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Pilot plant performance of rubbery polymeric membranes for carbon dioxide separation from syngas

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ABSTRACT

Pre-combustion carbon capture separates carbon dioxide from syngas before combustion. Rubbery polymeric membranes offer the ability to separate carbon dioxide from syngas, and in particular hydrogen, with reasonable selectivity. Here, the gas separation performance of three rubbery polymeric membranes, poly dimethyl siloxane (PDMS), cross-linked polyethylene glycol (PEG) and poly (ether-b-amide) (PEBAX 2533), are reported upon exposure to real unshifted syngas, as part of the CO2CRC Mulgrave capture project. At low temperatures, all three membranes were able to separate CO_2 from syngas; however competitive sorption by other syngas components significantly altered their performance relative to reported laboratory results. For PDMS, under syngas conditions CO_2 permeability was reduced compared to the pure gas permeability, but CO_2/H_2 and CO_2/N_2 selectivity were improved in the presence of syngas. This resulted in good CO_2 separation performance for this membrane. However over 24 h of exposure the performance decreased somewhat. In contrast, both PEG and PEBAX membranes demonstrated poor CO_2 separation performance upon exposure to syngas. In particular, low CO_2/H_2 selectivities where observed, indicating that both membranes upon exposure to syngas had poor selective ability.

1. Introduction

Increasing atmospheric carbon dioxide levels have been linked to climate change [1], which is associated with the world's dependence on fossil fuels. One viable option in reducing carbon emissions is the capture of carbon dioxide from large point sources such as power plants, with long term storage through geosequestration, known as carbon capture and storage [2]. Membrane technology holds a number of advantages for CO_2 capture [3,4]. The approach is operationally simple; the removal of gas through a selective film ensures high energy efficiency; and the equipment footprint is small leading to lower capital cost compared to conventional separation processes.

There are three main strategies for CO_2 capture from fossil fuel based power plants; post-combustion, oxy-fuel combustion and pre-combustion. For pre-combustion capture, fossil fuels are reformed into synthesis gas (syngas) comprised mainly of hydrogen and carbon monoxide [2,5]. This is further converted to more hydrogen through the water gas-shift reaction, resulting in high pressure CO_2 and H_2. Separation of these two components allows for the storage of CO_2, while H_2 can be used for a number of processes, such as power generation.

Pre-combustion processes can be further classified into those that use oxygen-blown gasification and those that use an air-blown gasifier. In the former case, the shifted syngas is as above; a fairly simple mixture of CO_2 and H_2. In such circumstances, a hydrogen-selective membrane is usually most appropriate, as the carbon dioxide can be retained at a high pressure for storage and a sweep gas can be used on the permeate side to ensure low permeate side partial pressures [6]. However, in air-blown gasification the syngas is diluted by a significant stream of nitrogen, complicating the carbon dioxide capture operation. In such operations, it may become more economic to use a CO_2-selective membrane, permeating carbon dioxide while retaining a hydrogen/nitrogen mixture which is suitable for direct combustion in a downstream turbine.

Hydrogen is a small molecule and so is readily separated from the other syngas components using a size-selective membrane. There are a range of polymeric, metallic and inorganic membranes that can achieve good H_2 separation from syngas. However the development of membranes that will instead retain the small molecular size of H_2 but permeate the larger CO_2 is a significant challenge [7] and can only be achieved through polymeric membranes [8]. Polymeric membranes can achieve this separation if they are strongly solubility selective [8], which favours CO_2, rather

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than diffusivity selective. In general, rubbery polymeric membranes, those operating above the glass transition temperature of the polymer, have this capability. This is because the high mobility of polymer chains in the membrane film permits a high diffusivity of all gases through the polymeric matrix and therefore differences in gas solubility within the polymeric matrix control the selectivity.

Here, we report on the performance of three rubbery polymeric membranes, poly dimethyl siloxane (PDMS), cross-linked poly ethylene glycol (PEG) and poly ether-b-amide (PEBAX 2533), in pre-combustion carbon capture pilot plant trials. These trials were part of the Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC) Mulgrave capture project [9,10]. The rubbery polymeric membranes are operated to separate CO_2 from unshifted syngas, generated from air-blown brown coal gasification. Our aim was to determine the membrane and strategy that has the most potential for successful implementation of carbon capture on an industrial scale [11]. The polymeric membranes, PDMS, PEG and PEBAX 2533 were chosen because of strong support within the literature for these polymers in CO_2 separation from H_2, based on laboratory results [7,12–15]. However, little research has focused on their performance under mixed gas conditions. Our own work has considered the impact of H_2S, CO and water on CO_2 permeation in PDMS [16] while Potreck et al. [17] and Sijbesma et al. [18] considered the impact of water on nitrogen permeation in PEBAX 1074. No information has been reported for their performance in actual syngas separation. This information is vital in the development of membrane technology for pre-combustion capture, to enable future membrane based capture plants to be designed and commissioned.

2. Experimental

Poly dimethyl siloxane composite membranes (PERVAP 4060) were supplied by Sulzer Chemtech (Switzerland). The composite membranes were composed of a PDMS film on a highly microporous support, with PDMS thickness ~10 μm, and used as supplied. PEBAX 2533 was supplied by Arkema, and cast in our laboratory as flat sheet membranes from 1-butanol (3 wt%). Cross-linked PEG was synthesized from poly (ethylene glycol) methyl ether acrylate (Mn 454 g/mol) (Aldrich) with 50% water, cast as flat sheet membranes with cross-linking promoted through 1-hydroxylcyclohexyl phenyl ketone (Irgacure 184) and UV light following the procedure established by Lin and Freeman [19]. Both PEG and PEBAX membranes where dried under vacuum at 80 °C for 12 h [20], producing membranes of average thickness 70 μm. The polymeric structures of all three membranes are given in Fig. 1.

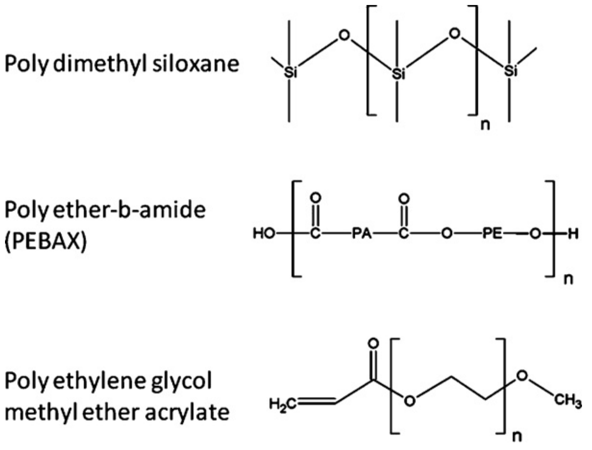

Fig. 1. Chemical structures of poly dimethyl siloxane (PDMS), poly ether-b-amine (PEBAX), where PA is the poly amide block and PE the poly ether block, and poly ethylene glycol methyl ether acrylate (PEG).

The CO2CRC Mulgrave capture project membrane pilot plant original design was undertaken by the CO2CRC and Process Group Pty Ltd., with further additions to the design performed by Pilot Plant Management Services Pty Ltd. (PPMS). Construction was undertaken by PPMS with assistance from the CO2CRC. The pilot plant process is shown in Fig. 2.

The membrane pilot plant was housed within a custom built cabinet (Erntec). All piping was 1/4″ stainless steel tube, except for the main feed line from the gasifier which was 1/2″ stainless steel tube, and the final exit stream to the onsite extraction unit (Nylon). All valves and fittings were made from stainless steel (Swagelok). Pressure gauges (Swagelok) and pressure transmitters (GEMS Sensors and Control – Basingstoke England) with displays (PR electronics) where positioned on all lines. A back-pressure regulator (Porter 08011) on the retentate of the membrane unit controlled the pressure within the module, with feed gas flowrate measured by a gas rotameter (0–10 L/min Kytala (Muurame Finland)). The retentate flowrate was measured by a gas meter (Ampy Email Model 750), while the permeate flowrate measured by a universal flowmeter (Agilent Technologies ADM3000). To prevent

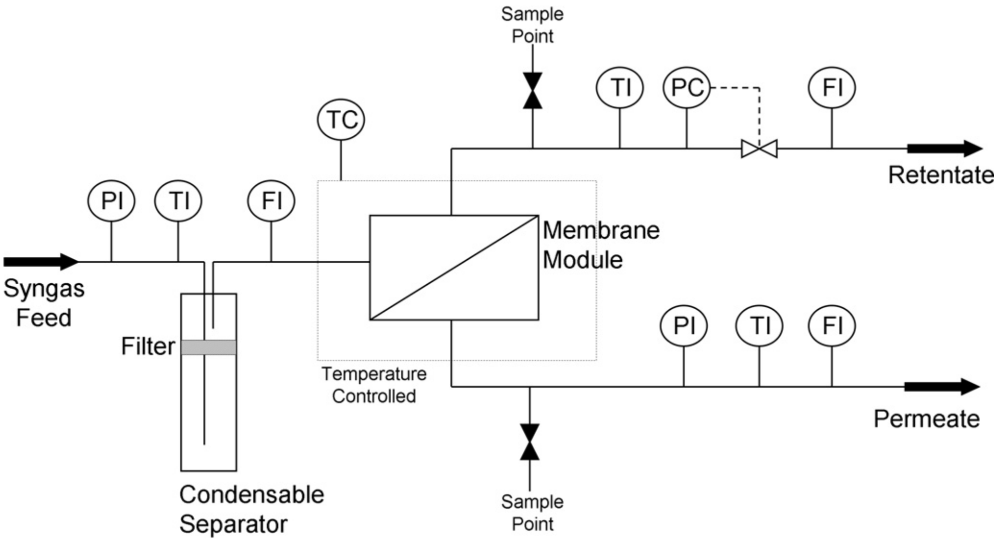

Fig. 2. CO2CRC Mulgrave Project Membrane Pilot Plant process diagram.