THE CO_2 AND H_2 PERMEABILITY OF MEMBRANES COMPOSED OF HIGHLY CO_2-PHILIC POLYMERS

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Membranes have the potential to be an integral part of the coal gasification/water-gas-shift reaction process to transform coal, oxygen and water feed streams into hydrogen for fuel and CO_2 for sequestration. The objective of this work is to design polymeric membranes that have very high CO_2 permeability and high selectivity toward CO_2 (i.e. very low H_2 permeability). It is our hypothesis that the favorable thermodynamic interactions that enable certain polymers to dissolve in dense CO_2 at extremely high pressure (~2000 – 10000 psia) will also allow membranes composed of these polymers to exhibit high CO_2 permeability at pressure conditions associated with pre-combustion separation. Polymer candidates include polydimethyl siloxane (PDMS), perfluoro polyether (PFPE), polypropylene glycol dimethyl ether (PPGDME), and polyethylene glycol dimethyl ether (PEGDME).

INTRODUCTION

CO_2 capture and sequestration are becoming an important part of industry today, especially from advanced power generation sources (eg IGCC). The separation and capture of carbon dioxide from such a plant is expected to significantly impact the cost of carbon capture and sequestration. If improvements can be made in the selective removal of CO_2, then the expense of the carbon capture and sequestration process could be diminished. Membranes hold significant promise in high pressure (pre-combustion) carbon capture because of their small footprint, mechanical simplicity, relatively low energy requirements, and single-step separation.

MATERIALS

Supported liquid membranes

The following polymers were used in this study: polydimethyl siloxane (PDMS) (Dow Corning, 10cSt, MW~1250g/mol), perfluoropolyether (PFPE) (Dupont Krytox oil, MW=960 g/mol), polypropylene glycol dimethyl ether (PPGDME) (Polymer Source, MW=1060 g/mol),

and polyethylene glycol dimethyl ether (PEGDME) (Sigma Aldrich, MW~500 g/mol). The porous support used was crosslinked nylon (BIODYNE, pore size 0.2μm). All the materials were used as received.

Dense Film Membranes

The following polymers were used in this study: polydimethyl siloxane (PDMS) (McMasterCarr, sheet 0.0005" thick, MW=unknown), perfluoropolyether diol (PFPE) (Solvay, MW=750 g/mol), polypropylene glycol diacrylate (PPGDA) (Sigma Aldrich, Mn~900 g/mol), polyethylene glycol diacrylate (PEGDA) (Sigma Aldrich, MW~700 g/mol).

Membrane Preparation

PDMS, PPGDME, PEGDME, and PFPE are liquid oligomers were produced by drop coating the oligomer onto the porous support and allowing diffusion of polymer into the pores for 3-4 hours. These supported liquid membranes were tested by measuring the steady-state flux of two components in a mixed gas stream permeating through the membrane.

The dense film membranes were produced by crosslinking diacrylate-terminated liquid oligomers. Initially the diacrylates were run through a separation column to remove the inhibitor before crosslinking. The diol was converted to a diacrylate according to the procedure described by Bloomquist et al [1]. A prepolymer solution of each acrylate was made using 0.1wt% AIBN, and this prepolymer solution was crosslinked into a film using a compression heater. The thickness was controlled using a spacer between two aluminium sheets. The PPGDA and PEGDA were crosslinked at 80 ˚C for 2 hrs and the PFPEDA was crosslinked at 120 ˚C for 2 hrs. These dense film membranes were used freestanding in the constant volume analysis.

METHODS

The permeability (P) in a non-porous polymeric membrane is the product of the diffusivity (D) and solubility (S) of the gas:

$$P = D * S \tag{1}$$

The selectivity (α) of a pair of gases is simply the ratio of their permeability and therefore also their diffusivity and solubility.

$$\alpha_{a/b} = \frac{P_a}{P_b} = \frac{D_a}{D_b} \frac{S_a}{S_b} . \tag{2}$$

In the separation of CO_2 from H_2, if one considers the diffusivity selectivity based on size, the diffusivity of H_2 will always be greater because of the dimensions of the molecules. The sorption capability of a gas is generally a function of the condensability of the component to be separated. Because CO_2 is more easily condensed than H2, the solubility of CO_2 in the polymer tends to be greater than that of hydrogen.

These polymers were chosen because they have favorable thermodynamic interactions that enable them to dissolve in dense CO_2 at extremely high pressure (2000-10000 psi), as detailed in the paper by Miller, Enick and Luebke being presented at this conference. It is our hypothesis that this will increase the solubility interaction that occurs between CO_2 and the polymer, leading to high CO_2 permeability at low pressure.

Constant Pressure Analysis

The constant pressure method is based on measuring the steady state flux of a mixed gas that is permeating through the membrane while keeping a constant pressure difference across the membrane, a constant composition of mixed gas flowing on the retentate side of the membrane, and a constant flow rate sweep gas on the permeate side that maintains the concentration of the permeate gases at low, abut accurately measurable, concentrations. The steady state flux is related to the permeability using Equation (3.

$$P_a = \frac{n_a t_m}{\Delta p} \qquad (3)$$

where P_a is the permeability, n_a is the flux through the membrane, t_m is the membrane thickness and Δp is the partial pressure difference across the membrane. The unit of permeability is barrer and is defined as:

$$barrer = 1 \times 10^{-10} \frac{cm^3 (STP) \, cm}{cm^2 \, s \, cmHg}$$

The permeate side is kept at atmospheric pressure, however a sweep gas is used to keep the partial pressures of the permeating gases low on the retentate side of the membrane. The permeation rate is measured by a bubble flow meter and the permeate gas and retentate gas are sent to a gas chromatograph to determine the gas composition. The permselectivity (α) is calculated by taking the ratio of the individual permeability values.

Constant Volume Analysis

The constant volume method measures the pressure drop as a function of time, and enable the permeability of a single gas component to be calculated using Equation (4.

$$p_f = p_i \exp\left(\frac{kART}{V} t\right) \qquad (4)$$

Where k is the permeance, A is the membrane area, R is the gas constant, T is the absolute temperature, V is the volume, t is the time, p_i is the pressure at t=0 and p_f is the pressure at t=t_f. The permeability is simply the product of the permeance and the membrane thickness. Only ideal selectivity, based on pure component fluxes, can be measured with this apparatus.

RESULTS

The permeance of each CO_2-philic polymer listed above was tested as supported liquid membranes as a function of temperature. Testing the polymers as a liquid provides an assessment of the limiting permeability of a membrane composed of the flexible crosslinked polymer because the crosslinking of the polymer will decrease the diffusivity of the gas through the membrane and probably diminish the solubility of the gas (unless the crosslinking groups are more CO_2-philic than the oligomer). Therefore one would expect that the permeability obtained in these supported liquid membrane tests would exceed the permeability of a flexible membrane composed of the crosslinked oligomer.

PEGDME (MW=500 g/mol) and PPGDME (MW = 1060 g/mol) were tested as a liquid supported on a cross-linked nylon membrane and tested in a constant pressure apparatus for mixed gas permeability (CO_2/H_2). The results for PEGDME showed that at the lowest temperature tested (37 ˚C) the CO_2 permeability was 797±105 barrers with a selectivity of 11.06±0.35. At the highest temperature (150˚C) the CO_2 permeability was 1220±6 barrers with a selectivity of 1.53±0.07. The results for PPGDME showed lower permeabilities compared to PEGDME (although the molecular weight of the PPGDME was greater than the MW of the PEGDME) where the CO_2 permeability at the lowest temperature tested (37 ˚C) was 518±2.88 barrers with a selectivity of 5.86±0.13 and at the highest temperature (150˚C) the CO_2 permeability was 994±25 barrers with a selectivity of 1.29±0.04.

Permeability and permselectivity are shown in Figures **1** and **2** as a function of temperature. For PEGDME the hydrogen permeability and selectivity show good Arrhenius dependencies; however, the CO_2 permeability has a weak Arrhenius dependence, which could be due to the extremely strong interactions between CO_2 and the polymer. For PPGDME, the CO_2 and H_2 permeability and permselectivity show very good Arrhenius dependencies. The activation energy for CO_2 permeation in PPGDME is 1.9 times greater than that for PEGDME; however the activation energy for H_2 permeation in both these samples remains the same.
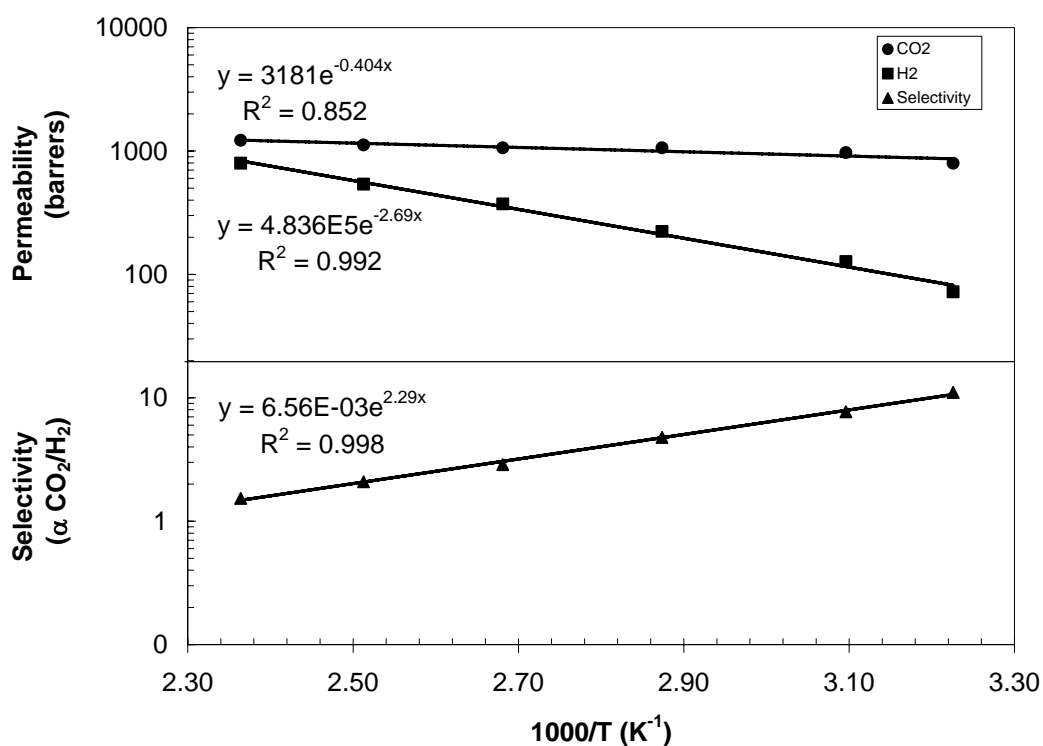
Figure 1 : $CO_2(\bullet)$ and $H_2(\blacksquare)$ mixed gas permeability as a function of temperature for PEGDME (M_n=500 g/mol) supported liquid membrane. The line indicates the exponential fit to determine the permeation activation energy.

Figure 2 : $CO_2(\bullet)$ and $H_2(\blacksquare)$ mixed gas permeability as a function of temperature for PPGDME (M_w=1060 g/mol) supported liquid membrane. The line indicates the exponential fit to determine the permeation activation energy.
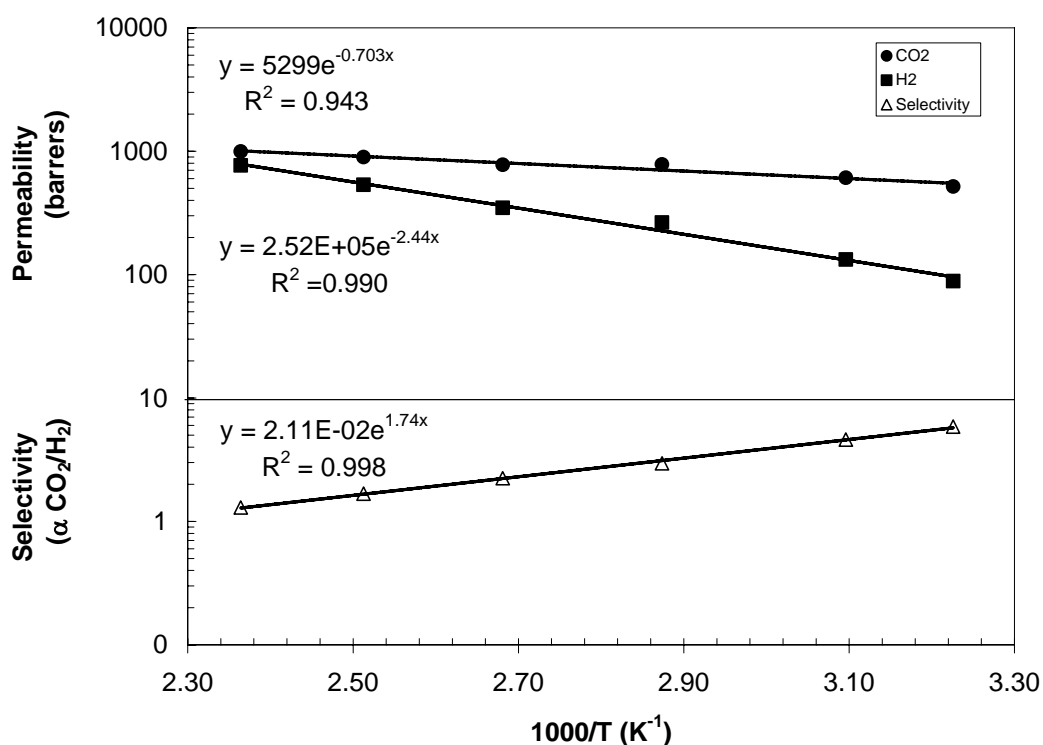
The crosslinked films were tested in the constant volume apparatus. The preliminary results for these polymers are listed in Table 1. Even from these preliminary results we can already see that the crosslinked PFPE shows a relatively high selectivity towards CO_2.

Table 1. Constant Volume Permeability Results

Polymer	CO_2 Permeability (barrers)	H_2 Permeability (barrers)	Selectivity ($\alpha CO_2/H_2$)
PFPEDA	365±62	83.2±7.2	4.4
PDMS	888	-	-
PEGDA	35	-	-
PPGDA	-	-	-

CONCLUSION

Several polymers were chosen based on their phase behavior in CO_2 at extremely high pressures to be good candidates for CO_2 selective membranes. Based on the dense film results to date; the PDMS membrane exhibits a high permeability for CO_2, the perfluorinated polyether has a relatively high permeance and a reasonably high selectivity such that this membrane's performance is at the Robeson limit for polymeric membranes for the CO_2/H_2 separation, and the PEGDME permeability is low. The remaining flexible crosslinked membrane data will be presented at the conference.

Based on the supported liquid membranes, the permeance of CO_2 shows much less temperature dependence than H_2 in the PPGDME and PEGDME membranes. PEGDME (Mw 1060) appears to exhibit a higher selectivity for CO_2 than PPGDME (Mw 500), however oligomers of the same number of repeat units or same Mw have not yet been studied. The remaining supported liquid membrane data will be presented at the conference.

ACKNOWLEDGEMENT

REFERENCES :

[1]. Blomquist, R. et al. "Low optical loss polymers". US Patent US20020122647, 2002.