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The CO_2 permeability and mixed gas CO_2/H_2 selectivity of membranes composed of CO_2-philic polymers

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ABSTRACT

The objective of this work was to design polymeric membranes that have very high CO_2 permeability and high mixed gas selectivity toward CO_2 rather than hydrogen. Therefore the membranes were based on "CO_2-philic" polymers that exhibit thermodynamically favorable Lewis acid:Lewis base and hydrogen bonding interactions with CO_2. CO_2-philic polymers that are solid at ambient temperature include polyfluoroacrylate (PFA); polyvinyl acetate (PVAc); and amorphous polylactic acid (PLA). Literature CO_2 permeability values for PVAc and PLA are disappointingly low. The cast PFA membranes from this study had low permeabilities (45 barrers at 25 °C) and very low CO_2/H_2 selectivity of 1.4. CO_2-philic polymers that are liquid at ambient conditions include polyethylene glycol (PEG), polypropylene glycol (PPG), polybutylene glycol with a linear -($(CH_2)_4O$)-repeat unit (i.e., polytetramethylene ether glycol (PTMEG)), polybutylene glycol (PBG) with a branched repeat unit, perfluoropolyether (PFPE), poly(dimethyl siloxane) (PDMS), and polyacetoxy oxetane (PAO). A small compound, glycerol triacetate (GTA) was also considered because it is similar in chemical structure to a trimer of PVAc. These liquids were tested as supported liquid membranes (SLM) and also (with the exception of PAO and GTA) as rubbery, crosslinked materials. Mixed gas permeability was measured using equimolar mixtures of CO_2 and H_2 feed streams at one atmosphere total pressure in steady-state flux experiments over the 298–423 K temperature range. The most promising SLMs were those composed of PEG, PTMEG, GTA, and PDMS. For example, at 37 °C the PEG-, PTMEG-, GTA- and PDMS-based SLMs exhibited CO_2/H_2 selectivity values of ~11, 9, 9, and 3.5, respectively, and CO_2 permeability values of ~800, 900, 1900, and 2000 barrers, respectively. Crosslinked versions of the PEG, PTMEG and PDMS membranes at 37 °C exhibited selectivity values of ~5, 6, and 3.5, respectively, and CO_2 permeability values of ~50, 300, and 3000 barrers, respectively.

1. Introduction

The capture of CO_2 from advanced power generation sources, such as the Integrated Gasification Combined Cycle (IGCC), and its subsequent geologic sequestration will increase the cost of power generation from these higher efficiency plants. However, improvements related to the selective removal of CO_2 from a post-water gas shift reactor stream rich in CO_2, H_2 and water could reduce these expenses. The two most common separation techniques being considered for the CO_2/H_2 separation are physical absorption with solvents and membrane-based separation. The attributes of membrane-based separation units include mechanical simplicity, relatively low energy requirements, and a single-step separation mechanism with no need for regeneration. Some of the disadvantages of membranes include large material cost for high throughput applications, fouling, limited commercial development, difficulty in attaining high product purity, and the limited thermal and chemical stability of many polymers.

Ideally, membranes would be able to maintain their mechanical integrity and favorable permeability and selectivity characteristics at the temperature of the water-gas shift reactor effluent, which is roughly 250 °C. The crosslinked polymers used in this study; however, would be viable only at temperatures less than 200 °C, the temperature at which conventional crosslinking groups become unstable. The supported liquid membranes could slowly volatilize at elevated temperatures or be displaced from the porous support if high differential pressures are applied across the membrane, and CO_2-philic solid polymer membranes typically have melting point values less than 100 °C. For strong size-selective (glassy polymers) separations permeability increases as temper-

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ature increases; however for rubbery polymers permeability and diffusivity can be temperature dependent [1,2]. Therefore it is expected that the water-gas shift effluent stream would have to be cooled substantially for polymeric membranes to be viable for this CO_2–H_2 separation. (For this reason, these CO_2-philic membranes will be subsequently examined for the CO_2–N_2 post-combustion separation, which is inherently low temperature.)

In this study, only reverse selective membranes (i.e., ones in which the larger gas molecule, CO_2, has a greater mixed gas permeability than the smaller gas component, H_2) were considered. For a dense polymeric material to act as a reverse selective solution–diffusion membrane, where permeability is the product of solubility and diffusivity, the solubility of CO_2 in the polymer must be so great that it more than compensates for the high hydrogen diffusivity in the polymer.

Membranes used for commercial gas separation processes are generally fabricated in the form of hollow fibers or rolled sheets. The types of membranes used in this lab-scale study, however, include thin cast or thermally pressed films of amorphous polymers, supported liquid polymer membranes (SLM) retained in a porous nylon fabric, or crosslinked polymeric films.

The films cast from a solvent or thermally pressed are composed of highly CO_2-philic solid polymers. Although this type of membrane is not used industrially, it is a convenient method for assessing the performance of membranes composed of the most CO_2-philic polymers that have ever been identified, which are the low melting point, amorphous solids such as poly(fluoroacrylate).

Although SLMs are easy to prepare and serve as excellent vehicles for quickly comparing the permeability and selectivity of polymers of oligomers, the slight vapor pressure of these liquids can compromise the integrity of the membrane placed in contact with flowing gases for extended periods of time. Ionic liquids, rather than polymers or oligomers, may be more appropriate for long-term supported liquid membrane use because these molten salts exert no detectable vapor pressure.

The flexible, crosslinked polymers, which are based on the same polymers used in the SLMs, are more practical membranes in that they are non-volatile and have excellent mechanical properties.

Polymers that have been previously assessed for removing CO_2 from a mixed gas CO_2/H_2 stream include polyphosphazenes, PEO-based materials, polymers with ultra-high free volume and fluoropolymers [3–17]. Polyphosphazenes were able to achieve CO_2 permeability of 250 barrers with a CO_2/H_2 selectivity of 10 at 30 °C [4]. Amorphous PEO had a CO_2 permeability of 140 barrers and a CO_2/H_2 of 6.8 at 35 °C [8]. Pure PEO has a tendency to crystallize at higher molecular weights, which greatly diminishes its permeability. PEG-containing copolymers of polyurethanes, polyimides and polyamides exhibited separation factors as high as ~7 [9]. PEBAX, a polyether-block-amide, has been studied as a CO_2 membrane material and as the matrix of a semi-interpenetrating membrane in conjunction with a CO_2-philic, PEG-based, liquid oligomer [10]. Pure PEBAX has shown a permeability of 73 barrers and a selectivity of 9.1 at 30 °C [16]. A 50:50 (wt%) PEBAX -poly(ethylene glycol) dimethyl ether (PEGDME) semi-interpenetrating network membranes had a CO_2 permeability of 606 barrers and a CO_2/H_2 selectivity to 15.2 at 30 °C [16]. Ultra-high free volume polymers generally yield highly permeable membranes (e.g., up to ~44000 barrers) but the selectivity of CO_2/H_2 is ~2 [17]. For most ultra-high free volume polymers the permeability order is $CO_2 > H_2 > He > O_2 > Ar > CH_4 > N_2 > Xe$ [18]. From the references mentioned here only one of the studies included mixed gas results [12], the rest of the results were performed using single gas permeation techniques, whereas this research is primarily focused on mixed gas permeability and selectivity.

The polymers chosen for this work have been previously shown to be highly "CO_2-philic" in that they are capable of dissolving in CO_2 at concentrations of ~5 wt% at extremely high pressure (1000–10000 psi), and/or they have been shown to be excellent solvents for the absorption of CO_2 [19–21]. The partial pressure of CO_2 in an IGCC plant is expected to be only several hundred psia, well below the pressure required for the polymer to dissolve in CO_2. Therefore there is no danger of these CO_2-philic membranes dissolving during the gas separation, particularly the crosslinked materials. These polymers, which are shown in Table 1, include: poly(heptadecafluorodecyl acrylate), a polyfluoroacrylate (PFA), probably the most CO_2-philic polymer that has been identified to date; polyvinyl acetate (PVAc), the most CO_2-philic oxygenated hydrocarbon-based polymer; amorphous polylactic acid (PLA); poly-3-acetoxy oxetane (PAO), a highly acetylated polymer designed via molecular modeling that exhibits a large number of multi-point interactions with CO_2; perfluoropolyether (PFPE), a polyhexafluoropropylene oxide Krytox® oil; polydimethyl siloxane (PDMS), commonly referred to as silicone oil; polyethyleneglycol dimethylether (PEGDME), a major constituent of the Selexol® CO_2 solvent; polypropyleneglycol dimethylether (PPGDME), which has a branched monomeric unit; polybutyleneglycol diacetate that is based on a linear $-((CH_2)_4O)-$ monomeric unit, also known as poly(tetramethylene ether glycol) diacetate (PTMEG-DAc), and polybutyleneglycol diacetate (PBGDAc) with a branched monomeric unit. A small compound, glycerol triacetate (GTA) was also selected for study as a supported liquid membrane because its structure is analogous to a trimer of PVAc (it is very difficult to synthesize low viscosity oligomers of vinyl acetate). The primary mechanism responsible for the remarkable levels of solubility in CO_2 are the multiple-point Lewis acid:Lewis base interactions and weak hydrogen bonding interactions between CO_2 and the backbone and side-chains of the polymers [19–21].

It is our contention that because these polymers have such favorable thermodynamic interactions with CO_2, they are excellent candidates for forming CO_2-permeable and CO_2-selective membranes. Specifically, it is expected that these favorable interactions between CO_2 and the polymer will enhance the solubility of the CO_2 in the polymer dramatically, thereby enhancing the CO_2 permeability and selectivity that will be reported in this study.

The only solid polymer used in this study, PFA, was knife cast into a dense film. This was the only manner in which this extremely fragile membrane, with a low melting point (~71 °C, measured by DSC) polymer could be made with enough mechanical integrity to be mounted and sealed into the membrane holder without tearing or cracking.

The liquid polymers, PFPE, PDMS, PEGDME, PPGDME, PTMEG-DAc, PBGDAc and PAO, and the small compound GTA were first tested as SLMs. Our intent in studying the supported liquid membranes was not primarily to propose such membranes for commercial application, where the high total pressure drop across the membrane and the appreciable vapor pressure of the oligomers would render them impractical for extended use. Rather, it was recognized to be a simple means of preparing a membrane that could be used to quickly assess the polymer's CO_2 permeability. Crosslinking typically diminishes CO_2 permeability because the crosslinking functionalities are less CO_2-philic than the polymeric segments and because of the "blockage" of free volume caused by crosslinked network, therefore it was expected that the SLM permeability values would exceed those of the corresponding crosslinked membranes.

PFPE, PDMS, PEG, PPG, PTMEG, and PBG were crosslinked in order to be assessed as rubbery, flexible films that serve as more robust membranes. PAO and GTA could not be end-functionalized for crosslinking, however.

Our results, along with prior literature results for CO_2-selective polymeric membranes, will be presented on a plot of mixed gas CO_2/H_2 selectivity vs. CO_2 permeability, facilitating the identifi-