Membrane-based Gas Separation: Principle, Applications and Future Potential

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1. INTRODUCTION
Separation processes constitute an integral part of chemical industries for isolation of products and recovery of reactants. Membrane methods of separation are modern techniques which could reduce capital investment, operating cost and process safety. Separation of binary gas mixtures is an important unit operation in a large number of industries to recover valuable gases and enable pollution control. Such separations are currently undertaken by conventional technology viz., cryogenic distillation, adsorption on solid surface and solvent absorption. Now membranes are increasingly finding application for gaseous separations and have exhibited tremendous potential. Large scale gas permeators have already been employed in industrial sectors in the US and some European countries. Membrane technology could compete as well as compliment conventional separation techniques due to its multidimensional character, which involves rapid mass transfer rate and high selectivity towards a specific gas. Inherent advantages of membrane gas separation process are as follows:

- Simplicity of operation and installation.
- Feasibility under mild conditions, for eg. air separation can be carried out at lower pressure and ambient temperature rather than extreme conditions in cryogenic distillation.
- Smaller footprint and flexibility of operation due to compactness of modules with huge reduction in consumption of electricity and fuel.
- No extra agents are required as compared to corrosive and polluting amine solvents in absorption process.
- Continuous mode of operation with partial or complete recycle of retentate/permeate.
- Possibility of integration with other separation units to constitute effective hybrid processes for achieving improved economy and desired purity levels.
- Membranes can be “tailored” to adapt to a specific separation task.
Figure 1. Schematic of Membrane Gas Separation Process

A simple sketch of gas separation by membrane is provided in Fig. 1. The feed gets split into permeate stream and an unpermeate stream also known as retentate. Depending upon the application, either the permeate or retentate could be the final product. The membrane preferably allows one component of the feed stream to pass through it due to preferential interaction and sorption combined with higher diffusivity of the same component owing to differences in molecular size. The kinetic diameters of a few of the common gases along with their other properties are provided in Table 1. The lower the kinetic diameter, the higher the diffusivity.

The development of a potential polymer is the key area of research in membrane technology. The aim in the development of new membranes is to increase the permeability and selectivity or increasing the permeability without compromising the selectivity or enhancing the selectivity at constant permeability. Several researchers have been working to synthesize and use different varieties of membranes for separation of O₂/N₂ from air, CO₂/CH₄ from landfill, biogas or natural gas, CO₂/N₂ in power plants, H₂ recovery in ammonia manufacture or water gas shift reaction and even olefin–paraffin separation in refinery. Membranes can be prepared from different polymers such as polycarbonates, polyimides, polyamides, polyetherimides, or polysulfones by various techniques.

Background and Milestones

The origin of membrane materials for gaseous separations can be dated back to nearly two centuries.
Fig. 2 displays the important milestones in the history and scientific origin of this unit operation as described by Baker in 2002. It is considered that the foundation for gas separation was laid by
Thomas Graham, a Scottish chemist and father of membrane science who studied diffusion of gases and liquids through various media who discovered that certain substances such as glue, gelatin and starch pass through a barrier more slowly than others like inorganic salts, leading to establishing a distinction between the two types of particles, made by the separating media or barrier. In 1855, Fick, an outstanding physiologist, studied gas transport through nitrocellulose membrane and postulated the concept of diffusion which is well-known as ‘Fick’s first law’, a quantitative description of material transport through barriers.

2. THEORY OF GAS PERMEATION

The driving force for gas separation is partial pressure gradient which is the product of total pressure and mole fraction. Most membranes used for gas separation are non-porous.

![Figure 3. Principle of Gas Permeation and Separation](image)

Separation takes place according to the morphology of the membrane which is based on different transport mechanisms. Porous polymer membranes have a pore size ranging from 0.5 to 10 µm and non-porous membranes with a polymer chain gap of $10^{-3}$ to $10^{-4}$µm induced by thermal vibration. Depending on the porosity of the membrane matrix, various transport mechanisms including Poiseuille (viscous) flow, Knudsen’s diffusion, molecular sieving, capillary condensation and solution–diffusion mechanism for gas transport through membranes are proposed as illustrated in Fig. 4. Porous membranes are used to separate the uranium hexafluoro (UF$_6$) isotope gas mixtures to isolate the radioactive U$^{235}$ isotope.
**Mass Transfer through Porous Membranes**

Knudsen’s diffusion occurs in a porous membrane, whose pore sizes are smaller than the mean free path of the gas molecules. Fig. 4(a) reveals the transport of gases through porous membranes by Knudsen diffusion mechanism. Gas molecules interact with the pore walls much more frequently than colliding with one another which allows lighter molecules to preferentially diffuse through pores. Knudsen’s diffusion principally takes place in membranes with a pore diameter in the range of 50-100Å [ref hand book]. Molecular sieving is primarily based on the precise size exclusion and shape discrimination amongst various gas molecules by the micropores of < 7Å in diameter as per Fig. 4 (b).

**Mechanisms of Permeation in Nonporous Membranes**

Transport of gases through nonporous polymeric membranes is usually described by solution–diffusion mechanism (Fig. 4(c)) which consists of three steps, (a) sorption of preferential permeate (solubility) at the upstream surface of the membrane, (b) activated diffusion through the membrane and (c) desorption at the downstream side. Solution-diffusion mechanism is driven by a difference in thermodynamic activities existing across the membrane and interacting forces working between membrane material and permeating molecules. The activity difference causes a concentration gradient that leads to diffusion in the direction of decreasing activity as depicted in Fig. 4 (d). Carbon molecular sieve (CMS) membranes and zeolites are the typical membranes dominated by molecular sieving mechanism and give high separation performance. Ratio of the gas molecular size to micropore diameter controls the permeation rate. Permeability ($P$) is the capability of a membrane to permeate gas molecules:

$$P = D \times S$$  \hspace{1cm} (1.1)

The ability of a membrane to separate two molecules, $A$ to $B$, is the ratio of their permeability, called as the membrane selectivity $\alpha$.

$$\alpha = \frac{P_A}{P_B}$$  \hspace{1cm} (1.2)

For a binary gas mixture the selectivity can also be determined from a molar concentration of the two gases in feed and permeate:

$$\alpha = \frac{y(1 - x)}{x(1 - y)}$$  \hspace{1cm} (1.3)

where $y$ is the permeate concentration of the fast permeating gas and $x$ is its feed concentration.
Gas permselectivity of a membrane can be enhanced by facilitated transport which involves reversible complexation and transport of permeant molecules across a membrane through utilization of a carrier species. The carrier reacts with a permeant molecule to form a labile complex. Within the membrane, the carrier shuttles the permeant across the membrane boundaries to downstream side where the carrier-gas molecule complex breaks allowing the gas to flow into the permeate stream. When a feed mixture contains only one species with which the carrier will react, the transport of that particular species will be “facilitated” or carrier-mediated across the membrane as illustrated in Fig. 5. The driving force in facilitated transport is a
concentration gradient of permeant-carrier complexes across the membrane. It has been found that olefin transport can be facilitated by transition metal ions such as Cuprous and Silver ions which possess vacant $d$-orbitals due to formation of a $\pi$-bond complex.

Fig. 5. Mechanism of Facilitated Transport

Gas separation using facilitated transport is most commonly done with “immobilized liquid” membranes, prepared by dissolving the carrier in an appropriate solvent to impregnate an electrically neutral but rigid microporous polymer matrix. Once formed, surface tension forces serve to hold the carrier molecules inside the membrane.

3. MEMBRANE DEVELOPMENT

**Polymer Selection**

Preliminary criteria for selecting polymeric material for gas separation are based on chemical resistance, sorption capacity and good mechanical strength. However, the key important factors are: (a) intrinsic membrane permeability, (b) ability of the polymer to resist swelling induced plasticization and (c) ability to process the polymer into a useful asymmetric or thin film composite morphology. The polymer should have good interaction, preferably with one of the components of the mixture, for inducing an effective separation. Molecular structure, specific nature of the material, crystallinity and membrane polarity are also some of the important factors, which affect membrane performance. Stability at moderate temperatures specific nature of feed gas feed components besides rubbery or glassy nature of polymers also decides the choice of membrane material. Rubbery materials have high permeabilities, but poor selectivities due to the paucity of polar groups, absence of crystallinity and low degree of cross-linking. Glassy polymers show higher permselectivity and are thus suitable for gas separation studies. Density of
the glassy polymer increases by annealing or plasticization. Hence, high permselectivity can only be obtained with polymers having rigid backbones structures and small inter-segmental gaps i.e., high $T_g$ and resistance to plasticization. In general, any glassy polymer is a combination of amorphous and crystalline phases and knowledge on how crystallinity influences separation would be essential in choosing the right membrane material. Polymers should also be inexpensive to the development of low cost pilot plants. Cellulose acetate, polysulfone, Pebax, PVDF and polyimide have been widely used for several commercial applications.

**Membrane Synthesis**

Membranes can be synthesized by solution casting followed by (a) controlled evaporation of solvent to obtain a dense (nonporous) membrane, (b) partial solvent evaporation and phase inversion in a non-solvent bath to obtain asymmetric film and (c) immediate phase inversion to obtain an ultraporous film. A dense membrane is prepared by casting a bubble free and sufficiently viscous polymer solution on a suitable surface such as an ultraporous polymer substrate or directly on a glass plate by using a doctor’s blade to a predetermined thickness. The blade consists of an adjustable metallic bar resting on metallic supports on either side to form a precise gap between the bar and the plate on which the film was cast. **Fig. 6(a)** illustrates the method used for preparation of a dense Pebax-1657 membrane by casting a 4% (w/v) solution of the polymer prepared in moderately volatile ethanol/water (70/30) solvent mixture. After casting, the solution is left to undergo controlled evaporation of solvent which leaves behind a thin, uniform polymer film. The glass plate is covered with a metal or glass cover and the solvent was made to escape by making a small opening at the edge of the dome with thin sheets of paper. Composite membranes are prepared by solution casting of a thin film of the critical polymer on an ultraporous support followed by solvent evaporation initially at ambient temperature and later at elevated temperature (60-80ºC). **Fig. 6(b)** represents controlled evaporation technique for preparation of dense membrane.

Asymmetric membrane of say cellulose acetate polymer is prepared in a highly volatile solvent such as acetone. After casting directly on a macroporous nonwoven fabric or glass plate, the solvent is evaporated for a time period of 0-60 sec following which it is immersed in a nonsolvent water bath for 5 min to obtain a membrane possessing a dense skin layer supported on a porous layer of the same polymer. The nonporous skin is formed due to almost total solvent evaporation from the upper surface of the cast film whereas residual solvent present in lower layers gets replaced by water molecules to produce pores during the precipitation process.
Physical morphologies of dense and asymmetric membranes are seen in Fig. 7 (a) and (b), respectively. Fig. 7 (c) represents a thin film composite membrane cast on porous substrate.

On the other hand, a porous polyethersulfone (PES) membrane of approximately 20,000 molecular weight cut off (MWCO) is prepared by phase inversion method wherein an 18% w/v solution of PES is prepared in a nonvolatile solvent such as DMF, DMAc or even NMP. 3% propionic acid is used as an additive and the dope is degasified before being cast on a non-woven polyester fabric. After casting, the fabric is immediately immersed in ice-cold water bath for 5 min to obtain a 45-50 µm thick ultraporous PES film which is further washed with water to remove residual solvent.

Fig. 6. (a) Schematic Representation of Doctor’s Blade and (b) Controlled Evaporation
Membrane Characterization

Gas membranes are generally characterized by: (i) Scanning Electron Microscopy (SEM) for studying microstructure, surface/cross-sectional morphology and membrane thickness, (ii) X-ray Diffraction (XRD) for zeolite phase identification in mixed matrix membranes, framework structure and orientation, crystallinity and the intersegmental $d$-spacing, (iii) Fourier Transform Infrared Radiation (FTIR) for determination of functional groups present in the substance, intermolecular interactions and extent of modification induced, (iv) Differential Scanning Calorimetry (DSC) for determination of thermal behavior and $T_g$, (v) Thermo Gravimetric Analysis (TGA) to measure the amount and rate of change in the weight of a material as a function of temperature and (vi) Universal Testing Machine (UTM) to assess tensile strength.

4. EXPERIMENTAL PROCEDURES

Design of Permeability Cell

Basic design of a permeability cell of stainless steel (SS-316) is presented in Fig. 8 which shows three basic components: (i) bottom plate, which houses the perforated plate and membrane, (ii) top plate, which has the provision for feed distribution across the membrane and (iii) locking...
ring to fasten the top plate onto the bottom plate for a leak proof arrangement. A step of 1.5 cm depth is provided in the bottom plate for insertion of a perforated plate. The membrane is fixed on a circular perforated plate of 8.4 cm outer diameter (OD) by applying vacuum grease at the edges. An ‘O’ ring made of neoprene or silicon rubber is placed on top of the membrane following which, the top plate is inserted onto the bottom flange and fastened.

Figure 8. Blowup of Gas Permeability Cell

Fig. 8 shows two internally threaded ports each on surface of top plate for feed inlet and at the downstream surface of the bottom plate for permeate outlet. Adaptors with one side having 1/8" external threading and another side suitable for ¼” nut and ferrule fittings are provided for connecting the cell to the manifold. Aligning pins of 2 mm OD were used during the insertion to ensure that membrane does not undergo movement during the tightening action of the internally threaded locking ring, which presses the top plate onto the rubber ‘O’ ring placed on top of the membrane. Overall thickness of the metal surrounding the membrane enclosure in this leak-proof arrangement is 2.64 cm, which is sufficient to withstand high pressure.

Permeability Measurement

The continuous flow method is most widely chosen to carry out permeability studies with dense membranes of thickness large enough to allow low permeation rates. In this method, a conveniently high gas pressure is applied on one side of the membrane under investigation, and the permeated gas is allowed to expand on the opposite side at low pressure, usually atmospheric. The change in the volume of permeate is then measured as a function of time. If
the permeation rates are low, the feed component permeates through the membrane into a flowing stream of inert gas in the permeate compartment. A schematic of typical gas separation manifold is provided in **Fig. 9** whereas its pictorial representation is given in **Fig. 10**.

![Figure 9. Process Flow Diagram of High Pressure Gas Separation Manifold](image)

The permeate line is evacuated by means of a vacuum pump. The feed gas mixture is introduced slowly into the upper chamber by means of ¼ inch SS 316 needle valves, keeping the outlet valve open for flushing out the retained gas. After flushing the feed line for 5 min, retentate needle valve is closed until the dial gauge indicated the desired pressure. Once the required pressure to measure the permeability was attained, the feed gas was kept in flowing condition near the membrane surface by partially opening the needle valve downstream of the membrane on the retentate line to minimize concentration polarization. Flow rate of permeate was measured with a soap bubble meter and the gas stream is analyzed online by gas chromatography (GC). Retentate gas flowing out of the system is also analyzed by GC simultaneously while doing the experimental studies. The feed gas was analyzed before commencing the experiment to determine exact gas composition with the values specified by cylinder supplier. Permeate, retentate and feed gas stream compositions are used to calculate the permeability and selectivity of the membrane.
After the permeation studies, both feed and retentate lines of the membrane are flushed with the inert gas (N\textsubscript{2}) and permeate line is evacuated to remove sorbed gas mixture to regenerate the membrane to its original state. The permeability of a gas through a membrane is measured at least thrice for reproducibility. For studies with spiral and hollow fiber membrane modules, the retentate valve in the experimental manifold is kept partially open to facilitate the continuous flow of feed gas across the surface of the fibers. The retentate flow is adjusted accordingly to achieve a constant stage cut through the membrane at increasing pressures. The permeate flow rate is directly measured using a wet gas meter and analyzed using the on-line GC equipment.

5. APPLICATIONS OF GAS SEPARATION TECHNOLOGY

*Separation of O\textsubscript{2} and N\textsubscript{2}*

Separation of oxygen (O\textsubscript{2}) and nitrogen(N\textsubscript{2}) from the essentially free air has wide applications. About 60\% of gas separation business involves air processing to produce purifiedN\textsubscript{2} or O\textsubscript{2}, which is fallout of the fact that O\textsubscript{2} and N\textsubscript{2} are the third and fifth largest bulk gases produced worldwide. N\textsubscript{2} is produced by membrane process for inert gas blanketing besides storing and shipping of flammable liquids, fresh fruits and vegetables. Currently, there is limited utility of membranes for commercial-scale production of O\textsubscript{2} and is primarily for medical purposes and industrial combustion. Oxygen-enriched air improves combustion efficiency of coal and is also a desirable feedstock for gasifiers. O\textsubscript{2} currently produced by organic membranes has a purity limit of 50\%. Ideally, new membrane materials with high permeability of ~250 Barrer and O\textsubscript{2} separation factor \( \geq 10 \) are desirable to enhance feasibility of industrial oxygen production.
Separation of H\textsubscript{2} from Hydrocarbon Gases

Hydrogen is the fuel of the future. Use of hydrogen as an energy source could address issues related to global climate change, energy security, and local air pollution. Recovery of H\textsubscript{2} by membranes is important in refineries where light hydrocarbon gases are also produced which need to be purged from the reaction system. H\textsubscript{2} value in the purge gas can be used as fuel. There are in fact two major incentives to recover hydrogen from refinery off gases. One is that H\textsubscript{2} in the purge stream, if recovered, can be as much as 20\% of the total H\textsubscript{2} generated in refinery plants. Additionally, the cost of H\textsubscript{2} manufacture is increasing for various critical refining processes including coking, hydrocracking and hydrodesulfurization. Membrane processing competes with other separation processes like pressure swing adsorption (PSA), cryogenics and oil scrubbing for these applications. Separation of H\textsubscript{2} from methane has been identified as one of the promising future applications of inorganic membrane technology in refineries.

Separation of H\textsubscript{2} and CO

Synthesis gas contains a mixture of mostly H\textsubscript{2} and CO plus low percentages of CO\textsubscript{2} and N\textsubscript{2}. Transition metal catalysis is used in a number of reactions for preparing variety of organic and inorganic compounds such as alcohols, aldehydes, acrylic acids and ammonia. The stoichiometry of feed gas for these reactions must be adjusted according to the process requirements. The ratios of H\textsubscript{2} to CO and other gases in the feed streams in those chemical production processes can be varied by selective removal of H\textsubscript{2} as permeate through a membrane. In this case, CO comes out at the retentate side at high pressure which is an advantage over other separation processes such as cryogenic distillation and PSA. Another important application is the removal of CO from H\textsubscript{2} produced during steam reforming of natural gas.

Separation of H\textsubscript{2}/N\textsubscript{2} Mixtures

Ammonia is typically made from synthesis gas at a temperature of 500 °C and pressure of 300bar. Incomplete conversion to ammonia results in a need to recycle unreacted gases back to the reactor. The purge gas contains valuable H\textsubscript{2} and N\textsubscript{2} as the major components. To reuse them after purge, H\textsubscript{2} and N\textsubscript{2} need to be separated from the purge gas, which can be achieved at lower cost using organic membranes. In this application, H\textsubscript{2} is separated as permeate at low pressure side of the membrane and recompressed to the pressure of the reactor before recycle.

Acid Gas Removal from Natural Gas

The worldwide market for latest natural gas separation purification is estimated at approximately US$ 5 billion/year. The natural gas treatment process is dominated by amine absorption. In
recent years, membrane process has been accepted as a promising technology for natural gas separation since high efficiency has been observed in membrane-based separation in upgrading natural gas through removal of water and acid gases H₂S and CO₂. To reduce toxicity these impurities must be removed from natural gas stream before delivering to a pipeline for minimizing pipeline corrosion and improve calorific value. Membranes can be used for bulk removal of CO₂ and H₂S from natural gas followed by final clean up using amine absorption to forge an economical and energy efficient integrated process that would involve lower amine circulation rates and hence lesser pollution. However, glassy polymeric membranes suffer from plasticization in the presence of trace quantities of condensable heavy hydrocarbons, which cause the loss of selectivity. Hence, the development of robust membrane materials is imperative to widespread commercialization of natural gas sweetening.

**Olefin/paraffin Separation**

Aliphatic unsaturated hydrocarbons play an important role in chemical synthesis. Thus, the separation of olefin-paraffin mixtures is of great significance in synthetic industrial processes. Propylene is one of the products of fluid catalytic cracking of hydrocarbon feed stocks. Liquefied petroleum gas (LPG) components include ethane (C₂H₆), ethylene (C₂H₄), propane (C₃H₈) and propylene (C₃H₆), as well as higher hydrocarbons like butane (iso and normal), butylene, pentanes etc. From this mixture the separation of propylene to >95% purity by economical means is a challenging task due to the similar molecular sizes and physical properties of most of these gases comprising the refinery gas mixture. Currently the separation of this mixture is carried out by distillation, which is highly energy intensive due to nearly 100 stages present in a long thin column called C₃ splitter where usually 66% C₃H₆+34% C₃H₈ is the feed. As a consequence, membrane separation with simple operation, low power consumption and better economy holds high potential for olefin/paraffin separations provided the right membrane material is developed.

**CO₂ Sequestration**

Global warming has been identified as one of the world’s major environmental issues. While it is impossible to completely stop the effects of anthropological global warming, it is possible to mitigate these effects via a variety of options. One such option is the reduction of greenhouse gas emissions through the capture of CO₂ from flue gases followed by underground sequestration. Flue gas is the gas exiting to the atmosphere for conveying exhaust gases from a fireplace, oven, furnace, boiler or steam generator. Quite often, the flue gas refers to
the combustion exhaust gas produced at power plants. Its composition depends on what is being burned in furnace such as solid-fuel-fired, gas-fired, gas turbine plants, oil-fired and coal-fired, but it will usually consist of mostly N\textsubscript{2} derived from the combustion air, CO\textsubscript{2} and water vapor as well as excess O\textsubscript{2} (also derived from the combustion air). CO\textsubscript{2} emissions from coal-fired power plants are believed to contribute significantly to global warming climate change. The direct approach to address this problem is to capture the CO\textsubscript{2} in flue gas and sequester it underground. In particular, the capture of CO\textsubscript{2} from high concentration sources allows storage options, such as geo-sequestration, to reduce emission levels. The conventional process for CO\textsubscript{2} capture is by reversible solvent absorption which is energy intensive and solvent regeneration requires high heating utility in the stripper. Membrane technology is an attractive and competitive alternative to conventional absorption technology in this case.

6. UPSCALING OF GAS MEMBRANE
The building block of a membrane system is called a module. All module types developed so far are based on two geometries: flat sheet and tubular. Configurations based on flat sheet membranes are plate-and-frame and spirally-wound modules, whereas tubular and hollow fiber modules are based on fine capillaries or tubes housed like a shell and tube heat exchanger. Photograph of a typical hollow fiber membrane prepared by melt extrusion of Poly(etheretherketone) (PEEK) polymer is depicted by Fig. 11.

Plate-and-Frame Module
Plate-and-frame modules are one of the earliest types of membrane assemblies. They are the closest to common laboratory set-ups. The membrane, feed spacer and product spacers are layered together, like in a sandwich as shown in Fig. 12 (a) between two end plates. The feed gas is passed across the membrane surface and the spacer plate distributes the feed flow within the module. Packing density in this module is 100 to 400 m\textsuperscript{2}/m\textsuperscript{3}.

Spiral-Wound Module
A spirally-wound module is a plate-and-frame system wrapped around a central perforated pipe collecting the permeate as shown in Fig. 12 (b). A spacer is placed in between the membranes to avoid contact of feed and permeate and also to provide clearance for gas to interact with the membrane. The entire permeate gas is collected in a pocket like envelope and carried to the perforated central tube. Precaution is taken to avoid bypass of feed by using an ‘O’ ring between the module outer circumference and shell inner diameter. The feed flows through the module in axial direction, whereas the permeate flows in radial direction towards the center. The packing
density of spirally-wound modules is higher than that of plate-and-frame modules (around 300-1000 m²/m³) and depends strongly on the channel height.

**Hollow Fiber Module**

Hollow fiber membrane module consists of thin, fine capillaries collected together and made into a bundle. This bundle is perfectly potted on both the ends to arrest any leakage between feed and permeate chambers and then placed in the housing as shown in Fig.12 (e). Hollow fiber modules can be operated in two ways, either “inside-out” where permeate is collected outside the membrane in the housing or “outside-in” where permeate passes into the membrane bore called lumen. Depending on feed and permeate flow patterns, modules can be operated in cocurrent or countercurrent mode. Fibers are generally between 1.0–1.5 mm in outer diameter and arranged parallel to one other to pass through tube-sheets at either one or both ends of the device. Seals are provided between the tube-sheet exterior and the pressure vessel to isolate the high-pressure feed from low-pressure permeate. The bore of the fibers are generally of 0.5–1 mm diameter.

The hollow fiber module is renowned for its high packing density which can reach values of 10,000-30,000 m²/m³.

**Tubular Module**

Tubular membranes are mostly nanoporous zeolite membrane layer supported on porous ceramic tube, mostly on the inner side of a support tube, with some coated on outer surface of the ceramic substrate as well. Tubes can be used individually or grouped together in a package shown in Fig.12 (d). Membranes are placed inside a support porous tube and these tubes are placed together in a cylindrical shell to form the unit module. The flow in a tubular membrane is usually inside out, which is due to weak attachment of membrane to the supporting layer. Tubular membranes are produced with inner diameters from 5–25mm, the most common is 12.5 mm.

![Fig. 11. Picture of PEEK Hollow Fiber for Gas Separation Supplied by PoroGen](image-url)
7. RESULTS ON PURIFICATION OF NATURAL GAS AND BIOGAS

Natural gas mainly consists of methane (79-84 mol %) as the major useful constituent, higher hydrocarbons, mostly paraffins (3-7%) besides impurities such as acid gases H₂S (ppm level) and CO₂ (5-8 mol%) and some moisture (ppm level). Natural gas is available at high pressures of 55–67 bar with specific gravity of 0.57-0.62 and gross heating value of 36-41 MJ/m³. The first pilot plant in India funded by DSIR, New Delhi was designed by EIL-Gurgaon and CSIR-IICT based on a thin film composite Pebax membrane developed by CSIR-IICT. Fig.13 exhibits a flow sheet for isolation of pure propylene by an integrated process of distillation and membrane gas separation. Propylene is a major feed stock for production of polypropylene, isopropanol, acrylonitrile, propylene oxide, epichlorohydrin and cumene. Propylene is produced by the catalytic dehydrogenation of propane which results in an equimolar mixture of the olefin and unreacted paraffin. The mixture is fed to a membrane unit which provides a permeate enriched in propylene that is further sent to a distillation column which enriches propylene as the top product. The bottom product of the distillation column is lean in propane and recycled back to the membrane unit. The C₃ splitter in a refinery is a long column comprising of 95 trays due
to the similar physical properties and molecular sizes of propane and propylene. This hybrid process configuration can be extended to petroleum refineries where the C\textsubscript{3} stream coming from debutanizer is sent to the membrane column first, and subsequently the propylene rich permeate is processed in a shorter C\textsubscript{3} splitter distillation column whose number of stages gets reduced due to the membrane stage. Top product from debutanizer would require compression to provide driving force for membrane separation. Such a venture needs funding and risk taking to enhance feasibility of commercialization.

**Fig. 14** displays a different attempt made by the authors to enrich methane present in biogas mixture by selective removal of the same acid gases which are produced along with CH\textsubscript{4} during the anaerobic digestion of solid waste material. This particular biogas mixture contains about 40-45 mol\% methane, 30-35\% CO\textsubscript{2}, 1000 ppm of H\textsubscript{2}S and N\textsubscript{2} (balance). The modules used here are commercial hollow fiber ones based on polysulfone supplied by Solvay, USA and Matrimid Polyimide procured from University of Twente, The Netherlands. The GC chromatograms show that nearly pure CO\textsubscript{2} is obtained in permeate at atmospheric pressure and ambient temperature, indicating high degree of separation. However, once the pressure is increased CH\textsubscript{4} molecules also passed through the barrier leading to lower efficiency of separation and fuel losses. Development of indigenous polyimide membrane is a big challenge which could enable lowering of capital and running costs. It is worth mentioning that most membranes allow more rapid permeation of moisture, followed by H\textsubscript{2}S and then CO\textsubscript{2}. However the selectivity of CO\textsubscript{2}/CH\textsubscript{4} gas pair is critical in achieving success.

**Factors that Influence Membrane Performance**

There are several factors affecting membrane performance in a gas permeation process including a change in feed composition which will directly affect the sorption phenomena or degree of swelling at the gas membrane interface as envisaged by the sorption-diffusion principles. Since diffusion of gaseous components in the membrane is dependent upon the concentration of the component or solubility of the components, permeation characteristics are greatly influenced by the feed composition. Coupling effects between two or more species could occur in multi-component feeds, which may considerably influence the selectivity. Similarly, higher concentration of condensable species could plasticize the membrane. The driving force in gas separation is the partial pressure gradient across the membrane. The flow of a component, say \textit{i}, across the membrane can occur only if its partial pressure at the feed side of the membrane is greater than that at the permeate side. In general, solubility decreases with increasing
temperature, while diffusivity increases. A membrane processing high selectivity at ambient temperature may yield poor separation at elevated temperatures.

**Figure 13. Proposed Process Integration of Distillation with Gas Separation for Propylene Recovery**

**Figure 14. Preliminary Results for Biogas Purification by Polysulfone and Polyimide Hollow Fiber Membranes**
In pressure driven processes, different individual component permeation rates generally cause an increase of the less permeable component in the boundary layer near the membrane surface. This inhibits the rate of transport of the more permeable species and subsequently, the selectivity. However, such effects are rare or nonexistent for gas separations due to the much greater gas phase external diffusion coefficients as against liquid feeds. Performance of any membrane depends upon the nature of its base material. Polarity is one of the polymer properties which contribute considerably to its separation performance. In order to separate a particular component in a particular feed mixture, the polarity of one of the components must be close to the polarity of the membrane.

8. STATE−OF−THE−ART AND FUTURE PROSPECTS

Compared to conventional separation technologies such as cryogenic distillation, absorption and adsorption, growing academic and industrial attentions are now focused on membrane-based gas separation. This is due to the fact that gas separation may offer inherent advantages such as energy efficiency with low capital investment, simplicity and ease of installation, low operation and maintenance cost, low weight and space requirement with high process flexibility.

Gas transport properties of polymer films are not only important for industrial production of high purity gases, but also in synthesis of barrier materials for food packaging and beverage industries. Membrane gas separation process is an emerging technology on industrial scale in the late seventies when Prism® was introduced in 1978. Since then the utilization of membrane technology in gas separation has rapidly expanded and undergone broad usage/interest in industrial sector. Membrane gas separation impacts the separation business with US$250 million a year. Prediction of the advancing economy of membrane based gas separations is presented in Table 2, wherein only the major applications for gas separation membranes are considered.

<table>
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<tr>
<th>Type of Separation</th>
<th>Membrane Market (US$ Million)</th>
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<tr>
<td></td>
<td>2010</td>
</tr>
<tr>
<td>Isolation of Inert N₂ from Air</td>
<td>100</td>
</tr>
<tr>
<td>O₂ Enrichment from Air</td>
<td>10</td>
</tr>
<tr>
<td>H₂ Recovery</td>
<td>60</td>
</tr>
<tr>
<td>CO₂ Removal from Natural Gas</td>
<td>60</td>
</tr>
<tr>
<td>Vapor/Nitrogen Separation</td>
<td>30</td>
</tr>
<tr>
<td>Vapor/Vapor Separation</td>
<td>20</td>
</tr>
<tr>
<td>Removal of Moisture from Air and others</td>
<td>30</td>
</tr>
</tbody>
</table>
A view of recent literature enables tracking of the development of novel polymers synthesized by researchers or types of commercial membranes used for industrial gaseous separations. Dense membranes show higher selectivity compared to porous membranes due to less free volume and the solution-diffusion made of mass transfer. Rubbery polymers exhibit high permeabilities and their selectivity is influenced by differences in the condensability of the gas species. In this area, polyurethanes, polyamides and poly(organo siloxanes) were studied in detail because of the vast utility of poly(dimethylsiloxane) (PDMS) which has a very low glass transition temperature. This silicone polymer has a flexible backbone but exhibits adequate selectivity.

Various types of membranes have been developed for specific industrial applications, but are unable to see the light of day due to problems arising in scale-up of such membranes to modular configurations which is a very challenging task. Since the early beginning of gas permeation, several membranes have been synthesized with the earliest ones being based on polysulfone and cellulose acetate. Table 3 reveals the established global system suppliers for various applications in the field of membrane gas separation. One of the recent small applications shown in the table is natural gas dehydration. These polymer types still predominate but have been joined by polyimides, polyamides, polycarbonates, polyetherimide and sulfonated aromatic polymers as seen from Table 4.

**Future Prospects and Scope for Further Research**

- Integration of membrane gas separation with amine absorption for treatment of natural gas, landfill gas and biogas for enrichment of methane.
- Development of hybrid process of membrane and adsorption with molecular sieves for recovery of hydrogen from refinery off-gases.
- Synthesis of facilitated transport membranes for enrichment of oxygen from air and separation of olefin-paraffin mixtures.
- Development of both flat sheet and hollow fiber mixed matrix membranes consisting of organic polymers incorporated with inorganic fillers to enhance both flux and selectivity.
- Scale-up of mixed matrix and facilitated transport membranes for industrial application.
- Mathematical modeling and computer simulation for design of more efficient gas permeators.
Table 3. Major Global Suppliers of Gas Membrane Systems

<table>
<thead>
<tr>
<th>Gas Mixture</th>
<th>Application</th>
<th>Supplier</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂/N₂</td>
<td>Nitrogen generation</td>
<td>Perma (Air Products), Generon (IGS), IMS (Praxair), Medal (Air Liquide), Parker Gas Separation, Ube</td>
<td>USA</td>
</tr>
<tr>
<td></td>
<td>Oxygen enrichment</td>
<td></td>
<td>USA</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Canada</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>USA</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>USA</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>USA</td>
</tr>
<tr>
<td>H₂/Hydrocarbons</td>
<td>Refinery H₂ recovery</td>
<td>Air Products, Air Liquide, Ube, Praxair</td>
<td>USA</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Canada</td>
</tr>
<tr>
<td>H₂/CO</td>
<td>Syngas ratio adjustment</td>
<td>Air Products, Air Liquide, Ube, Praxair</td>
<td>USA</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Canada</td>
</tr>
<tr>
<td>H₂/N₂</td>
<td>Recovery of H₂ from ammonia purge gas</td>
<td>Air Products, Air Liquide, Ube, Praxair</td>
<td>USA</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Canada</td>
</tr>
<tr>
<td>CO₂/CH₄</td>
<td>Acid gas treatment, Enhanced oil recovery, Upgrading landfill gas</td>
<td>Cynara (NATCO), Air Products, Ube, Kvaerner</td>
<td>USA</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>USA</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Norway</td>
</tr>
<tr>
<td>H₂S/ Hydrocarbons</td>
<td>Sour gas treatment</td>
<td>Cynara (NATCO), Air Products, Ube, Kvaerner</td>
<td>USA</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>USA</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Norway</td>
</tr>
<tr>
<td>H₂O/ Hydrocarbons</td>
<td>Natural gas dehydration</td>
<td>Kvaerner, Air Products.</td>
<td>Norway</td>
</tr>
<tr>
<td>H₂O/Air</td>
<td>Air dehydration</td>
<td>Air Products, Parker Balson, Praxair</td>
<td>USA</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Canada</td>
</tr>
<tr>
<td>Hydrocarbons/Air</td>
<td>Pollution control, Hydrocarbon recovery</td>
<td>Borsig, GMT, MTR</td>
<td>Germany</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Canada</td>
</tr>
</tbody>
</table>

Table 4. List of Commercial Gas Membranes and their Modular Configurations

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Module type</th>
<th>Gas Mixture System</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polysulfone</td>
<td>Hollow fiber</td>
<td>O₂, N₂, H₂, H₂O, CO₂</td>
<td>Perma (Air products)</td>
</tr>
<tr>
<td>Polyimide/polyaramide</td>
<td>Hollow fiber</td>
<td>H₂,N₂,O₂</td>
<td>Medal (Air Liquide)</td>
</tr>
<tr>
<td>Tetrabromo polycarbonate</td>
<td>Hollow fiber</td>
<td>N₂</td>
<td>Generon (MG Industries)</td>
</tr>
<tr>
<td>Polyimide</td>
<td>Hollow fiber</td>
<td>N₂, H₂O</td>
<td>IMS (Praxair)</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>Spiral wound</td>
<td>CO₂</td>
<td>Kvaerner</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CO₂, H₂</td>
<td>Separex (UOP)</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>Hollow fiber</td>
<td>CO₂</td>
<td>Cynara (Dow)</td>
</tr>
<tr>
<td>Polyimide</td>
<td>Hollow fiber</td>
<td>Air dehydration</td>
<td>Perker Hannifin</td>
</tr>
<tr>
<td>Polyimide</td>
<td>Hollow fiber</td>
<td>O₂, N₂, H₂</td>
<td>Ube</td>
</tr>
<tr>
<td>Silicone rubber</td>
<td>Plate and frame</td>
<td>VOCs</td>
<td>GKSS licensees</td>
</tr>
<tr>
<td>Silicone rubber</td>
<td>Spiral wound</td>
<td>VOCs</td>
<td>MTR</td>
</tr>
</tbody>
</table>
REFERENCES

**About the Authors**

**Dr. S. Sridhar** is a Chemical Engineer working as Principal Scientist and Project Leader of Membrane Separations Group at CSIR-Indian Institute of Chemical Technology (IICT), Hyderabad, India. He has developed several technologies for solvent recovery, gas purification and wastewater treatment for chemical industries. He has also contributed immensely to rural welfare through water purification besides academia & education by training 200 students. He has published 173 research papers including 89 in peer reviewed journals, 6 popular science articles, 73 publications in proceedings of symposia/conferences and 4 book chapters. Dr. Sridhar has 7 international patents to his credit and is a recipient of 14 prestigious awards including CSIR & Scopus Young Scientist awards and Engineer of the Year Award from A.P. State Govt.

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