Establishing the suitability of symmetric ultrathin wall polydimethylsiloxane hollow-fibre membrane contactors for enhanced CO$_2$ separation during biogas upgrading

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ABSTRACT

A hollow fibre membrane contactor (HFMC) comprised of nonporous symmetric ultrathin wall polydimethylsiloxane (PDMS) fibres has been studied for biogas upgrading to establish if the ultrathin wall can enable low resistance to mass transfer coupled with enhanced selectivity for carbon dioxide (CO$_2$). For a feed gas CO$_2$ mole fraction of 80%, a CO$_2$ flux of 1.25×10^{-4} mol m^{-2} s^{-1} was recorded which was higher than expected and is ostensibly due to the thin wall and the absence of a support layer which can limit gas transfer due to concentration polarisation. Maximum CO$_2$ flux was recorded at the highest liquid velocity tested due to a reduction in the thickness of the liquid phase boundary layer. Resistance in series analysis demonstrated that by limiting liquid phase resistance, mass transfer was controlled by the PDMS membrane and selectivity toward CO$_2$ was analogous to the ideal selectivity imparted by PDMS. In comparison, mass transfer was liquid phase controlled for a microporous HFMC that comprised of fibres with equivalent wall thickness. Whilst PDMS presents a higher theoretical selectivity when compared to the gas filled pore of a microporous fibre, higher selectivity was provided by the microporous fibre due to the solvents selectivity, which established that selectivity is dependent upon the controlling phase boundary. Though higher CO$_2$ fluxes were achieved with microporous fibres, ultrathin PDMS fibres are potentially beneficial for gases with a low CO$_2$ mole fraction due to their greater resistance to wetting. However, at higher CO$_2$ mole fraction, PDMS HFMC are only viable by increasing CO$_2$ flux through overpressure or reduction in wall thickness, though the feasibility is impingent upon validating the fibres mechanical integrity for both conditions.

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1. Introduction

There is increasing demand for technology capable of separating carbon dioxide (CO$_2$) from biogas to enable delivery of a purified gas product suitable to supplement natural gas supply. To achieve the appropriate purity, the methane (CH$_4$) content must be increased to equivalent or higher than natural gas ($> 81\%$) from a typical inlet composition of 60:40 CH$_4$:CO$_2$, though CO$_2$ content can vary widely between 15% and 60%, dependent upon biogas source [1,2]. Conventional gas/liquid absorption contactor processes have been most frequently employed as the separation technology. Absorption relies upon the difference in solubility between CO$_2$ and CH$_4$ in the solvent phase to deliver the required selectivity. According to a survey of European installations, 69% of the 31,935 m^3 h^{-1} of biogas upgrading capacity is delivered through gas/liquid absorption columns and whilst numerous absorption solvents are commercially available, water has been predominantly used as the absorption solvent [1].

Hollow-fibre membrane contactors (HFMC) are a gas/liquid contactor process that supports an analogous absorption mechanism to conventional absorption columns. Whereas absorption columns are dependent upon direct contact between gas and liquid phases, for microporous HFMC, the hydrophobicity of the membrane facilitates the separation of the liquid phase from the gas phase with the gases free to diffuse through the open pore structure. Furthermore, due to the increase in specific surface area, the technology presents an inherent advantage in reducing both process scale and absorption solvent consumption, relative to conventional columns. Herzog and Pederson [3] noted economic advantages for natural gas treatment (*ca.* 10% CO$_2$) using an amine based solvent coupled with a microporous polytetraflouroethylene (PTFE) based HFMC. The authors presented a 70–75% technology weight reduction and 65% space reduction for the membrane absorber and stripper in comparison to standard absorber design.

Whilst the potential of microporous HFMC has been demonstrated, pore wetting by the absorption solvent is a common constraint that can reduce process efficiency [4].

Nonporous or dense membrane HFMC can alternatively be used to form the boundary between the two phases enabling retardation to solvent penetration. Furthermore, the nonporous membrane can enhance selectivity for CO_2 over methane since separation is mediated by diffusion through the polymeric membrane substrate. However, diffusion through the nonporous membrane wall can incur significant resistance to mass transfer (k_m):

$$k_m = \frac{P_i}{\delta} \quad (1)$$

where P_i is the permeability, and δ is the membrane thickness. To diminish resistance attributable to the nonporous material, previous authors have utilised polydimethylsiloxane (PDMS) as this polymer exhibits high gaseous permeability due to its low glass transition temperature [5,6]. However, current commercially available PDMS hollow fibres typically comprise wall thicknesses between 165 μm and 1000 μm [7,8,9] which incurs significant resistance and as such wall thickness has been cited as the limiting factor in the practical application of PDMS for HFMC applications [6]. To overcome this barrier, in the following study, an ultra thin wall PDMS hollow-fibre with a wall thickness of 35 μm is tested. For illustration, this wall thickness is equivalent to the skin layer (38 μm) of a thin film composite (TFC) PDMS membrane previously tested for the separation of polypropylene from nitrogen [10]. Whilst TFC have been previously developed to limit the resistance of the selective dense material, the support layer increases the overall membrane wall thickness. In this study, the PDMS fibre wall is symmetric. Consequently, with no support layer, total wall thickness is reduced as is the potential effect of internal concentration polarisation. This ultrathin wall symmetric PDMS membrane is therefore evaluated to determine its suitability as a highly selective absorption process for biogas upgrading. The nonporous PDMS fibre is compared to microporous polypropylene (PP) fibres of an equivalent wall thickness (40 μm) to investigate: (i) differences in mass transfer between fibres over a broad range of feed gas CO_2 mole fractions (y_{CO_2}); and (ii) enhancement in selectivity (α_{CO_2/CH_4}) provided by the nonporous PDMS fibre.

2. Materials and methods

2.1. Experimental set-up

The experimental set-up was similar to that used by Atchariyawut et al. [11] (Fig. 1). Carbon dioxide (CO_2, 99.7%) and methane (CH_4, 99.995%) (BOC gases, Ipswich, UK) were therefore blended in binary mixtures to simulate biogas at numerous CH_4/CO_2 compositions to vary y_{CO_2} from 20% to 80%. The CO_2 and CH_4 gas flow rates were regulated from each gas cylinder using calibrated mass flow controllers (range 0.01–1.0 l min^{-1}, Roxspur Measurement and Control Ltd., Sheffield, UK). Following in-pipe mixing, the gas was passed through the shell-side of the hollow fibre modules. The nonporous module comprised of a polydimethylsiloxane (PDMS) based hollow-fibre (PermSelect® PDMSXA-1.0, MedArray, Ann Arbor, USA) whilst the microporous module comprised of polypropylene (PP) based hollow fibres (1.7 × 5.5 MiniModule®, Membrana GmbH, Wuppertal, Germany) (Table 1). Fibre wall thickness and pore morphology were confirmed using scanning electron microscopy (SEM) at an accelerating voltage of 10 kV (XL30, FEI, Oregon, US) whilst surface roughness was performed by the atomic force microscopy (AFM) (Dim3100, Veeco, Santa Barbara, US) and roughness data was obtained using the accompanying software (version 4.42r4). Deionised water (DI) was used

as the CO_2 absorption solvent with a nominal conductivity of < 1 μS cm^{-1}. The DI water was stored in a PVC tank, which was fixed within a water bath fitted with an ancillary heater (1.5 kW, Grant Instruments Ltd., Shepreth, UK) to regulate temperature between 19 °C and 22 °C. The temperature of the liquid outlet, tank inlet and air temperature were monitored at each experiment. The DI water was passed counter-currently through the lumen side of the membrane using centrifugal pumps for flow rates (Q_L) up to 6 l min^{-1} (50010 Series, Jabsco GmbH, Norderstedt, Germany) and for Q_L up to 24 l min^{-1} (DC15/5, Totton Pumps, Southampton, UK). Liquid flow rate was controlled using a needle valve between the pump and module. Gas flow rates were measured with a 50 ml soap film bubble flow metre calibrated for a flow range between 10 and 300 ml min^{-1} (Restek, Bellefonte, USA). Due to slight differences in shell and lumen side priming volumes between modules, L/G was based on velocity rather than flow with maximum V_L of 2.46 cm s^{-1} and 1.66 cm s^{-1} used for the micro-porous and non-porous membranes respectively. The gas and liquid side pressure drops across the module were measured using four pressure transducers sited upstream and downstream of the module (range 0–1 bar, Sensit, Roxspur Measurement and Control Ltd., Sheffield, UK). Pressure data was recorded using a 16-bit analogue to digital converter (ADC-16, Pico Technology, Eaton Socon, UK).

When operating the microporous polypropylene membrane, trans-membrane pressure was regulated at *ca.* 0.25 barg to limit gas bubble formation on the liquid side and to minimise wetting. The liquid outlet was sampled using pre-evacuated 22.7 ml glass vials fitted with chlorobutyl/PTFE gas tight caps (Chromacol, Welwyn Garden City, UK). The liquid was collected under vacuum to ensure no exposure to environmental conditions [9]. In accordance with the method of Cookney et al. [9], liquid samples were permitted to reach equilibrium prior to analysis of the headspace. The resultant data was applied to a mass balance procedure to determine the liquid phase CH_4 and CO_2 concentrations [9,12]. Gas outlet samples were collected in capped, evacuated GC vials for subsequent analysis by gas chromatography with a thermal conductivity detector (200 Series GC, Cambridge Scientific, Ely, UK). Validation gas samples were collected using 100% CH_4 in the gas line. The integrated areas of the validation samples were compared with a pure methane standard (99.99%, Scientific Technical Gases Limited, Newcastle, UK) and were within 1% of the expected result. To reach steady-state conditions for each run of experiments, sampling was started after three retention times or a minimum of 2 min depending on which was the longest. Gas outlet and liquid outlet samples were collected and analysed in triplicate and analysed following each change in process conditions.

2.2. Mass transfer analysis

The CO_2 flux into the absorption solvent was estimated by [13]

$$J_{CO_2} = \frac{(Q_{g,i}c_{ii} - Q_{g,o}c_{io})273.15\,K}{22.4\frac{L}{mol}T_g A_m} \quad (2)$$

where $Q_{g,i}$ and $Q_{g,o}$ are the inlet and outlet volumetric gas flow rates, c_{ii} and c_{io} the CO_2 concentrations in the feed and gas retentate, T_g the gas temperature and A_m the membrane area based on the inner fibre diameter. Methane is a partially soluble gas and as such results in low methane fluxes. Consequently, methane flux was evaluated based upon liquid phase data using the dissolved methane concentration to determine flux, J

$$J_{CH_4} = \frac{(Q_{l,i}c_{l,i} - Q_{l,0}c_{l,0})}{M_{CH_4}A_m} \quad (3)$$

where $c_{l,i}$ and $c_{l,o}$ are the inlet and outlet liquid CH_4 concentrations, $Q_{l,i}$ and $Q_{l,o}$ are the liquid flow rates, M_{CH_4} is the molar mass of CH_4