New Directions in Membranes for Gas Separation

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Introduced commercially in 1979, membrane-based gas separation has become a successful and accepted new unit operation in chemical engineering. Gas-separation membranes complement as well as compete with older separation technologies such as cryogenic distillation, selective adsorption and absorption processes. Gas separation membranes are now applied in a wide range of processes, including the production of nitrogen from air, hydrogen recovery from refinery, petrochemical and ammonia-purge streams, carbon dioxide removal from natural-gas streams and other mixtures with hydrocarbons and dehydration of compressed air.

Growth in traditional membrane markets has been driven by technology developed in the 1970s and 1980s by the major chemical companies and later implemented and driven by the industrial gas companies. However, the demands of the markets have now changed, and new technology is needed to spawn further expansion. Membrane companies face significant challenges that will require creative solutions to develop the next-generation technology.

Historical Perspective

The foundation for today's commercial gas-separation membranes was established in the 1960s and 1970s, primarily by the major chemical/plastics companies (e.g. DuPont, Monsanto, General Electric, Dow). Several technology areas were critical to success, but none more than the development of the membrane and membrane processing.

Materials Development

DuPont recognized in the mid-1950s that gas diffusion through polymers could be used to separate gases. By 1958, hundreds of polymers had been tested for various gases and the list grew to thousands by the mid-60s. It was clear from the beginning that there is a tradeoff between permeability and permselectivity. Polymers with high permeability generally have low selectivity and *vice versa,* and there is an apparent upper bound to this relationship. Over the last 40 years, polymer scientists have tried to push the limits of this upper bound, but for the most part advances have been evolutionary. In fact, some believe that significant advances in traditional polymeric membranes will be difficult to attain because we are currently close to the limit of the technology. Since the research on new polymeric membrane materials has been significantly scaled back in the industrial gas membrane companies, one cannot expect further significant advances in membrane performance and capabilities. Thus another approach is needed for future membranes if continued improvement is sought.

Membrane Processing

To maximize the flux through a membrane, it is essential to minimize the membrane thickness. This is accomplished by making the membrane a composite of a very thin effective separating layer and a porous support layer. To maximize the productivity of a membrane module, the surface area must also be maximized. Depending on the final module configuration, hollow-fiber membranes have greater membrane area for specific module volume than flat-film membranes by a factor of 4-10. Module surface area is inversely proportional to fiber size, so smaller fibers are generally better, although pressure drop and flow dynamics must also be taken into consideration.

Significant advances in membrane processing have been made over the past 30 years to achieve near-ultimate performance. The first hollow fiber membrane for gas separation developed in DuPont was a melt-spun polyester with an outside diameter of less than 40 microns and a wall thickness of about 10 microns. By today's standards, this would be a very inefficient membrane. Nonetheless, a full commercial system using this membrane was installed in 1969 for the adjustment of the H_2/CO ratio in a syngas plant in Louisiana. During the '70s a large effort was expended on developing the process technology to fabricate highly efficient asymmetric (Loeb-Sourirajan) hollow-fiber membranes. This allowed making a separating layer of tenths-of-micron thickness and in turn an order-of-magnitude improvement in transmembrane flowrate. A large effort was also expended on packaging the hollow fibers into an efficient module.

These efforts came to commercial fruition in the late 1970s and 1980s. In 1978, Monsanto brought their "multicomponent" polysulfone/polysiloxane membrane (today, owned by Air Products/Permea) to the market for the recovery of hydrogen in refinery or petrochemical streams. In 1980, Dow/Cynara initiated a field test of an asymmetric cellulose acetate membrane for the separation of CO_2 from natural gas in Texas. In the early '80s, Separex, Envirogenics and Grace began installing membranes to remove CO_2 from natural gas. By 1985, Permea and Dow launched first-generation commercial membranes for nitrogen. Early materials and manufacturing technology for gas-

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separation membranes were derived from other membrane technologies, particularly reverse osmosis. The first-generation membranes were successful, but at best marginally profitable because of high capital and operating costs.

Around 1985, the major players set out to develop new polymers, improved membrane and permeator design and new separation process design. At the same time, the leading industrial gas companies entered the field via acquisitions and joint ventures; this provided more direct access to gas markets and additional commitment to enable rapid development and reduction to practice. New manufacturing processes and equipment were custom developed for gas separation membranes, displacing older technology borrowed and adapted from other membrane fields. In 1986, DuPont introduced its asymmetric polyaramide membrane (now owned by Air Liquide/Medal) for hydrogen applications; and in 1988, an asymmetric polyimide membrane for nitrogen production. In 1987, Dow/Generon introduced a high-performance asymmetric brominated polycarbonate membrane for nitrogen production (now owned by Mg Industries). Also in 1987, Union Carbide introduced a composite polysulfone/ethyl cellulose hollow fiber (now owned by Praxair/Innovative Membrane Systems). The profusion of development and commercialization activity provided credibility for membranes in industrial gas separation processes and allowed rapid growth and market acceptance.

Whereas the late '70s and '80s represented an era of intense membrane innovation, the '90s represented the industrialization and growth phase of the life cycle. R&D became more "D", with effort focused on improved membrane efficiency and reduced membrane manufacturing costs. An example of a significant advance is Medal's development of a one-step process to produce "asymmetric-composite" membranes based on multicomponent fiber spinning technology. This technology enabled low-cost production of asymmetric hollow fibers utilizing a relatively high-cost polymeric separating layer.

Two features in this timeline merit additional comment. The first is that there was no step change in the performance of the membrane materials. Most of the improvements came from gains in cost or in membrane thickness or geometry or in bundle efficiency. Today's commercial membranes are based on materials developed before 1990, with only evolutionary changes since (and forthcoming). The second is that low capital cost was a key enabling factor for today's membranes, all based on polymers. Next-generation membranes will have to be similarly inexpensive in final module form to be commercially attractive. This is perhaps the most difficult challenge.

The Need for New Technology

Now that membrane technology is widely recognized as a viable and often favored separation technology, advances in technology will quickly be accepted. Membranes with improved permselectivity, higher temperature and pressure capability and resistance to contaminants in the feed gas will spawn new growth. However, it is critical that the new technology be tailored for each specific application.

Nitrogen Production

Existing membranes are well suited for on-site production of nitrogen up to 99.5% purity. It is estimated that membranes supply almost one third of all gaseous nitrogen production. However future growth is limited due to several factors:

- worldwide nitrogen production is expected to parallel global industrial growth;
- the cost of producing nitrogen from small on-site cryogenic units is now competitive with membrane-produced nitrogen;
- development of new membranes with improved performance has plateaued.

Technical focus should be on improved permselectivity. It is estimated that an O_2/N_2 selectivity of 10 at room temperature (with no decrease in oxygen permeance) will reduce the operating costs for producing nitrogen by 15-20% and allow penetration into applications of higher purity. There is some but not compelling incentive for improved permeance; the attendant gain in membrane capital cost would benefit only small, equipment-type applications. There is little need for improved durability, since membrane nitrogen is produced under mild conditions with respect to temperature, pressure and impurities (with the exception of lubricant oil vapor).

Hydrogen Purification/Recovery

Membrane systems for the recovery of hydrogen have been relatively successful since the commercial introduction of Monsanto's Prism membranes in 1978 and are now widely accepted. Today's membranes have high H_2/CH_4 selectivity (35-200 at 80 °C) but need several improvements for continued growth.

For next-generation membranes in traditional applications, the major requirements are lower capital cost (which translates into higher membrane permeance), capability to operate at higher temperature and pressure and better resistance to hydrocarbons and other contaminants in the feed streams. It is conceivable that several of these attributes may be achieved with polymeric membranes; however, alternative approaches are also worthy of pursuit. One approach has been with palladium membranes that provide H_2-specific transport with very high selectivity and high temperature capability. However, high cost and scale-up issues have limited use of this technology to specific and small applications. Moreover, H_2/CH_4 selectivity higher than that of polymeric membranes is not needed in most applications.

The need also exists for a membrane that retains the hydrogen on the high pressure side of the membrane and passes the higher molecular weight components. Today's membranes pass hydrogen and recover it at low pressure. For example, if the feed pressure is 1,500 psi, the hydrogen-rich permeate stream may be at 400-500 psi or lower. In many cases, this stream must be recompressed for further use. The "surface selective flow" carbon membranes developed by Air Products operate on the principle of rapid transport of the adsorbed species (in this case hydrocarbons) versus hydrogen, the transport of which is hindered. Pilot scale tests have demonstrated the concept; however, full commercialization has been impeded by the high cost of the membrane.

Alternative approaches for direct production of hydrogen at high pressure have been to use (a) membranes of high-free-volume polyacetylene with a "nanopore" structure that provides a permeation/separation mechanism similar to Air Products' carbon, or (b) membranes of rubbery polymers with solubility selectivity favoring condensibles over hydrogen. These approaches have been proven in selected applications, but their viability remains to be established.

Natural Gas Sweetening

This is probably the most demanding large-scale industrial application for membranes. Typical feed pressure ranges from 900 psi to 1,300 psi at temperatures from 50-80 °C. Carbon dioxide levels may be as high as 50% mole, and each gas reservoir has a different make-up of hydrocarbons as well as water vapor and hydrogen sulfide. The objective is to reduce carbon dioxide and hydrogen sulfide to less than 2% and 3 ppm respectively. Depending on the feed composition and product requirements, extensive pretreatment of the feed gas may be required, and often multistage design is needed to get sufficient separation.

Today's commercial membrane systems (Separex/Uop, Cynara, Grace/Kværner, Medal) have made inroads against traditional amine scrubbing systems. However, two major improvements are required to establish membranes as the preferred technology. The CO_2/CH_4 selectivity must be increased from the current level of 15-20 under actual operating conditions to at least 50, without significant loss of carbon dioxide permeance. The membranes must also be endowed with greater tolerance to aromatic and high aliphatic hydrocarbons. Existing polymeric membranes require extensive pretreatment to remove hydrocarbon and polar organic constituents (e.g. glycols used for dehydration). The cost of pretreatment can be as much as 40% of the operating cost of the membrane process.

Other Applications

A number of other separations are under development or study. Some are simply building on existing membranes. An example is the recovery of perfluorocarbon gases from mixtures with N_2. But others cannot be done with off-the-shelf polymeric membranes and require the development of new, specialized membranes. Examples include: the separation of olefins from paraffins (e.g. ethylene from ethane, propylene from propane); the removal of nitrogen from natural gas; the recovery of carbon dioxide from flue gas; the removal of acid gases from syngas while maintaining hydrogen and CO at high pressure. Some of these represent significant challenges and will require breakthrough technologies.

The Solution is not Easy

The historical focus on polymers as membrane materials has been driven by the polymers' ease of processing into efficient membranes with small effective thickness and high area/volume ratio and by the relatively low material and processing cost. Today, however, polymers have only marginal room for improvement left.

Improvement of the O_2/N_2 selectivity from the current level of 5-6.5 to 10 at 25 °C requires breaking through the upper bound barrier for polymers and may be better served by inorganic materials with higher specificity toward O_2 such as carbon and zeolites. Improvement of the CO_2/hydrocarbon selectivity from the current level of 15-20 in practical operating conditions to 50 requires either breaking through the upper bound barrier or resorting to polymers with high CO_2 solubility that are likely vulnerable to plasticization and damage by CO_2. New approaches under consideration include crosslinked glassy polymers, soft/hard-segment block copolymers and inorganic materials with sorption specificity toward CO_2. Improvement of the membranes' resistance to contamination or damage by organic components in the feed stream in H_2/hydrocarbon and CO_2/hydrocarbon separations also requires a step change in the membrane materials. Existing manufacturing processes use soluble polymers, which by their nature, have limited resistance to organics. Materials thoroughly resistant to organic impurities would probably require new manufacturing processes.

Not surprisingly, manufacturers are reluctant to venture outside the scope of existing manufacturing processes. After all, considerable investment has been made in developing the existing process technology and production equipment and it is recognized that a new material will probably require development of a new manufacturing process with new investment. However, to succeed, it will be necessary to break away from the current paradigm focused on polymeric membranes.

A New Game Plan

Discovery R&D at the major membrane companies was slowed down in the early '90s as resources were redirected to facilitate the growth of the business. That cycle has been broken. Several research groups are now working on new membrane materials that reach above existing technology.

Molecular sieving ceramic or carbon membranes are capable of operating at high temperature and in hostile environments. Both of these technologies have received considerable research attention over the past two decades and we are beginning to see encouraging results from these efforts. Hollow fiber carbon membranes (Carbon Membranes Limited) are purported to be on the brink of commercialization. Ceramic membranes continue to attract significant resources academically and industrially and significant advances have been made; however, it is too early to predict the outcome of this research. Once these materials are developed, it will be essential to develop low cost manufacturing processes and to package them into efficient membrane devices.

An alternative approach to purely inorganic membranes is to combine the separation characteristics of inorganic molecular sieves with the ease of processing of polymeric membranes. The concept is not new, but considerable effort is required to bring it to the point of commercial viability. Several academic and industrial research groups are currently working on this concept. A number of other "clever" membranes, with high gas/gas selectivity, are under aggressive development. Ion-conducting membranes made of solid oxides with high permeability to oxygen ions and very high selectivity for O_2/N_2 are under development at two large research consortia of companies and universities. Work is also under way on new facilitated transport membranes with specificity toward olefins and CO_2.

A problem that companies face is that these technical challenges require considerable resources. It is critical that resources be directed where the benefit is perceived to be the greatest. A practical way to bring together the critical mass and knowledge needed to succeed is to form partnerships with governmental agencies and universities. Several large membrane research consortia have emerged over the past few years that involve industrial cooperation and partial funding by US government agencies. Such inter-company research initiatives are more likely to leverage new development.

The new crop of membranes on the horizon will extend the growth of gas-separation membranes, both in existing and new applications. The membranes will succeed at first in separations not viable with polymeric membranes… particularly in separations that require very high selectivity. They will displace polymeric membranes in some of the existing separations, but not immediately… only after they are reduced into membrane geometry efficient enough to match the commodity-like low capital cost of polymeric membranes.

As pointed out earlier, this promises to be the most difficult challenge.