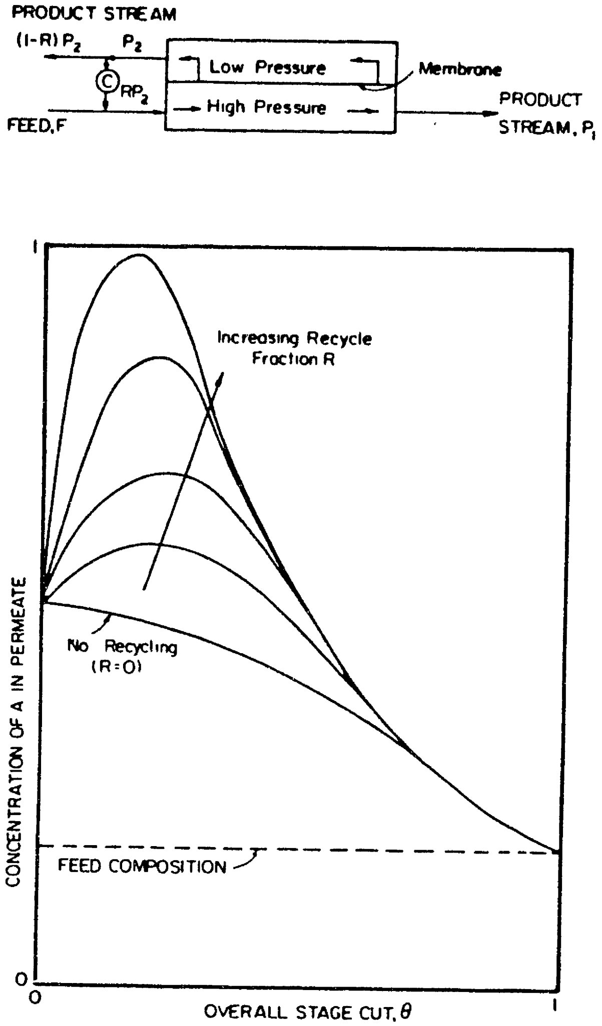
Recycling a portion of the permeate stream into the feed stream is one means for obtaining a product purity greater than the maximum obtainable in a single stage. However, it entails the additional costs of a compressor and a lower throughput or a larger surface area. Therefore, the optimal recycle ratio is determined by economic considerations subject to technical feasibility. The effect of recycle on the separation of a binary mixture in a countercurrent flow membrane separator is shown qualitatively in Fig. 3.4. Note that the effect of recycle on product purity is greatest at relatively low stage cuts (typically 0.1-0.3), and that the maximum is fairly sharp.

Recycle can of course be used within a cascade as well as around a single module. Further information and results on the effects of recycle are given by Heit, Majumdar and Sirkar (1982), Stern, Perrin and Naimon (1984), and by Teslik and Sirkar (1985).

A cascade is a network of multiple membrane modules. Adding modules in parallel increases overall throughput, flexibility and

Fig. 3.4

EFFECT OF RECYCLE ON PRODUCT PURITY IN A SINGLE-STAGE SYSTEM



Source: Stern, Perrin and Naimon (1984)

reliability. Adding modules in series increases the purity or recovery of the products. The modules may have different sizes, membrane elements and operating conditions. Multiple feed and product streams, and multiple recycle streams can also be provided. Thus, cascading provides great flexibility via many degrees of freedom.

However, cascading generally requires interstage compression and it may entail interstage mixing losses, which lead to higher costs. The mathematical analysis, design and optimization of cascades is complex (Pan and Habgood, 1978).

Additional information on membrane cascades is given by Hwang and Kammermeyer (1975), King (1980), MacLean, Stookey and Metzger (1983), and Matson, Lopez and Quinn (1983).

The use of two or more different types of membranes in different stages of a cascade (Fig. 3.5a-c) or within the same stage (Fig. 3.5d) has been investigated. The behavior of such systems shows that the latter is quite effective in achieving high permeate product purities in the separation of binary gas mixtures (Fig. 3.5e). The separation of ternary gas mixtures into three product streams has been investigated by Sirkar (1980) and by Sengupta and Sirkar (1984).

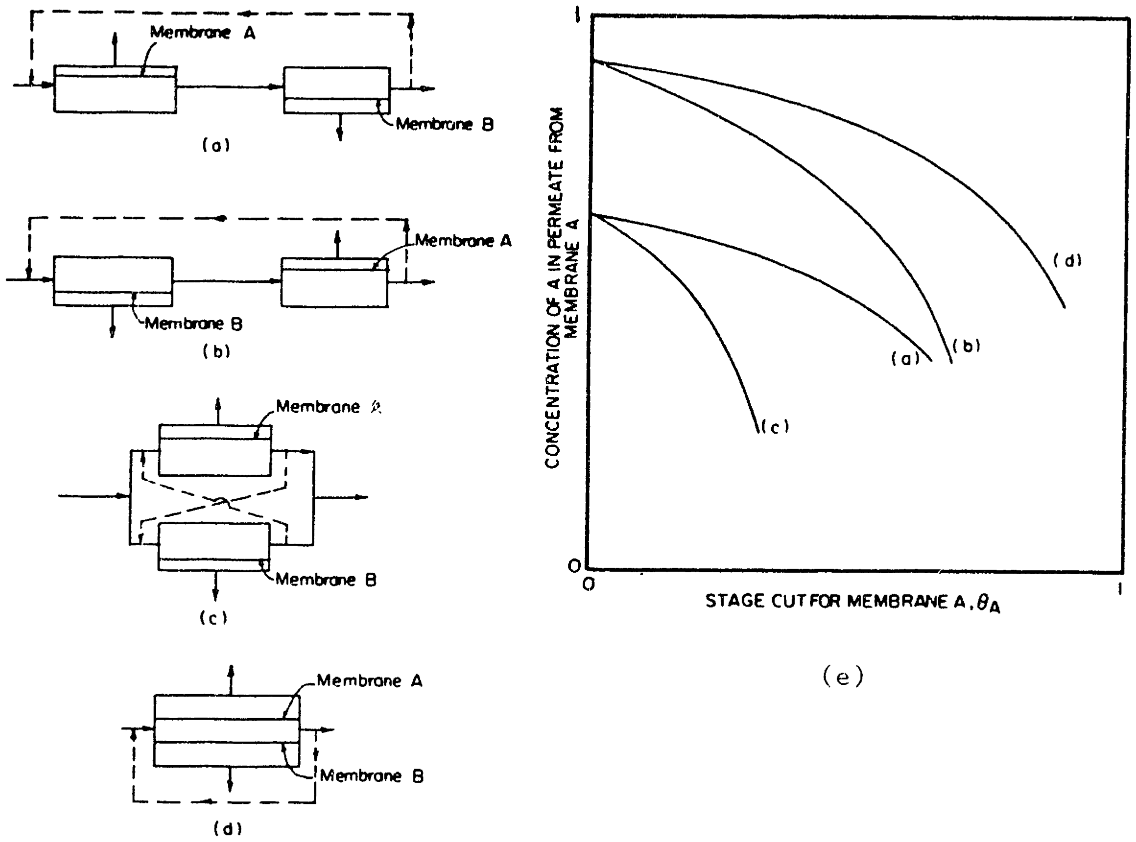
3.3 The Continuous Membrane Column

The continuous membrane column (CMC) is a special case of a recycle permeator. It has an enriching section and (optionally) a stripping section as well (Fig. 3.6). Typical performance curves for each type of CMC in a binary gas separation are shown directly beneath the corresponding diagrams in Fig. 3.6. Note the similarity between the CMC with enriching section only (Fig. 3.6b) and the single recycle permeator shown in Fig. 3.4. The key difference is because the feed is introduced on the low pressure side in the CMC, and on the high pressure side in the conventional permeator.

The behavior of the full CMC (Fig. 3.6a) is quite different in two respects. First, the permeate concentration declines monotonically as the stage cut increases. Second, the effect of the recycle ratio is significant only at low values of the stage cut. The maximum degree of separation is achieved at the limit of total recycle.

Fig. 3.5

THE USE OF DIFFERENT TYPES OF MEMBRANES TOGETHER IN ONE SYSTEM



The membrane permeation systems with permeators connected in series (a, b) and in parallel (c). Each permeator contains a different type of membrane. The products are both permeated (low-pressure) and unpermeated (high-pressure) streams. A two-membrane permeator (d), i.e., a permeation system in which both membranes are contained in the same vessel, is shown for comparison. The dashed lines indicate recycle options. Membrane A is more permeable to component A of the mixture, and membrane B is more permeable to component B. The ordinate shows on a linear scale the concentration (in mole fraction) of component A in the permeated (low-pressure) product stream from membrane A. The abscissa is also on a linear scale. Stage cut θ_A is variable while stage cut θ_B is constant.

Source: Stern, Perrin and Naimon (1984)

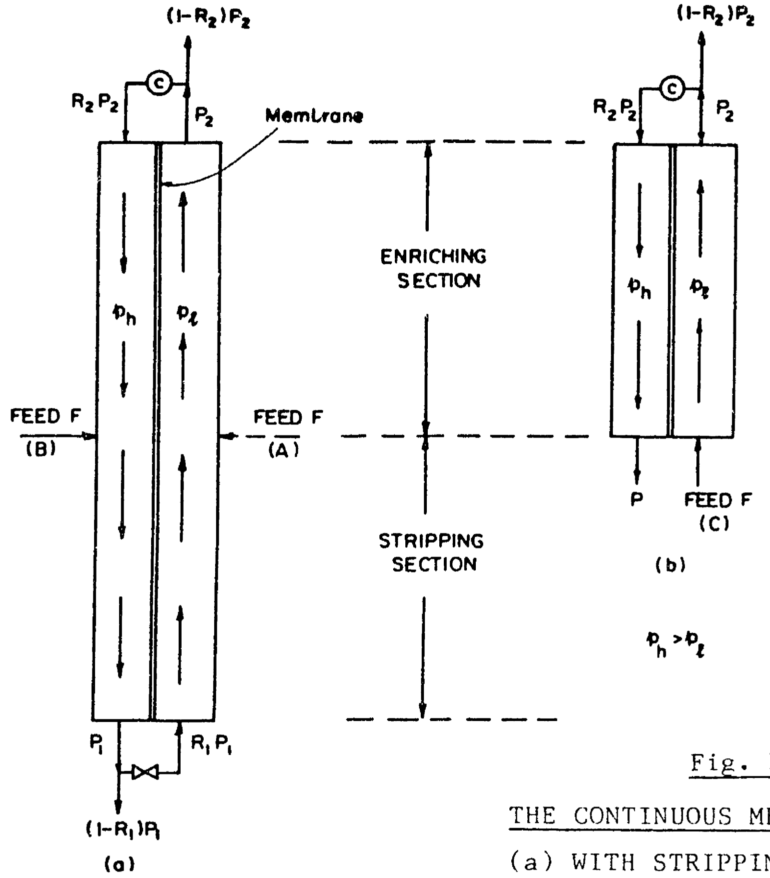
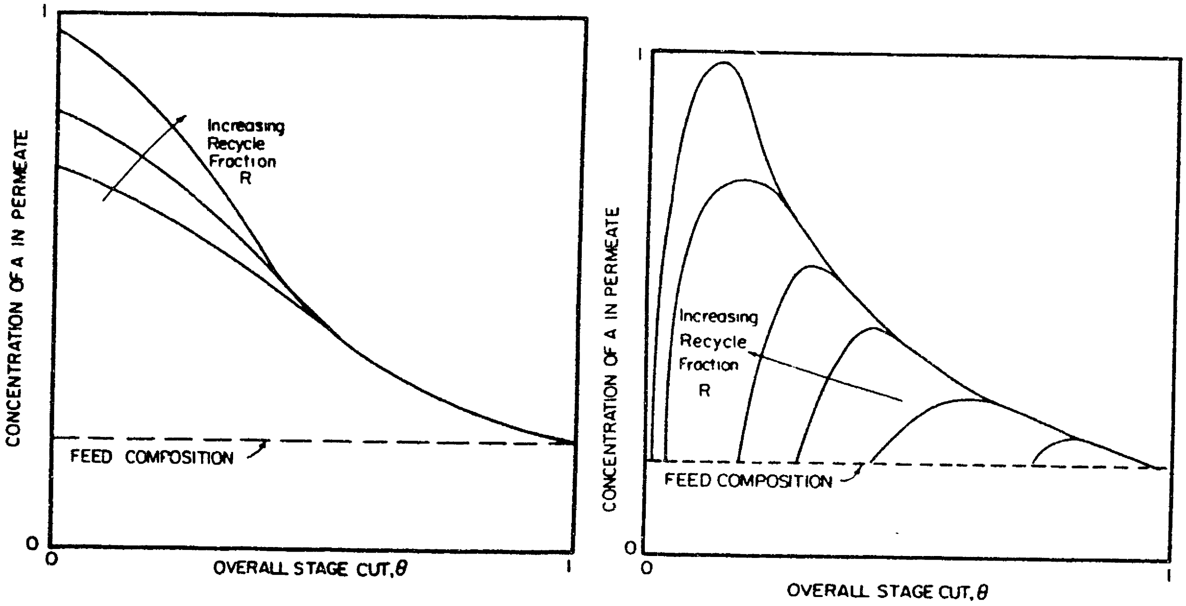


Fig. 3.6

THE CONTINUOUS MEMBRANE COLUMN

(a) WITH STRIPPING SECTION
(b) WITHOUT STRIPPING SECTION



Source: Stern, Perrin and Naimon (1984)

The main technical advantage of the CMC is that a highly enriched product can be obtained in relatively simple equipment, with only one recycle compressor, instead of the multiplicity of compressors and membrane modules that consititute a cascade. It overcomes the inherent enrichment limit of a single-stage permeator. Nevertheless, this "revolutionary separation device" (as it was described by Hwang and Thorman, 1980) has not yet been commercialized (Hwang, 1985). So a potential technical advantage does not necessarily imply an economic advantage in this case and in general.

The CMC was invented by Pfefferle, who filed a U.S. patent application in 1960 and was granted a patent in 1964. This patent, which has now expired, was assigned to Engelhard Industries, Inc. The concept remained dormant and obscure until the late 1970's, when R&D programs on it began at a few universities.

Much of the theoretical analysis has centered around analogies between the CMC and equilibration separation processes such as distillation. For example, Hwang and Thorman (1980) defined the terms NMU (no. of membrane units) and HMU (height of a membrane unit), by analogy to the classical NTU (no. of transfer units) and HTU (height of a transfer unit), respectively, for packed columns used in continuous countercurrent contactors (CCC). Thus, the total length of a CMC is obtained analogously to the length of a CCC, as follows:

$$Z_{CCC} = (NTU)(HTU) \quad (3.3.1)$$

$$Z_{CMC} = (NMU)(HMU) \quad (3.3.2)$$

The analogy between the CMC and distillation in plate columns, including a graphical McCabe-Thiele-type design method for the CMC, was developed by Schulz, Michele and Werner (1982a,b). The McCabe-Thiele method and the derivation of equation (3.3.1) are explained by King (1980). The analogy between rate-governed and equilibration separation processes cannot be carried too far due to their intrinsic differences.

Computer simulation models of the CMC by numerical solution techniques were reported by Schulz and Werner (1984), Yoshisato and Hwang (1984) and Teslik and Sirkar (1985).

Direct comparisons of the characteristics of various CMC's, recycle permeators and cascades, for given feed mixtures and types of membranes, have been reported by Hwang, Yuen and Thorman (1980), Schulz, Michele and Werner (1982), Matson, Lopez and Quinn (1983), and by Teslik and Sirkar (1985). A two-stage series cascade with recycle has significantly lower membrane area and power requirements than a CMC (enriching section only) and a single recycle permeator, for air enrichment to 50% and 90% (Table 3.1). Only one compressor was required in each case. Such a comparison is a good indicator of the relative economics which is a function of membrane area and type, and the power needed for compression.

The comparative studies cited above led to the analysis and development of various modifications and extensions of the original CMC concept. For example, a system of two CMC's in series was proposed for separating the ternary mixture of CO_2, CH_4 and N_2 typically encountered in natural gas processing (Hwang and Ghalchi, 1982). A CMC with one countercurrent permeator stage in the recycle loop was shown to be an improvement over either one individually (Schulz and Werner, 1984). The additional stage is analogous in position and function to the condenser at the top of a distillation column.

Another related concept under development is the continuous membrane reactor separator, in which the reaction and separation are carried in the same equipment. The products of reaction are separated as soon as they are formed (Membranes Simplify Catalytic Reactions, 1980; Shinnar and Feng, 1985). The basic concept is not new, and there is an analogous commercial process called "catalytic distillation."

R&D on the CMC and related systems is continuing at several universities, including the Stevens Institute of Technology, Syracuse University, the University of Cincinnati, and the University of Iowa in the U.S. (Section 4.4), and at the University of Dortmund in W. Germany. Further R&D is needed if the CMC is to become economically competitive with other membrane-based separation systems.

TABLE 3.1

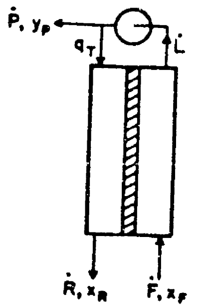
Comparison of membrane oxygen enrichers

Case (i): 50% O_2, $\phi = 0.10$, $\alpha^* = 2.2$

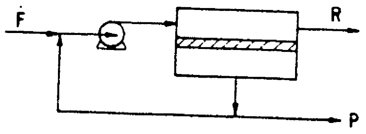
System	Area	Power
Continuous Membrane Column Enricher	1.00	1.00
Recycle Permeator	1.04	0.97
Two-Unit Series Cell	0.60	0.70

Case (ii): 90% O_2, $\phi = 0.10$, $\alpha^* = 4.8$

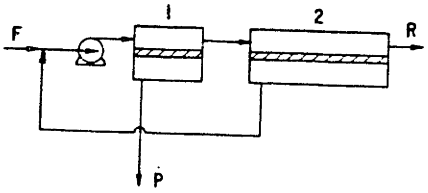
System	Area	Power
Continuous Membrane Column Enricher	1.00	1.00
Recycle Permeator	0.98	0.91
Two-Unit Series Cell	0.35	0.25



(a) continuous membrane column



(b) recycle permeator



(c) two-unit series cell

Source: Matson, Lopez and Quinn (1983)

3.4 Economics of Membrane Separation Systems

The selection, design and optimization of membrane separation systems must be based on economic criteria applied to the technically feasible alternatives. The economics of the total process plant are specific to that plant and entail assumptions and estimates of many variables. The costs of raw materials, utilities, labor and land vary widely from site to site, and over time at each site. Therefore, detailed economic evaluation must be done on a case by case basis. The general discussions and conclusions presented here and by others are subject to exceptions.

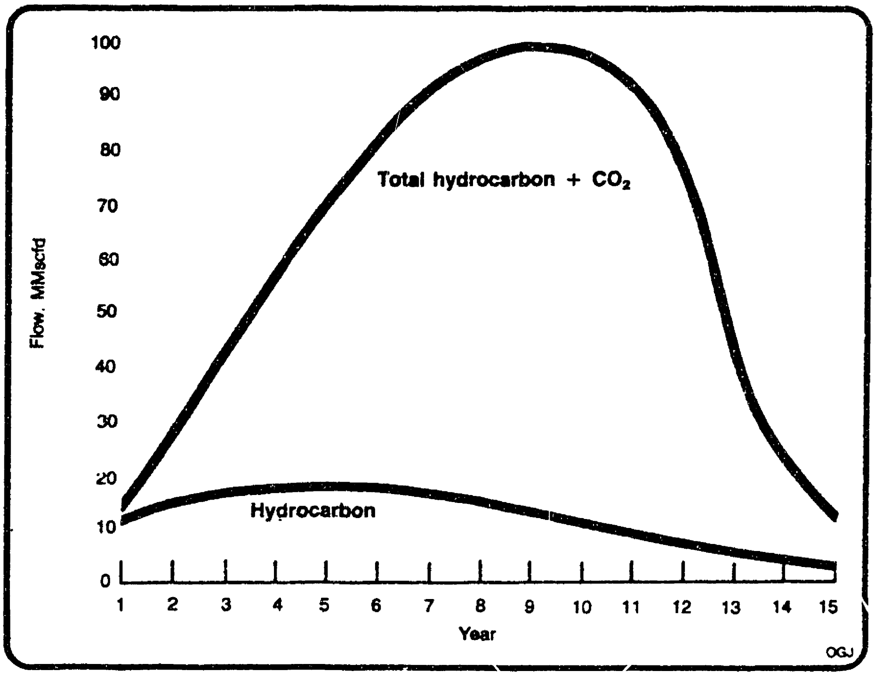
The published economic analyses are mostly comparative studies of two types: those comparing membrane-based and non-membrane-based gas separations, and those comparing alternative membrane-based separation schemes. Normalized data reflecting only relative rather than absolute magnitudes, or imcomplete data are sometimes published for reasons of confidentiality.

The economics of separating CO_2 from light hydrocarbons in enhanced oil recovery (EOR) operations have been studied by several authors. The separation plant recovers CO_2 at a sufficiently high purity (95-97% CO_2) and pressure (2,000 psig) for reinjection into the reservoir. It also recovers natural gas liquids (NGL), H_2S, and water vapor, so that the hydrocarbon product stream meets pipeline gas specifications. The feed gas flow rate and composition vary widely during the life of the project (Fig. 3.7). The separation system under consideration may be a base-load unit, or an addition to an existing gas processing plant for handling the additional quantities of gas. These are important factors that affect the economics of the project.

The economics of CO_2 separation by cryogenic fractionation, DEA and TEA absorption, and membrane permeation, as reported by Goddin (1982) are summarized in Fig. 3.8. In all cases, the unit costs of the product decline with increasing CO_2 content of the feed. The costs for CO_2 sweetening by the Selexol process, shown separately in the figures, are excluded from the costs for the cryogenic separation but are included in the costs of the other processes. In other words, if a sweetened CO_2 product were not required, then the costs of the

Fig. 3.7

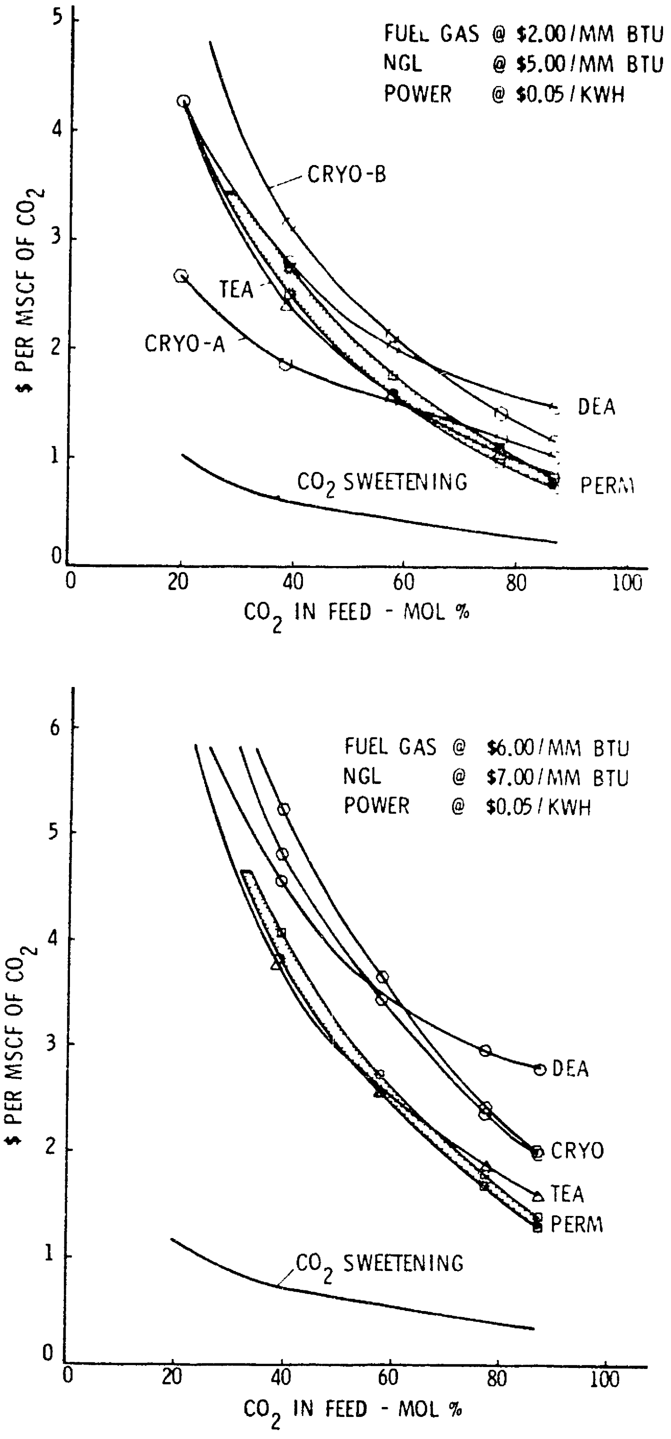
GAS FLOW RATE AND COMPOSITION IN A TYPICAL CO_2 EOR PROJECT



Source: Schaffert and Ryan (1985)

Fig. 3.8

COSTS OF CO_2 REMOVAL vs. CO_2 CONTENT OF THE FEED GAS IN AN EOR PROJECT



Source: Goddin (1982)

non-cryogenic processes would be lowered by the costs of sweetening. The membrane permeation processes tend to be more competitive at higher concentrations of CO_2 in the feed, and when fuel costs are higher, due to higher partial pressure gradients and greater energy efficiencies, respectively.

The curves for membrane permeation in Fig. 3.8 are shown as a shaded band bounded by two lines, each representing different permeation parameters. The capital costs of the membrane systems are assumed to be \$6/ft^2, consisting of \$2.70/ft^2 for the membrane modules and \$3.30/ft^2 for the piping, instrumentation, and other equipment. Compressors were assumed to be electrically driven, reciprocating units costing \$600/BHP. The compressors cost about 2.5 times as much as the permeators themselves. This shows the importance of comparing gas separation processes at the same feed and delivery pressures, and including compression costs. Further details of the assumptions and data are given by Goddin (1982).

The capital costs per unit CO_2 production rate as a function of the latter, as reported by Radovich (1983), are shown in Fig. 3.9. Data on total costs and the underlying assumptions were not published, to protect the proprietary information of Warren Petroleum Co., the sponsor of the study. Nevertheless, these published data do indicate the economies of scale associated with membrane separation systems.

The relationship between the capital cost (K) of a plant and its capacity (Q) is usually expressed by:

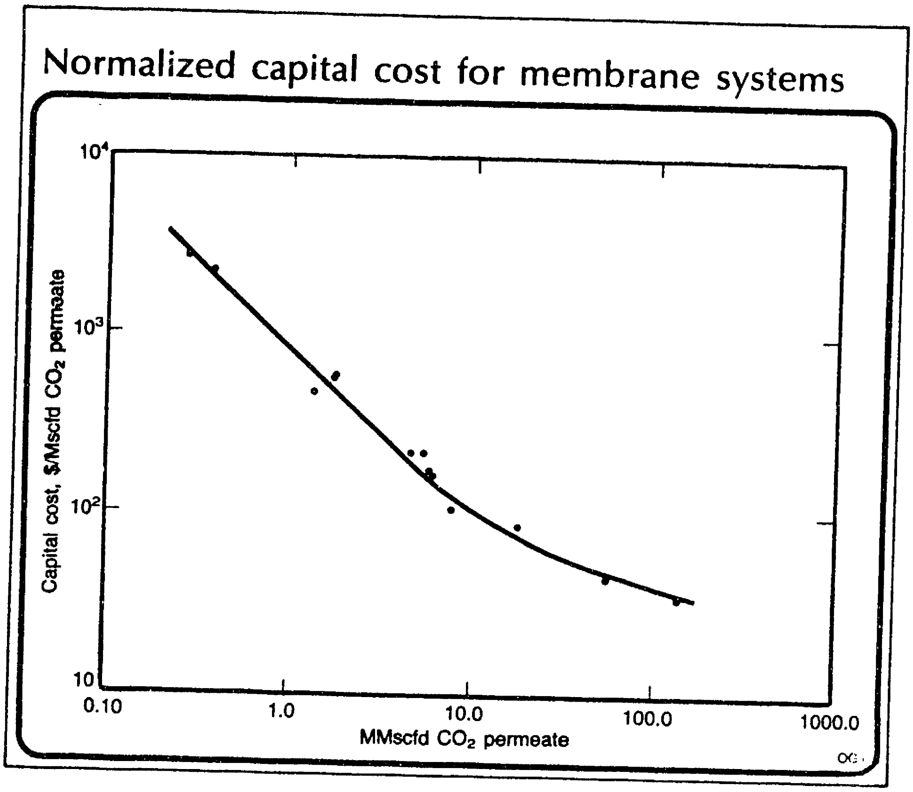
$$K_1/K_2 = (Q_1/Q_2)^n \qquad (3.4.1)$$

or equivalently,

$$\frac{K_1/Q_1}{K_2/Q_2} = (Q_1/Q_2)^{n-1} \qquad (3.4.2)$$

If the scale factor (n) is constant over some range of the variables, then log-log plots of K vs. Q or K/Q vs. Q would be linear, with slopes

Fig. 3.9



Source: Radovich (1983)

of n or n-1, respectively. The data in Fig. 3.9 are plotted in the form corresponding to equation (3.4.2). The entire line is not linear, but it can be approximated by two linear segments joined by a short curved segment. The values of n in each segment are as follows:

Q, MMSCFD CO_2	n	Economy of Scale
0.2 - 8	~0	Strong
8 - 20	varies	Intermediate
20 - 150	0.6	Normal

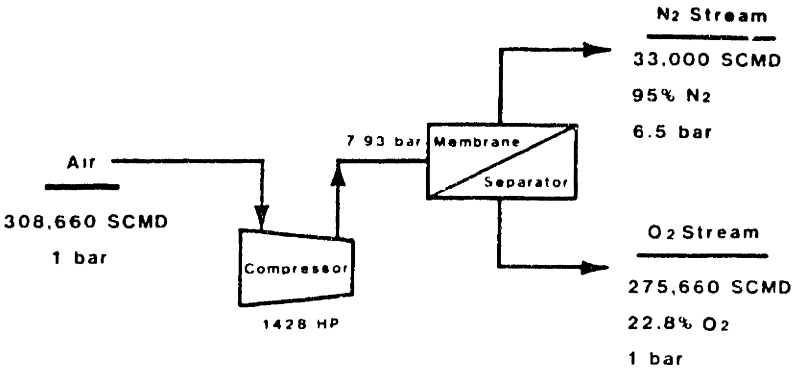
A scale factor of 0 implies that the capital cost remains essentially constant at its minimum value. A scale factor of 0.6 is typical of commercial-scale continuous processing plants in the chemical industry. At larger capacities beyond the range of the data in Fig. 3.9, we would expect the curve to level out, as the scale factor approaches unity. This is because such large capacities are attainable only by adding more membrane modules and compressors, rather than by enlarging the same number of modules and compressors.

The trade-offs among the throughputs, recoveries and purities of the products strongly affect the economics of any separation system, including membrane-based ones. The technical aspects of these trade-offs have been discussed earlier (see for example Sections 2.3 and 3.1). The following example illustrates the economic aspects of these trade-offs, and their implications for membrane selection.

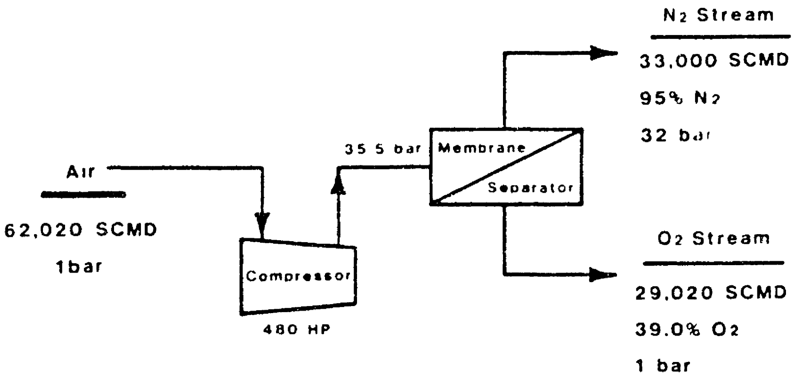
Consider the design of a system to make 33,000 SCMD of 95% pure nitrogen from air. Two commercially available types of membranes are compared for this application. The composite dimethyl silicone (DMS) membrane has a high permeability for most gases, but an O_2/N_2 selectivity of 2. The asymmetric cellulose acetate (CA) membrane has a lower permeability for most gases, but a higher O_2/N_2 selectivity of 5. The material and energy balances and the relative economics of these two cases are shown in Fig. 3.10, taken from Schell (1985).

The capital cost and the replacement cost of the membrane modules alone are much greater for the CA membrane. But the capital and operating

Fig. 3.10 COMPARATIVE ECONOMICS OF DMS AND CA MEMBRANE SYSTEMS FOR AIR SEPARATION



O_2/N_2 separation with DMS membrane.



O_2/N_2 separation with CA membrane.

Membrane system cost comparison

	CA	DMS
Membrane system cost	9.20	1.00
Compressor cost	8.40	22.84
Total capital cost	17.60	23.84
Annual operating costs		
Membrane repl.	17.00	1.00
Power	39.25	116.50
Total operating costs	56.25	117.50

Source: Schell (1985)

costs of the compressors are much greater for the DMS membrane. The total operating costs of the more permeable DMS membrane are about twice as great as those of the more selective CA membrane, in this application.

The final system design must be based on a detailed evaluation that considers many other factors as well. But the above analysis indicates the dominant effects of membrane selectivity, and of compression costs, on a project's economics.

The key points and trends discussed in this section on the economics of membrane gas separation were illustrated by data selected from the literature. A few supplemental sources of pertinent data published after 1975 are listed below.

The economics of hydrogen recovery from the purge gas stream of ammonia plants by membrane and other means are presented by Gardner, Crane and Hannan (1977), Van Gelder (1982), and Schendel, Mariz and Mak (1983). The economics of hydrogen recovery in oil refineries, mainly from hydroprocessing recycle streams, are discussed by Maciula (1980a,b), Schendel, Mariz and Mak (1983), Bollinger, Long and Metzger (1984), Schell (1985) and Yamashiro et al. (1985). They found the membrane process to be more economical than PSA in these applications. A membrane system was found to be more economical than a cryogenic system for recovering hydrogen in the HYTORT oil shale conversion process (Colton and Medvetz, 1983).

The economics of CO_2 separation from light hydrocarbons in EOR applications have been reported by Goddin (1982), Mazur and Chan (1982), Kulkarni et al. (1983), Flynn (1983), Boustany et al. (1983), Schell, Houston and Hopper (1983), Newman (1985), and many others. The economics of membranes, distillation, and their combinations are compared by Schendel, Mariz and Mak (1983), Schendel (1984) and Schendel and Seymour (1985).

The economics of air separation are discussed by Fischer and Burnett (1978), Metzger, Handermann and Stookey (1984), Gollan (1984), McReynolds (1985) and Schell (1985).

The vendors of membrane separation systems and engineering firms are good sources of economic estimates for specific applications.

4. MARKETS AND ORGANIZATIONS

The rapid growth of membrane-based gas separation during the past decade, and its bright future prospects, are attributable to both technology-push and market-pull forces (Sections 1.1 and 2.1). The relevant aspects of the technology have been covered in the preceding chapters. The market for gas separation by membranes, at present and in the future, and the organizations participating in this market, form the subjects of this chapter.

4.1 The Membrane Gas Separation Market

The number of commercial membrane gas separation systems, and their total capacity, have grown rapidly during the past decade. Just a handful of commercial units had been built before 1977. Most of these early installations, other than isotope separation plants, separated hydrogen or helium from various gas mixtures (Section 2.1). Monsanto installed its first large-scale Prism system in its petrochemical plant at Texas City in 1977. This marked the beginning of the rapid growth phase in the life cycle of membrane gas separation.

There will be over one hundred commercial membrane systems worldwide by the end of 1985. Their total capacity will be about 760 (10^6) SCFD of feed gas, with the following breakdown:

Vendor Source	No. of Units	Rated Capacity 10^6 SCFD	%
Monsanto Prism:			
U.S.	40	387	51
Foreign	43	291	38
Subtotal	83	678	89
Dow Cynara	2	70	9
All Others	20	12	2
Total	105	760	100

The above data represent a rough estimate only, subject to change within a short time, due to the dynamism of this industry and market. Monsanto has the dominant market share, domestically and internationally. The dominant technology, which is embodied in Monsanto's and Dow Chemical's products, consists of synthetic (noncellulosic) polymeric membranes in the form of hollow fibers.

The capacities of these commercial membrane separation systems are typically in the range of 0.1 - 25 (10^6) SCFD of feed gas. The largest single system to date, with a capacity of 75 (10^6) SCFD, is a Monsanto Prism system for CO_2 recovery in an EOR project.

The installed costs of membrane separation systems range from $50,000 to several millions of dollars.

Published estimates of the size of the membrane-based gas separation market at present and in the foreseeable future, are summarized in Table 4.1. The disparity among these data, especially the future projections, should not cause concern. After all, these are rough estimates of moving targets -- industries and technologies in a state of rapid evolution -- and these estimates involve many economic and technical assumptions.

A plausible scenario for the growth of the U.S. and worldwide membrane-based gas separation system markets over the next 15 years could be based on the following assumptions:

- Worldwide market: $60 million in 1985.
- Average annual growth rate: 12%.
- U.S. share: 50% of the worldwide market.

These imply the following growth schedule:

Year	U.S. Market $ Millions	Worldwide Market $ Millions
1985	30	60
1990	53	106
1995	93	186
2000	164	328

Table 4.1

ESTIMATED SIZE AND GROWTH RATES OF THE MEMBRANE-BASED GAS SEPARATION MARKET

Base Year	Base Market $ Millions	Future Year	Future Market $ Millions	Growth Rate*	Basis	Reference
1982	10-15	--	--	--	Worldwide market, total systems, including membrane lungs (blood oxygenators).	Lonsdale (1982b)
1983	10	1993	30	12%	U.S. market, membrane modules.	Crull (1983, 1984)
1984	6	1990	145	70%	Worldwide market, U.S. share is 2/3. Membranes only, system values would be double.	T.A. Sheets Co. estimates, reported by Parkinson (1984)
1984	50	1994	130	10%	Worldwide market, total systems.	Monsanto estimates, reported by Parkinson (1984)
1984	55	1999	300	12%	Worldwide market, total systems.	Saltonstall (1985)
--	--	1995	1,000	--	(Not specified by author.)	Pappas (1984)

---

*Average annual compounded growth rate between the base year and the future year.

The separation of hydrogen in refineries, petrochemical plants and ammonia plants is the largest commercial application of membranes up to the present time. However, the largest application after 1990 will probably be for acid gas removal in various processing plants (Table 1.1), mainly for the separation of CO_2 from hydrocarbons and flue gases. Membrane separation could eventually capture 80% of the market for separating CO_2 in EOR operations, according to a study by Battelle Columbus Laboratories (Parkinson, 1984).

The markets for membranes in applications other than gas separation are described in the market research publications listed in Table 2.2. The leading organizations that are participating in and shaping this market are identified and discussed in the following sections.

4.2 Industrial Companies

There are over twenty U.S.-based companies that have some activities related to gas separation by membranes. They are listed alphabetically in Table 4.2. These companies may be classified into three groups.

Monsanto is the market leader by a wide margin. Its share of the worldwide installed capacity is about 89%. There are more Prism units in commercial service than any other kind, and they are used in all the major applications of membranes for gas separation. Because no other companies come close to Monsanto in market position, Monsanto is the only company in the first group. Even if Monsanto loses some share of this expanding market over the next decade, it will most probably retain the largest market share during this period. Thus, any company considering entry into this business should regard Monsanto as its principal potential competitor.

The second group of companies consists of Dow Chemical, Signal/UOP, W.R. Grace, and Parker Drilling Co. (which owns Separex). Envirogenics Systems Co. might have been included here, but its gas separation business is up for sale, so its future presence in this market is not definite.

The above companies are fully integrated vendors of membrane systems, i.e., they do R&D, manufacturing, system design, engineering and installation of complete systems; they have commercial products

Table 4.2

U.S. COMPANIES WITH SIGNIFICANT ACTIVITIES RELATED TO GAS SEPARATION BY MEMBRANES

Name	Location of Main Activity	Main Activities		Trade Name	Affiliation	Comments
		R&D	Commercial Products & Services			
A/G Technology Corp.	Needham MA 02194	x				Air Separation with hollow fibers
Airco	Murray Hill NJ 07974	x			Subsidiary of BOC Int'l	Major producer of industrial gases
Air Products & Chemicals Inc.	Allentown PA 18105	x				Major producer of industrial gases
Albany Int'l Membrane Dev. Venture	Norwood MA 02062	x			Joint venture with a large U.S. company	Hollow fiber membranes
Allied Corp.	Morristown NJ 07960	x	x		Joint owner of Enstar	Bipolar membranes for flue gas desulfurization
Bend Research Inc.	Bend OR 97701	x	x		Joint venture with W.R. Grace & Co.	Contract R&D for Gov't agencies and private companies; liquid membranes; facilitated transport
Cynara Co.	Houston TX 77079		x	Cynara	90% owned by Dow Chemical	CO_2/Hydrocarbon separations
Dow Chemical USA	Midland MI 48674	x	x	GENERON		Hollow fiber systems for air separation
Du Pont Corp.	Wilmington DE 19898	x		Permasep		Formerly made hollow fiber membranes for H_2 separations. Now reentering the market.

Table 4.2 (continued)

Enstar Engineering Inc.	Houston TX 77036		x	DELSEP	A div. of Enstar Corp., partially owned by Allied Corp.	Employs Envirogenics spiral-wound membrane modules
Envirogenics Systems Co.	El Monte CA 91731	x	x	GASEP	Subsidiary of Sogex Int'l Ltd. (Paris, France)	Spiral-wound cellulose acetate membranes. Gas separation business is for sale.
Exxon Research & Engineering Co.	Annandale NJ 08801	x			Subsidiary of Exxon Corp.	Former R&D effort in liquid membranes, many patents, some licensed to others.
General Electric Co.	Schenectady NY 12345	x				Facilitated transport, ultrathin silicone polycarbonate membranes
Fluor Corp.	Irvine CA 92711		x			Technical/economic studies, patent on membrane plus distillation process
Membrane Technology & Research Inc.	Menlo Park CA 94025	x				Spiral-wound membranes for separating organic compounds from air or water
Monsanto Co.	St. Louis MO 63167	x	x	Prism		Hollow fiber composite membranes for a wide range of separations. World market leader in number and total capacity of commercial installations.

Table 4.2 (continued)

Osmonics, Inc.	Minnetonka MN 55343	x	x	OSMO		Spiral-wound membrane modules
Oxygen Enrichment Co. Ltd.	Schenectady NY 12301	x	x	OECO Enricher	Holds exclusive license from GE	Oxygen-enriched air for medical purposes
Parker Drilling Co.	Tulsa OK 74103				Wholly owns Perry Gas Cos., Separex Corp. and Spectrum Separations	Oil & gas contract drilling, gas processing
Separex Corp.	Tyler TX 75711	x	x	Separex	(See above)	Spiral-wound cellulose acetate membranes
Signal UOP Research Center	Des Plaines IL 60016	x			Corp. R&D center for the Signal Cos.	Contract and proprietary R&D on membrane-based and other separations
UOP Fluid Systems Div.	San Diego CA 92117	x	x	SPIRAGAS	Subsidiary of Signal Cos.	Air separation by a composite dimethyl silicone polysulfone spiral-wound membrane
W.R. Grace & Co.	Houston TX 77092	x	x	Gracesep	Contract w/ Bend Research, Inc.	Spiral-wound cellulose acetate membranes, mainly for oil & gas applications.

for multiple applications; and their technologies are covered by patents. They are all large, diversified multinational companies. Their membrane separation businesses, which represent a small fraction of their total business, are not broken out separately in their financial reports. They are all NYSE-listed companies, except for Envirogenics which is owned by a privately held foreign company. All these companies except Separex also make membrane-based products for applications other than gas separation.

Du Pont, the company that pioneered the commercial use of hollow-fiber polymeric membranes for gas separation, withdrew from this market in the mid-1970's, but is now re-entering it. Du Pont could join the second group of companies in a couple of years, since it has prior experience in the field and current experience in related fields.

The third group consists of the remaining companies that have a minor position in this market. Some of them are large companies that are doing membrane-related R&D in-house or are sponsoring such work at other companies. Some are small, specialized contract R&D firms, which might well be the source of the next generation of technology in this field. A few of these small companies were started by former employees of the larger companies.

Some of the companies in the third group have made significant technical contributions to the field of membrane separations, but they do not make or sell any commercial products. For example, Exxon R&E and General Electric did pioneering and significant work in liquid membranes, but these have not been commercialized (Parkinson, 1983).

Foreign companies' activities in membrane-based gas separation consist mostly of R&D or joint efforts with U.S. companies. In Japan, two consortia that have significant R&D programs are the Research Association of Polymer Basic Technology, and the Research Association for C-One Chemistry. Their member companies and R&D programs are reported by Parkinson (1984). A commercial-scale air enrichment system using supported silicone rubber membranes, developed by the Osaka Gas and Matsushita Electric companies, is described by Ito (1983).

The U.S.-based companies are far ahead of the rest of the world in this technology and its commercial development. However, the foreign companies could compete with domestic companies for business in the former's home countries.

This is why a joint venture or similar alliance between a U.S.-based and a foreign company is usually mutually advantageous. The U.S. company provides the commercial product and some related technical services; the foreign company contributes marketing expertise and also some services to the customers. For instance, Monsanto and Maritime Protection A/S of Norway formed a joint program to develop and market an onboard nitrogen generator for marine vessels (Monsanto and a Partner ..., 1983; Metzger et al., 1984).

The strategies critical to commercial success in the membrane separation business may be inferred by comparing the actions taken by Du Pont and Monsanto, and the resulting outcomes.

Around 1961-1962, Du Pont initiated a R&D program to develop hollow-fiber membranes for gas separation. The initial target application was the recovery of helium from natural gas. The Textile Fibers Department had developed melt-spun homogeneous hollow fibers for textile applications by that time.

The first laboratory-scale permeator was about 0.3 m long and contained about 100 hollow fibers made of Dacron polyester. The first commercial-scale device was called the Permasep B-1 (for Barrier-1). A separation system containing such devices was installed and successfully operated to recover helium from natural gas in Texas (Edwards, 1971, 1972).

In 1969, Du Pont introduced its first commercial device for desalination by reverse osmosis, the Permasep B-9. This product belonged to the next generation of technology for RO and gas separation, being based on anisotropic Aramid (aromatic polyamide) hollow fibers made by solution spinning (Hoehn, 1985).

From 1969 to 1972, Du Pont installed a few Permasep gas separation units for recovering hydrogen from streams in refineries and petrochemical plants, mostly ones owned by Du Pont. Du Pont received the prestigious Kirkpatrick Chemical Engineering Achievement Award for this innovation in 1971 (Why Hollow-Fiber Reverse Osmosis Won..., 1971).

In the mid-1970's, Du Pont dropped out of the gas separations market, but it continued improving and selling its Permasep line of products for desalination.

Du Pont recently renewed its R&D effort and established an internal venture group in its Polymer Products Department (PPD) to develop and commercialize the next generation of polymeric membranes for gas separation. Its main target market appears to be oil and gas production and processing. Test units have been installed at a Conoco refinery in Oklahoma and at a Conoco oil field in West Texas.

Du Pont thus appears to be staging a belated comeback into the business that it pioneered but later ceded to Monsanto. This is consistent with Du Pont's strategy of expansion into specialty polymers and engineered products (Pappas, 1984). R&D on polymer products represents 40% of Du Pont's total R&D expenditures (Webber, 1984b). Du Pont's corporate technology strategy, R&D budget and R&D organization are described by Webber (1984b) and De Young (1985).

Monsanto started its formal R&D program on membrane gas separation in its Corporate R&D Department around 1974-1975. The initial target application was the recovery of hydrogen in refineries and chemical plants. Monsanto's invention of the RM Composite hollow-fiber membrane system gave it the competitive advantage of having superior technology.

After a remarkably short elapsed time of 2-1/2 years, Monsanto installed its first commercial membrane gas separation system in its own petrochemical plant in Texas City. Having demonstrated the technical feasibility in in-house installations, Monsanto started marketing these systems under the trade name of "Prism" in 1979. Monsanto then broadened the Prism product line to additional applications, including carbon dioxide separation from hydrocarbons in oil and gas production, air separation into oxygen and nitrogen, and gas dehydration. For this successful innovation, Monsanto received the Kirkpatrick Award in 1981, exactly ten years after Du Pont won the same award for the same type of product (Rosenzweig, 1981).

Monsanto established an autonomous, self-supporting Separations Business Group at Research Triangle Park, NC. This group carried out applied R&D, design, manufacturing, marketing, and service. Only basic research continued at the Corporate R&D Center in St. Louis.

In 1984, Monsanto relocated the group from Research Triangle Park to St. Louis. It is now part of the Engineered Products Division. Monsanto's corporate technology strategy, R&D budget and R&D organization are described by Webber (1984a).

The entries by Du Pont and Monsanto into the membrane gas separation business had many aspects in common. Both were internal ventures established to exploit and commercialize hollow-fiber polymer technology. Both ventures were initiated as R&D projects in Corporate R&D centers. Both companies field-tested and demonstrated the commercial feasibility of their systems in in-house petrochemical facilities. Both companies received the Kirkpatrick Award in recognition of their innovations, although a decade apart.

However, even seemingly minor differences in action or procedure can result in major differences in outcome. The two technologies were generically the same, but differed in important details. Monsanto's membrane materials, fabrication methods, and engineering designs for the Prism system were superior to Du Pont's. Monsanto worked closely with its customers throughout this period, and formed various alliances with some of them, such as the one with Maritime Protection A/S mentioned earlier. Du Pont's gas membrane activities were technically and organizationally too close to their traditional fiber spinning activities, and not close enough to the market.

Monsanto's superior strategy, technology and execution, its organization in the early stages as an independent business unit, and its cooperative activities with users, contributed to its success, even though it entered the market several years later than Du Pont.

Now that Du Pont's market familiarity is higher than it was at the time of original entry, its re-entry has a better chance of success. Its new products must embody much more advanced technology than the present products on the market. Du Pont must also target its product design and marketing efforts at several major markets for gas separation.

4.3 Government Agencies

Several U.S. Government agencies are supporting R&D related to membrane separation technology. These programs range from basic research through applied R&D to pilot plants. Most of the information thus obtained is in the public domain, except for some information on the separation of isotopes.

The U.S. Department of Energy (DOE) supports membrane-related R&D through its Office of Basic Energy Sciences, its Office of Industrial Programs, and through in-house R&D performed at its National Laboratories.

Bend Research, Inc.'s promising R&D program for developing a liquid membrane system that can produce up to 90% oxygen from air in a single stage is sponsored by the DOE Office of Basic Energy Sciences (Hanson, 1982). Small, specialized contract R&D firms such as Bend Research, Inc. rely heavily on Government funding to make their significant contributions to the advancement of membrane technology.

The DOE Office of Industrial Programs sponsors a variety of R&D programs that are generally aimed at energy-efficient separation technologies. Current progress is reported by the contractors at the annual Membrane Technology R&D Workshops. The most recent one was held at Clemson, SC in October, 1984. Programs on membrane-based systems for making oxygen-enriched air, and the latter's use in combustion processes, have been sponsored by this office of DOE.

DOE has commissioned reviews of membrane technology, including the ones by Lonsdale (1982a) and by Leeper et al. (1984).

The National Science Foundation (NSF) will spend about $371,000 this year to support 7 R&D programs on membrane gas separation (Table 4.3). The NSF is establishing a few new Engineering Research Centers, one of which might be devoted to separation processes (Zanetti, 1984).

The National Bureau of Standards (NBS) of the U.S. Department of Commerce has several R&D activities related to the fundamentals of transport through membranes. Its Polymer Science and Standards Division develops Standard Reference Materials (SRM) and standard techniques for the measurement of permeability and related parameters (Barnes, 1983). The National Engineering Laboratory is conducting basic research on facilitated transport and liquid membranes (Flynn

TABLE 4.3
NSF RESEARCH PROJECTS IN GAS PERMEATION

In The Chemical, Biochemical and Thermal Engineering Division

Grant No.	PI/Inst/Title	FY '85 Budget
CPE-8312761	Lloyd, Douglas and Martin; Univeristy of Texas; "Aspects of Membrane Permeation"	$66,281
CPE-8306952	Paul, Don; University of Texas; "Equilibrium and Permeation Properties of Glassy Polymers"	$52,495
CPE-8314443	Belfort, George and Drew, Don; Rensselaer Polytechnic Institute; "Particle Fluid Mechanics Applied to Membrane Fouling"	$65,510
CPE-8351932	Koros, William J.; University of Texas; "Permeation in Membranes" (Presidential Young Investigator)	$62,500
CPE-8441444	Hwang, Sun-Tak; University of Cincinnati; "Continuous Membrane Reactor Separator"	$61,603
CPE-8442928	Hwang, Sun-Tak; University of Cincinnati; "Improvement and Application of Continuous Membrane Columns"	$24,581
CPE-8442700	Datta, Ravindra; University of Iowa; "Continuous Membrane Reactor Separator for Homogeneous Catalysis"	$38,244
	Total	$371,214

and Way, 1982). This year's budget for research directly related to gas separation is about $400,000.

The U.S. Navy has sponsored R&D programs related to the recovery and purification of helium. Helium of high purity (>99.8%) is mixed with oxygen to form the gas breathed by divers. Under contract to the U.S. Navy, Westinghouse developed an onboard helium recovery system using spiral-wound cellulose acetate membranes (Martin, Snyder and Lahoda, 1983).

The Office of Water Research and Technology (OWRT), and its prodecessor, the Office of Saline Water (OSW), both of the U.S. Department of the Interior, supported a considerable amount of membrane-related R&D from the 1950's through the 1970's.

Government support of membrane-related R&D, by multiple agencies with different missions, has contributed significantly to the advancement of membrane technology and to the growth of the membrane separations industry. The DOE will probably remain the major source of Government funding of R&D related membrane separation technology in the near future.

4.4 Universities and Other Nonprofit Institutions

Much of the basic R&D in the disciplines underlying membrane-based separation technology has been performed at academic and other nonprofit institutions. Such institutions have made significant contributions in the areas of transport mechanisms through membranes, structure-property relationships, measurement and correlation of permeability data, and computer-aided modeling, design and optimization of multi-stage membrane separation systems.

Of the many universities throughout the world doing R&D that is somewhat relevant to the subject, a few U.S. universities that have especially strong R&D programs related to membrane-based gas separation are listed in Table 4.4.

Some of these programs are sponsored by private industry, reflecting the growing trend of university-industry collaboration. For example, the Center of Excellence for Membrane Technology at the University of Cincinnati was established with the aid of a $2 million grant from the Standard Oil Company of Ohio. The Separations Research Program (SRP) at the University of Texas at Austin has 32 industrial firms as sponsors who contribute $20,000 per year (Zanetti, 1984). In a survey last year, these firms ranked gas separation by membranes as the R&D area of highest priority among eight areas of separation technology (Fair, 1984).

The following four U.S. nonprofit organizations have performed and/or sponsored significant activities related to membrane separation technology:

- Battelle Columbus Labortories (Columbus, OH)
- Gas Research Institute (Chicago, IL)
- Institute of Gas Technology (Chicago, IL)
- SRI International (Menlo Park, CA)

TABLE 4.4

U. S. UNIVERSITIES WITH MAJOR R&D PROGRAMS RELATED TO GAS SEPARATION BY MEMBRANES

Name	Department or Center	Address	Key Faculty Member
Montana State University	Chem. Eng.	Bozeman MT 59717	F. P. McCandless
North Carolina State Univ.	Chem. Eng.	Raleigh NC 27695	H. B. Hopfenberg V. T. Stannett
Stevens Inst. of Technology	Chemistry & Chem. Eng.	Hoboken NJ 27695	K. K. Sirkar
Syracuse University	Chem. Eng. & Materials Science	Syracuse NY 13210	S. A. Stern
Univ. of Cincinnati	Chem. & Nuclear Eng; Center of Excellence for Membrane Tech.	Cincinnati OH 45221	S. T. Hwang
Univ. of Iowa	Chem. Eng.	Iowa City IA 52242	K. Kammermeyer
Univ. of Missouri at Rolla	Chem. Eng.	Rolla MO 65401	H. Yasuda
	Chemistry		J. Stoffer
Univ. of Texas at Austin	Chem. Eng; Center for Energy Studies	Austin TX 78712	W. J. Koros D. R. Paul

5. CONCLUSIONS AND RECOMMENDATIONS

The key conclusions of this thesis are summarized below.

The separation of gases by membranes on a commercial scale has grown rapidly since the mid-1970's, due to both technology-push and market-pull incentives. Although the technical feasibility of gas separation by selective permeation through membranes has been known for over a century, such separation first became economically feasible in the 1970's. This was mainly due to the rapid advancement of membrane technology during the postwar period, culminating in the RM Composite technology that is embodied in Monsanto's Prism products (Section 2.1).

The increased demand for energy-efficient gas separation processes, specialty chemicals, hydroprocessing capacity in oil refineries, and carbon dioxide for enhanced oil recovery in the 1970's resulted from the sharp rise in the cost of fossil fuels. These trends generated certain market opportunities in which gas separation by membranes gained a relative economic advantage over the alternative processes (Chapter 1 and Section 2.1).

However, membrane technology will not completely displace alternative gas separation technologies. It will substitute for the latter only in those applications in which it has a relative economic advantage.

Membrane technology can also augment or complement other gas separation technologies. The Fluor process of membranes with distillation (Fig. 1.6), and the Cynara membrane system upstream of a gas-liquid absorption plant (Fig. 1.7), are examples of synergistic combinations of membrane-based and other gas separation processes. This is why membrane separation should be evaluated by itself and in combination with other processes in a given application (Section 1.2).

The separation of hydrogen from gas streams in ammonia plants, petrochemical plants and oil refineries has been the largest commercial application of membrane-based gas separation to date. Both Du Pont and Monsanto operated their early membrane systems in hydrogen separation service in their in-house petrochemical plants (Section 4.2). The permeability ratio of hydrogen to carbon monoxide through Monsanto's Prism membranes is about 35 (Henis and Tripodi, 1980, 1981). This is high enough to make membrane separation competitive with the alternative cryogenic distillation process for this application.

The largest future application of membrane separation, after 1990, will most probably be for acid gas removal from hydrocarbon streams and flue gases (Table 1.1). The largest single membrane gas separation plant is a Monsanto Prism plant to recover CO_2 in an EOR project in Texas. Its capacity is 75 (10^6) SCFD of feed gas (Section 4.1). Membranes are well suited for processing the streams of variable flow rate and composition that occur in EOR projects (Fig. 3.7).

It has been generally been uneconomical to recover CO_2 from combustion flue gases, which represent the largest potential source of CO_2. Furthermore, regulations to control "acid rain" emissions will require multibillion dollar investments in flue gas desulfurization (FGD) equipment (Boom Market for FGD Equipment, 1984). CO_2/CH_4 permeability ratios of 25-35 are exhibited by commercial membranes (Table 2.6). The facilitated transport membranes of the future will have even higher selectivities.

Air separation and the dehydration of gases and vapors are also significant growth markets for membranes. These and other current and future applications are discussed in Section 1.3.

Membranes are generally competitive in the following situations:

- When a membrane having the requisite selectivity, durability and other properties is commercially available.
- For small to medium capacities, or variable feed rates or compositions.
- For bulk separation or composition adjustment, rather than final purification to products of high purity.
- When a high partial pressure gradient of the desired component(s) in the permeate stream is available or can be readily maintained.

A longer more detailed list is given in Table 1.2. The correct identification of those applications in which membranes would be economically competitive is a critical factor for success. This point is supported by the following comments on Monsanto by Lonsdale (1982a):

"The Monsanto group made two types of breakthroughs. The first

> was technical...The second sort of breakthrough was not so obvious, but was equally important in our opinion: they identified industrially important and feasible applications for the new separation technology... Identifying these viable applications has led to a new industry of rapidly growing importance. It is this identification of feasible applications...that we believe will have the greatest payoff.'

There are complex trade-offs among the key variables that govern membrane system performance. High selectivity is generally of greater economic value than high permeability in the choice of membrane materials. This is because highly selective membranes require fewer stages in series and fewer interstage compressors than would more permeable but less selective membranes. The costs of compression and related hardware may often exceed the costs of the membrane modules themselves in a multistage cascade. These points are illustrated by a comparison of the economics of CA and DMS membranes for air separation (Fig. 3.10). The total cost of separation by the more selective, less permeable CA membrane was about half that of the less selective, more permeable DMS membrane.

The capital cost of a membrane separation system is a function of the total membrane area, the number of compressors and their power consumption. Modules cost \$2-3/ft^2, and total systems cost about \$6/ft^2 (Section 3.4). The total operating cost is a function of compressor power consumption and membrane replacement costs, the latter usually being the smaller of the two.

Economies of scale occur up to but not beyond the scale of the individual stage or module. Optimization should be done on the economics of the overall processing plant containing one or more membrane separation systems. Overall plant economics depend on many variables and assumptions that are specific to a particular application.

Facilitated transport, which represents the next generation of membrane separation technology, will probably be in commercial use by 1990. The principle has already been demonstrated on a laboratory scale, and it has been observed operating in biological systems. Facilitated transport would provide greater extents of separation per stage, than the current technology. For example, the experimental air enrichment system developed by Bend Research, Inc. can generate 88% pure oxygen in a single stage, versus the 28-39% purity achievable by current commercial membranes (Baker et al., 1982).

There will be over one hundred membrane gas separation systems in commercial service worldwide by the end of 1985. Their total capacity will be about 760 (10^6) SCFD of feed gas (Section 4.1).

The total worldwide market for membrane gas separation systems, worth about $60 million in 1985, might reasonably be expected to grow at 12% per year over the next 15 years. The U.S. share of the world market might be about 50% on the average over the next 15 years. Unexpected increases in oil prices, in the use of CO_2 for EOR, in natural gas production, in gas recovery from unconventional sources, or in synthetic fuels production, would increase demand for membrane gas separation (Section 1.1).

Future breakthroughs in membrane separation technology, whose nature, significance and timing are difficult to predict, might accelerate the penetration of membrane gas separation into new applications.

On the other hand, a scenario of lower oil prices, lower use of unconventional energy sources, or slower technological advancement, would have the opposite effect.

Monsanto is the leading company in the industry by a wide margin. Its present share of the world market is about 89%. Although it was not the first company to enter this market, it was the first one to succeed in it, for reasons discussed in Section 4.2.

The following strategies for success were inferred from a case study of Du Pont and Monsanto, and from other evidence:

- Understand the market and the competition. Pursue several major applications in which membrane-based separations would have a competitive advantage over alternative technologies or would complement them.

- Maintain superior technology through a strong multi-disciplinary R&D program, and protect it by patents.

- Be a fully integrated vendor. Form alliances with other firms as required for this purpose.

- Establish an autonomous, entrepreneurial form of organization that can respond rapidly to the changes in the market, the competition and the technology.
- Monitor and utilize appropriate scientific and technological developments occurring outside your firm, especially at universities, nonprofit research institutes and Government laboratories.

The most promising agenda for future research and development should be shaped by the technical barriers and by the economic incentives and trade-offs that characterize the current state of the art. The following agenda is recommended for the industry:

1. Membrane elements having more favorable selectivity and permeability properties (Sections 2.3, 2.4).
2. Membrane elements having greater strength, stability and durability, especially with respect to temperature, pressure and chemical species in the feed (Section 2.4).
3. Methods of fabrication of membrane elements that are uniform, reproducible, inexpensive, preferably in hollow-fiber form, and easily replaced in the field (Section 3.1).
4. A more comprehensive theory of membrane transport phenomena, aging and structure-property relationships, leading to better membrane materials (Section 2.3).
5. Computer-aided modeling, synthesis, control, economic analysis and optimization of multistage membrane separation systems (Chap. 3).
6. Improved equipment configurations, such as continuous membrane columns, multiple membrane systems, and membrane-walled reactors (Chap. 3).
7. Facilitated transport systems having improved stability, durability and fabricability (Section 2.1).
8. Expert systems for selecting and specifying the most appropriate membrane for a given application.
9. A shorter innovation cycle, i.e. the time from scientific discovery or invention to first commercial use (Section 2.1).

A more detailed discussion of each point may be found in the sections or chapters referenced above.

The economic and competitive advantage of having superior technology was demonstrated by the case of Monsanto (Section 4.2).

The appropriate R&D strategy and resource allocation of a particular firm depends on that firm's business strategy, market position, areas of expertise, and size. Complete coverage of all the areas listed above would be appropriate for large, fully integrated vendors, such as the firms in the first and second groups defined in Section 4.2. Selective but in-depth activity in a few areas would be appropriate for the more specialized firms in the third group.

Academic, nonprofit and Government institutions, and the latter's contractors, should focus on fundamental, long-range R&D programs in the disciplines underlying membrane separation technology.

6. GLOSSARY

ACS	American Chemical Society
BHP	Brake Horsepower
CA	Cellulose Acetate
CCC	Continuous Countercurrent Contactor
CMC	Continuous Membrane Column
DEA	Diethanolamine
DMS	Dimethyl Silicone
DOE	Department of Energy
ELM	Emulsion Liquid Membrane
EOR	Enhanced Oil Recovery
FGD	Flue Gas Desulfurization
GPA	Gas Processors Association
GRI	Gas Research Institute
HMU	Height of a Membrane Unit
HTU	Height of a Transfer Unit
IIASA	International Institute for Applied Systems Analysis
ILM	Immobilized Liquid Membrane
NGL	Natural Gas Liquids
NMU	Number of Membrane Units
NSF	National Science Foundation
NTIS	National Technical Information Service
NTU	Number of Transfer Units
NYSE	New York Stock Exchange
OPEC	Organization of Petroleum Exporting Countries
PSA	Pressure Swing Adsorption
PSI	Pounds (force) per Square Inch
PVA	Polyvinyl Alcohol
RM	Resistance Model
RO	Reverse Osmosis
SACROC	Scurry Area Canyon Reef Operating Committee
SCFD	Standard Cubic Feet per Day
SCFH	Standard Cubic Feet per Hour
SCMD	Standard Cubic Meters per Day
SNG	Synthetic Natural Gas

STP	Standard Temperature and Pressure
TEA	Triethanolamine
TFC	Thin Film Composite
UCLA	University of California at Los Angeles

7. REFERENCES

Akin, S.O., King, C. et al., Interim Report to US DOE No. DOE/ID/12293-T1, Washington, DC, March 8, 1984.

Andrews, S.P.S., Third BOC Priestley Conference, London, Sept. 1983, Royal Society of Chemistry, London, 1984.

Antonson, C.R., Gardner, R.J., King, C.F., and Ko, D.Y., Ind. Eng. Chem. Process Des. Develop., 16 (4), 463-469, Oct. 1977.

Astarita, G., Savage, D.W. and Bisio, A., "Gas Treating with Chemical Solvents," Wiley, New York, 1983.

Baker, R.W., Roman, I.C., Smith, K.L. and Lonsdale, H.K., Industrial Heating, 49 (7), 16-18, July 1982.

Barnes, J.D., Amer. Chem. Soc. Symp. Series, 223, 75-88, Washington, DC, 1983.

Blaisdell, C.T. and Kammermeyer, K., Chem. Eng. Science, 28, 1249-1255, 1973.

Blaisdell, C.T. and Kammermeyer, K., AIChE J., 18 (5), 1015-1019, Sept. 1972.

Bollinger, W.A., Long, S.P. and Metzger, T.R., Chem. Eng. Progress, 80 (5), 51-57, May 1984.

Bollinger, W.A., MacLean, D.L. and Narayan, R.S., Chem. Eng. Progress, 78 (10), 27-32, Oct. 1982.

"Boom Market for FGD Equipment," Chem. Eng., 91 (14), 36-38, July 9, 1984.

Boucif, N., Majumdar, S. and Sirkar, K.K., Ind. Eng. Chem. Fundam., 23 (4), 470-480, 1984.

Boustany, K., Narayan, R.S., Patton, D.J. and Stookey, D.J., Proc. 62nd Annual Convention, Gas Processors Association, 146-149, 1983.

Brandrup, J., Immergut, E.H. and McDowell, W. (Editors), "Polymer Handbook," 2nd Ed., Wiley, New York, 1975.

Brooks, K.W., Chem. Week, 136 (3), 21-24, Jan. 16, 1985a.

Brooks, K.W., Chem. Week, 136 (13), 32-33, March 27, 1985b.

Brubaker, D.W. and Kammermeyer, K., Ind. Eng. Chem., 44 (6), 1465-1474, June 1952.

Cabasso, I., "Hollow-Fiber Membranes," Kirk-Othmer ECT, 3rd Ed., 12, 492-517, Wiley, New York, 1980.

Chern, R.T., Koros, W.J., Hopfenberg, H.B. and Stannett, V.T., "Material Selection for Membrane-Based Gas Separations," ACS Symp. Series, 269, 25-46, 1985.

Chern, R.T., Koros, W.J., Sanders, E.S., Chen, S.H. and Hopfenberg, H.B., "Implications of the Dual-Mode Sorption and Transport Models for Mixed Gas Permeation," in Whyte, Thaddeus E., Yon, Carmen M. and Wagener, Earl H. (Editors), "Industrial Gas Separations," Amer. Chem. Soc. Symp. Series, 223, Chap. 3, 47-73, 1983.

Chi, C.W. and Cummings, W.P., "Adsorptive Separation (Gases)," Kirk-Othmer ECT, 3rd Ed., 1, 544-563, Wiley, New York, 1978.

Chowdhury, J. and Lewald, R., Chem. Eng., 91 (23), 30-35, Nov. 12, 1984.

Coady, A.B. and Davis, J.A., Chem. Eng. Progress, 78 (10), 44-49, Oct. 1982.

Colton, J.W. and Medvetz, S.S., Inst. Gas Tech. Symposium Papers, 447-471, Synthetic Fuels from Oil Shale and Tar Sands, Louisville, KY, May 17-19, 1983.

Cooper, A.R. (Editor), "Polymeric Separation Media," Plenum Press, New York, 1982.

Crank, J. and Park, G.S. (Editors), "Diffusion in Polymers," Academic Press, New York, 1968.

Crull, A., "Membranes in Separations and as Supports," Business Opportunity Report No. P-041N, Business Communications Co., Stamford, CT, August 1983.

Crull, A.W., High Technology, 4 (7), 83, July 1984.

De Young, H.G., High Technology, 5 (1), 11-14, Jan. 1985.

Eckhouse, J.G., Conser, R.E. and Meier, G.G., UOP Process Division Technology Conference, Chicago, IL, 1982.

Edwards, V.H., CHEMTECH, 1, 367-370 and 425-431, 1971.

Edwards, V.H., Recent Developments in Separation Science, 2, 269-280, 1972.

Egli, S., Ruf, A. and Buck, A., Swiss Chem., 6 (9), 89-126, 1984.

Fair, J.R., Chem. Eng. Education, 18 (4), 190-195, Fall 1984.

Fayed, A.S., Oil & Gas J., 81 (1), 92-96, Jan. 3, 1983.

Finken, H., "Asymmetric Membranes for Gas Separations," ACS Symp. Series, 269, 245-271, 1985.

Fischer, J. and Burnett, L.J., Argonne National Laboratory, ANL-78-108, March 1979.

Flynn, A.J., Proc. 62nd Ann. Convention, GPA, San Francisco, CA, March 14-16, 1983.

Flynn, T.M. and Way, J.D., Energy Progress, 2 (2), 79-82, June 1982.

Fox, J.L., Chem. & Eng. News, 60 (45), 7-12, Nov. 8, 1982.

Frank, W.H. (Editor), "Adsorption Separation of Gas Streams," Amer. Chem. Soc. Symp. Series, 135, Washington, DC, 1980.

Frisch, H.L. and Stern, S.A., Critical Reviews in Solid State and Materials Science, 11 (2), 123-187, 1983.

Gantzel, P.K. and Merten, U., Ind. Eng. Chem. Process Des. Develop., 9 (2), 331-332, 1970.

Gardner, R.J., Crane, R.A. and Hannan, J.F., Chem. Eng. Progress, 73 (10), 76-78, Oct. 1977.

"Gasification Units to Use Shell-Koppers Process," Chem. & Eng. News, 58 (33), 36-38, Aug. 18, 1980.

Goddin, C.S., Hydrocarbon Processing, 61 (5), 125-130, May 1982.

Gollan, A., "The Economics of Oxygen-Enriched Air Production via Hollow-Fiber Membranes," Membrane Technology R&D Workshop, Clemson, SC, Oct. 1984.

Hanson, D., Chem. & Eng. News, 60 (50), 28-29, Dec. 13, 1982.

Heit, L.B., Majumdar, S. and Sirkar, K.K., "Oxygen Enrichment by a Recycle Permeator," AIChE Spring National Meeting, Anaheim, CA, June 8, 1982.

Henis, J.M.S. and Tripodi, M.K., Separation Sci. & Tech., 15 (4), 1059-1068, 1980a.

Henis, J.M.S. and Tripodi, M.K., U.S. Patent 4,230,463, Oct. 28, 1980b.

Henis, J.M.S. and Tripodi, M.K., J. Membrane Science, 8, 233-246, 1981.

Henis, J.M.S. and Tripodi, M.K., "Composite Hollow Fiber Membranes for Gas Separation: The Resistance Model Approach," in Cooper, Anthony (Editor), "Polymeric Separation Media," pp. 75-78, Plenum Press, New York, 1982.

Henis, J.M.S. and Tripodi, M.K., Science, 220 (4592), 11-17, April 1, 1983.

Herzog, M., U.S. Patent 307,041, Oct. 21, 1884a.

Herzog, M., U.S. Patent 307,042, Oct. 21, 1884b.

Hoehn, H.H., "Aromatic Polyamide Membranes," in Lloyd, Douglas R. (Editor), "Materials Science of Synthetic Membranes," Amer. Chem. Soc. Symp. Series, 269, Chap. 4, 81-98, Washington, DC, 1985.

Holmes, A.S., Ryan, J.M., Price, B.C. and Styring, R.E., 61st Annual Convention, Gas Processors Association, Dallas, TX, March 15-17, 1982.

Hopfenberg, H.B. (Editor), "Permeability of Plastic Films and Coatings to Gases, Vapors, and Liquids," Plenum Press, New York, 1974.

Hughey, A., Wall St. J., 201 (25), 27, Feb. 4, 1983.

Hwang, S.-T., Personal Communication, March 26, 1985.

Hwang, S.-T. and Ghalchi, S., J. Membrane Science, 11, 187-198, 1982.

Hwang, S.-T. and Kammermeyer, K., "Membranes in Separations," Wiley, New York, 1975.

Hwang, S.-T. and Kammermeyer, K., "Membrane Processes" in Elving, Philip J. et al. (Editors), "Treatiste on Analytical Chemistry," 2nd Ed., Part I, Vol. 5, 185-238, Wiley, New York, 1982.

Hwang, S.-T. and Thorman, J.M., AIChE J., 26 (4), 558-566, July 1980.

Hwang, S.-T., Yuen K.H. and Thorman, J.M., Separation Science & Tech., 15 (4), 1069-1090, May 1980.

Hyne, J.B., CHEMTECH, 12 (10), 628-637, Oct. 1982.

Ito, H., Proc. Int'l Gas Research Conference, 879-888, Gov't Institutes, Rockville, MD, 1983.

Kammermeyer, K., Chem. Ing. Tech., 48 (8), 672-675, Aug. 1976.

Kesting, R.E., "Synthetic Polymeric Membranes: A Structural Perspective," 2nd Ed., Wiley, New York, 1985.

King, C.J., "Separation Processes," 2nd Ed., McGraw-Hill, New York, 1980.

Kulkarni, S.S., Funk, E.W., Li, N.N. and Riley, R.L., AIChE Symp. Series, 79 (229), 172-178, 1983.

Lee, H.L., Lightfoot, E.N., Reis, J.F.G. and Waissbluth, M.D., "The Systematic Description and Development of Separations Processes," in Li, N.N. (Editor), "Recent Developments in Separation Science," 3, Part A, 1-69, CRC Press, Cleveland, OH, 1977.

Leeper, S.A. et al., "Membrane Technology and Applications: An Assessment," U.S. Department of Energy, Report EGG-2282, Washington, DC, Feb. 1984.

Lloyd, D.R. (Editor), "Materials Science of Synthetic Membranes," American Chemical Society Symposium Series, 269, Washington, DC, 1985.

Loeb, S. and Sourirajan, S., U.S. Patent 3,133,132, May 12, 1964.

Loeb, S. and Sourirajan, S., UCLA Report No. 60-60, 1960.

Loeb, S. and Sourirajan, S., Adv. Chem. Ser., 38, 117-132, ACS, Washington, DC, 1963.

Loeb, S. and Sourirajan, S., U.S. Patent 3,223,424, Dec. 14, 1965.

Lonsdale, H.K., "Membrane Separation Technology in the 1980's," Final Report by Bend Research, Inc. for the U.S. Dept. of Energy, Jet Propulsion Laboratory, DOE/JPL-9950-691, Contract No. 956158, March 1982a.

Lonsdale, H.K., J. Membrane Science, 10, 81-181, 1982b.

Maciula, E.A., Hydrocarbon Processing, 59 (5), 115-118, May 1980a.

Maciula, E.A., Oil & Gas J., 78 (21), 63-68, May 26, 1980b.

MacLean, D.L., Stookey, D.J. and Metzger, T.R., Hydrocarbon Processing, 62 (8), 47-51, August 1983.

Makino, H., Kusuki, Y., Yoshida, H. and Nakamura, A., U.S. Patent 4,378,324, March 29, 1983.

Marchetti, C., "When Will Hydrogen Come?," Working Paper WP-82-123, Int. Inst. Appl. Systems Analysis, Laxenburg, Austria, Nov. 1982.

Margis, P., German Patent 17,981, August 7, 1881.

Martin, F.E., Snyder, T.S. and Lahoda, E.J., "Helium Recovery Using Semipermeable Membranes," in Industrial Gas Separations," Amer. Chem. Soc. Symposium Series, 223, 1-25, Washington, DC, 1983.

Matson, S.L., Lopez, J. and Quinn, J.A., Chem. Eng. Science, 38 (4), 503-524, 1983.

Mazur, W.H. and Chan, M.C., Chem. Eng. Progress, 78 (10), 38-43, Oct. 1982.

Mazur, W.H., Jakabhazy, S.Z. and Mendia, M., "Gas Separation Membranes -- Now and Tommorrow," Presented at the Europe-Japan Congress on Membranes and Membrane Processes, Stresa, Italy, June 18-22, 1984.

McCandless, F.P., J. Membrane Science, 19 (1), 101-113, April 1984a.

McCandless, F.P., J. Membrane Science, 17, 323-328, 1984b.

McReynolds, K.B., "GENERON Air Separation System," AIChE Spring National Meeting, Houston, TX, March 29, 1985.

Meares, P. (Editor), "Membrane Separation Processes," Elsevier, New York, 1976.

"Membranes Simplify Catalytic Reactions," Chem. & Eng. News, 58 (30), 35-36, July 28, 1980.

"Membranes Vie for On-Site Nitrogen Output," Chem. & Eng. News, 63 (9), 26, March 4, 1985.

Metzger, T.R., Handermann, A.C., Stookey, D.J. and Rygg, A., "Shipboard Inert Gas Generation," 18th Annual Loss Prevention Symposium, AIChE Summer National Meeting, Philadelphia, PA, August 22, 1984.

Michaels, Alan S., Pure & Appl. Chem., 46, 193-204, 1976.

Mitchell, J.K., J. Roy. Inst. Gt. Britain, 2 (4), 101-118, and 2 (5), 307-321, 1831.

Mix, T., "Low Energy Separations," Kirk-Othmer ECT, 3rd Ed., Supplement, 806-845, John Wiley, New York, 1984.

"Monsanto and a Partner Develop a New Application of Prism Separators," Chem. Eng., 90 (21), 10, Oct. 17, 1983.

"Monsanto Tests Separators for Dehydration," Chem. & Eng. News, 63 (17), 16, April 29, 1985.

Newman, S.A. (Editor), "Acid and Sour Gas Treating Processes," Gulf Publishing Co., Houston, TX, 1985.

Othmer, D.F. and Frohlich, G.J., Ind. Eng. Chem., 47 (5), 1034-1040, May 1955.

Pan, C.Y., AIChE J., 29 (4), 545-552, July 1983.

Pan, C.Y. and Habgood, H.W., Ind. Eng. Chem. Fundam., 13 (4), 323-331, Nov. 1974.

Pan, C.Y. and Habgood, H.W., Can. J. Chem. Eng., 56, 197-209 and 210-217, April 1978.

Pappas, N., "Partners in Progress: A High-Growth Future for the High-Tech Plastics Industry," SPI/SPE Conference, Philadelphia, June 22, 1984.

Parkinson, G., Chem. Eng., 90 (17), 22-27, August 22, 1983.

Parkinson, G., Chem. Eng., 91 (8), 14-19, April 16, 1984.

Parro, D., Oil & Gas J., 82 (39), 85-88, Sept. 24, 1984.

Pattison, D.A., Chem. Eng., 75 (12), 38-42, June 3, 1968.

Paul, D.R. and Morel, G., "Membrane Technology," Kirk-Othmer ECT, 3rd Ed., 15, 92-131, John Wiley, New York, 1981.

Pauley, C.R., Simiskey, P.L. and Haigh, S., Oil & Gas J., 82 (20), 87-92, May 14, 1984.

Perry, R.H., Green, D.W. and Maloney, J.O. (Editors), "Perry's Chemical Engineers' Handbook," 6th Ed., McGraw-Hill, New York, 1984.

Pfefferle, W.C., U.S. Patent 3,144,313, Aug. 11, 1964.

Proc. 1st GRI Gas Separations Workshop, Denver, CO, Oct. 22-23, 1981.

Pusch, W. and Tanioka, A., "Structure Investigations of Homogeneous Cellulose Acetate Membranes by Gas Permeation Measurements," Desalination, 46, 425-434, 1983.

Pusch, W. and Walch, A., J. Membrane Science, 10, 325-360, April 1982a.

Pusch, W. and Walch, A., Angew. Chem. Int. Ed. Engl., 21 (9), 660-685, 1982b.

Radovich, J.M., Oil & Gas J., 81 (11), 61, March 14, 1983.

Rain, C., High Technology, 3 (11), 69-76, 87, Nov. 1983.

Raucher, D. and Sefcik, M.D., "Gas Transport and Cooperative Main-Chain Motions in Glassy Polymers," (Chap. 5, 89-110), and "Sorption and Transport in Glassy Polymers: Gas-Polymer-Matrix Model," (Chap. 6, pp. 111-124) in Whyte, T.E., Yon, C.M. and Wagener, E.H. (Editors), "Industrial Gas Separations," Amer. Chem. Scc. Symp. Ser., 223, Washington, DC, 1983.

Rony, P.R., Separation Science, 3, 239-248, 1968.

Rosenzweig, M.D., Chem. Eng., 88 (24), 62-66, Nov. 30, 1981.

Saltonstall, C.W., "Gas Membranes: What's Happening?," Proceedings 1984 Membrane Conference, Business Communications Co., Stamford, CT, 1985.

Saltonstall, C.W., Lawrence, R.W. and Niu, D., "Calculation of Performance in Membrane Gas Separation," AIChE Spring National Meeting, Houston, TX, March 1983.

Sanders, B.H. and Choo, C.Y., Petr. Refiner, 39 (6), 133-138, June 1960.

Schaffert, F.W. and Ryan, J.M., Oil & Gas J., 83 (4), 133-136, Jan. 28, 1985.

Scharle, W.J. and Wilson, K., "Oxygen Facilities for Synthetic Fuel Projects," ASME Cryogenic Processes and Equipment Conference, San Francisco, CA, Aug. 19-21, 1980.

Schell, W.J., J. Membrane Science, 22 (2&3), 217-224, Feb. 1985.

Schell, W.J., Hydrocarbon Processing, 62 (8), 43-46, August 1983.

Schell, W.J. and Houston, C.D., Hydrocarbon Processing, 61 (9), 249-252, Sept. 1982a.

Schell, W.J. and Houston, C.D., Chem. Eng. Progress, 78 (10), 33-37, Oct. 1982b.

Schell, W.J., Houston, C.D. and Hopper, W.L., Oil & Gas J., 81 (33), 52-56, August 15, 1983.

Schendel, R.L., Chem. Eng. Progress, 80 (5), 39-43, May 1984.

Schendel, R.L., Mariz, C.L. and Mak, J.Y., Hydrocarbon Processing, 62 (8), 58-62, Aug. 1983.

Schendel, R.L. and Seymour, J., Oil & Gas J., 83 (7), 84-86, Feb. 18, 1985.

Schulz, G., Michele, H. and Werner, U., J. Membrane Science, 12, 183-194, 1982a.

Schulz, G., Michele, H. and Werner, U., J. Membrane Science, 11 (3), 311-319, Oct. 1982b.

Schulz, G. and Werner, U., Desalination, 51, 123-133, 1984.

Scott, J. (Editor), "Hollow Fibers: Manufacture and Application," Noyes Data Corp., Park Ridge, NJ, 1981.

Seader, J.D., "Separation Systems Synthesis," Kirk-Othmer ECT, 3rd Ed., 20, 698-726, John Wiley, New York, 1982.

Sengupta, A. and Sirkar, K.K., J. Membrane Science, 21 (1), 73-109, Oct. 1984.

Shinnar, R. and Feng, C.A., Ind. Eng. Chem. Fundam., 24 (2), 153-170, May 1985.

Sirkar, K.K., Chem. Eng. Sci., 32, 1137-1145, 1977.

Sirkar, K.K., Separation Science & Tech., 15 (4), 1091-1114, 1980.

Sirkar, K.K., Separation Science & Tech., 13 (2), 165-171, 1978.

"SNG Process is a Potential CO_2 Source," Oil & Gas J., 80 (26), 116-117, June 28, 1982.

Sourirajan, S. (Editor), "Reverse Osmosis and Synthetic Membranes: Theory-Technology-Engineering," National Research Council of Canada, Ottawa, 1977.

Stannett, V., J. Membrane Science, 3, 97-115, May 1978.

Stannett, V.T., Koros, W.J., Paul, D.R., Lonsdale, H.K. and Baker, R.W., Adv. Polymer Science, 32, 69-121, 1979.

Steiner, W.A. and Weller, S.W., U.S. Patent 2,597,907, May 27, 1952.

Steinmeyer, D., "Process Energy Conservation," Kirk Othmer ECT, 3rd Ed. Supplement, 669-697, John Wiley, New York, 1984.

Stern, S.A., "Industrial Applications of Membrane Processes: The Separation of Gas Mixtures" in "Membrane Processes for Industry: Proceedings of the Symposium," 196-217, Southern Research Institute, Birmingham, AL, May 19-20, 1966.

Stern, S.A. and Frisch, H.L., Ann. Rev. Materials Science, 11, 523-550, 1981.

Stern, S.A. Mauze, G.R. and Sampat, S.R., "Mechanisms of Gas Permeation Through Polymer Membranes," U.S. Dept. of Energy, Report DOE/ER/05015, Washington, DC, Dec. 1984.

Stern, S.A., Perrin, J.E. and Naimon, E.J., J. Membrane Science, 20 (1), 25-43, July 1984.

Strathmann, H., J. Membrane Science, 9, 121-189, August 1981.

"Synfuels Market Makes Oxygen Producers Giddy," Chem. Eng., 87 (8), 82-84, April 21, 1980.

Teslik, S. and Sirkar, K.K., "Comparative Analysis of the Role of Recycle or Reflux in Permeators Separating a Binary Gas Mixture" in Li, N.N. and Calo, J.M. (Editors) "Recent Developments in Separation Science," 9, CRC Press, Boca Raton, FL, 1985.

"The Petroleum Handbook," 6th Ed., Elsevier, Amsterdam, 1983.

Torrey, S. (Editor), "Membrane and Ultrafiltration Technology: Developments Since 1981," Noyes Data Corp., Park Ridge, NJ, 1984.

Turbak, A.F. (Editor), "Synthetic Membranes," (in 2 volumes), Amer. Chem. Soc., Symp. Series, 153 and 154, Washington, DC, 1981.

Van Gelder, J.M., "Hydrogen Recovery from Ammonia Plant Purge Gas via Prism Separators," Technical Conference on Ammonia Fertilizer Technology, Beijing, PRC, March 13-28, 1982.

Vieth, W.R., Howell, J.M. and Hsieh, J.H., J. Membrane Science, 1 (2), 177-220, July 1976.

Webber, D., Chem. & Eng. News, 62 (52), 6-13, Dec. 24, 1984a.

Webber, D., Chem. & Eng. News, 62 (6), 7-12, Feb. 6, 1984b.

Weller, S. and Steiner, W.A., Chem. Eng. Progress, 46 (11), 585-590, Nov. 1950a.

Weller, S. and Steiner, W.A., J. Appl. Phys., 21 (4), 279-283, April 1950b.

Wensley, C.G. and Jakabhazy, S.Z., "High Performance Gas Separation Membranes," Presented at the AIChE Winter National Meeting, Atlanta, March 11-14, 1984.

"Why Hollow Fiber Reverse Osmosis Won the Top CE Prize for Du Pont," Chem. Eng., 78 (27), 54-59, Nov. 29, 1971.

Whyte, T.E., Yon, C.M. and Wagener, E.H. (Editors), "Industrial Gas Separations," ACS Symp. Series, 223, Washington, DC, 1983.

Wilson, K.B., Oil & Gas J., 80 (42), 105-110, Oct. 18, 1982.

Yamashiro, H., Hirajo, M., Schell, W.J. and Maitland, C.F., Hydrocarbon Processing, 64 (2), 87-89, Feb. 1985.

Yasuda, H. and Stannett, V., "Permeability Coefficients" in Brandrup, J., Immergut, E.H. and McDowell, W. (Editors), "Polymer Handbook," 2nd Ed., III-229, Wiley, New York, 1975.

Yoshisato, R.A. and Hwang, S.-T., J. Membrane Science, 18, 241-250, 1984.

Zanetti, R., Chem. Eng., 91 (18), 18-21, Sept. 3, 1984.

Zavaleta, R. and McCandless, F.P., J. Membrane Science, 1, 333-353, 1976.