The potential for use of cellulose triacetate membranes in post combustion capture

H.T. Lu, S. Kanehashi, C.A. Scholes, S.E. Kentish*

Department of Chemical and Biomolecular Engineering, The University of Melbourne, Parkville, VIC 3010, Australia

ABSTRACT

Cellulose triacetate (CTA) membranes occupy much of the gas separation market in natural gas processing. With a high CO_2/N_2 selectivity, this material may also be prospective for post-combustion carbon capture, if the permeance can be optimised. In capture applications, the impacts of liquid water condensate of variable pH, SO_x and NO_x on the gas separation performance are of critical interest to ensure maximum membrane lifetime. In this work, dense CTA membranes were aged in pH solutions of 3, 7 and 13 for a total of 60 days. It was found that the plasticisation of the CTA membrane when aged in pH 3 and pH 7 solutions enhanced the permeability of CO_2 and N_2 by over 30% with little impact on CO_2/N_2 selectivity. Conversely, the membrane aged at pH 13 failed due to hydrolysis reactions. The membrane was selective for SO_2 over CO_2 with a SO_2 permeability of 20 Barrer. Conversely, NO did not readily permeate, so that the permeate composition was below the level of detection. CTA membranes stored in SO_2/N_2 and pure N_2 for a 120 day period at 22 °C were relatively stable, with a slight loss in permeability due to membrane aging. Conversely, a significant loss in permeability was observed when these membranes were exposed to 0.74 kPa of NO for the same period. The performance loss appeared to relate to reaction of alcohol groups within the cellulose acetate structure with trace levels of NO_2 in the gas mixture. The results highlight the possibility for use of CTA membranes in post-combustion capture, if the active layer thickness can be reduced to enhance gas flux.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Carbon dioxide (CO_2) emissions are the leading cause for anthropogenic global warming, (Lashof and Ahuja, 1990; Preston and Jones, 2006; EPA, 2011; Cubasch et al., 2013), with the major source being the combustion of fossil fuels. Carbon Capture and Storage (CCS) is one potential pathway for achieving CO_2 emission reduction targets, securing a sustainable energy industry while taking advantage of vital resources. Membrane gas separation is one technology proposed for the carbon capture step that combines high energy efficiency with high surface area-to-volume ratios and is 'chemical free' (Wang et al., 2011).

Membrane gas separation is already commercialised for carbon capture, in natural gas sweetening for the removal of H_2S and CO_2. Cellulose triacetate (CTA) membranes have the greatest industry acceptance for this application, making up to 80% of this membrane market (Baker, 2004; Henis and Tripodi, 1980). CCS from coal-fired power station flue gas is another proposed strategy, known as post-combustion capture, where membrane gas separation has potential. While CTA membranes prepared by the phase inversion technique do not have the ideal permeability for post combustion capture, their high CO_2/N_2 selectivity, commercial readiness and proven industrial resilience means that they could have strong potential. Thin film composite CTA membranes have been prepared by other workers (Taajamaa et al., 2011; Niinivaara et al., 2016; Li and Huang, 1997) and emerging membrane fabrication technologies such as layer by layer (Sullivan and Bruening, 2003) and continuous assembly of polymers (CAP) (Fu et al., 2016) approaches could allow the thickness of the active layer to be reduced further, which would result in adequate permeance to meet gas flux requirements. Alternatively, the use of porous additives within the active layer to form a mixed matrix structure could also improve the permeability of the structure, without compromising the selectivity (Kanehashi et al., 2015).

However, flue streams normally contain moisture (100 ppm–20 wt% (Jecht, 2004; Løkken et al., 2008)) which is known to alter the separation performance of many membrane materials (Baker, 2000; Chen et al., 2011; Azher et al., 2014). Chen et al. showed that the presence of water vapour at low partial pressures reduced the permeability of CO_2 and CH_4 through dense CTA

* Corresponding author.
E-mail address: sandraek@unimelb.edu.au (S.E. Kentish).

membranes due to competitive sorption and "anti-plasticisation" behaviour (Chen et al., 2015). Conversely, higher water vapour pressures plasticised or swelled the membrane resulting in an increase in gas permeability and a decline of gas selectivity (Chen et al., 2015; Paulson et al., 1983). Upstream processing can also result in liquid water occasionally reaching the membrane unit, as droplets. In a post-combustion application, highly alkaline water may result from entrained fly ashes or the caustic slurry used in desulfurisation (Aitken et al., 1984; Satriana, 1981). Conversely, acidic water may overflow from a direct contact cooler if desulfurisation is not employed (Aitken et al., 1984; Mumford et al., 2011). As one of the earliest polymers used in membrane applications for both gas separation and water treatment, the hydrolysis of the cellulose acetate polymer in liquid water has been well studied across a range of pH conditions (Toprak et al., 1979; Dias et al., 1998; Vos et al., 1966). The overall hydrolysis rate constant, k, can be expressed as:

$$k = k_{H+} \left[H^+ \right] + k_{OH-} \left[OH^- \right] + k_{H_2O} \tag{1}$$

where the quantities in brackets are the ion activities. At ambient temperature, this results in a hydrolysis rate of around $5.4 \times 10^{-10} \, s^{-1}$ at pH 3, 1.4×10^{-10} at pH 7 and $0.0014 \, s^{-1}$ at pH 13. However, the impact of this hydrolysis on the gas separation performance of the membrane is less well understood.

Post-combustion flue gas typically contains 200–5000 ppmv SO_x when it exits the combustion chamber (Thambimuthu et al., 2005; Kuehne and Friedlander, 1980). If flue gas desulphurisation is used, this reduces the SO_x content to between 10 and 50 ppmv (Thambimuthu et al., 2005). This is mainly in the form of SO_2, with some SO_3 also present. Many polymeric membranes are selective for SO_2 relative to other major gases, because of the strong condensability of SO_2 (Scholes et al., 2009; Dytnerskii et al., 1989; Zavaleta and McCandless, 1976; Seibel and McCandless, 1974). The permeability of SO_2 within a composite CTA membrane has been reported by Kuehne and Friedlander, who focused on the impact of SO_2 pressure and membrane fabrication technique (Kuehne and Friedlander, 1980). However, the impact of SO_2 on a CTA membrane at different temperatures was not considered, which is important given the range of temperatures that can be present in flue gas. Further, the long term effects of SO_2 on CTA membrane performance have not been established.

The concentration of nitrogen oxides in power station flue gas is in the range of 150–300 ppmv, with nitric oxide (NO) the major component and <10 ppmv nitrogen dioxide (NO_2), with some variation dependant on combustion technologies (Mumford et al., 2011). Again, these levels can be reduced through the use of selective catalytic reduction (SCR), which can remove 85 to 98% of these pollutants (Thambimuthu et al., 2005; Faucett et al., 1977), but this is not always in place. To the best of the authors' knowledge, there is no reported information on the impact of NO on a CTA membrane, though the effect on another class of polymeric membranes, polyimides, is reported (Scholes et al., 2011). It is expected that NO will have higher diffusivity than CO_2 because of smaller kinetic diameter, but the solubility of NO will be lower than CO_2, based on critical temperature behaviour (Yampolskii et al., 2006). An understanding of the impact of NO on CTA membranes is of vital importance if they are to be applied to post-combustion capture.

In this investigation, the gas transport performance of CTA membranes in single gas and mixed gas feeds of CO_2, N_2 and impurities (H_2O, SO_2 and NO) are reported. In addition, the impact of these impurities on the CTA membrane over 60–120 day periods is reported. This information will assist in evaluating the potential for CTA membranes to be used in this emerging industrial application.
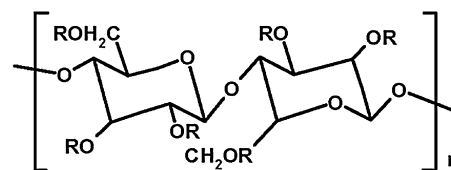
Fig. 1. Chemical structure of cellulose triacetate polymer.

2. Experimental

2.1. Membrane fabrication

The basic chemical structure of CTA is shown in Fig. 1. The CTA polymer utilised in the study was supplied by Cellulose Company – Daicel Corporation, Japan with an acetylation degree of 61.6%. Prior to membrane fabrication, the polymer powder was dried overnight under vacuum at 100 °C to remove the moisture. At least two membranes were tested in each experiment to confirm the reproducibility.

Dense membranes were fabricated using dicholoromethane (ChemSupply, Australia) as the solvent. The solution (1 wt%) was filtered and cast into glass petri dishes that were kept covered for 24 h for solvent evaporation. The thickness of each membrane was measured with a micrometer and found to be in the range of 60–80 μm.

A thin film CTA membrane was also fabricated by spin coating to measure the permeability of SO_2 and NO (Huang and Paul, 2007; Scofield et al., 2016). A 4 wt% CTA in dichloromethane solution was spin coated onto a hydrophilic polytetrafluoroethylene (PTFE) membrane filter of 0.2 μm nominal pore size (Omnipore™, Merck Millipore, Australia). The spinning rate was set at 1500 rpm for 20 s and the substrate was pre-wetted by deionised water to reduce the pore penetration of polymer and solvent (Scofield et al., 2016). The thickness of the thin film composite CTA was measured by Scanning Electron Microscopy (FEI Quanta 200 ESEM FEG). The membrane was gold-coated by a Dynavac Mini Sputter Coater prior to imaging. The thin film thickness was found to be in the range of 3–6 μm.

All membranes were dried under vacuum at 35 °C for 24 h and then 100 °C for a further 24 h. The fabricated membranes were kept in a desiccator to minimise the exposure to moisture. The membranes were stored for 14 days prior to permeability measurements. Densification due to loss of free volume (physical aging) is greatest for any glassy membrane during these first two weeks and hence the delay ensured that this densification did not overpower any other more subtle changes in membrane permeability. Further, in engineering practice, at least 14 days would be needed to transport and install the membrane module after fabrication, hence the performance in this initial period is less relevant.

2.2. Characterisation

The sorption kinetics of the membrane was determined by immersing the membrane samples into solutions at 35 °C. Solutions of pH 3.0, 7.0 and 13.0 were prepared from sulphuric acid (Chemsupply, Australia), purified water (Millipore Elix) and sodium hydroxide (Sigma Aldrich, Australia). After a specified immersion time, the membrane was removed from the solution, excess liquid droplets on the membrane surfaces removed by wiping with a tissue, and weighed on an analytical balance (XS205 Mettler Toledo Australia) with maximum error of 0.06% (Potreck et al., 2009). The