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**A LITERATURE-REVIEW OF  
GAS SEPARATION MEMBRANES**

ERL 91-72 (CS)



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**A LITERATURE REVIEW OF  
GAS SEPARATION MEMBRANES**

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Sept. 1991**

**ENERGY RESEARCH LABORATORIES  
DIVISION REPORT ERL 91-72(LS)**

# A LITERATURE REVIEW OF GAS SEPARATION MEMBRANES

by

T.M. Giddings and B.A. Farnand

## ABSTRACT

A literature review has been made of membranes for the separation of gases. Applications which are presently feasible include the recovery of hydrogen from ammonia purge streams, catalytic cracker purge gas, hydrotreater off-gas, separation of carbon dioxide from hydrocarbons for enhanced oil recovery, and purification of nitrogen gas from compressed air. Selectivity of membranes to various gas streams depends on differences in molecular weight and also on large differences in chemical properties such as hydrophobicity and hydrophylicity. Although many gas separations are presently possible, further development is required to separate other gas streams such as hydrogen sulphide/carbon dioxide or organic vapours.

## INTRODUCTION

The impact of membranes on industry is evident in many technologies. Their use is becoming well established in areas such as hydrocarbon processing, chemical purifications, water desalination, liquid waste processing and pharmaceutical and biotechnological processing. More recently membranes have been applied to refineries, chemical plants, and natural gas reservoirs for the separation or purification of mixed gas streams<sup>(1,2)</sup>.

Membrane separation of air for the enrichment of O<sub>2</sub> has applications to the medical field. Also in industry, air enriched in oxygen (to approximately 35% O<sub>2</sub>) can produce higher furnace temperatures as well as reducing the volume of parasitic nitrogen to be heated, thus lowering total energy consumption.<sup>3</sup>

Separations of CH<sub>4</sub>, Ar and H<sub>2</sub> show potential to be the dominant separation process in the purification of purge gas in ammonia production plants. Recovery of H<sub>2</sub> from the purge gas stream which consists of N<sub>2</sub>, Ar, CH<sub>4</sub> was performed by cryogenic separation<sup>(2,4)</sup>. However, membrane processes offer the advantages of operating at near ambient temperatures, and having no moving parts, resulting in lower operating and maintenance costs<sup>(5)</sup>. Data available on the lifetimes of membranes is incomplete due to the relatively short period of time that the technology has been commercialized, however, membrane manufacturers offer guarantees up to 5 years on the performance of their membranes for gas separation<sup>(6)</sup>.

Membranes have been tested for the recovery of hydrogen from light hydrocarbon streams of hydrotreater off-gas as an alternative to the use of selective molecular sieves in pressure swing adsorption which have high capital costs. Membranes also have the potential to be used for separating CO<sub>2</sub> from hydrocarbons in enhanced oil recovery operations, H<sub>2</sub>S removal for natural gas sweetening, and separation of H<sub>2</sub> in coal gasification processes<sup>(2,4)</sup>.

Concerning gas separations using membranes, one drawback is the lack of an adequate database and theory available for the selection of a polymeric membrane to give optimum gas selectivity for many applications<sup>(1)</sup>. There are, however, several transport models, which although still new and subject to further modification, claim to specify the membrane, and predict the permeabilities of several pure gases, as well as the separation of some binary mixtures.

## THEORETICAL CONSIDERATIONS

Three different theories which attempt to describe membrane separations are "solution diffusion", "dual mode sorption", and "preferential sorption capillary flow". The preferential sorption capillary flow mechanism assumes that all polymeric gas separation membranes have pores, and that gas permeation can only occur through these pores. Transport across the membrane is predicted by the bulk flow properties of the gas, and surface diffusion of the gases on the polymer along the pore (which is assumed to be of cylindrical structure). The bulk flow is a combination of Knudsen, slip, and viscous flows. The contribution of each is dependent on the pore size distribution, the nature of the permeating gas (mean free path), and operating temperature and pressure<sup>(7)</sup>.

The solution diffusion model assumes that transport of gases can occur only by the dissolution of gases into (obeying Henry's law) and diffusion (obeying Fick's first and second laws) through the polymeric material of the membrane. This model predicts the performance of rubbery polymers much more accurately than glassy ones. The dual mode sorption model is similar to the solution diffusion model but is adapted to account for glassy polymeric membranes. Pores are viewed as being non-existent in most gas separation membranes by the solution diffusion and dual mode sorption models<sup>(8,9)</sup>.

Further investigation into the preferential sorption capillary flow mechanism suggests that for very small pore sizes surface diffusion through the membrane pore would be the primary contribution to permeation. Permeability, and therefore selectivity would depend on the chemical properties of the gases. As the membrane pore size increases, permeation rates would be expected to increase as well as the contribution to flow by the bulk flow mechanisms such as Knudsen, slip, and viscous flow. The extent to which each of these mechanisms contributes relative to one another depends on the mean free path of the gas (inversely proportional to the collision diameter of the molecules). The magnitude of the Knudsen flow and slip flow are inversely proportional to the square of the molecular weight of the gas. It can be predicted that membranes having small pore sizes would be preferentially permeable to gases having greater interactions with the membrane material. Also, membranes having a larger pore size distribution would be more selective to gases having smaller molecular weights. For example, Chen, Fouda, and Matsuura<sup>(10)</sup> describe the permeation of methane, and carbon dioxide through cellulose acetate membranes. CO<sub>2</sub> was found to have higher interactions with the polymer material. At very small pore sizes, CO<sub>2</sub> had higher permeation rates than CH<sub>4</sub>. As pore size increased, the permeation rate of CH<sub>4</sub> (which has the lower molecular weight) exceeded that of CO<sub>2</sub>.

Both the surface pore flow and the dual mode sorption models describe and predict membrane performance with reasonable accuracy. The solution diffusion based (dual sorption) model is the theory which is most widely accepted to describe the mechanism of transport of gases across membranes, although it

appears to be some time before either model is proven to be superior.

#### CURRENT TECHNOLOGY

The membrane units presently available are selective to the bulk flow properties of gases and to large differences in their chemical properties, for example hydrophobicity and hydrophylicity. Therefore, different gases which are crudely similar in terms of chemical properties, for example,  $\text{CH}_4$  and  $\text{C}_2\text{H}_{10}$ , may be separated on the basis of molecular weight by commercially available membrane units. Separations are also possible for some systems in which one of the components has a much stronger interaction with the polymeric membrane than the rest of the feed mixture, e.g.,  $\text{CO}_2$  from  $\text{CH}_4$ .

As an example of the operating specifications for membranes available for industrial applications, a cellulose acetate based polymeric membrane produced by Monsanto is listed to have an operating temperature range of  $0^\circ\text{C}$  to  $60^\circ\text{C}$ , a maximum operating pressure of 1100 psig, and product rates between 1,400 and 2,800,000  $\text{m}^3$  per day. The operating specifications and separation properties for the membranes made from polysulfone, polyaramide, and polyimide are similar, but can withstand higher temperatures. Operating pressures higher than 110 psig are possible with some systems are also listed by the manufacturers, but separation efficiency may be reduced.

A good indication of the separation properties of a given membrane can be obtained by testing the permeabilities of pure gases. Table 1 lists the relative permeabilities<sup>(11)</sup> for common gas components through a Monsanto cellulose acetate membrane<sup>(12)</sup>. Separations which are currently possible using commercial membrane units are listed in Table 2.

Membrane technology is presently being used for many industrial processes<sup>(13)</sup>. The selective removal of  $\text{H}_2$  for example has many applications in petroleum refining and petrochemical industries which are listed in Tables 3 and 4 respectively<sup>(14)</sup>. An example of the implementation of membranes for the enrichment of hydrogen is the purification of purge gas from catalytic hydroprocessing units. At Conoco Inc.'s Ponca City Refinery, a gas oil hydrotreater high pressure purge stream at 1050 psig and 71 mol % hydrogen was fed into a "Medal" gas separation membrane at 12 MMSCFD. The purity of the hydrogen enriched stream was 95% at 75% recovery which was collected at 430 psig and 7 MMSCFD, then fed into the light cycle oil hydrodesulphurizer. The product stream depleted of hydrogen was then sent to the cryogenic liquefied petroleum gas recovery unit. Off-gas collected from the light cycle oil hydrodesulphurizer at 90% hydrogen was recycled to the gas oil hydrotreater make-up compressor. Benefits included enhanced light cycle oil hydrodesulphurizer productivity, lower operating temperature for the gas oil hydrotreater, and lower refrigeration costs for the cryogenic liquefied petroleum gas recovery unit<sup>(15)</sup>.

## FUTURE TECHNOLOGY

The separation of gases of similar molecular weights differing only moderately in chemical properties requires further work before permeabilities are up to commercial standards. Separations which would be successful by bulk properties alone are complicated by a gas with a larger molecular weight which interacts strongly with the membrane material. These gases have a relative permeability higher than that predicted on the basis of molecular weight. Applications which would require technological advancement are listed in Table 2<sup>(1)</sup>.

Improvements to the current technology would have many benefits. Higher membrane selectivities will reduce capital (number of membrane units) and operating (compression power) costs. Higher temperature resistance will eliminate the need for heat exchange on high temperature feed streams, and would result in lower membrane area requirements. Increased chemical resistance to impurities would increase the flexibility of operations<sup>(1)</sup>. Compounds such as aromatic hydrocarbons, alcohols, ketones and chlorinated hydrocarbons are considered to be good solvents for cellulose acetate membranes. For these membranes, the partial pressure of these compounds should be limited to 10% of their pure vapour pressure to avoid condensation within the membrane module.<sup>16</sup>

Separation of compounds such as ethane and ethene by present technology would likely favour the permeation of ethene by a very small margins. Permeates having ethene of 98% purity from feed solutions of 1:1 ethene/ethane have been obtained by "liquid membranes".<sup>5</sup> This process utilizes a liquid of low volatility which contains low volatile components having a high affinity for one of the components in the feed gas mixture. The liquid is either sandwiched between two membranes, or suspended within a dense membrane. For the separation of ethene from ethane, the liquid can consist of silver ions dissolved in water. The theory which describes this separation process is Facilitated Transport.<sup>17,18</sup> This process suffers the disadvantages of (a) mass transport of the permeating species being very slow; and (b) the carrier solvent eventually being lost, and the membrane drying out.

## CONCLUSION

Several gas separations are possible through the use of membranes. The technique of gas separation using membranes is still relatively new and does have its limitations. One major limitation is the lack of a complete database. Although research is becoming increasingly active in the area of producing new, more highly selective membrane materials, the current technology is not nearly fully exploited.

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Table 1 - Relative Permeabilities of Gases in Cellulose Acetate Membrane<sup>(1)</sup>.

Compound	Relative Permeability
H <sub>2</sub> O	100
He	15
H <sub>2</sub>	12
H <sub>2</sub> S	10
CO <sub>2</sub>	6
O <sub>2</sub>	1.0
CO	0.3
CH <sub>4</sub>	0.2
N <sub>2</sub>	0.18
C <sub>2</sub> H <sub>6</sub>	0.10

Table 2 - Gas separations that are possible by current membrane technology and separations which may be possible by future membrane technology<sup>(1)</sup>.

CURRENT TECHNOLOGY	FUTURE TECHNOLOGY
H <sub>2</sub> / C <sub>1</sub> +	H <sub>2</sub> / CO <sub>2</sub>
H <sub>2</sub> / CO	H <sub>2</sub> S / CO <sub>2</sub>
He / C <sub>1</sub> +	NH <sub>3</sub> / C <sub>1</sub> +
H <sub>2</sub> O(v) / C <sub>1</sub> +	NH <sub>3</sub> / N <sub>2</sub>
H <sub>2</sub> S / C <sub>1</sub> +	NH <sub>3</sub> / H <sub>2</sub>
CO <sub>2</sub> / C <sub>1</sub> +	SO <sub>2</sub> / CO <sub>2</sub>
CO <sub>2</sub> / N <sub>2</sub>	SO <sub>2</sub> / C <sub>1</sub> +
CO <sub>2</sub> / CO	NO <sub>x</sub> / C <sub>1</sub> +
NO <sub>x</sub> / CO	N <sub>2</sub> / C <sub>1</sub> +
NO <sub>x</sub> / N <sub>2</sub>	C <sub>1</sub> / C <sub>2</sub> +
O <sub>2</sub> / N <sub>2</sub>	Ar / Air
CO <sub>2</sub> / Air	Organic Vapours

+ indicates hydrocarbons heavier than CH<sub>4</sub> or C<sub>2</sub>H<sub>6</sub>.

Table 3 - Typical Hydrogen Membrane Performance Petrochemical Applications<sup>(15)</sup>.

Process stream	Primary separation	Feed purity (%)	Permeate purity (%)	Recovery (%)
Ammonia Purge Gas	H <sub>2</sub> /C <sub>1</sub>	60-70	80-95	90-95
Methanol Purge Gas	H <sub>2</sub> /C <sub>1</sub> -CO <sub>2</sub>	55-85	90-96	80-95
Aniline Reactor Off Gas	H <sub>2</sub> /C <sub>1</sub>	55-65	90-95	90-95
Cyclohexane Feed Gas	H <sub>2</sub> /C <sub>1</sub>	60-70	90-95	90-95
Propylene Purge Gas	H <sub>2</sub> /C <sub>3</sub>	50-60	90-95	80-90
Ethylene	H <sub>2</sub> /C <sub>1</sub>	50-60	85-95	70-90

Table 4 - Typical Hydrogen Membrane Performance Refining Applications<sup>(15)</sup>.

Process stream	Primary separation	Feed purity (%)	Permeate purity (%)	Recovery (%)
Catalytic Reformer Off-Gas	H <sub>2</sub> /C <sub>1</sub> -C <sub>4</sub>	70-80	90-97	75-95
Cryogenic Unit Feed and Off Gas	H <sub>2</sub> /C <sub>1</sub> -C <sub>4</sub>	15-20	80-90	70-80
FCC Off Gas	H <sub>2</sub> /C <sub>1</sub> -C <sub>4</sub>	15-20	80-90	70-80
Hydrocracker Purge	H <sub>2</sub> /C <sub>1</sub> -C <sub>4</sub>	60-80	85-95	80-95
Hydrotreater Purge	H <sub>2</sub> /C <sub>1</sub> -C <sub>4</sub>	60-80	85-95	80-95
PSA	H <sub>2</sub> /C <sub>1</sub> /CO <sub>2</sub>	50-60	80-90	65-95