

Gas Separation Using Polymeric Membranes: The Recent Development and Its Future.

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Abstract

Membranes separation technology has been widely accepted as an alternative to the conventional separation techniques. Reverse osmosis, ultrafiltration and microfiltration are examples of the application of membrane separation technology which has been practiced in the chemical industry. Advances in these areas gradually led to the development of membrane made from polymeric materials for gas separations. The polymeric membrane has found acceptance in a range of industrial, medical and laboratory applications. The paper will discuss the recent development, advantages, challenges, applications and future of polymeric membranes in gas separation applications.

Introduction

Membrane technology for the separation of liquid/liquid and liquid/solid streams has been practiced in industry for many years in reverse osmosis, ultrafiltration, microfiltration, and other applications. Advances in these areas gradually led to the development of membranes suitable for industrial gas separation. Introduced commercially only in late 1979, this technology has found acceptance in a range of industrial, medical and laboratory applications.

Principles of gas membrane separation (1).

An example of a gas membrane separation process is air separation. In this process, air is separated into its nitrogen and oxygen components by passing the feed stream across a membrane surface. Gas membrane separation is a concentration-driven process which, for gases, is directly related to the pressure of the feed and permeate streams. The feed air is compressed to provide this driving force and the air stream is passed across the membrane surface in a cross-flow arrangement, as opposed to the "dead-end" setup used with particulate filters. The membrane is more permeable to oxygen than to nitrogen and thus the oxygen permeates through the membrane to the low pressure permeate side. The remaining stream is enriched in nitrogen and exits as the high pressure residue stream. Although where shows complete separation, membrane permeation is a rate-controlled process and complete separation is not achieved. The degree of separation is determined by the selectivity of the membrane and by the conditions of the separation, including pressure, temperature, flow rate and membrane area.

Advantages

Membrane gas separation competes with cryogenic distillation and a wide range of

adsorption and absorption processes such as pressure swing adsorption and amine treatment (2). Membranes also compete with the on-site delivery of gases such as oxygen and nitrogen. Because gas separation membranes do not offer a separation that is particularly unique, they must compete primarily on the basis of overall economics and convenience (3).

An obvious advantage of gas membranes is their simplicity of operation and installation. There are no rotating parts or circulating liquids, so supervision and maintenance costs are reduced. In many applications, membranes have a lower capital outlay and require no utilities unless a compressor is needed. They are generally weight and space efficient, which is important in transportation or offshore platform applications. Membrane processes are flexible; additional capacity is easily added to an existing plant. Their environmental impact is low because they contain no toxic liquids and are compact in size. These advantages have enabled the penetration of membranes into many commercial applications (Table 1 and 2).

Development in membrane formation technology

There are three key performance attributes that affect a membrane's economic utility for a particular application (1). The first is its selectivity, which directly affects the degree of the separation, both recovery and purity, and indirectly affects membrane area. The second parameter is membrane flux or permeability, which simply dictates the capital investments or the amount of membrane required. The third is the life of the membrane which includes maintenance and replacement costs. These parameters depend on the type of membrane polymer selected, how it is formed into a membrane, and how that membrane is packaged and designed into a process.

There are many polymeric materials that have good selectivities for specific gas separation problems. Examples of such materials are polysulfone and cellulose acetate which were the earliest commercial membranes. These types still predominate but have been joined by polyimides, polyamides, polycarbonates, polyetherimide and sulfonated polysulfone (4). The real challenge for industrial application was to fabricate these polymers into membranes having both economically high permeability rates and high durability in the gas stream environment.

Large-scale commercial gas mixture separation plants started to operate in the late 1970s (5). Membranes having useful selectivities were known since 1960s but were too slow and too expensive to be economical. Both of these problems were solved in the late 1960s and early 1970s by the developers of another membrane process, reverse osmosis. The problem of slow permeation was overcome by the development of asymmetric membranes (6,7). This method is known as the Loeb-Sourirajan method. The membranes produced consist of a permselective surface film supported by a much thicker microporous substrate. It was applied to cellulose acetate membranes. In this technique, a solution containing approximately 20% polymer is cast on a moving web and then precipitated by immersion in a bath of water. The water rapidly precipitates the top surface of the cast film, forming the permselective skin. This skin then slows the entry of water into the underlying polymer solution, which thus precipitates much more slowly, forming a more porous substructure. However, strong, defect-free membranes require the permselective top skin of the membrane to be rather thick. Consequently, the gas flux through these membranes is low.

The problem of low gas flux through the Loeb-Sourirajan gas separation membranes has been partially solved by workers at Monsanto (8). The Monsanto group made Loeb-Sourirajan membranes (principally from polysulfone) and then coated the membranes with a thin layer of silicone rubber, which is extremely permeable but has rather low selectivity. The layer of silicone rubber does not function as a selective barrier but rather plugs up and reduces to negligible amounts the flow-through defects in the permselective polysulfone film. The increase in flux resulting from this thinner polysulfone membrane more than compensates for the slight reduction in flux due to the silicone rubber sealing layer.

A third membrane, developed by Ward (9), Riley (10) and others, is a composite structure in which a permselective membrane, usually silicone rubber, is directly coated onto a high-permeability support membrane. In these membranes, mechanical strength is provided by the microporous support and permselectivity by the thin surface layer. This allows relatively weak, rubbery materials to be used for the permselective layer, with a strong material such as microporous polysulfone providing mechanical strength.

The problem of producing low-cost membrane modules was also solved during the development of modules for reverse osmosis membranes (11). There are two principal module designs currently in use: the spiral-wound module (12) and the hollow-fiber modules (13). Both configurations are considerably less expensive than the older plate-and-frame systems.

Hollow-fiber membranes are produced by a spinning process that has much in common with conventional fiber spinning. As a result, the cost of producing the membrane on a square-foot basis is quite low. Most of the cost of producing hollow-fiber modules is incurred when fibers are mounted (potted) inside the module shell. Hollow-fiber modules usually are used with the feed gas circulated around the outer surface of the fibers.

There are a number of spiral-wound module designs. The first and simplest consists of a membrane envelope wound around a perforated central collection tube. The wound module is placed inside a tubular or pressure vessel, and feed gas is circulated axially down the module across the membrane envelope. A portion of the feed permeates into the membrane envelope, where it spirals toward the center and exits through the collection tube.

The flat-sheet membranes used in spiral-wound modules usually have higher fluxes than capillary and hollow-fiber membranes made from the same material. This is because it is difficult to make hollow-fiber permselective skins as thin as flat-sheet skins. For this reason, although spiral modules are usually two to five times more expensive on a square-foot basis than hollow-fiber membranes, they are competitive in many applications.

Applications (1)

Typical applications of polymeric membranes in gas separation are as follows :

a) Air Separation And Dehumidification.

The first truly competitive membranes for air separation did not reach the market until 1986, but this is quickly becoming the largest application for gas separation membranes. The combination of more highly permeable membranes and the reduction in membrane prices has brought the cost of air separation down to levels where it can be competitive with on-site deliveries of cryogenically produced gases for many applications. The use of membranes for the dehumidification of air is relatively new.

The products of membrane air separation are oxygen (permeate) and nitrogen (residue). At present the vast majority of membrane applications produce nitrogen as the gas of interest. In principle, a given membrane could be used for either nitrogen or oxygen production. The system design, however, is quite different depending on which product is desired. The current state of membrane technology does not allow high purity levels to be economically achieved in most cases. Membranes are most efficient when producing nitrogen in the 95-99% range and oxygen at 30-45% purity. Current membranes generally have low separation factors (4,14,15,16,17).

Nitrogen production via membranes is growing rapidly for applications requiring inert gas

blanketing. These include storage and shipment of flammable liquids and fresh fruits, vegetables, and flowers. Perishable products must be shipped via air to minimize spoilage, but shipping in a nitrogen atmosphere dramatically reduces the spoilage rate so that ocean or land shipment becomes possible. Membrane units are installed as a part of the container and are far more weight and space efficient than liquid nitrogen tanks or on-board pressure swing adsorption units. Membranes are also replacing gas-fired inert gas generators for stationary applications because of their ease of operation and safety.

Membranes are also successfully challenging the delivery of liquid nitrogen for a wide variety of applications. Customers generally like the ability to produce gases on demand and the membrane units eliminate storage tanks and delivery problems. Membranes also produced gas more cheaply than delivered nitrogen for lower volume applications (18).

Oxygen production is not a major commercial endeavor because of the relatively low oxygen purities that are currently possible. There is limited use of membranes for medical oxygen production, particularly in Japan, but there are no major applications for large-volume oxygen production via membranes. A potential market exists for enhanced combustion applications, and several companies are actively involved. Small oxygen units are proving useful in biological and laboratory applications where enriched air can be used to accelerate cell metabolism (18).

Another application for membranes is in the air dehumidification process (19). The conventional processes involve the use of desiccants or refrigerant driers. The advantage of using membranes is that they have very high moisture permeability and selectivity which makes removal of moisture from a pressurized air stream easy. Dew points of -35°C or lower can be reached depending on the conditions of the process. Dehydration is achieved with some loss of feed air to carry the moisture out with the permeate. The membrane approach eliminates regeneration cycles, dust and noise, and can operate without power.

b) Hydrogen separation and recovery

The use of membranes to recover hydrogen is widespread in the ammonia and refinery industries and, to a lesser extent, in the petrochemical industry (Table 3). In most applications, membranes allow inexpensive hydrogen recovery from waste gas streams for recycle back to the plant. In many cases, hydrogen was simply burned for its fuel value because separation was prohibitively expensive. Membranes compete with cryogenic, catalytic, and pressure swing adsorption (PSA) processes for hydrogen separation and have many potential applications.

Ammonia is typically produced by reacting hydrogen and nitrogen at high pressure and temperature over a catalyst. Hydrogen feedstock is provided by the steam reforming of natural gas, and nitrogen is supplied from air. Conversion to ammonia is incomplete and the unreacted gases are recycled back to the feed side to improve yield. Inert gases such as argon (from air) and unreacted methane would build up if this were a closed loop, and so a continuous gas purge is maintained to keep these contaminants at a constant, tolerable level. This purge gas contains valuable hydrogen, which can now be removed. Membranes provide a cost-effective separation that results in energy savings and an effective capacity increase (20).

Refinery hydrogen recovery is expected to grow over the next decade in response to several factors such as:

- i) increasing levels of sulfur in crude require more hydrodesulfurization
- ii) heavier feedstock require more hydroprocessing
- iii) refiners are improving their product slate through increased coking and hydrocracking.

Hydrogen will be supplied by direct production and from the recovery of off-gases from existing processes that generate hydrogen as a by product. Membranes have been shown to provide a highly cost-effective solution to hydrogen recovery from these streams (21). Competitive recovery processes include oil scrubbing, PSA, and cryogenics.

Synthesis gas is a mixture of hydrogen and carbon monoxide that is used in a variety of petrochemical and metallurgical processes. It is produced from natural gas, oil, or coal via different processes. Syngas can be used for the production of methanol and other oxygenated chemicals such as acetic acid, ethylene glycol, and ethanol. The stoichiometry of the feed gas must be adjusted depending on the process. Membranes can be used to vary the stoichiometry by selectively removing hydrogen (22). Traditional methods for separating synthesis gas have been cryogenics separation and blending or PSA to provide the desired hydrogen purity. However, both of these processes provide carbon monoxide at low pressure, while membranes provide this gas at high pressure.

c) Natural gas treatments

Some natural gas contains impurities such as carbon dioxide and hydrogen sulfide which require removal prior to delivery to a pipeline. Both are corrosive to the pipeline, and hydrogen sulfide is also toxic. Almost all natural gas needs to be dehydrated prior to delivery to a pipeline to prevent corrosion and hydrate formation. Natural gas is typically produced at the high pressures ideal for membrane operation. Membranes separate carbon dioxide, hydrogen sulfide, and moisture into the permeate stream. The methane stream product is delivered with essentially no pressure loss.

Removal of gas contaminants is often accomplished in centrally located processing plants into which many small gas wells are fed. The most common process for removing carbon dioxide and hydrogen sulfide is amine absorption. Membrane systems for natural gas treating can offer significant advantages in capital investment, ease of operation, and weight and space savings over amine systems (23). Membranes are particularly useful for remote locations (24).

Carbon dioxide enhanced oil recovery uses carbon dioxide pumped into dying oil reservoirs to recover the remaining oil. The CO₂ is pumped into the formation on the periphery of the reservoirs at high pressures, and then diffuses through the formation to drive residual oil toward existing wells. Over time, the CO₂ also arrives at the well and begins to "contaminate" the natural gas associated with the oil. This contamination can reach as high as 95% as the project matures. Membrane systems are very effective at removing high levels of CO₂ (25).

Landfills generate methane that is contaminated with approximately 50% carbon dioxide. Landfill gas at atmospheric pressure is available only at low flow rates and is expensive to upgrade. However, the gas is essentially free and collection satisfies certain environmental interests. Also, this gas is usually more valuable than wellhead gas because it is often located near industrialized areas where the value of energy is much higher. Several landfills currently use membranes to provide a high quality gas.

Many industrial processes produce waste air streams containing hydrocarbon vapors. In addition to the lost of valuable hydrocarbons, these emissions represent health, environmental, and safety problems. Membranes can be utilized to remove and concentrate these vapors (26). If desired, these hydrocarbon can be collected and recycled.

Recent increases in air pollution standards in Europe and Japan have generated interest in this. Membranes can be used for the separation of helium gases from dirigibles or deep sea diving

atmospheres. Reclamation involves separating the helium from air contamination. Membranes provide a very effective option for this applications.

Membranes are also proposed for the on-site purification of hydrogen produced from ammonia dissociators for sale to small-volume hydrogen consumers. Considerable effort is also being placed on the development of membranes suitable for the removal of nitrogen from natural gas, which is a particularly difficult separation even with non-membrane technology.

Future

The future of polymeric gas membrane is promising with many exciting developments and opportunities remain for gas separation membranes. Research and development estimated to be in excess of US\$100 million worldwide is being invested in this technology, and the availability of gas membranes is creating applications that were not even thought of just a few years ago (1). Over the past two years, membranes have appeared that are 200-400% more efficient than the ones that entered the marketplace in 1979. These improvements will continue for the foreseeable future, albeit at a slower rate, and will have a profound impact on the acceptance of membranes in many applications.

During the next decade, considerable improvement in available gas separation membranes is expected with membranes specifically designed for gas separation replacing membranes adapted from reverse osmosis. Membrane fluxes at the same selectivity will probably increase twofold within a few years, and five-to tenfold by 1995. In the United States the only major company in the field currently is Monsanto but several others are beginning to offer competition. Thus, significant reductions in the capital cost of the membranes will probably occur. The U.S. Army is sponsoring development of membranes that will recover water from vehicle exhaust for field troops in arid or in situations where the water supply may be contaminated. Judging from the patent literature, gas separation with membranes is also under active development in Japan. The Japanese government is funding a study on the recovery of carbon dioxide from flue gas to reduce the greenhouse effect, including evaluation of membranes for the separation. In Malaysia, a Membrane Research Unit (MRU) has been established at the Faculty of Chemical and Natural Resources Engineering, University Teknologi Malaysia and has received encouraging supports in terms of finance and manpower resources. Among the objectives of MRU are to develop membranes for gas separations and to design membrane system for gas processing (27).

Although the recent development in polymeric membranes is encouraging, it is unlikely that it will displace other gas separation techniques, such as cryogenics, as the principal method of separating oxygen and nitrogen in air - the largest gas separation process. Membranes, however, could find a much larger application if facilitated transport membranes could be developed into a viable process (28).

Present day membranes are capable of separation mainly inherently "fast" gases (e.g., H_2 , CO_2) from inherently "slow" gases (e.g., N_2 , CH_4). Current technology is not sufficiently refined to efficiently separate different traditionally slow gases (such as N_2 from CH_4 hydrocarbons from each other). Such separations can, in principle, be achieved by facilitated transport. In this process, imitating the function of biological membranes, the membrane contains a compound interacting specifically with only one of the feed constituents. With appropriate binding constants and binding kinetics, very efficient separations can be obtained. To date most work in this area has been confined to liquid membranes (thin liquid films, liquid in liquid microcapsules or liquid impregnated solid films). Transport facilitation was demonstrated for O_2 , N_2 , CO_2 , H_2S and ethylene

(extensive work was done on ion transport in liquids). The most practically advanced facilitated gas transport system has been the ethylene/ethane separation studied at Amoco (29). This separation, based on aqueous silver ion, was scaled up to pilot plant size. Technical problems that have not yet been solved in these systems are associated mainly with the need for water in the membrane and hence in the feed streams. It is difficult to prevent the membrane from drying at all times, especially at high pressure differentials. Once such problems are solved in an economical way, new, previously impractical gas separation should become possible.

Conclusion

The development and advancement of the gas separation technology using the polymeric membrane is very promising. The problem of low flux in the early 1960s was solved with the development of asymmetric membrane through the Loeb Sourirajan method in the late 1970s. Further improvement was made through the development of composite membrane. There is a world wide interest for further research and developmental work with more than \$250 Million Ringgit being invested. The future of this technology depends on the advancement and refinement of the technology to be able to separate slow gases such as N_2 and CH_4 from each other efficiently. Such separation can be achieved by facilitated transport and once this technology is developed, previously impractical gas separations should become possible.

Reference

- 1) Spillman, R.E.; Sherwin, M.B. Gas Separation Membranes: The First Decade; Chemtech June 1990.
- 2) MacLean D.L.; The Structure of Gas Separation Technology: The structure of Gas Separation Technology; Fourth BOC Priestly Conference.
- 3) Spillman, R. W. Chem. Eng. Prog. 1989, 85(1), 41.
- 4) Fritzsche, A. K.; Narayan, R. S. Chem. Econ. Eng. Rev. 1987, 19(205).
- 5) Baker, R.W.; Blume, Ingo; Permselective Membrane Separate Gases; Chemtech April 1986.
- 6) Loeb, S., Sourirajan, S. Sea Water Demineralization by Means of an Osmotic Membrane; ACS Advances in Chemistry Series 38; American Chemical Society: Washington, 1963; p. 117.
- 7) Rozelle, L. T., Cadotte, J.E., Cobian, K.E; Kopp, C. V. In Reverse Osmosis and Synthetic Membranes; Sourirajan, S., Ed.; National Research Council of Canada: Ottawa, Ont., 1977.
- 8) Henis, J.M.S.; Tripoli, M. K. Sep. Sci. Technol. 1980, 15, 1059.
- 9) Ward, W.J., III; Browall, W.R.; Salemme, R.M. J. Membr. Sci. 1976 1, 99.
- 10) Riley, R.L.; Grabowsky, R.L. U.S. Patent 4,234,701, 1984.
- 11) Gooding, C. H. CHEMTECH 1985, 15(6), 348-55.
- 12) Kremen, S.S. In Reverse Osmosis and Synthetic Membrane; Sourirajan, S. Ed.; National Research Council of Canada: Ottawa, Ont., 1977.
- 13) Baum, B.; Holley, W. Jr.; White, R.A. In Membrane Separation Processes; Meares, P., Ed.; Elsevier Scientific: Amsterdam, 1976.
- 14) Fain, D. E. "Gas separation Processes: Technology/Business Review;" Presented at the 1988 BCC Membrane/Planning Conference: Boston, MA, Nov. 2, 1988.
- 15) Fleming, H. L. "Molecular Sieving Inorganic Membranes;" Presented at the 1989 BCC Membrane/ Technology Planning Conference: Cambridge, MA, October 17-19, 1989.
- 16) Rautenbach, R.; Albracht, R. Membrane Processes; Otto Salle Verlag GmbH & Co.: Frankfurt, Germany, 1989; pp. 422-454.
- 17) Kesting, R.E. Synthetic Polymer Membranes, 2nd Ed.; Wiley Interscience: N.York, 1985

- 18) Beaver, E. R.; Bhat, P.V.; Sarcia, D.S. AIChE Symposium Series 261, 1988, p.84.
- 19) Haggin, J.; Chem. Eng. News, July 18, 1988, p. 35.
- 20) Shirley, J.; Borzik, D. Chem. Proc. 1982, 42, 30.
- 21) Stookey, D. J.; Patton C. J.; Malcolm, G. L. Chem. Eng. Prog. 1986, 82(11), 36.
- 22) Schott, M. E.; Houston, C. D.; Glazer, J. L.; DiMartino, S. P. "Membrane H₂/Co Ratio Adjustment," AIChE National Meeting: Houston, TX, Apr. 1987.
- 23) Babcock, R. E.; Spillman, R. W.; Goddin, C. S.; Cooley, T. E. Energy Prog. 1988, 8(3), 135; Cooley, T. E.; Dethloff, W. L. Chem. Eng. Prog. 1985, 81(10), 45.
- 24) Cooley, T. E.; Spillman, R. W. "Membrane Gas Treating;" Presented at the 68th Annual Gas Processors Association Convention: San Antonio, Texas, March 14, 1989.
- 25) Goddin, C. S. "Comparison of Processes for Treating Gases with High Carbon Dioxide Content: "Presented at the Gas Processors Association: Dallas, TX, March 1982.
- 26) Peinemann, K. V.; Mohr, J. M.; Baker, R. W. AIChE Symposium Series 250, 1986, Vol. 82, p. 19.
- 27) Hamdani Saidi; Ramlan Aziz; Ahmad Fauzi Ismail; Ahmad Sahar; Intan Salleh ; Processing the Natural Resources of The Islamic Countries Using Membrane Technology; Conference on Technological Development for the Islamic Countries-Issues And Options.
- 28) Stern, S.A.; Frisch,H.L.; The Selective Permeation of Gases Through Polymers, Ann. Rev. Mater. Sci. 1981 11:523-50
- 29) Steigelman, E.F. U.S.Pat. 4,014,665 (1977)

Table 1. Advantages of gas separation membrane processes

Low capital investment
Ease of installation
Simple operation
No rotating parts ^a
No utilities required ^a
High process flexibility
Low weight and space requirements
Low environmental impact

^a Unless a compressor is needed

Table 2. Gas membrane application areas

Gases separated	Applications
O ₂ /N ₂	Nitrogen generation, oxygen enrichment
H ₂ O/Air	Air dehumidification
H ₂ /Hydrocarbons	Refinery hydrogen recovery
H ₂ /CO	Syngas ration adjustment
H ₂ /N ₂	Ammonia purge gas
CO ₂ /Hydrocarbons	Acid gas treating, Landfill gas upgrading
H ₂ O/Hydrocarbons	Natural gas dehydration
H ₂ S/Hydrocarbons	Sour gas treating
He/Hydrocarbons	Helium separations
He/N ₂	Helium recovery
Hydrocarbons/Air	Pollution control, Hydrocarbon recovery

Table 3. Hydrogen separation applications for membranes

Ammonia synthesis purge
Ammonia synthesis gas
Catalytic reformer
Catalytic cracker purge
Hydrocracker purge
Hydrotreater purge
Methanol synthesis purge
Oxo-alcohol synthesis purge
Hydrogenator purge PSA purge