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A Review of Membrane Technology for Gas Separation

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ABSTRACT

Membrane separation is now worldwide acknowledged as a cost-effective process to produce moderate purity streams containing up to 98 - 99.5 % nitrogen or 25-40 % oxygen. Therefore, the demand for higher product purity of membrane air separation had motivated carrying out of this study. The objective of this study is to testing a suitable membrane for gas separation, gas separation membranes are extensively used for the separation of gas. Polymeric membranes have mechanical strength, reproducibility and economical processing capacity. However they suffer from upper bound trade-off between permeability and selectivity. Inorganic membranes have high selectivity, robustness, thermal and chemical stability but these membranes are economically unfavourable due to high capital and maintenance cost. In mixed matrix membrane superior gas separation properties of inorganic membranes and economical processes ability of polymeric membranes are exploited by combining the inorganic particles in polymer matrix. In case of glassy polymer, poor distributions of dispersed phase in polymer matrix and week contact of particles in polymer matrix are the challenges in mixed matrix membrane. For rubbery polymers, poor selectivity of mixed matrix membrane is the core problem. Blending of a glassy and a rubbery polymer with amines is suggested to develop a polymeric blend membrane by coating the polymer blend with different amines of high selectivity and permeability. The developed membrane will be characterized and its performance will be evaluated for the separation of gas terms of selectivity and permeability.

Keywords: Membrane Technology, Gas Separation, Rubbery Polymers, Mixed Matrix Membrane, Polymeric Membranes.

I. INTRODUCTION

Gas separation is an important unit operation employed widely throughout the chemical industries. Examples include the separation of air into oxygen and nitrogen, and the removal of volatile organic compounds from effluent streams. The traditional methods used for such separations include cryogenic distillation and adsorbent bed processes. In recent times, however membrane-based gas separation is becoming increasingly popular due to its inherent advantages over the more traditional methods. These include low capital and operating costs, lower energy requirements and generally ease of operation. A membrane may be simply defined as an interphase between two bulk phases [1]. During the last 30 years, the use of membranes in separation processes has grown at a very rapid pace. Presently membrane-based processes are being used in a wide array of applications, such as microfiltration, ultrafiltration, nanofiltration, reverse osmosis and electrodialysis [1, 2]. Gas separation in membranes occurs due to differences in permeability's of the species flowing through the membrane. With a few exceptions, membranes used for gas separation can be broadly categorized into two major classes: porous inorganic and dense polymeric. Porous membranes have a well-defined static pore structure, which depending on the formation process can be highly connected and torturous or non-connected and straight. Pores in inorganic membranes can be classified according to their size as macropores (>500A°), mesopores (500–20A°) or micropores (<20A°) [3]. Across these pore size regimes, gas transport in inorganic membranes may occur via a host of four different types basic principles or mechanisms of gas separation Representation is given the figure 1:

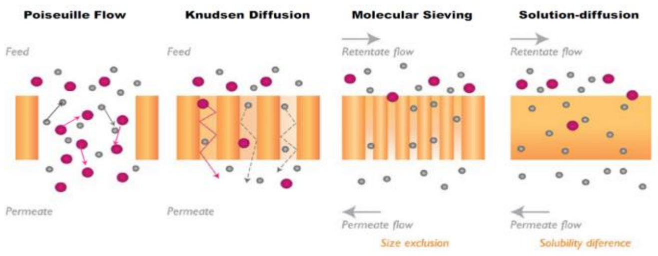


Figure 1: Schematic diagram of transport mechanism in gas separation membranes [4]

1.1 Poiseuille Flow

Poiseuille flow is also known as viscous flow. It occurs when the pore radius (r) inmembranes is larger than the mean free path (λ) of the gas penetrants. The mean freepath refers to the average distance traversed by a gas molecule during collisions and is represented by equation (2.1). During collisions, the membrane contains pores largeenough to allocate convective flow, where gas molecules collide exclusively with each other and there is no separation between the gas components. Poiseuille flow takes place when the membranes have much larger pore sizes than gas molecules which are larger than 10 μm[4-6].

$$\lambda = \frac{3\eta}{2P}\left(\frac{\pi RT}{2M}\right)^{0.5} \qquad \text{Equation 2.1}$$

Where η is the gas viscosity, P is the pressure, T is the temperature, R is the universal gas constant and M is the gas molecular weight [4].

1.2. Knudsen diffusion

Knudsen diffusion happens when the pore size of the membrane decreases to 50-100Å in diameter. The penetrant gas flows through the membrane almost independent from each other during Knudsen diffusion. For an equimolar feed, the selectivity, α induced by Knudsen diffusion is inversely proportional to the square root of the molecular weight of the respective two gases as shown in the following equation[4-6]

$$\alpha_{x/y} = \sqrt{\frac{M_y}{M_x}} \qquad \text{Equation 2.2}$$

Where M_{x} and M_y are the gas molecular weights of gas x and gas y, respectively. Membrane with Knudsen diffusion is not favorable for industrial application due to its relative low gas-pair selectivity [4-6].

1.3 Molecular Sieving

Molecular sieving mechanism is the separation based on the size discrimination between gas penetrant in the pores less than 7Å in diameter. In this transport mechanism, gases with small molecular size and high diffusion rate are able to permeate through the ultra-microspores of the polymer while the gases with large molecular size will experience a stronger repulsive force and restricted them from passing through. In general, molecular sieving is the main mechanism for inorganic separation such as zeolites and carbon molecular sieves. The porous membrane yields high permeability while the selectivity is based on the size discrimination between the gases [4-6]

1.4 Solution diffusion

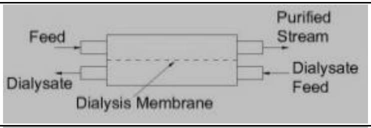
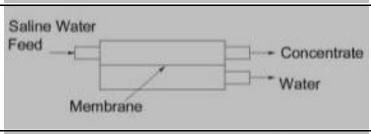
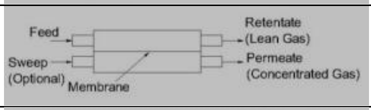
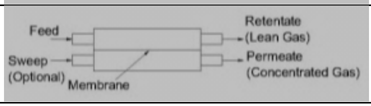
The solution diffusion mechanism is most profound in explaining the transportation ofgases in dense or non-porous polymeric membranes. Conceptually, this mechanism comprises of three steps. Firstly, gases adsorb into the polymer at the boundary in contact with the feed. Secondly, gas molecules diffuse across the membranes through a concentration gradient. Thirdly, gases desorb at the permeate side [4-6]

II. METHODS AND MATERIAL

2. Literature Review

Membrane technology covers all engineering approaches for the transport of substances between two fractions with the help of permeable membranes. In general, mechanical separation processes for separating gaseous or liquid streams use membrane technology. Membrane separation processes operate without heating and therefore use less energy than conventional thermal separation processes such as distillation, sublimation or crystallization, etc. The separation process is purely physical and both fractions (permeate and retentate) can be used. Cold separation using membrane technology is widely used. Membrane separation processes have a very important role in the separation industry.

Membrane separation processes differ based on separation mechanisms and size of the separated particles. Some of the widely used membrane processes are shown in the table 2.1 [7].

Process	Concept	Materials Passed	Driving Force	Materials Retained
Dialysis		Ions and Low-Molecular Weight Organics	Concentration Difference	Dissolved and Suspended Material with Molecular Weight > 1000
Reverse Osmosis		Water	Pressure Difference, Typically 100-1500 psi	Virtually All Suspended and Dissolved Material
Gas and Vapor Separations		Gases and vapors	Pressure Difference, Typically 15-1500 psi	Membrane-Impermeable Gases and Vapors
Vapor-Liquid Separation		Vapors	Pressure Difference and Vapor-Liquid Equilibrium	Membrane-Impermeable Liquids and Vapors

2.1 What is Membrane

A membrane is a selective barrier; It allows some things to pass through but stops others. Such things may be molecules, ions, or other small particles. The influent of an artificial membrane is known as the feed-stream, the liquid that passes through the membrane is known as permeate, and the liquid containing the retained constituents is the retentate or concentrate [8-9]. The ideal representation of the membrane concept is shown in the figure 2 below.

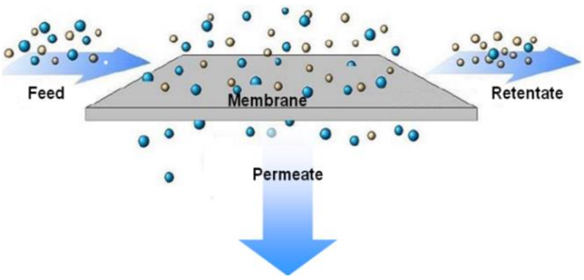


Figure 2: Idealized membrane flow concept. (Source: Internet)

2.2 Industrial Applications of Membrane in Gas Separation

Membrane separation processes have very important role in separation industry because membrane separation processes is that it operate without heating. Nevertheless, they were not considered technically important until mid-1970. The industrial gas separation is widely spread by using the membrane in last 25 years. The multiple application of gas separation Membrane is listed in Table 2.2.1[7, 16]

Gas Separation	Application
O_2/N_2	Oxygen enrichment, Nitrogen (Inert Gas) Separation
H_2/Hydrocarbons	Refinery hydrogen recovery
H_2/CO	Syngas ratio adjustment
H_2/N_2	Ammonia purge gas
CO_2/Hydrocarbons	Acid gas treatment enhanced oil recovery, landfill gas upgrading
H_2S/Hydrocarbons	Sour gas treating
H_2O/Hydrocarbons	Natural gas dehydration
He/Hydrocarbons	Helium separation
H_2O/Air	Air dehydration
He/N_2	Helium recovery
Hydrocarbon/Air	Pollution control, hydrocarbon recovery
Hydrocarbons from process streams	Organic solvent recovery, monomer recovery

2.3 Issues and Challenges in Membrane Applications for Gas Separation

The following issues and challenges occur in membranes application for gas separation [7-9]

2.3.1 Membrane Fouling
2.3.2 High Cost
2.3.3 Concentration of Polarization
2.3.4 Lack of selectivity
2.3.5 Lack of mechanical resistance
2.3.6 Sensitivity to chemical attack
2.3.7 Membrane cleaning

2.3.8 Module Design

2.4 Materials for Gas Separation Membrane

The selection of material membrane is the most important factor for Gas Separation. Chemical interaction between a membrane material and a gas penetrant determined the separation efficiency of a membrane separation process [10]. The choice of material is based on the application and cost-effectiveness. The most important requirements of effective separation material are:[11,12]

2.4.1. Engineering feasibility.
2.4.2. Good chemical resistance.
2.4.3. High separation efficiency with reasonable high flux.
2.4.4 Good mechanical stability.
2.4.5. High thermal stability.
2.4.6. Low cost.

2.5 Membrane used for Gas Separation

2.5.1 Polymeric Membranes

Polymeric membranes perform their process by different mechanisms which are based upon the properties of membrane means physical and chemical structure, interaction between membrane, component and nature of gas [13]. It can be classified into two types: porous and non-porous [14, 16]. A porous membrane is a rigid, highly voided structure with randomly distributed interconnected pores like a conventional filter. Separation is dependent on molecular size of polymer and pore size distribution. These membranes exhibit high fluxes but they are inherently low selective. Non porous membrane also called as dense membrane consists of a dense film. Permeate molecules are first absorbed and then diffused through polymer matrix under the driving force of pressure or concentration gradient. Dense membranes are highly selective but transport of gas through the polymer medium is very low. Permeate of similar sizes can be separated by dense membranes if they have significantly different solubility in polymer. Polymeric membranes can be classified on the basis on polymer material.

Glassy Polymer At a low temperature the amorphous regions of a polymer in the glassy state, the molecules are frozen on place. They may be able to fluctuate slightly, but they do not have any segmental motion in which portions of the molecule wiggles around. Whenever the amorphous regions of a polymer are in the glassy state, it generally will be brittle, hard and rigid [14, 16].

Rubbery Polymer If the polymer is heated it eventually will reach its glass transition temperature. The molecules can start to wiggle around at this temperature. The polymer now is in its rubbery state. The rubbery state tends to softness and flexibility to a polymer. Semi-crystalline solids have both crystalline and amorphous regions. Accordingly the temperature, in the amorphous regions can be either in the rubbery or glassy state. Temperature at which the transition in the amorphous regions between the glassy and rubbery state occurs is called the glass transition temperature. The amorphous portion of semi-crystalline solid contains the glass transition property. During the glass transition the crystalline portion remains crystalline. There is a general tradeoff between permeability and selectivity for polymeric membranes with rubbery polymeric membranes with high permeability and low selectivity and vice versa for glassy polymeric membranes. Despite their mechanical strength, reproducibility and economical processing capacity, dense membranes are still not much attractive because they suffer from upper bound tradeoff between permeability and selectivity [14, 16].

2.6 Comparison of Polymeric, Inorganic and Mixed Matrix Membranes

A comparison of polymeric, organic and mixed matrix membrane is given in table in terms of cost, chemical and thermal stability, and mechanical strength, compatibility to solvent, swelling, separation performance and handling. It is clear from the table that polymeric membranes are economical to fabricate and have good mechanical strength. Their separation performance and stability is moderate and these are robust in handling. Their main disadvantage lies in swelling and compatibility to solvent. However still for industrial applications polymeric membranes are preferred. Different techniques are being used to improve the performance of polymeric membranes to withstand required duties. Blending is a cost and time effective method to develop materials with desired properties [15, 16].

Properties	**Polymeric membranes**	**Inorganic membranes**	**Mixed matrix membranes**
Cost	Economical	High	Moderate
Chemical and thermal stability	Moderate	High	High
Mechanical Strength	Good	Poor	Excellent
Compatibility to solvent	Limited	Wind Range	Limited
Separation Performance	Frequently Occurs	Free of swelling	Free of swelling
Swelling	Moderate	Moderate	Exceed Robeson upper boundary
Handling	Robust	brittle	Robust

III. CONCLUSION

The present research addresses the current needs of having high permeability and selectivity membrane for removal of gas. The developed polymer blend membranes have improved flexibility, reduced cost, improved process ability, and enhanced selectivity and/or permeability compared to the comparable polymer membranes that comprise a single polymer. It will be possible to develop polymeric blend membrane for separating high pressure gas streams at their processing pressure. This advantage could offer cost savings that may provide a new incentive for polymeric blend membranes. This result opens a new tool for studying gas separation by polymeric blend membranes.

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