



The separation of oxygen from air using commercial, plasticized, and nonplasticized polymeric membranes
by Mark David Mus

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in
Chemical Engineering
Montana State University
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Abstract:

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The selectivity of the various membranes was compared using the traditional separation index, α , where $\alpha = Y(1 - X)/X(1 - Y)$ and Y is defined as % oxygen in the permeate while X is % oxygen in the feed.

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In general, it was found that using phenyl compounds as modifiers increased the separation index of the membrane more than did the use of aliphatic chains.

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of a thesis submitted by

Mark David Mus

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TABLE OF NOMENCLATURE

A	Area
C	Concentration
CP	Permeability coefficient
D	Diffusivity
D_0	Coefficient in Arrhenius expression for diffusivity
E	Activation energy
H	Henry's Law constant
H_0	Coefficient in Arrhenius expression of Henry's Law constant
L	Membrane thickness
$L_{(2)}$	Molar flowrate of permeate
N	Flux
P	Pressure
R	Gas constant
S	Solubility of gas in membrane
T	Temperature
X	Mole fraction of oxygen in feed
Y	Mole fraction of oxygen in permeate
Z	Length coordinate
r	Pressure ratio

Subscripts

a	Component a
b	Component b

x

d Diffusivity property

m Membrane property

s Solubility property

Superscripts

* Ideal

Greek Letters

α Separation factor = $Y(1 - X)/X(1 - Y)$

ABSTRACT

The oxygen enrichment of a product stream by selective permeation through a membrane was investigated using both commercially available polymeric films and membranes made by including various plasticizing agents (amines, glycols, and ethers) in polyvinylidene fluoride resin. Tests were conducted at various temperatures and constant pressure. The permeate samples were tested for oxygen and nitrogen content using a gas chromatograph.

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In general, it was found that using phenyl compounds as modifiers increased the separation index of the membrane more than did the use of aliphatic chains.

INTRODUCTION AND PURPOSE

Oxygen enriched air has a number of important uses including smelting, welding, and increasing the combustion temperature of fuels. With the advent of higher oil and natural gas prices another important use will be in coal liquefaction and gasification. Current U.S. oxygen production is at approximately 60-70,000 tons/day. Future needs of oxygen for coal gasification are estimated at 1/5 to 1/3 ton of oxygen per ton of coal [1, p. 116]. Currently the cheapest method of producing oxygen is the cryogenic distillation of air. In this process air is liquefied, then, due to its lower boiling point, nitrogen is removed in a distillation column [2]. This process is energy intensive.

With the increasing consumption of oxygen and the rise in energy costs, cheaper methods for oxygen production need to be explored. Previous research [3] has indicated that separation of oxygen from air using facilitated transport liquid membranes has the potential of replacing the cryogenic process. This research showed that a permeate containing 88% oxygen could be achieved in a single pass using these liquid membranes. Advantages of these membranes could be smaller process units and less energy. It has been estimated that a membrane producing 90% oxygen from air would require 1/3 the power of cryogenic distillation [4, p. 8]. However, a highly selective membrane is required for high purity oxygen.

Possible reasons for selective permeation through modified and nonmodified polymeric membranes could be a greater solubility of one component versus another and a difference in molecular size of the permeate components.

The goals of this research were as follows:

1. The screening of membranes for selectivity was to be conducted. Commercial polymeric films and modified polyvinylidene fluoride membranes were to be tested.
2. The effect of temperature on the oxygen selectivity of the various membranes was to be studied.

THEORETICAL BACKGROUND

The Theory of the Permeation Process

The permeation of a gas through a polymeric membrane involves three transport processes (see Fig. 1).

These stages are as follows:

1. Diffusion from the bulk phase of the gaseous mixture through the gas film-membrane interface to the membrane surface.
2. Diffusion through the membrane to the opposite face.
3. Diffusion from the membrane surface through the membrane-gas film interface to the bulk gas phase.

Transport Through a Gaseous Film

The flux of gaseous molecules through a gas film can be described by a modification of Fick's first law for steady state diffusion [5, p. 12].

$$N_a = (N_a + N_b) \frac{C_a}{C_a + C_b} - D \frac{\partial C_a}{\partial Z} \quad (1)$$

The first term in the above equation is due to bulk flow while the second term describes molecular diffusion.

The resistance to the flux in a membrane is much greater than that in the gas film [6, p. 11]. Therefore, the resistance in the membrane is the dominant factor of the flux. The resistance in the gas film can be assumed to be negligible.

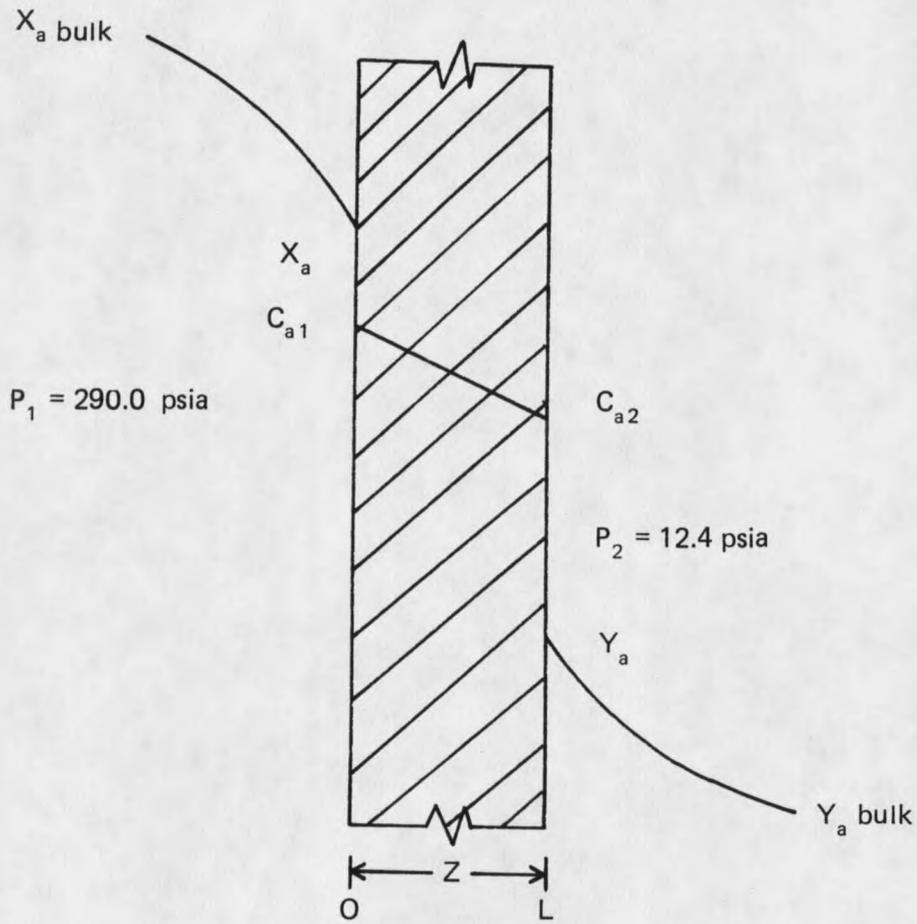


Figure 1. Concentration profile of component a in the membrane and its vicinity.

Note: $Y_a \text{ bulk} > X_a \text{ bulk}$

Transport Through a Polymeric Membrane

The flux of component a in a binary gas mixture through a polymeric membrane can be described by another modification of Fick's first law [6, p. 20]:

$$N_a = -D \frac{\partial C_a}{\partial Z} - \frac{D}{2C_m} \frac{\partial^2 C_a}{\partial Z^2} \quad (2)$$

This equation reflects the assumption that the diffusion process is at steady state. It differs from Fick's first law by the addition of the second term which is needed to describe the nonlinear relationship of the flux to the concentration gradient within the membrane. In gaseous diffusion the effect of the second term is generally negligible [6, p. 21]. The resulting equation is

$$N_a = -D \frac{\partial C_a}{\partial Z} \quad (3)$$

which is Fick's first law for steady state diffusion. Because the concentration is only a function of distance through the membrane, whole derivatives may be used.

$$N_a = -D \frac{dC_a}{dZ} \quad (4)$$

Appropriate boundary conditions are required to solve the equation. The boundary conditions used are

$$\text{at } Z = 0 \quad C_a = C_{a1}$$

$$\text{at } Z = L \quad C_a = C_{a2}$$

where L is the thickness of the membrane. Integrating Equation 4 with these boundary conditions results in

$$N_a \int_0^L dZ = -D \int_{C_{a1}}^{C_{a2}} dC_a \quad (5)$$

With further rearrangement, Equation 5 becomes

$$N_a = \frac{D}{L} (C_{a1} - C_{a2}) \quad (6)$$

Thus, if flux and concentration are measured and the thickness of the membrane is known, the overall diffusion coefficient can be calculated. The overall diffusion coefficient includes the effects of gas diffusion and the effect of the membrane on the diffusion process.

To find the effect of the temperature and membrane type on flux, the solubility of the gas in the membrane must be defined. Since the diffusion of the gas is slow and the pressures are relatively low, Henry's law can be used to describe an equilibrium relationship between component a at the membrane interface and its concentration in the membrane.

$$H_1 X_a P_1 = C_{a1} \quad (7)$$

$$H_2 Y_a P_2 = C_{a2} \quad (8)$$

Defining Henry's constant H as the solubility coefficient S gives

$$C_{a1} = S_1 X_a P_1 \quad (9)$$

$$C_{a2} = S_2 Y_a P_2 \quad (10)$$

Substituting Equations 9 and 10 into Equation 6 gives

$$N_a = \frac{D}{L} (S_1 X_a P_1 - S_2 Y_a P_2) \quad (11)$$

If solubility is a function of temperature only for an individual membrane and both sides of the membrane are at the same temperature, then

$$S_1 = S_2 = S \quad (12)$$

and

$$N_a = \frac{SD}{L} (X_a P_1 - Y_a P_2) \quad (13)$$

From Equation 13 it can be seen that the flux of a gas is dependent on the solubility and diffusivity of this gas in the membrane. Thus, increasing the solubility of one of the components (oxygen) of the feed gas (air) will enhance the separation.

Polymer-Structure Effects on Transport

The transport of gases through an unmodified membrane can be visualized in the following manner: The polymer used in this research (polyvinylidene fluoride) is a highly crystalline material, above 68% [7, p. 1769] with the void spaces being thought of as amorphous regions. In the diffusional process the penetrant molecule travels through these amorphous regions due to the concentration gradient. It has been shown that diffusion through a crystalline polymer depends strongly on two factors [8, p. 53]. The two factors are degree of crystallinity and crystallite size. Larger crystallites in combination with a greater degree of crystallinity causes the diffusional tortuosity to increase. This decreases the diffusion of the penetrant molecule through the polymer. Michaels et al. [7, p. 1772] has shown that the crystallites in vinylidene fluoride polymer have a flat planer structure.

The solubility of a penetrant molecule in the polymer depends primarily on the crystallinity of the polymer [9, p. 412]. With an increase in polymer crystallinity the solubility decreases. This is due to the amount of amorphous material present. For a less amorphous polymer there is less space available for the penetrant molecule which decreases the solubility.

There are several methods to change the degree of crystallinity of a polymer. One way is to change the method of polymer manufacture. Another is to cool the molten polymer to its solid state faster. The polymer becomes less crystalline and the crystallite size decreases. A third way is to add a plasticizer (modifier). An ideal modifier is one in which the desired penetrant molecule is preferentially soluble over the other molecules in the gas mixture. This would increase the flux and the separation of the preferred molecule. A

modifier also serves to increase the amount of amorphous material in the membrane. This increase reduces the diffusional tortuosity and increases the solubility of the penetrant molecule in the polymer. The total effect is to increase the flux of a gas through the membrane.

No particular method was used in choosing the main chemical group (i.e., amines, glycols, etc.) for use as modifiers. Different modifiers within each chemical group were tried in the hope that they would give clues for the direction that future research should take.

Temperature Effects on Transport

Temperature Effects on Gas Solubility

Work done on the permeation of gas into solid polymeric membranes has shown that the solubility of a gas in a membrane follows an Arrhenius behavior with respect to temperature [8, p. 53].

$$H = H_0 \exp\left(-\frac{E_s}{RT}\right) \quad (14)$$

Thus, an increase in temperature increases the solubility of the gas in the membrane.

The effect of temperature on gas solubility in a modified membrane is more complex. Although the solubility of a gas in a liquid modifier is generally higher than its solubility in a solid polymer, the effect of temperature on this solubility is different. The solubility of a gas in a liquid decreases as the temperature increases. Thus the overall temperature effect on gas solubility is a function of modifier and polymer properties.

Temperature Effects on Diffusion

Studies have shown that temperature effects on diffusion in modified polymers also follow an Arrhenius behavior [10, p. 106].

