



Effects of water vapor on the separation of methane and carbon dioxide by gas permeation through polymeric membranes  
by Gerald Thomas Paulson

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:

Three commercially available films and a vinylidene fluoride film modified with sulfolene were tested for the separation of carbon dioxide from carbon dioxide, methane and water vapor mixtures. Flux and separation factor values were obtained over a temperature range from 23 to 90°C and a feed gas moisture content from 0.0 to 1.32%. A feed gas containing 60% carbon dioxide and 40% methane on a dry basis was used at an operating pressure of 2068 kPa.

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The sulfolene modified film also provided good separation. Separation factor values for carbon dioxide ranged from 9.6 to 33.6. Flux values ranged from  $10.E-05$  to  $5.7 \times 10E-05$  cu cm(STP)/sq cm(sec).

Strong trends towards increasing flux and decreasing percentage of carbon dioxide in the permeate with increasing temperature were observed with all films.

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The sulfolene modified film tended towards constant or increasing percentage of carbon dioxide in the permeate with increasing water content. The flux tended to remain constant or decrease with increasing water content.

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EFFECTS OF WATER VAPOR ON THE SEPARATION OF METHANE  
AND CARBON DIOXIDE BY GAS PERMEATION  
THROUGH POLYMERIC MEMBRANES

by

GERALD THOMAS PAULSON

A thesis submitted in partial fulfillment  
of the requirements for the degree

of

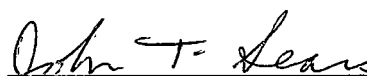
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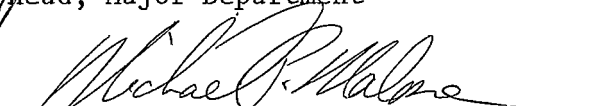
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## ABSTRACT

Three commercially available films and a vinylidene fluoride film modified with sulfolene were tested for the separation of carbon dioxide from carbon dioxide, methane and water vapor mixtures. Flux and separation factor values were obtained over a temperature range from 23 to 90°C and a feed gas moisture content from 0.0 to 1.32%. A feed gas containing 60% carbon dioxide and 40% methane on a dry basis was used at an operating pressure of 2068 kPa.

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## INTRODUCTION AND PURPOSE

The separation of a gas mixture by a membrane process involves the selective transport of a given species through a film. This method of separation has made considerable progress in recent years in areas such as the development of more selective and permeable membranes, as well as simple and efficient equipment for large scale operations.

The separation of carbon dioxide and methane is important in a number of areas, particularly in the manufacturing of Substitute Natural Gas (SNG). A substantial amount of SNG can be produced from biomass and gaseous effluent from anaerobic sewage treatment plants, landfills, oil fields, coal mines and agricultural waste digesters(1). The upgrade of biogas to SNG requires the removal of carbon dioxide, hydrogen sulfide and water. Biogas from anaerobic digestion varies from 40 to 60% methane and 60 to 40% carbon dioxide, contains traces of hydrogen sulfide and is saturated with water vapor(2). In order to provide pipeline quality gas, the SNG must be approximately 98% methane, a few parts per million hydrogen sulfide and dried(3). Many commercial processes capable of meeting these standards are available. However, biogas membrane processes are estimated to be in the order of a third to a half the cost of traditional systems(4-5).

Membrane surface area requirements are of significant economical interest. Studies indicate that as much as 95% of the total investment costs of a gas permeation process is determined by the area(6-7). To minimize area requirements it is necessary to know the dependence of

gas permeation rates over a wide range of variables. This work was conducted in an attempt to contribute to the ultimate goal of an economical membrane separation process for biogas purification. The specific objectives of this research were:

1. to test various commercially available polymeric films to determine permeation rate and selectivity for carbon dioxide.
2. to test a plasticizer in a vinylidene fluoride film to determine permeation rates and selectivity for carbon dioxide.
3. to determine the effect of temperature on selectivity for carbon dioxide in the various membranes.
4. to determine the effect of temperature on permeation rates in the various membranes.
5. to determine the effect of water vapor on the selectivity for carbon dioxide in the various membranes.
6. to determine the effect of water vapor on permeation rates in the various membranes.
7. to determine the permeation rates of water vapor in the various membranes.

## REVIEW OF THE LITERATURE

### A. BIOGAS PURIFICATION PROCESSES

Carbon dioxide, hydrogen sulfide and water removal technologies include a large number of commercial processes. In addition to membrane separation systems; four major groupings can be identified in gas removal processes(8).

Physical absorption involves the dissolution of the gas in a liquid solvent. Solvent regeneration usually can be accomplished by simple flashing or by stripping with an inert gas. Historically, water scrubbing was the first method used for carbon dioxide removal.

Chemical absorption involves the formation of a reversible chemical bond between the solvent and the solute. Regeneration involves breaking those bonds. Most solvents are either aqueous solutions of amines or aqueous solutions of alkaline salts. Potassium carbonate solutions can be used to chemically absorb carbon dioxide and hydrogen sulfide.

Chemical conversion can be utilized to reduce an undesirable gas concentration. Several commercial processes are available for converting hydrogen sulfide to elemental sulfur. Carbon dioxide when mixed with hydrogen can be catalytically converted to methane and water(9).

Gas removal by condensation is achieved by cooling, compression or a combination of both. Commercial trials of biogas purification by condensation have not been successful because of high capital costs and low thermal efficiency(10).

## B. POLYMERIC MEMBRANES USED FOR GASEOUS SEPARATION

Several gas permeation processes have been studied in detail. Differences in solubilities, mass transfer resistances or both account for membrane selectivity. Separation of a gas mixture is achieved by the flow of one component at a greater rate than the others.

Silicone rubber is used as a membrane for the separation of oxygen from air(11). A three-stage cascade of hollow fiber permeators results in a product stream of 38% oxygen. Oxygen could be enriched to 32.6% in a one stage process(12).

The recovery of helium from natural gas has received much attention. Union Carbide has conducted large scale tests using cellulose acetate films in a two-stage process(13). Some tests have been conducted using a Teflon FEP film(14). Teijin Limited of Japan has announced a method that employs an undisclosed hollow fiber system to recover helium(15).

A commercial installation for the separation of hydrogen from a refinery gas stream has been in operation since 1969(16). The system uses hollow fibers of dacron polyester and is marketed by the Du Pont Company.

The removal of rare gas fission products has been studied by the nuclear industry(17). Silicone rubber membranes is used in a flat plate permeator for the tests.

Polymer membrane processes have been tested for a large number of laboratory systems. Brubaker and Kammermeyer tested polyethylene, trifluoromonochloro-ethylene and cellulose acetate over a wide variety of gas mixtures(18). Tajar and Miller reported data for the permeation of carbon dioxide, oxygen and nitrogen in a membrane consisting of polyethyleneamine, polyvinylbutyral, epoxy and water(19).

Modified poly(vinylidene fluoride) membranes have been used in four studies. Seibel and McCandless used sulfolane modified films to separate sulfur dioxide from nitrogen(20). Zavaleta studied a number of modified films for separating sulfur dioxide from nitrogen(21). Heyd studied eight modified films as well as six commercially available films for separating hydrogen sulfide from nitrogen(22). Ellig, Althouse and McCandless tested several films for separating carbon dioxide from methane(23). Their study is discussed in the following section.

#### C. LABORATORY MEMBRANE PROCESSES FOR BIOGAS PURIFICATION

General Electric Company has experimented with immobilized liquid membranes for carbon dioxide removal(24). The liquid membrane is immobilized by a hydrophobic porous support membrane. The liquid membrane consists of a hydrophilic porous membrane whose pores are filled with an aqueous carbonate solution. This membrane utilizes the phenomenon described as "facilitated transport" by the addition of carbon dioxide hydrolysis catalysts to the aqueous carbonate solution. Reported values



of carbon dioxide permeability vary from 0. to 160. (cc/sq cm sec) (cm/cm Hg) with a membrane thickness of 0.0015cm and a carbon dioxide feed gas with partial pressure varying from 5 to 200 cm Hg. Humidity control is critical.

The Monsanto Company has developed coated membranes(25). The process involves a multicomponent membrane consisting of a porous film and a thin(<0.005cm) coating. The film is either cellulose acetate, polycarbonate or polysulfone and the coating is either polysiloxanes or polystyrene. The combinations of films and coatings will separate carbon monoxide, nitrogen, argon, methane, ethane, carbon dioxide and sulfur hexafluoride.

Ellig, Althouse, and McCandless tested 16 membranes for the removal of carbon dioxide from a 60 percent carbon dioxide and 40 percent methane mixture(26). A moisture-free feed gas was used. Thirteen commercial membranes were tested. The best separations were obtained with polyethersulfone, polysulfone and cellulose acetate. Three modified poly(vinylidene fluoride) membranes were made by dissolving vinylidene fluoride and a modifier in dimethyl formamide. The films were cast on glass plates between thicknesses of masking tape. The solvent was evaporated by placing the plates in an electrically heated oven. The membrane modified with sulfolene demonstrated the best separation of the three. Observed separation factors ranged from less than 0.1 to 40.2

with fluxes up to 0.044 cu cm (STP)/sq cm sec . The highest fluxes were obtained from the films with the lowest separation factors.

#### D. COMMERCIAL PROCESSES FOR BIOGAS PURIFICATION

The General Electric Company is currently marketing a Permaselective Membrane Process(27). A 27.8 standard cubic meter per day system is operating on sewage digester gas in Southern California. A 278.0 standard cubic meter per day system is planned for the Fresh Kills Landfill located in New York City(28).

The General Electric Permaselective Membrane Process operates by a pressure differential and allows carbon dioxide to pass through the membrane surface while methane is retained in the high pressure gas stream. A second stage is used to recover methane in the carbon dioxide effluent. The system uses a silicone- polycarbonate membrane with thicknesses as thin as 200 angstroms. Water is removed from the gas prior to injection into the membrane system.

## THEORETICAL BACKGROUND

### A. THE NATURE OF THE TRANSPORT PROCESS

Permeation through a polymeric membrane is thought to involve the following series of steps(29):

- (i) transport from the bulk mixture to the membrane surface.
- (ii) solution of the gas into the membrane at the interface.
- (iii) transport through the membrane(diffusion).
- (iv) release of the gas from solution at the opposite interface.
- (v) transport from the membrane interface to the permeate stream.

The term permeation is used to describe the overall mass transport of gas through this sequence.

### B. ORDERING ANALYSIS

Each of the five steps represents a resistance to mass transfer of various magnitude. The resistances of some steps are negligible in comparison with other steps. In gas-phase permeation, steps (i), (ii), (iv) and (v) may be negligible(30).

### C. DIFFUSION THROUGH A MEMBRANE

For membrane diffusion the basic transport equations are:

$$N_A = -D \frac{\partial C_a}{\partial z} - \frac{D}{2C_m} \frac{\partial C_a^2}{\partial z} \quad (1)$$

and

$$\frac{\partial C_a}{\partial t} = \frac{\partial}{\partial z} D \frac{\partial C_a}{\partial z} + \frac{\partial}{\partial z} D \frac{C_a}{C_m} \frac{\partial C_a}{\partial z} \quad (2)$$

These equations differ from Fick's basic diffusion equations by the addition of the second terms due to the presence of the membrane.

The effect of the second term may be negligible in instances of large permeation fluxes.

#### D. SIMPLIFIED MODEL OF PERMEATION OF ONE COMPOUND

Assuming steady state diffusion through the membrane to be the rate controlling step and neglecting the second term of the diffusion equation (presence of the membrane), permeation reduces to Fick's basic diffusion equation.

$$N_a = -D \frac{dC_a}{dz} \quad (3)$$

Integration of this equation using the appropriate boundary conditions yields:

$$-N_a (z_1 - z_2) = -D(C_1 - C_2) \quad (4)$$

or

$$N_a = \frac{D}{L}(C_1 - C_2) \quad (5)$$

Assuming equilibrium between the gas and the interface, a Henry's Law expression,  $C = (S)(p)$ , is applicable.  $S$  is the solubility coefficient of the gas in the polymer. The resulting equation becomes:

$$N_a = \frac{DS}{L}(p_{a1} - p_{a2}) \quad (6)$$

The adequacy of Fick's and Henry's Law are questionable in many polymers(31). However, equation (6) does provide a basis for the study of permeation.

### E. TEMPERATURE EFFECTS

For unmodified films  $D$  and  $S$  usually obey an Arrhenius type relationship:

$$D = D_0 e^{(-E/RT)} \quad (7)$$

$$S = S_0 e^{(-\Delta h/RT)} \quad (8)$$

$E$  is the activation energy and  $h$  is the heat of solution for diffusion. Both diffusivity and gas solubility increase with increasing temperature.

For films modified with a liquid, the solubility of gases in the modifier usually decreases as temperature is increased. The flux could actually decrease with increasing temperature.

### F. EFFECT OF GAS MIXTURES ON PERMEATION

For the case of a gas mixture in contact with a membrane, equation (6) becomes:

$$N_a = \frac{DS}{L}(p_{a1} - p_{a2}) \quad (9)$$

or in terms of the total pressure:

$$N_a = \frac{DS}{L}(P_1 X_{a1} - P_2 Y_{a2}) \quad (10)$$

The effect of a gas mixture on permeation is dependent on the polymer and the gaseous components. Mixtures of nitrogen and oxygen permeate in an additive fashion(32). Each gas permeates independently. Both the gases have low solubilities in most polymers.

Nitrogen and carbon dioxide mixtures, and oxygen and carbon dioxide mixtures permeate dependently(33). Oxygen has been reported to permeate at rates up to three times faster in the presence of large amounts of carbon dioxide than in pure oxygen.

#### G. EFFECT OF WATER VAPOR ON GAS PERMEATION

Possible interaction of water vapor with the membrane will influence the mechanism of permeation. In hydrophilic membranes a solution of water in the polymer will occur(34). This results in a softening or plasticizing effect, and may cause swelling. In hydrophobic membranes water should not interact with the polymer.

Few studies have been conducted on the effect of water vapor upon gas permeation. Simril and Hershberger reported a 50-fold increase in carbon dioxide permeability through cellophane as the relative humidity increased from 0. to 100%(35). Pilar reported a 1000-fold increase for the same conditions(36). Two methods have been adopted for the study of the effects of water on permeation. The first method preconditions the film with water and the film is then tested. The second method uses a test gas that is humidified. The results of the two methods vary(37).

In general, the permeability of gases increased as the moisture content of the film is increased. However, transmission of water vapor is pressure dependent. The solubility of water in films is reported to increase in a nonlinear fashion with pressure(38).

Some data is available on the commercial films used in this study(39). Water absorption in 24 hours for cellulose acetate, polysulfone and polyethersulfone is 8.5, 0.3 and 2.1 weight percent respectively.

#### H. POLYMER CHEMISTRY ASPECTS

Gases are transported through polymeric nonporous membrane by means of diffusion. The partial pressures of the gases are the driving forces and the film thickness, gas solubility and gas diffusivity control permeation rates.

Plasticizers (or modifiers) in a polymer have several effects. The addition of a plasticizer increases the diffusivity of gases in a polymer. Solubilities of gases or vapors may also increase, particularly when the gas or vapor is soluble in the modifier. The overall effect of plasticizers is generally an increase in the permeate flux.

Zavaleta studied the effect of plasticizer content and concluded that 18% sulfolene in poly(vinylidene fluoride) yielded the maximum flux(40). Films with a higher sulfone content were prone to leak.

#### I. SEPARATION FACTOR DEFINITION

The degree of separation of components A and B is commonly expressed in terms of a separation factor. It is defined by the concentration ratio:

$$\alpha_a = \frac{(C_a/C_b)_p}{(C_a/C_b)_s} \quad (11)$$

In terms of mole fractions the separation factor is:

$$\alpha_a = \frac{Y_a/(1-Y_a)}{X_a/(1-X_a)} \quad (12)$$

For the case of perfect mixing on the high pressure side, the overall separation factor is identical to the separation factor at any point along the membrane length.



## EXPERIMENTAL EQUIPMENT, MATERIALS AND PROCEDURES

### A. EXPERIMENTAL EQUIPMENT AND MATERIALS

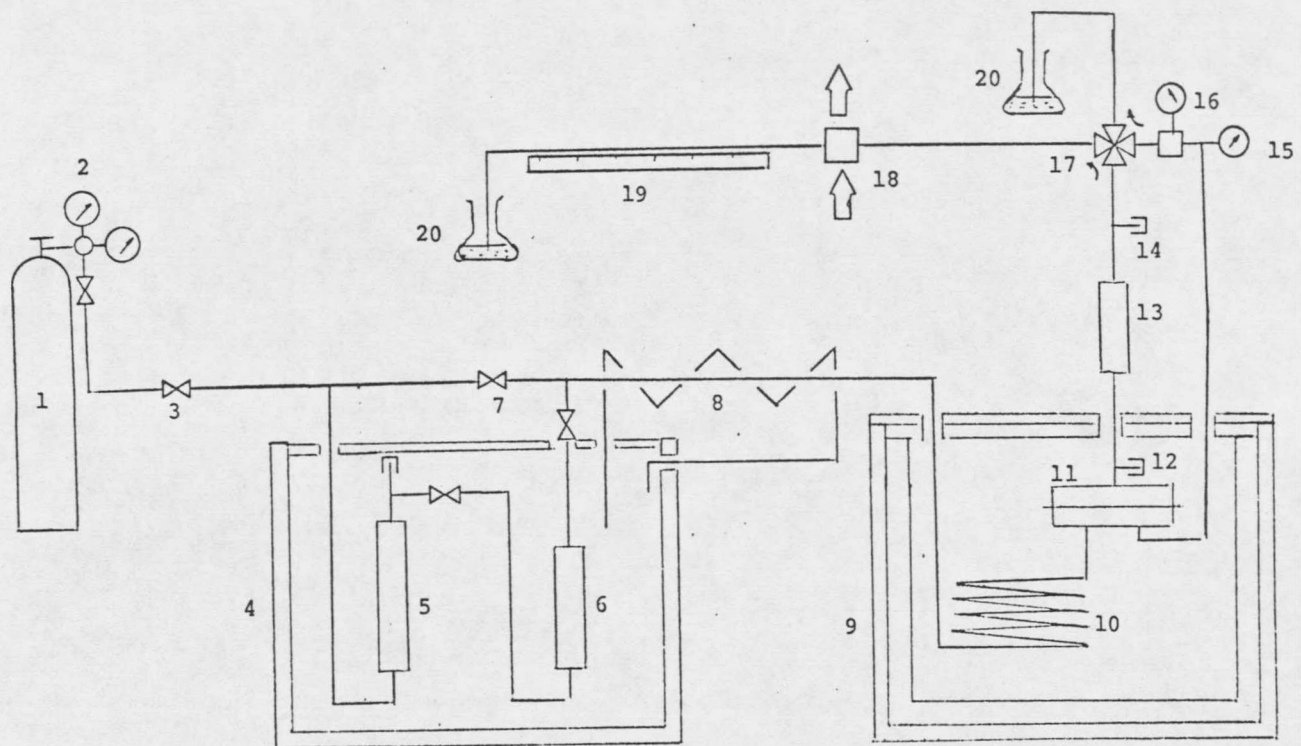
A schematic diagram of the experimental equipment is shown in Figure IV-1. The equipment consisted of a gas supply system, water vapor control equipment, permeation cell, a constant temperature enclosure for the cell, a permeate stream drier, permeate flow measurement equipment and gas composition analysis equipment. A description of each subsystems follows.

#### 1. GAS SUPPLY SYSTEM

The feed gas was stored in a National Cylinder Gas Division of Chemetron Corporation gas cylinder. An operating pressure of 2068 kPa was set by a Grove "Mighty Mite" back pressure regulator and was measured by a Matheson Company pressure gauge. A Matheson pressure regulator located on the outlet of the high pressure cylinder was maintained at a pressure slightly above the operating pressure. A feed flow rate (approximately 2 liters/hour) was set using a Whitey micrometering valve. The gas rate was measured periodically by a Varian Inc. bubble meter. The gas was vented through an oil seal.

#### 2. WATER VAPOR CONTROL EQUIPMENT

The water vapor control equipment consisted of two columns in series that were submerged vertically in a Forma Scientific Masterline model 2095 company water bath(-30 to 72°C range). Feed gas enters a 2.0 cm diameter column that was filled with water and packed with 0.3 cm Fenske rings. The column was 20.3 cm in length. The wet gas continued



- (1) Feed Gas Cylinder (2) Pressure Regulator (3) Needle Valve (4) Constant Temperature Bath (5) Packed Column (6) Glass Wool Column (7) By-pass Valves (8) Feed Line Trace Heating (9) Cell Enclosure (10) Tubing Coil (11) Permeation Cell (12) Wet Permeate Sampling Septum (13) Permeate Drier (14) Vacuum Septum (15) Pressure Gauge (16) Back Pressure Regulator (17) Two Way Valve (18) Sampling Valve (19) Length Measurement (20) Oil Seal

FIGURE IV-1. SCHEMATIC DIAGRAM OF PERMEATION EQUIPMENT

through a 15.2 cm length of 1.2 cm in diameter column that was packed with glass wool. The glass wool column eliminated water droplets in the feed gas. The resulting gas was saturated at the temperature of the water bath. The bath temperature was varied to produce a feed gas of different water vapor concentrations. The gas feed line from the constant temperature bath to the permeation cell enclosure was heated by circulating water from the bath through a 0.6 cm in diameter copper line to prevent condensation. The two lines were wrapped in 2.5 cm thick fiberglass insulation. The columns were by-passed for runs requiring a moisture free feed gas.

### 3. PERMEATION CELL

A diagram of the permeation cell is shown in Figure IV-2. A cavity was machined into each of two stainless steel blank flanges which were 1.6cm thick and 11.4cm in diameter. A porous stainless steel disk covered with filter paper was placed in the cavity on the low pressure side to support the membrane. The membrane was sealed between two teflon gaskets and the permeation cell was assembled with eight equally spaced bolts. The gasket opening, which determine the exposed membrane surface, had an area of 20.3 sq cm. The high pressure side of the cell had a tubular thermocouple well. A sampling septum was located on the low pressure side of the cell. The septum was used to remove moist samples of the permeate.



























































































































