Quantifying the loss of methane through secondary gas mass transport (or ‘slip’) from a micro-porous membrane contactor applied to biogas upgrading

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Abstract

Secondary gas transport during the separation of a binary gas with a micro-porous hollow fibre membrane contactor (HMFC) has been studied for biogas upgrading. In this application, the loss or ‘slip’ of the secondary gas (methane) during separation is a known concern, specifically since methane possesses the intrinsic calorific value. Deionised (DI) water was initially used as the physical solvent. Under these conditions, carbon dioxide (CO$_2$) and methane (CH$_4$) absorption were dependent upon liquid velocity ($V_L$). Whilst the highest CO$_2$ flux was recorded at high $V_L$, selectivity toward CO$_2$ declined due to low residence times and a diminished gas-side partial pressure, and resulted in slip of approximately 5.2 % of the inlet methane. Sodium hydroxide was subsequently used as a comparative chemical absorption solvent. Under these conditions, CO$_2$ mass transfer increased by increasing gas velocity ($V_G$) which is attributed to the excess of reactive hydroxide ions present in the solvent, and the fast conversion of dissolved CO$_2$ to carbonate species reinitiating the concentration gradient at the gas-liquid interface. At high gas velocities, CH$_4$ slip was reduced to 0.1 % under chemical conditions. Methane slip is therefore dependent upon whether the process is gas phase or liquid phase controlled, since methane mass transport can be adequately described by Henry’s law within both physical and chemical solvents. The addition of an electrolyte was found to further retard CH$_4$ absorption via the salting out effect. However, their applicability to physical solvents is limited since electrolytic concentration similarly impinges upon the solvents capacity for CO$_2$. This study illustrates the significance of secondary gas mass transport, and furthermore demonstrates that gas-phase controlled systems are recommended where greater selectivity is required.

Keywords: Binary gas; slipping; slippage; fugitive; solvent recirculation; gas/liquid
1. Introduction

Biogas is a renewable source of methane (CH$_4$) produced on a large scale at wastewater treatment works during anaerobic digestion. Typically the biogas has a CH$_4$ content of 55-60 % by volume, compared to >90 % CH$_4$ for natural gas. Carbon dioxide (CO$_2$) is the key balancing gas contributing 35-50 % of the total gas volume. As an inert gas, CO$_2$ lowers the calorific value (CV) of the biogas from 36 MJ m$^{-3}$ for natural gas to 21 MJ m$^{-3}$ (Ryckebosch et al., 2011). Whilst the lower CV of biogas is appropriate for direct utilisation in combined heat and power (CHP) applications, the CV must be upgraded for use as ‘biomethane’, or natural gas alternative, principally through the selective separation of the CO$_2$. As a result of incentivisation schemes, it is increasingly preferable to upgrade biogas for ‘gas to grid’ instead of electricity generation via CHP because of the disparity in value of the gas for these applications. For example, as a consequence of the ‘renewable heat incentive’ (RHI) in the UK, a cubic meter of biogas is worth approximately 32 pence (p) if used as a natural gas alternative but only 19 p when applied to CHP (Read et al., 2011).

Several technologies exist for selective CO$_2$ removal, including pressure swing adsorption (PSA), dense membrane separation and absorption columns using either water or a chemical as the absorption solvent. Whilst the specific mechanism for gas separation differs between technologies, these current process options are not able to offer definitive selectivity during separation, thus some loss of the secondary gas can be expected. The term ‘slip’, corresponds to the loss of this secondary gas, in this case methane, from the product side due to either co-permeation, in the case of dense permeation membranes, or co-dissolution during absorption. The significance of slip to process operation is application specific. For example, in the case of dilute hydrogen sulfide (H$_2$S) absorption from air for odour treatment (Jefferson et al., 2005; Esquiroz-Molina et al., In Press), the co-solubilisation of the ternary gases nitrogen and oxygen (and low concentration CO$_2$) are not quantified, or considered. However, for biogas upgrading the significance of methane ‘slip’ is considerable since methane possesses the intrinsic value as the product gas. Few published studies have sought to quantify slip. Early studies of full-scale dense gas membranes for CH$_4$ recovery from
landfill gas reported up to 18% methane slip (Ho and Sirkar, 1992) though this has since been reduced using multiple membrane arrays to enable subsequent treatment of the retentate gas stream which comprises low concentration methane. By comparison, 8% and 13.1% CH₄ slip have been reported for PSA and absorption respectively, the latter using water as the solvent and a pressurised gas phase of between 20-25 bar (Baldwin, 2011; Läntelä et al., 2011).

For biogas upgrading at sewage works, packed tower absorption is the predominant technology employed with water used as the absorption solvent, for process simplicity, and due to the wide availability of treated final effluent onsite. Water demonstrates a reasonable selectivity for CO₂ since methane is only a partially soluble gas. Consequently, analysis of methane transport during process evaluation is often neglected. However, high liquid flow rates are demanded in absorption technologies that result in high methane slip over long operational periods. Several authors have considered the application of hollow fibre membrane contactors (HFMCs) as an alternative absorption technology to conventional packed towers for biogas upgrading (Atchariyawut et al., 2007; Simons et al., 2009). The hydrophobic membrane enables separation of the gas and liquid phases, with gaseous diffusion facilitated through the micro-porous membrane which enhances mass transfer and increases specific surface area availability compared to conventional absorbers. Consequently, Nii and Takeuchi (1992) noted an order of magnitude reduction in liquid flow rate when comparing a polydimethylsiloxane HFMC with a conventional packed absorption column to achieve comparable removal of CO₂ from flue gas. Whilst enhanced mass transfer has been ascertained, the fate of the secondary gas, or the slip, during absorption has not been examined and is central to understanding process efficacy. This study therefore seeks to quantify: (i) the mass transfer of the two principal biogas components methane and carbon dioxide to determine the significance of methane slip from HFMC applied to upgrading; (ii) the capacity to mitigate methane slip through manipulating solvent chemistry; and (iii) evaluating the impact of multiple solvent cycles on methane slip compared to single pass operation.
2. Materials and methods

2.1 Equipment setup and operation

Methane (99.995 %) and carbon dioxide (99.7 %) (BOC gases, Ipswich, UK) gases were controlled using mass flow controllers (0.01-1.0 L min\(^{-1}\), Roxspur Measurement and Control Ltd., Sheffield, UK) and were mixed in-line to provide an initial 60/40 CH\(_4\)/CO\(_2\) gas composition to the shell-side of the HFMC (Liqui-Cel\textsuperscript{®} 1.7x5.5 MiniModule\textsuperscript{®}, Membrana GmbH, Wuppertal, Germany)(Figure 1). The outlet gas flow rate was measured using a bubble flow meter (50 mL, Restek, Bellefonte, USA).

Absorbent was stored in a 50 L PVC tank and maintained at 24-26 °C by a thermostat circulator (GD120, Grant Instruments Cambridge Ltd., Shepreth, UK) sited in the water bath. The absorbent was passed through the fibre lumen in counter-current mode using a centrifugal pump (max. 6 L min\(^{-1}\), 50010 series, Jabsco GmbH, Norderstedt, Germany). The HFMC comprised 7400 polypropylene (PP) fibres, with a nominal outer diameter (OD) and length of 300 µm and 0.113 m respectively, yielding a surface area of 0.58 m\(^2\) (based on inner fibre diameter, ID of 220 µm). The fibres were characterised with a nominal pore size of 0.03 µm and porosity of 40 %. The fibres were potted in polyurethane fixed in a polycarbonate shell with an ID of 0.0425 m resulting in a packing density of 0.369.

Solvent recirculation was investigated to compare multiple passes (or cycles) of solvent use to single pass solvent use. For these experiments, a 10 L absorbent reservoir was incorporated into the liquid side of the experimental design to minimise the impact of sampling from the liquid phase on the resultant mass transfer data. The vessel was magnetically stirred to ensure complete mixing of the bulk solvent. During multiple-pass (MP) experiments, a smaller HFMC was employed to ensure that the MP tests could be conducted with a reasonably short timeframe. This smaller module (Liqui-Cel\textsuperscript{®} 1x5.5 MiniModule\textsuperscript{®}, Membrana GmbH, Wuppertal, Germany) comprised of 2300 identical hollow fibres (OD 300 µm/ ID of 220 µm/pore size 0.03 µm) but 0.10 m in length, yielding a surface area of 0.18 m\(^2\).
All absorbents were based on de-ionised (DI) water with a resistivity of 18.2 MΩ-cm. For experiments using chemically based solvents, either sodium chloride (NaCl) or sodium hydroxide (NaOH) was used (NaCl 99% and NaOH 98% pellets, Fisher Chemicals, Loughborough, UK). Chemical solutions were initially prepared as concentrates by adding 1755 g NaCl and/or 1320 g NaOH to 10 L of DI water with thorough mixing to ensure complete dissolution. Concentrates were then diluted in the absorbent tank to provide 1.0 M solutions. To determine liquid phase concentrations, the method adapted from Alberto et al., (2000) was used in which evacuated vials were employed to ensure no exposure of aqueous solvent samples to the environment. Prior to use, the 22.7 mL GC-MS glass vials were capped and sealed with gas-tight PTFE/aluminium crimp caps (Fisherbrand, Fisher Scientific, Loughborough, UK). Vials were then evacuated for 20 s using a vacuum pump (CAPEX L2C, Charles Austen Pumps, Byfleet, Surrey, UK) at fixed pressure to ensure consistent vacuum pressures in each vial (0.3 atm). Aqueous solvent samples were collected from a luer lock needle fitted on the liquid outlet. The reduced vial pressure imposed a vacuum on the liquid side enabling collection of a liquid sample, which when complete, had equilibrated to atmospheric pressure. Liquid samples were agitated for 7 minutes (maximum speed, Multi Reax, Heidolph, Schwabach, Germany), and were subsequently left to equilibrate overnight. The resultant dissolved phase concentrations were calculated based on a mass balance (Alberto et al., 2000). Methane flux was calculated using:

\[
J_{CH4} = \frac{(Q_{i,l} \times c_f) - (Q_{i,0} \times c_r)}{M_{r,CH4} \times A_m}
\]

(equation 1)

Where \(J_{CH4}\) is methane flux (mol m\(^{-2}\) s\(^{-1}\)), \(Q_{i,l}\) and \(Q_{i,0}\) are the inlet and outlet liquid flow rates respectively (m\(^3\) s\(^{-1}\)), \(c_f\) and \(c_r\) are CH\(_4\) concentrations in the liquid feed and retentate respectively (g m\(^{-3}\)), \(M_{r,CH4}\) is the relative molecular mass of methane and \(A_m\) is the active surface area of the HFMC.

Gas samples were taken from GC septa fitted on the gas-side upstream and downstream of the
contactor and injected onto a gas chromatograph. The CO₂ flux was calculated according to Atchariyawut et al. (2007):

\[
J_{CO_2} = \frac{[(Q_{gi} \times c_{f}) - (Q_{go} \times c_{r})] \times 273.15 \times 1000}{22.4 \times T_g \times A_m}
\]

(equation 2)

Where \(J_{CO_2}\) is the CO₂ flux (mol m⁻² s⁻¹), \(Q_{gi}\) and \(Q_{go}\) are the inlet and outlet gas flow rates respectively (m³ s⁻¹), \(c_{f}\) and \(c_{r}\) are the CO₂ mole fraction in the gas feed and gas retentate respectively, \(T_g\) is the gas temperature (K) and \(A_m\) is the active surface area (m²). Selectivity was calculated using (Rongwong et al., 2011; Lu et al., 2006):

\[
Selectivity = \frac{R_{CO_2}}{F_{CO_2}} / \frac{R_{CH_4}}{F_{CH_4}}
\]

(equation 3)

Where \(R_{CO_2}\) and \(R_{CH_4}\) are the CO₂ and CH₄ concentrations in the retentate liquid (g L⁻¹), and \(F_{CO_2}\) and \(F_{CH_4}\) are the CO₂ and CH₄ concentrations in the gas feed (g L⁻¹). All samples were analysed in triplicate.

2.3 Analysis

A gas chromatograph (GC) fitted with a thermal conductivity detector (TCD) was used to analyse the gas and liquid samples (200 Series GC-TCD Cambridge Scientific Instruments Ltd., Witchford, UK). Gas solutes were separated on an Alltech® CTR I concentric packed column which has a concentric column with a 1/4” outer column surrounding an 1/8” inner column (Alltech Associates Inc., Deerfield, Illinois, USA). Samples were introduced onto the column in a 1mL volume and eluted using Helium as the carrier gas at an entry pressure of 4.2 bar(g). The isothermal method used an injector temperature of 150 °C, an oven temperature of 30 °C and a detector temperature of 180 °C. The instrument was calibrated using certificated CO₂ and CH₄ gas standards (Scientific Technical Gases Ltd., Staffordshire, UK) prior to each analysis. A sharp methane peak eluted from the inner column containing mixed porous polymer packing at a retention time of 30 s followed by the CO₂ peak at 90 s. Concentration of chemically absorbed CO₂ in NaOH containing solutions, existing as carbonate,
was ascertained by titration of retentate absorbent with 1.0 M HCl using BaCl$_2$ to neutralise the carbonate ions (Benedetti-Pichler Cefola, 1939).

3. Results

3.1 Impact of solvent chemistry on biogas component flux

A CO$_2$ flux of 7.6x10$^{-5}$ mol m$^{-2}$ s$^{-1}$ was recorded when using DI water as the absorption solvent, at a fixed $V_0$ of 0.0047 m s$^{-1}$ and $V_L$ of 0.0054 m s$^{-1}$, which corresponded to an L/G of 1.15, with a Reynolds number (Re) of 1.32 (Figure 2a). The L/G was progressively increased by increasing $V_L$ to a maximum of 0.024 m s$^{-1}$ (Re = 5.90), upon which a CO$_2$ flux of 1.7x10$^{-4}$ mol m$^{-2}$ s$^{-1}$ was recorded, representing an increase in CO$_2$ flux of approximately 200%. Analogous behaviour was observed for CO$_2$ flux when NaCl was added as a simple electrolyte, where $V_L$ ranged from 0.0074 m s$^{-1}$ (Re = 1.71) to 0.022 m s$^{-1}$ (Re = 5.12). Re values for the gas on the shell side ranged between an initial Re = 10.5 (accounting for viscosity of initial gas mixture and $V_0$ of 0.0047 m s$^{-1}$; Jackson, 1956) to a minimum Re = 4.2 (accounting for change in gas mixture composition and $V_0$) at the HFMC outlet for DI solvent. Substitution of the DI and NaCl ‘physical’ solvents for a 1 M NaOH ‘chemical’ absorbent resulted in a CO$_2$ flux of 2.98x10$^{-4}$ and > 99 % CH$_4$ concentration in the outgas, which remained unchanged when $V_L$ was varied from 0.0122 m s$^{-1}$ (Re = 2.47) to 0.0242 m s$^{-1}$ (Re = 4.90). This corresponded to a plateau in CO$_2$ flux with increasing $V_L$, indicating that the process was gas phase controlled (Li and Chen, 2005; Esquiroz-Molina, In Press). Gas velocity ($V_G$) was subsequently increased from 0.0047 m s$^{-1}$ to a maximum of 0.031 m s$^{-1}$ at a fixed $V_L$ of 0.0089 m s$^{-1}$ to reduce the L/G ratio and identify the impact upon CO$_2$ flux (Figure 2b). CO$_2$ flux was found to be dependent upon $V_G$, with the highest CO$_2$ flux of 1.74x10$^{-3}$ mol m$^{-2}$ s$^{-1}$ recorded at a $V_G$ of 0.031 m s$^{-1}$. Similarly to DI water, no quantifiable difference in CO$_2$ flux could be noted following the inclusion of NaCl to NaOH. Since both physical and chemical systems were ostensibly controlled by differing phases, direct comparison is difficult to ascertain. However, both $V_L$ (0.009 m s$^{-1}$) and $V_G$ (0.0047 m s$^{-1}$) were identical for DI and NaOH at an L/G of 1.92 which corresponded to the minimum CO$_2$ flux of 2.98x10$^{-4}$.
The highest CH$_4$ flux was recorded using DI water. At an L/G of 1.15, CH$_4$ flux was 2.03x10$^{-6}$ mol m$^{-2}$ s$^{-1}$ which increased to a maximum flux of 1.15x10$^{-5}$ mol m$^{-2}$ s$^{-1}$ at an L/G of 5.2 (Figure 3). Methane flux diminished markedly with the inclusion of NaCl to DI water. To illustrate, a CH$_4$ flux of 6.2x10$^{-6}$ mol m$^{-2}$ s$^{-1}$ was recorded at L/G 4.7 compared to 8.6x10$^{-6}$ mol m$^{-2}$ s$^{-1}$ for DI water at the lower L/G of 4.2. For the NaOH solvent, CH$_4$ fluxes were comparable to those of NaCl below L/G 2.6. However, at L/G greater than 2.6, CH$_4$ flux recorded for the NaOH solvent apparently increased as an exponent of L/G, subsequently recording a CH$_4$ flux of 9.7x10$^{-6}$ mol m$^{-2}$ s$^{-1}$ at L/G 5.2, only 15 % below that observed for DI water. Addition of NaCl to NaOH introduced the greatest limitation to CH$_4$ flux, recording between 8.9x10$^{-7}$ and 4.6x10$^{-6}$ mol m$^{-2}$ s$^{-1}$ for L/G ranging 1.4 to 5.

Following process optimisation using the rate limiting phase ($V_G$ in the case of chemical based solvents NaOH and NaOH/NaCl; and $V_L$ for the physical solvents DI water and aqueous NaCl), selectivity toward CO$_2$ was estimated for each solvent (Figure 4). For physical solvents, selectivity was greater when using NaCl. However, a linear decrease toward CO$_2$ selectivity was noted for both solvents when $V_L$ was increased. For example, for DI water, selectivity decreased from 166 at L/G 2.4 to 106 at L/G 5.2. The NaCl/NaOH solvent increased selectivity for CO$_2$ at L/G 0.29 from 1030 for NaOH to 2250. At higher L/G, selectivity diminished to that observed for physical solvents.

Data was selected from the reported datasets to enable an approximate comparison of slip, from the solvents evaluated. To normalise the datasets, an outlet gas composition of 85 % methane, equivalent to North Sea natural gas (Persson et al., 2006), was selected (Table 1). The highest slip was observed when using DI water at 5.2 %. In comparison, the chemical solvent reduced methane
slip to 0.1%. Adding the NaCl electrolyte reduced methane slip in both physical and chemical solvents to 4.0% and 0.03% respectively.

3.2 Application of solvent recirculation to minimise slip

Single pass solvent use was compared to recirculating the solvent in multi-pass (MP) to enable greater utilisation of the available solvent (Figure 5). Cumulative losses were compared following subsequent solvent uses (without regeneration) based upon a parameter normalised to CO₂ removal (CH₄ lost per gram CO₂ absorbed, g g⁻¹). For both solvents, a pseudo-plateau was evidenced following one recirculation which can be explained by the saturation of the solvent with CH₄ after one circulation. This is supported by the measured dissolved phase methane concentration which stabilised following approximately one recirculation. However, methane losses were lower using the NaOH solvent. For example, following two solvent recirculations, losses were 0.086 g g⁻¹ and 0.709 g g⁻¹ for the NaOH and DI solvents respectively. Over five solvent recirculations, the chemical solvent supported an outlet gas phase concentration of >99% CH₄ (Figure 6). In contrast, outlet gas quality rapidly diminished for the DI solvent following less than one use.

4. Discussion

A significant finding in this study was that methane slip was dependent upon whether the process was gas phase or liquid phase controlled. For physical solvents such as DI water, the liquid phase presented the rate limiting condition to CO₂ mass transfer. This manifested as an increase in CO₂ flux, and therefore an enhancement in gas-side methane purity, when V_L was increased. The DI solvent approached saturation for CH₄ at low V_L. This can be explained by the partial solubility of methane in water, yielding a predicted saturation concentration of 13.5 mg L⁻¹ at a partial pressure of 60% (Willhelm et al., 1977). A proportionate increase in methane flux was subsequently observed with an increase in V_L and can be explained by the continual saturation of newly introduced solvent at the solvent-membrane boundary. In contrast, dissolved CO₂ concentration diminished at high V_L.
from a maximum of 500 mg\textsubscript{CO\textsubscript{2}} L\textsuperscript{-1} at \(V\textsubscript{L} 0.011\) m s\textsuperscript{-1}, to 387 mg\textsubscript{CO\textsubscript{2}} L\textsuperscript{-1} at \(V\textsubscript{L} 0.024\) m s\textsuperscript{-1}. This can be explained by a combination of the lower residence time available for absorption which limited radial gas transport from the solvent-membrane boundary due to under-developed laminar flow conditions (\(Re \ll 2100\)) observed throughout for DI water (\(Re_{max} = 5.90\)) (Dindore et al., 2005), and a reduction in gas-side CO\textsubscript{2} partial pressure at higher \(V\textsubscript{L}\). This reduction in CO\textsubscript{2} solvent concentration subsequently reduced selectivity toward CO\textsubscript{2} with an increase in \(V\textsubscript{L}\) (Figure 4). The hydrodynamic conditions were comparable for all solvents across the \(V\textsubscript{L}\) ranges examined, with insufficient difference in viscosity and density of electrolytic solutions for any significant change in flow regime (Zhang et al., 1996; Sipos et al., 2000; Laliberte, 2007).

For the chemically reactive NaOH solvent, the process was gas phase controlled, which is illustrated by the negligible gradient recorded for CO\textsubscript{2} flux following an increase in \(V\textsubscript{L}\) (Figure 2a). This chemical reaction is described as ‘fast’ (11,000 m\textsuperscript{3} kmol\textsuperscript{-1} s\textsuperscript{-1}), such that dissolution can no longer be predicted by Henry’s Law, as upon penetration the CO\textsubscript{2} reacts to form bicarbonate (HCO\textsubscript{3}) (Kucka et al., 2002; Pohoricki and Moniuk, 1988). Consequently, whilst operated within the low \(Gz\) number range applied to physical solvents, this conversion to carbonate species, in the presence of a high reactant concentration, was sufficient to re-establish the concentration gradient at the membrane-solvent boundary. The excess of reactive [OH\textsuperscript{-}] within the reaction zone further enabled a reduction in the operational L/G ratio. This limited CH\textsubscript{4} flux, as the physical dissolution of CH\textsubscript{4} in NaOH can be similarly described by Henry’s law and is thus attributable to solvent flow rate. To illustrate, to achieve an equivalent outlet CH\textsubscript{4} purity of 85 %, the L/G required for DI and NaOH solvents were 5.2 and 0.33 yielding ‘slip’ of 5.2 % and 0.1 % respectively. Interestingly, when using the chemical solvent at L/G >1, the gas-side CO\textsubscript{2} concentration was reduced to below the limit of detection and was coincident with a non-linear increase in methane flux (Figure 3). It is posited that this CH\textsubscript{4} flux enhancement arises from the increase in gas-side CH\textsubscript{4} partial pressure suggesting that an optimum L/G should be identified to limit ‘slip’ in addition to gas-side CO\textsubscript{2}. 
Selectivity was enhanced in both chemical and physical absorption systems by the inclusion of NaCl (Figure 4). The NaCl behaved as an electrolyte, which induced ‘salting out’ of the physically absorbed gas species resulting in a reduction in the attainable saturation constant. Setschenow (1889) supposed that ‘salting out’ was induced by a preference of water molecules to hydrate and dissolve ionic species rather than the uncharged gas candidates. Latterly Masterton and Lee (1970) used ‘scaled particle theory’ (SPT) to suggest that salting out increased the work required to form a cavity (within the condensed liquid phase) of sufficient size to accommodate a gas solute. Consequently, electrolyte addition to the physical solvent (DI) reduced methane slip to 4 % compared to 5.2 % for DI water. The use of NaCl to improve outlet gas quality was also assessed by Atchariyawut et al. (2007). The authors based the improvement in outlet gas quality on the electrolytes capacity to reduce water vapour content. Whilst the author’s hypothesis of reduced water activity is valid, clearly the contribution of reduced methane ‘slip’ must also be considered.

Due to the inclusion of NaCl, the CO₂ saturation constant was reduced by 22 %. However, the measured dissolved CO₂ concentration was below this saturation concentration and hence the impact on CO₂ flux was seemingly negligible (Figure 2a). It is posited that further lowering of the solubility constant will impede absorption performance. Interestingly, whilst the chemical solvent reduced slip through enabling lower L/G operation, NaOH similarly dissociates into ionic form, presenting a synergistic effect since slip is therefore also retarded through salting out of the [Na⁺] and [OH⁻] ions (Weisenberger and Schumpe, 1996), and is supported by the diminished CH₄ flux recorded for NaOH when compared to DI (Figure 3). Consequently, the addition of NaCl to NaOH absorbent effectively doubled the electrolytic solvent concentration, further inhibiting CH₄ flux and subsequently enhanced selectivity for CO₂ by approximately 200 %. Since the chemical solvent’s reactivity offsets the lower physical absorption constant for CO₂, it is suggested that higher electrolytic concentrations can be implemented and methane ‘slip’ further decreased.

Using multi-pass absorption enables further cessation of ‘slip’ since both physical and chemical solvents are essentially saturated with CH₄ in a single pass, thus subsequent solvent
recirculation should retard further CH₄ flux, tending measured CH₄ flux to zero. However, the
capacity to utilise physical solvents in multi-pass absorption is limited as approximately 50 % of the
maximum CO₂ load is also reached in single-pass. In comparison, the CO₂ flux and outlet gas quality
recorded for the chemical solvent following five recirculations was analogous to single pass,
demonstrating a sustained excess of highly reactive hydroxide [OH⁻] ions. Based on an idealised
stoichiometric conversion of 2:1, [OH⁻]: CO₂ (Vas Bhat et al., 2000) and an L/G of 5.2, approximately
37 chemical solvent recirculations are possible before reaching a [OH⁻] concentration of 0.1 M.
Interestingly, whilst an order of magnitude lower in chemical concentration, 0.1 M NaOH has been
shown sufficient to maintain a >99 % CH₄ outlet gas concentration under analogous hydrodynamic
conditions (Galan-Sanchez, 2011).

Physical absorption in HFMC demonstrated methane slip of 5.2 %. Although direct comparison to
conventional water scrubbers cannot be made due to differences in gas-side preconditioning and
scale, this is markedly lower than the 13.1% slip recorded for a pilot scale unit applied to landfill gas
(Läntelä et al., 2011) and is ostensibly a function of lower solvent consumption; an observation
which is supported by previous authors (Nii and Takeuchi, 1992; Herzog and Pederson, 2000). Lower
‘sip’ values of 4 % to 5 % have been recorded for full-scale water scrubbers, though it is unclear
whether the balance includes the use of abatement technologies such as thermal oxidisers which
oxidise the slipped methane to CO₂ (Patterson et al., 2011; Wolf and Nettelnbreker, 2011). In
addition, to the financial significance of enhancing the recovery of biomethane through minimising
slip, financial incentivisation now also rewards installations which operate at ‘slip’ below 0.5 % (Wolf
and Nettelnbreker, 2011). Based on this study, to reach this target without the use of abatement
technologies, chemical solvents are required as this enables the shift to gas-phase control which
minimises ‘slip’ through minimum solvent consumption; though the energy penalty associated with
solvent regeneration must also be considered. The characteristically low absorbent demand of
HFMCs could conceivably limit the energy necessary for chemical regeneration through a reduction
in liquid volume, which is also coupled to a significantly reduced pumping requirement. This is in
addition to the revenue from the methane that would otherwise have been lost at higher slip. For example, assuming biogas production of 1000 m$^3$ hour$^{-1}$ (a moderate full-scale flow rate) with 60 % initial CH$_4$ content, an upgrading plant operating at 5.2 % slip would lose approximately £87,500 year$^{-1}$ at 32 p m$^{-3}$. In contrast, a NaOH solvent with 0.1 % slip would only lose £1,700 year$^{-1}$. Only £500 year$^{-1}$ would be lost at 0.03 % slip in a NaOH + NaCl absorbent.

In practice, there is a trade-off between CAPEX and OPEX, such that the application of highly reactive chemical solvents will be used to reduce asset scale by increasing throughput, consequently, the number of achievable solvent recirculations could be lower than presented in this study. However, both energy and carbon returns demonstrate that operation greater than one recirculation is sufficient to derive a net energy benefit through minimising methane slip (Figure 7).

A criticality in L/G was also demonstrated where unnecessary operation at L/G >1 could impinge upon methane losses. This underpins a tacit advantage of HFMCs versus conventional packed columns in that the latter are operationally limited to turnup/turndown during process perturbation such as inlet gas composition or flow variation. By comparison HFMCs can achieve more rapid transitions in V$_L$ due to phase separation which enables HFMCs to operate at minimum V$_L$ and thus limit further ‘slip’.

5. Conclusion

The significance of methane slip during biogas upgrading was dependent upon whether the process was gas phase or liquid phase controlled since methane transport was governed by Henry’s law and hence independent of chemical reactivity.

- For physical solvents, absorption was dependent upon V$_L$. However, at high V$_L$, selectivity toward CO$_2$ declined due to low residence times and an underdeveloped regime;
- For chemical solvents, CO$_2$ mass transfer was dependent upon V$_G$ which was driven by an excess of [OH$^-$] ions available in the solvent for chemical reaction;
Electrolytes can retard CH$_4$ absorption via the salting out effect. In physical solvents, electrolytic concentration is limited by the effect upon CO$_2$ solubility. However, in chemical solvents, CO$_2$ absorption is decoupled from physical constants, thus an excess of electrolyte can enhance selectivity further; and

Multi-pass chemical solvent recirculation enables further methane slip prevention. Initial saturation of the solvent for CH$_4$, ensures that CH$_4$ flux tends toward zero following subsequent uses for CO$_2$.

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References


Figure 1. Schematic of the experimental set-up used for determining ‘slip’ from a polypropylene microporous hollow fibre membrane contactor (HFMC, 0.03 µm pore size).
Figure 2. (a) Impact of liquid velocity ($V_L = 0.0054$ m s$^{-1}$ to 0.024 m s$^{-1}$) with fixed initial gas velocity ($V_G = 0.0047$ m s$^{-1}$) on CO$_2$ flux in DI, NaCl, and NaOH absorbents fixed at 24-26 °C (b) Impact of gas velocity ($V_G = 0.0017$ m s$^{-1}$ to 0.031 m s$^{-1}$) with fixed liquid velocity ($V_L = 0.0089$ m s$^{-1}$) on CO$_2$ flux in NaOH and NaOH + NaCl absorbents fixed at 24-26 °C
Figure 3. The impact of liquid velocity ($V_L$ from 0.0046 m s$^{-1}$ to 0.024 m s$^{-1}$) on CH$_4$ flux in four solvents DI, NaCl, NaOH, and NaOH/NaCl. Absorbent solvent temperature fixed at 24-26 °C.

Figure 4. Influence of hydrodynamic conditions on CO$_2$ selectivity. Liquid velocity ($V_L$) varied from 0.0074 m s$^{-1}$ to 0.024 m s$^{-1}$ for DI and NaCl solvents and gas velocity ($V_G$) fixed to 0.0047 m s$^{-1}$. For NaOH and NaOH/NaCl, $V_G$ varied between 0.0046 m s$^{-1}$ and 0.031 m s$^{-1}$, with $V_L$ fixed at 0.0089 m s$^{-1}$. 
Figure 5. Methane losses measured over multiple solvent recirculations with DI or NaOH solvents. Methane losses normalised to CO$_2$ removed during gas separation. Operating L/G were selected that enabled effective CO$_2$ separation based on favourable CO$_2$ flux and gas-side purity. DI solvent $V_l$ 0.024 m s$^{-1}$ and $V_g$ 0.0031 m s$^{-1}$ (L/G 7.7); NaOH solvent $V_l$ 0.032 m s$^{-1}$ and $V_g$ 0.058 m s$^{-1}$ (L/G 0.42).

Figure 6. Outlet gas composition measured during sequential solvent recirculations using DI and NaOH absorption solvents. Solvent temperature 24-26 °C, $V_l$ 0.024 m s$^{-1}$ and $V_g$ 0.0031 m s$^{-1}$ (L/G 7.7); NaOH solvent $V_l$ 0.032 m s$^{-1}$ and $V_g$ 0.058 m s$^{-1}$ (L/G 0.42).
Figure 7. Energy and carbon balance based on methane slip during single pass (SP) and multi-pass (MP) solvent recirculation. A net energy gain is determined once solvent is recirculated more than once. Carbon neutrality requires greater than five solvent recirculations based on the modelled hydrodynamic conditions (assumptions 0.52 kg CO$_2$ kWh$^{-1}$; 40% electrical efficiency).

Table 1. Methane slip in DI, NaCl, NaOH, and NaOH + NaCl absorbents at 24-26 °C under conditions affording a relative output gas composition of 85 % CH$_4$.

<table>
<thead>
<tr>
<th>Absorbent</th>
<th>L/G</th>
<th>Liquid velocity $V_L / V_G$</th>
<th>Gas velocity $V_G$, m s$^{-1}$</th>
<th>CH$<em>4$ slip vol. $V</em>{CH4}$, m$^3$ h$^{-1}$</th>
<th>CH$<em>4$ slip vol. $Q</em>{CH4}$ out, m$^3$ h$^{-1}$</th>
<th>CH$_4$ slip % CH$_4$ out</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI</td>
<td>5.18</td>
<td>0.0241</td>
<td>0.0047</td>
<td>16.0</td>
<td>5.8</td>
<td>0.011</td>
</tr>
<tr>
<td>1 M NaCl</td>
<td>5.00</td>
<td>0.0233</td>
<td>0.0047</td>
<td>9.6</td>
<td>4.1</td>
<td>0.010</td>
</tr>
<tr>
<td>1 M NaOH</td>
<td>0.33</td>
<td>0.0089</td>
<td>0.0300</td>
<td>10.0</td>
<td>1.3</td>
<td>0.136</td>
</tr>
<tr>
<td>1 M NaOH + 1 M NaCl</td>
<td>0.55</td>
<td>0.0089</td>
<td>0.0173</td>
<td>4.6</td>
<td>0.6</td>
<td>0.179</td>
</tr>
</tbody>
</table>