

Controlling shell-side crystal nucleation in a gas-liquid membrane contactor for simultaneous ammonium bicarbonate recovery and biogas upgrading

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Abstract

A gas-liquid hollow fibre membrane contactor (HFMC) process has been introduced for carbon dioxide (CO₂) separation from biogas where aqueous ammonia (NH₃) is used to chemically enhance CO₂ absorption and initiate heterogeneous nucleation of the reaction product ammonium bicarbonate at the membrane-solvent interface. Aqueous ammonia absorbents (2 to 7 M) were initially used in single pass for CO₂ separation from a synthetic biogas where nucleation of ammonium bicarbonate crystals was observed at the perimeter of the micropores. Recirculation of the aqueous ammonia absorbent encouraged the growth of ammonium bicarbonate crystals on the shell-side of the membrane that measured several microns in diameter. However, at high aqueous NH₃ concentrations (3-7 M), lumen side crystallisation occurred and obstructed gas flow through the lumen of the HFMC. The suggested mechanism for lumen-side crystallisation was absorbent breakthrough into the lumen due to pore wetting which was promoted by low absorbent surface tension at high NH₃ concentration. Preferential shell-side nucleation can therefore be promoted by: (1) raising surface tension of the absorbent; and, (2) selection of a membrane with a more regulated pore shape than the PTFE membrane used (d/L 0.065) as both actions can diminish solvent ingress into the pore. This was evidenced using 2 M NH₃ absorbent where shell-side crystallisation was evidenced without the onset of lumen side crystallisation. Raising surface tension through the inclusion of salt into the chemical absorbent also promoted greater CO₂ flux stability. Importantly, this study demonstrates that chemically enhanced HFMC are an attractive prospect for gas-liquid separation applications where reaction product recovery offers further economic value.

Keywords: biomethane, membrane crystalliser, chemical absorption, crystallisation

1. Introduction

Many water utilities are now refining biogas into biomethane rather than using directly for electrical production due to the potential for higher revenue. To illustrate, in the UK, through support under the Renewable Heat Incentive (RHI), the revenue expected from biomethane is €0.39 m⁻³ which compares to only €0.23 m⁻³ for electrical production (Read et al., 2010). The biomethane product must achieve methane quality that is equivalent or higher than natural gas (>81%) which therefore demands the separation of carbon dioxide (CO₂) from biogas. This is generally facilitated using absorption in a packed column and is analogous to those currently trialled for carbon capture and storage (CCS). In CCS applications, process intensification is provided through the inclusion of a chemical solvent (e.g. monoethanolamine) that reacts with CO₂ to enhance the separation. However, the energy demanded for chemical solvent regeneration, coupled with solvent losses (due to volatility and degradation pathways) and the demand for specialist operators has limited uptake of chemical absorption for biogas upgrading by water utilities (Heile et al., 2014).

Ammonia is now recognised as an emerging chemical absorbent in CCS due to its higher absorption efficiency, greater chemical stability and lower energy demand for regeneration (Shuangchen et al., 2013; Makhoulfi et al., 2014). Aqueous ammonia (NH₃) absorption therefore presents comparable advantages for water utilities undertaking biogas upgrading, but also offers the unique opportunity to utilise the ammonia rich wastewater produced onsite as a low cost absorbent feedstock for enhanced CO₂ separation. The reaction between free NH₃ and CO₂ is known to proceed by (Eq. 1) where ammonium bicarbonate (NH₄HCO₃) is the reaction product formed:



When recovered in crystalline form, NH₄HCO₃ can be used as an ammonia rich fertiliser as well as a feedstock in commercial manufacture. Consequently, controlled production of a crystalline NH₄HCO₃ reaction product from ammonia rich wastewaters posits several advantages for biogas upgrading at sewage works including: further reduction in energy demand for absorbent regeneration; a

reduction in load onto nitrification/denitrification processes (€3 kgN^{-1}); and, production of NH_4HCO_3 as a new revenue stream (bulk cost €111 tonne^{-1}) (Thornton, 2007).

To enable recovery of crystalline products within a controlled environment, Curcio et al. (2001) introduced the membrane crystallisation reactor (MCR). In their work, a microporous hydrophobic membrane contactor (HFMC) was used to facilitate non-dispersive contact between a heated undersaturated crystallising solution (on the retentate side) and cooled pure water on the permeate side. The temperature differential provided the gradient for vapour transport from the crystallising solution through the membrane pores enabling an increased solute concentration (sodium chloride, NaCl) which upon exceeding its solubility limit, initiated nucleation and growth of NaCl crystals (Figure 1). The underpinning mechanism by which the MCR operates therefore corresponds to evaporation-migration-condensation (Di Profio et al., 2010) and has been used to recover NaCl and magnesium sulfate from nanofiltration retentate as crystalline products (Drioli et al., 2004) and for the controlled production of Lysozyme crystals (Di Profio et al., 2003).

The same microporous HFMC technology used to control crystallisation in MCR systems has now also been used to enable CO_2 separation from biogas through supporting an analogous absorption mechanism to conventional absorption columns (Heile et al., 2014). In this case, the hydrophobic membrane facilitates non-dispersive contact between the chemical absorbent and gas phase with the gases free to diffuse through the open pore structure. Due to the increase in specific surface area afforded by the membrane contactor, the technology presents an inherent advantage in reducing both process scale and absorption solvent consumption, relative to conventional columns (Herzog and Pederson, 2000). In this study, we therefore seek to introduce a gas-liquid membrane absorption crystallisation reactor that enables both the selective separation of CO_2 through reaction with ammonia and the subsequent nucleation and growth of the crystalline ammonium bicarbonate reaction product for recovery. The mechanism for nucleation and growth of NH_4HCO_3 crystals in this study differs from classical MCR systems in that supersaturation is achieved by counter diffusion of solutes through the transport of CO_2 molecules from the gas phase into the

crystallising fluid (an aqueous ammonia absorbent) where the driving force for CO₂ transport to the crystallising fluid is the enhancement in solubility provided by the chemical reaction with NH₃. Nucleation is then dependent upon CO₂ reaching sufficient concentration to initiate local supersaturation of the solvent (Figure 1).

Makhloufi et al. (2014) recently screened a number of hollow-fibre membrane materials to determine compatibility for CO₂ absorption into aqueous ammonia for chemically enhanced post combustion CCS. The authors remit precluded an interest in recovering NH₄HCO₃ as a byproduct and determined that microporous fibres were inappropriate for application to CCS due to CO₂ flux instability caused by ammonium bicarbonate precipitation on the gas-side (lumen-side) of the membrane. In this study, we therefore seek to introduce the mechanism underpinning controlled nucleation and growth of ammonium bicarbonate on the shell-side (absorbent side) of a microporous HFMC to illustrate the potential of the gas-liquid membrane absorption crystallisation reactor for simultaneous gas separation with reaction product recovery. A microporous polytetrafluoroethylene (PTFE) HFMC is therefore used to investigate: (i) the potential for chemical absorption in a microporous membrane to enable shell-side (absorbent side) crystal nucleation; (ii) investigation of absorbent conditions required to enable crystal growth; and (iii) the role of the microporous substrate in controlling nucleation. To our knowledge, this is the first study to describe the use of hydrophobic microporous membranes for the controlled nucleation and growth of a reactant product following chemical absorption from the gas phase.

2. Experimental

2.1 Fabrication, setup and operation of equipment

Hydrophobic micro-porous PTFE fibres obtained from Markel Corporation (Plymouth Meeting, Pennsylvania, USA) and comprised a 200 µm wall thickness and 44% porosity (Table 1). To enable characterisation of crystal growth with minimal disturbance, single fibre modules were manufactured. Modules comprised a transparent PVC shell with an inner diameter of 0.004 m and

were completed with two acetal push-fit T-union-joints (1/4" Speedfit, John Guest Ltd., Middlesex, UK). Fibres were potted in epoxy resin (Bostik Ltd., Stafford, UK). For dense membrane experiments, polydimethylsiloxane (PDMS) fibres with a wall thickness of 65 µm were used in an identical module construction (Trelleborg sealing solutions, Stuttgart, Germany).

Methane (CH₄, 99.995%) and carbon dioxide (CO₂, 99.7%) (BOC gases, Ipswich, UK) were mixed in controlled proportions using mass flow controllers (0.2-20.0 l min⁻¹, Roxspur Measurement and Control Ltd., Sheffield, UK) to provide an initial 50:50 CH₄:CO₂ gas composition and introduced through the fibre lumen (Figure 2). Liquid was pumped co-currently into the shell-side. Transmembrane pressure (TMP) was monitored by digital pressure gauges (DPG1000, Omega Engineering Ltd., Manchester, UK) and liquid and pressure flow controlled using needle valves.

2.2 Sampling and analyses

Ammonia absorbents were prepared through dilution of an NH₃ concentrate (35 %, Fisher Chemicals, Loughborough, UK) using de-ionised (DI) water (15.0 MΩ cm⁻¹). Absorbent pH was fixed to pH 11 to ensure 100% of the ammoniacal nitrogen was available as un-ionised free NH₃ (Thurston et al., 1979). Ammonia concentrations were confirmed by use of an ammonium cell test (4-80 mg l⁻¹, VWR International Ltd., Poole, UK) with subsequent determination by spectrophotometry (Spectroquant Nova 60, Merck-Millipore, Darnstadt, Germany). Gas composition was determined using an infrared biogas analyser sited on the gas outlet (range 0-100 %, accuracy <0.2 % full-scale; Yieldmaster, Bluesens gas sensor GmbH, Herten, Germany). Subsequently, CO₂ removal efficiency was determined based upon the binary gas composition before and after the membrane module:

$$CO_2 \text{ removal efficiency (\%)} = \frac{(c_{G,in} - c_{G,out})}{c_{G,in}} \times 100 \quad (2)$$

where $c_{G, in}$ and $c_{G, out}$ are gas phase CO₂ concentrations before and after the HFMC respectively (mol mol⁻¹). Gas flow rate exiting the contactor was measured using a bubble flow meter (50 ml, Restek, Bellefonte, US) and used to calculate carbon dioxide flux (J_{CO_2} , mol m⁻² s⁻¹):

$$J_{CO_2} = \frac{[(Q_{G,in} \times c_{G,in}) - (Q_{G,out} \times c_{G,out})] \times 273.15 \times 1000}{(22.4 \times A_m \times T_G)} \quad (3)$$

where $Q_{G, in}$ and $Q_{G, out}$ are gas flow rate before and after HFMC respectively ($m^3 s^{-1}$), A_m is the membrane surface area for absorption (m^2) and T_G is the gas temperature (K) (Atchariyawut et al., 2007).

Examination of the PTFE microporous membrane pore structure was determined using a scanning electron microscope (SEM) equipped with a field emission gun (sFEG) (XL30, FEI, Hillsboro, Oregon, USA). Pores size data was subsequently analysed to provide a size distribution using a log-normal distribution function (Li et al., 2000):

$$f_L(r) = \frac{1}{\sqrt{2\pi}r} [\ln(1 + \sigma^2)]^{-0.5} \times \exp \left[-\frac{(\ln(r/r_m)(1+\sigma^2)^{0.5})^2}{2 \times \ln(1+\sigma^2)} \right] \quad (4)$$

Surface roughness of the virgin fibres was characterised using atomic force microscopy (AFM, Dimension 3100, Bruker, Massachusetts, US). Examination of sacrificial membrane samples to determine crystal nucleation and growth was conducted using SEM (upto x10000 magnification) for the finer diameter PTFE fibres, and optical microscope for the wider diameter PDMS fibres. Fibre samples for SEM were first coated with gold-palladium (Au-Pd) using a cool sputtering SEM coating unit (E5100, Polaron Equipment/Quorum Technologies Ltd., Lewes, UK). Spectroscopic elemental analysis was performed in tandem with SEM by energy dispersive x-ray spectroscopy (EDX) using Aztec software (Oxford Instruments NTS, Abingdon, UK). Solvent surface tension was determined using a Du Noüy ring tensiometer (Kruss K6, Bristol, UK).

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151 **3. Results**

152 *3.1 Characterisation of the PTFE and PDMS membranes*

Pore size analysis by SEM indicated that average pore radius of the PTFE fibres was $0.157 \mu m$ with radii distributed within a range between $0.13 \mu m$ and $0.21 \mu m$ (Figure 3). This closely approximates to pore width data provided by the manufacturer (Table 1). The stretched length of the pores was approximately $4.9 \pm 3.1 \mu m$, yielding a pore diameter to length ratio (d/L) of 0.065. Average surface

roughness of the PTFE fibres was 82 nm which is similar to that measured for the nonporous PDMS membrane (77 nm).

3.2 Removal of CO₂ using NH₃ as a chemical absorbent

The PTFE HFMC was initially tested in single pass mode (without absorbent recirculation). Gas velocity, V_G , was varied between 0.28 m s⁻¹ and 18.62 m s⁻¹ whilst both liquid velocity (V_L) and aqueous ammonia absorbent concentration were fixed at 0.02 m s⁻¹ and 7 mol l⁻¹ respectively (Figure 4). Maximum CO₂ removal efficiency of 72 % was observed at the lowest V_G examined which corresponded to a G/L ratio of 3. For these fixed conditions, methane content increased from 50% at the inlet to 86% CH₄. As V_G was increased, CO₂ removal efficiency decreased to a minimum of 3.6% which was recorded at the highest V_G tested (18.62 m s⁻¹). Whilst CO₂ removal efficiency declined with an increase in V_G , CO₂ flux increased from 0.015 to 0.116 mol m⁻² s⁻¹ within the gas velocity range tested (Figure 4). Microscopic analysis of the shell-side of a PTFE fibre that had been used with 7 mol l⁻¹ aqueous ammonia solution and a G/L ratio of 10, showed white specks formed around the pore mouths indicating that crystal nucleation had been initiated (Figure 5).

3.3 Identification of heterogeneous crystal growth

Crystal growth on the shell side of the module was identified within each of the 2 to 5 M NH₃ absorbents used (V_G = 0.93 m s⁻¹, G/L 10) with carbon (C), oxygen (O) and nitrogen (N) peaks confirmed in the crystals formed by EDX (Table 2). Crystals that had grown in 3 to 5 molNH₃ l⁻¹ absorbents generally developed planar structures that were oriented roughly parallel to the membrane surface with multiple points of contact, whereas those formed in the 2 molNH₃ l⁻¹ absorbent developed perpendicular to the membrane surface with fewer crystal-membrane contact points. Following two to five absorbent recirculations (five second residence time per recirculation in the PTFE HFMC), a progressive decline in CO₂ flux was observed at each free ammonia concentration tested (Figure 6). After 6 and 13 recirculations respectively (30 s to 65 s), the 3 and 5 mol l⁻¹ NH₃

absorbent experiments were stopped due to lumen-side crystallisation which blocked the flow of gas (Figure 7). Lumen side crystals were tightly packed and propagated along the length of the hollow fibre. A similar progressive decline in CO_2 flux was also observed using $2 \text{ molNH}_3 \text{ l}^{-1}$ absorbent. However, whilst shell-side crystallisation was evidenced in the $2 \text{ molNH}_3 \text{ l}^{-1}$ absorbent (Table 2), lumen-side crystallisation was not observed following 34 absorbent recirculations (170 s).

3.4 *Using membrane type to control lumen-side crystallisation*

Performance of a nonporous PDMS membrane (Figure 8) was compared to the microporous membrane performance by recirculating $5 \text{ molNH}_3 \text{ l}^{-1}$ absorbent and fixing hydrodynamic conditions sufficient to yield equivalent CO_2 fluxes to the PTFE membrane (G/L 0.39, Figure 8). Under these conditions the NH_3 solvent had a 1 s residence time within the PDMS HFMC. A steady state period was observed between 400 and 800 solvent recirculations, which corresponded to CO_2 fluxes of around $0.014 \text{ mol m}^{-2} \text{ s}^{-1}$. However, after around 800 recirculations a progressive decline in CO_2 flux was noted and the experiment was terminated after 931 recirculations. Whilst crystals were observed to have grown on the shell-side of the PDMS fibre (Figure 9), the reduction in CO_2 flux after 800 recirculations coincided with the formation of crystalline solid within the fibre lumen inducing deformation of the cylindrical fibre structure.

3.5 *Manipulating solvent chemistry to promote shell-side nucleation on PTFE fibres*

Carbon dioxide flux provided by the PTFE membrane using $3 \text{ molNH}_3 \text{ l}^{-1}$ absorbent during recirculation were compared when using 1% wt. glycerol as an additive to the $3 \text{ molNH}_3 \text{ l}^{-1}$ absorbent as the addition of glycerol has been shown to diminish the volatility of ammonia (Shuangchen et al., 2013)(Figure 10). With the glycerol added, initial mean CO_2 flux was 3.5 % lower than without glycerol addition and after 12 recirculations, CO_2 flux was 23 % lower than with the pure $3 \text{ molNH}_3 \text{ l}^{-1}$ absorbent. Conversely, the addition of 5% wt. NaCl to the $3 \text{ molNH}_3 \text{ l}^{-1}$ absorbent increased CO_2 flux

stability. To illustrate, after 13 recirculations of the 3 molNH₃ l⁻¹ absorbent with 5% wt. NaCl added, CO₂ flux was 91% of initial flux in comparison to only 81% for the 3 molNH₃ l⁻¹ absorbent.

The change in surface tension following an increase in NaCl or aqueous ammonia concentration to deionised water was studied (Figure 11). With the inclusion of between 0.1 and 1 M NaCl (5.85% wt.), surface tension increased by up to 2.2 mN m⁻¹. However, a reduction in surface tension of between -0.8 and -8.7 mN m⁻¹ was measured for concentrations between 0.3 and 7 molNH₃ l⁻¹ which is within the range of aqueous ammonia absorbents studied and is consistent with the literature (Weissenborn et al., 1995). The addition of 5% wt. NaCl to aqueous ammonia reduced the change in surface tension. For example, at a concentration of 3 molNH₃ l⁻¹ a reduction in surface tension of -6.7 mN m⁻¹ was recorded whereas with the inclusion of 5% wt. NaCl, the change in surface tension reduced to only -3.9 mN m⁻¹.

4. Discussion

In this study, the use of a liquid phase chemical reaction to enhance CO₂ absorption and produce a crystalline reaction product has been demonstrated using a PTFE microporous hydrophobic hollow fibre membrane to promote the nucleation and growth of ammonium bicarbonate. During single pass experiments using a 7 mol l⁻¹ ammonia absorbent, an increase in V_G increased CO₂ flux into the receiving ammonia absorbent. In chemically reactive absorption systems, an increased gas phase flow rate is often observed to mediate solute flux (Esquiroz-Molina et al., 2013) as this enables replenishment of CO₂ at the solvent-membrane interface and maintenance of a high bulk gas CO₂ partial pressure (Zeng et al., 2013). When operating at high V_G (G/L 10) using 7 mol l⁻¹ ammonia absorbent (CO₂ flux 0.116 mol m⁻² s⁻¹, Figure 4), an absorption rate of 44.2 kmol m⁻³ h⁻¹ was recorded (kmolCO₂ m⁻³ absorption reactor volume h⁻¹). For comparison, Zeng et al. (2013) recorded a CO₂ absorption rate of 3.3 kmol m⁻³ h⁻¹ in a packed column using aqueous ammonia (4.5 mol l⁻¹), which illustrates the high rate of CO₂ transfer achieved with the micro-porous HFMC. For this high flux condition, activation of a substantial number of nucleation sites around the micro-pores on the

shell-side of the PTFE was demonstrated (Figure 5). This is supported by the work of Di Profio et al. (2003) where increased solute concentration enhanced supersaturation leading to an excess of nucleation. Interestingly, crystallisation is generally not observed in CO₂ /aqueous ammonia packed columns unless the ammonia concentration exceeds around 6 mol l⁻¹ (Budzianowski et al., 2011). In this study, nucleation and crystal growth was observed at 2 mol l⁻¹ (Table 2). The enhanced nucleation potential of the hydrophobic PTFE membrane can be explained by the high contact angle exhibited (around 129° for PTFE-water: Guillen-Burrieza et al., 2013; Zhu et al., 2013) which favours heterogeneous nucleation over homogeneous nucleation (Figure 12). The contact angle reflects the three phase line at the perimeter of the pore mouth, where the CO₂ gas phase, aqueous ammonia phase and PTFE solid phase interact (Figure 1; Curcio et al., 2006) and accounts for the proximity of nucleation sites relative to the pore mouth. The inclusion of pores reduces the thermodynamic preference for heterogeneous nucleation, although this is compensated for by the selection of a more hydrophobic material. Additionally, the provision of specific sites for nucleation at three phase line around the pore mouths, materials with increased porosity show an enhanced rate of nucleation, offering a kinetic preference for nucleation upon the membrane that complements the stability due to high contact angle (Curcio et al., 2006). It is proposed that the nucleation mechanism is analogous to that underpinning evaporation-migration-condensation as seen in MCr which is thought to follow: (1) surface adsorption through non-specific attractive interaction; (2) hindrance of lateral migration by the irregular pore structure causing packing; and (3) molecular entrapment which induces relatively higher supersaturation (Di Profio et al., 2010). However, within the gas crystallisation process proposed, CO₂ will migrate from the gas phase through the stagnant region of the solvent meniscus resident within the pore to the nucleation site, the rate of which will be determined by the reactivity of the solvent.

Growth of ammonium bicarbonate crystals on the shell-side of the membrane was demonstrated following recirculation of the ammonia absorbent (Table 2). Crystals grown within 3 and 5 molNH₃ l⁻¹ absorbents differed from those grown within 2 molNH₃ l⁻¹ absorbent which were

characterised by growth perpendicular to the membrane surface and from a comparatively limited number of nucleation points. Lowering the aqueous ammonia concentration to $2 \text{ mol NH}_3 \text{ l}^{-1}$ results in two effects: (1) this is close to the nominal limiting saturation concentration for the reactant product (NH_4HCO_3 , 2.24 mol l^{-1}); and (2) the flux of CO_2 into the aqueous phase is reduced due to the lower absorbent reactivity. The crystal orientation identified at low fluxes is indicative of conditions favouring crystal growth over nucleation, and is analogous to observations made previously when employing low solvent fluxes for evaporative MCr (Zhang et al., 2008) which results in production of fewer larger crystals. Controlling preference for the growth of fewer, larger crystals perpendicular to the membrane surface may be key to harvesting of the NH_4HCO_3 product, where it has been indicated that shear stresses due to axial liquid flow are sufficient to detach crystals grown upon the hydrophobic surface (Di Profio et al., 2010).

Following extensive solvent recirculation, crystal growth was observed on the lumen side of the PTFE fibre (Figure 7). In a preliminary evaluation of CO_2 absorption into aqueous NH_3 using oxyphan® microporous hollow fibres, Makhoulfi et al. (2014) postulated that the CO_2 flux decline observed was due to lumen-side (gas-side) crystallisation which initiated through high ammonia slip into the humidified gas phase. To investigate this mechanism, in this study, glycerol (1%) was added to the aqueous ammonia absorbent used with the microporous PTFE membranes as this is commonly employed to suppress NH_3 volatility by the glycerol hydroxyl group bonding to the free ammonia (Shuangchen et al., 2013). However, with the inclusion of glycerol, CO_2 flux declined more rapidly than without glycerol addition suggesting that glycerol-ammonia bonding also retarded mass transfer (Cheng et al., 2003). Direct measurement of ammonia slip could not be made in this study due to scale. However, ammonia slip has been measured by this group using a larger contactor scale (0.79 m^2) and similar process conditions ($5 \text{ mol l}^{-1} \text{ aq. NH}_3$; G/L 7.5) and a slip of only 0.015 % NH_3 noted which is ostensibly insufficient to grow the crystal mass observed within the fibre. The low slip can be explained by the low liquid velocities imposed, for which the depletion of ammonia through reaction with CO_2 extends radially away from the fibre wall toward the bulk (Figure 13). This is

experimentally corroborated at high G/L ratios where high CO₂ fluxes are coincident with diminished CO₂ removal efficiency (Figure 4) due to the decrease in mole ratio between NH₃ and CO₂ in the reaction zone (Zeng et al., 2013). At a G/L of 3, the methane content in the outlet gas exceeding the CH₄ content of North Sea natural gas (Persson et al., 2007) which indicated that the gas treatment objective can be met whilst limiting the free ammonia concentration (and hence slip) at the gas-liquid interface.

Higher aqueous ammonia concentrations were demonstrated to lower absorbent surface tension considerably (Figure 11). Lower surface tension is known to decrease breakthrough pressure for a cylindrical pore (Franken et al., 1987) which notably enhances the probability for wetting:

$$\Delta P_{B.P.} = \frac{-4B\sigma \cos\theta}{d_{\max}} \quad (5)$$

It is suggested that the reduction in surface tension observed at high aqueous ammonia concentration enables penetration of the ammonia rich absorbent into the pore and into the CO₂ rich gas phase initiating crystal nucleation in the lumen side of the microporous membrane. This was evidenced by the faster onset of lumen-side (gas-phase) crystal growth within aqueous ammonia concentrations greater than 3 M, which were characterised by a relatively large reduction in surface tension ($\Delta\sigma$ -5.6 to -9.6 mN m⁻¹, Figure 11). For comparison, whilst shell-side crystallisation was noted within the lower concentration 2 molNH₃ l⁻¹ absorbent, lumen-side crystal growth was absent. However, the progressive and gradual decline in CO₂ flux noted for the 2 molNH₃ l⁻¹ absorbent remains indicative of progressive pore wetting (Bougie et al., 2013); it is therefore asserted that the lower surface tension change measured at 2 molNH₃ l⁻¹ was insufficient to enable complete breakthrough into the lumen side. The role of surface tension in inhibiting both lumen-side crystallisation and wetting was confirmed through the addition of 5% wt. sodium chloride which counteracted the transition in surface tension introduced by the aqueous ammonia. Whilst the inclusion of NaCl increased surface tension of the aqueous ammonia by only 2.8 mN m⁻¹, a marked increase in CO₂ flux stability was observed (Figure 10, Figure 11).

Dense PDMS hollow fibre membranes were also evaluated as an approach to diminish lumen side crystallisation observed with microporous membranes at high aqueous concentrations, as they increase resistance to absorbent breakthrough whilst also being hydrophobic (contact angle with water approximately 110° : Aerts et al., 2006; Jadav et al., 2012). Whilst some crystal growth was observed on the shell-side of the PDMS membrane, crystal growth predominated on the lumen-side of the membrane within the gas phase (Figure 9). To generate analogous flux rates to those of the PTFE membrane, a high liquid velocity was used (G/L 0.39) which enhances surface renewal of free ammonia at the absorbent-membrane boundary and hence the potential for ammonia slip. Furthermore, since ammonia is a smaller and more condensable molecule than CO_2 , it is more permeable through PDMS (Makhloufi et al., 2014). Consequently co-permeability of both free ammonia and water vapour in the dense PDMS membrane promoted crystal growth within the fibre lumen and within the dynamic free volume network of the rubbery PDMS membrane which induced fibre wall distortion. Wetting and subsequent lumen-side crystallisation can be ascribed to the stretched pore shape of the microporous membrane in this study in addition to the surface tension of the absorbent. Stretched pores are a common feature of several commercially available hydrophobic polymeric microporous membranes (d/L 0.48, Heile et al., 2014) but was exacerbated within the PTFE fibre studied (d/L 0.065). Franken et al. (1987) introduced a pore geometry coefficient (B) to the Laplace-Young equation (Eq. 5) where non-cylindrical pore shape was classified by a coefficient of between $0 < B < 1$. This emphasises that pore wetting is exacerbated as pore shape tends away from that of a cylinder (Bougie et al., 2013). Consequently, microporous membranes with tighter pore shape together with surface tension regulation of the solvent are recommended to encourage preferential shell-side crystallisation and enhanced CO_2 flux stability in gas-liquid membrane absorption crystallisation reactors.

5. Conclusions

The use of microporous hollow fibre membrane contactors has been introduced to enable the nucleation and growth of crystalline reaction products initiated through chemically facilitated CO₂ separation from the gas phase. This represents the first membrane crystallisation reactor where the solubility limit to initiate nucleation is reached through counter diffusion of solutes from the solvent bulk to the membrane and of solutes from the 'permeate-side' through the membrane micropores into the membrane-solvent boundary. Lumen-side crystallisation can be avoided in favour of preferential shell-side nucleation and more stable CO₂ fluxes by: (1) raising surface tension of the absorbent through either limiting aqueous ammonia concentration or addition of a surface tension regulator; and, (2) selection of a membrane with a more regulated pore shape than the PTFE membrane used (d/L 0.065) as both actions can diminish solvent ingress into the pore. Although limiting aqueous ammonia concentration will diminish solvent reactivity and CO₂ flux, which suggests a larger process scale, the value ascribed to controlled production of the reaction product must also be weighted. Further refinement is required to ensure that longer term CO₂ flux stability can be ascertained simultaneously with ammonium bicarbonate growth. However, the progressive decline in CO₂ flux with the lower ammonia absorbent concentration was notably a result of wetting rather than interference of shell-side crystal growth. Whilst a high initial aqueous ammonia concentration initiated a large number of nucleation sites, the absorbent ammonia concentration also influenced morphology of crystals formed on the shell-side. Crystals formed within lower absorbent ammonia concentration (and lower CO₂ fluxes) possessed fewer nucleation sites and are characteristic of crystals preferentially grown under low flux conditions to favour growth over nucleation. This represents a potentially favourable characteristic for the continued detachment (and hence recovery) of the ammonium bicarbonate crystals formed, where the low shear stresses applied in continuous MCr have been shown sufficient to enable detachment and downstream recovery of the crystalline product (Di Profio et al., 2010).

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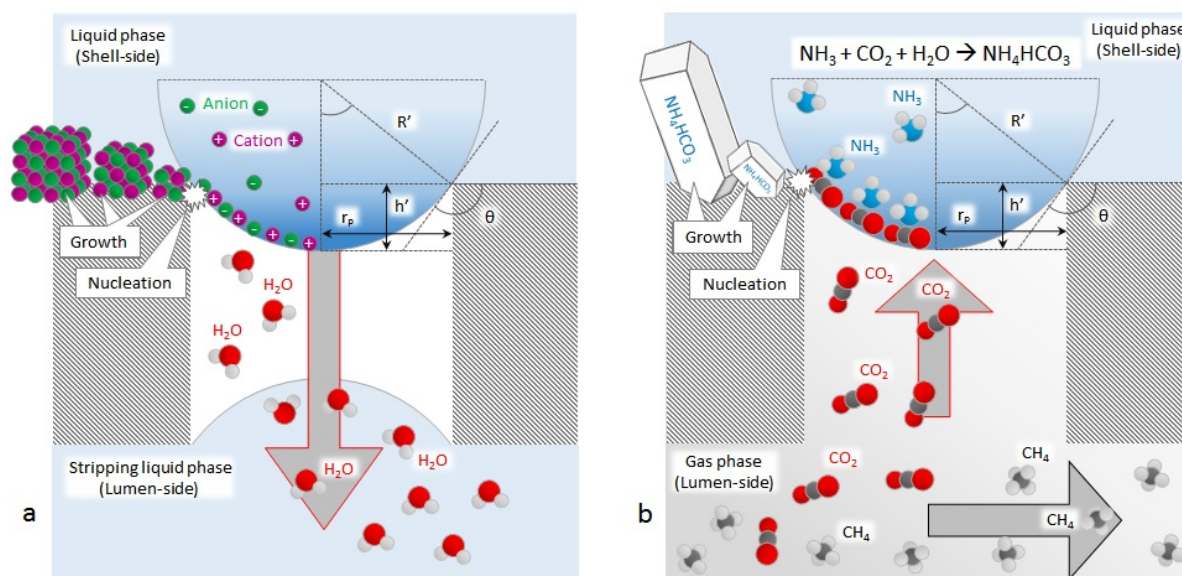


Figure 1. Mechanisms of crystallisation introduced: (a) membrane crystallisers typically achieve supersaturation through removing solvent (often water) as vapour to induce heterogeneous nucleation; and (b) the proposed gas-liquid membrane crystalliser where CO₂ absorbed within an NH₃ rich solution induces supersaturation through continuous CO₂ flux from the gas phase leading to nucleation of an NH₄HCO₃ product.

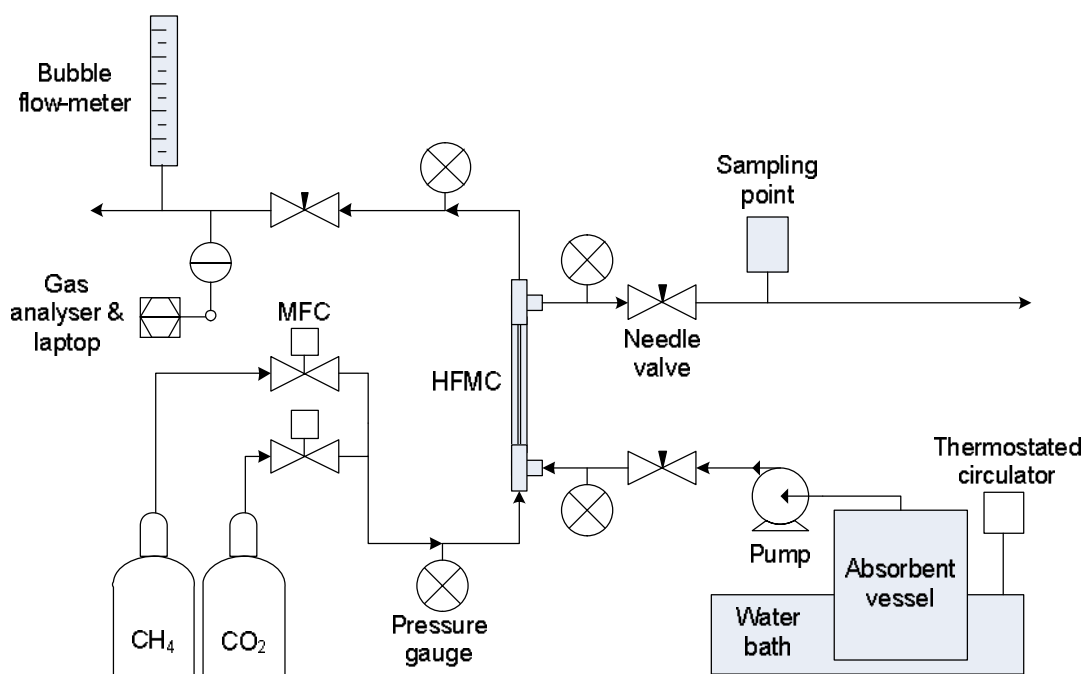


Figure 2. Schematic of experimental apparatus.

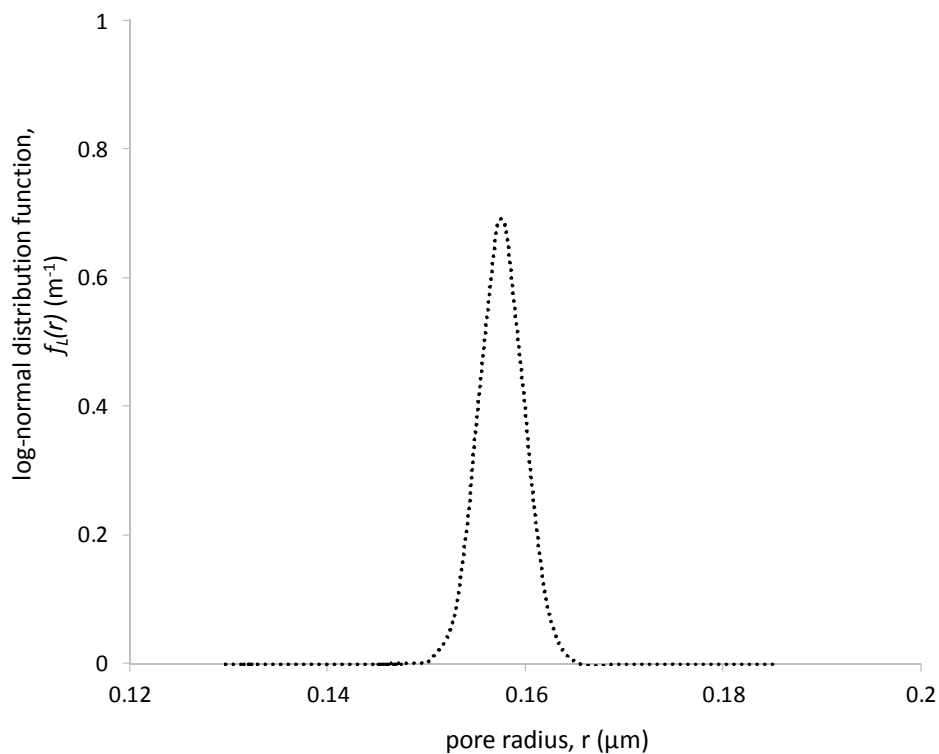


Figure 3. Statistical determination of pore radii using log-normal distribution.

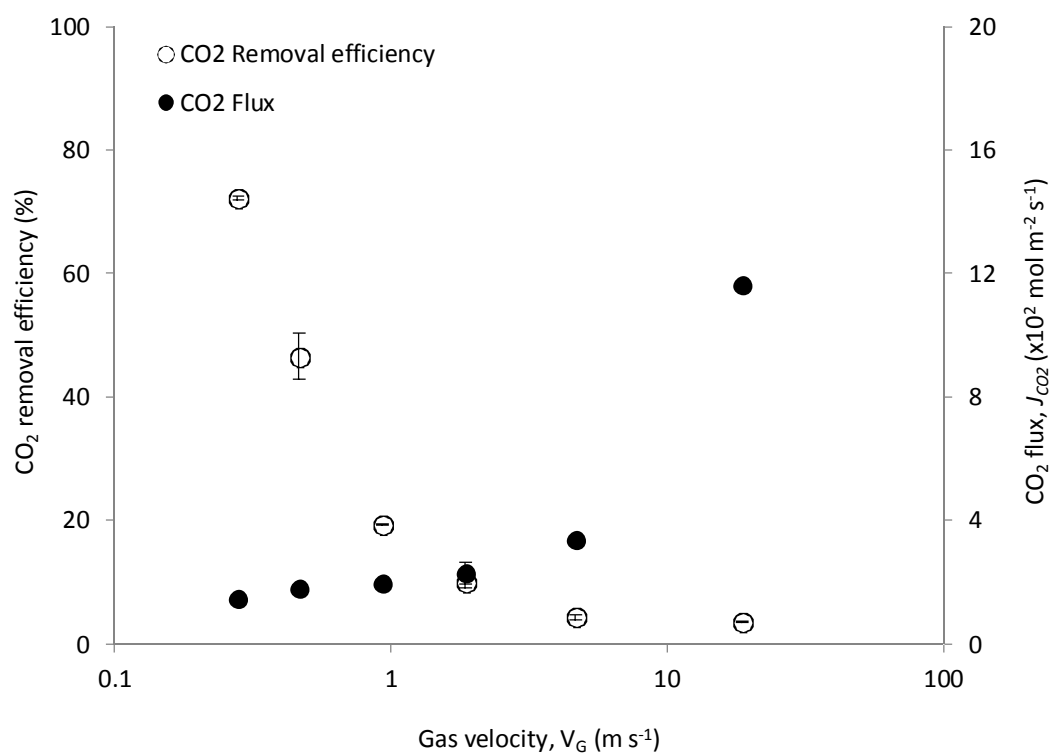


Figure 4. Effect of variable gas velocity (V_G) upon CO_2 removal efficiency; and CO_2 flux, during absorption from a 50:50 CO_2 : CH_4 gas mixture using 7 mol l^{-1} aqueous ammonia solution at fixed liquid velocity (V_L , 0.02 m s^{-1}) in a single fibre PTFE HFMC. Error bars indicate standard error.

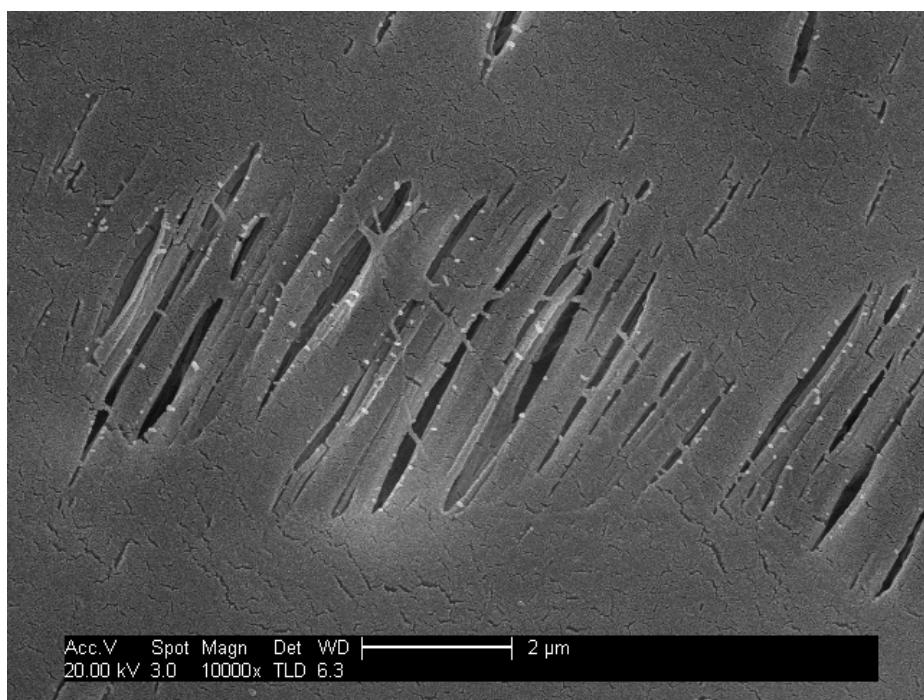


Figure 5. SEM surface analysis of NH_4HCO_3 crystal nucleation at the membrane-absorbent interface (shell-side) following CO_2 absorption using a 7 mol l^{-1} NH_3 solution in single pass operation (x10000).

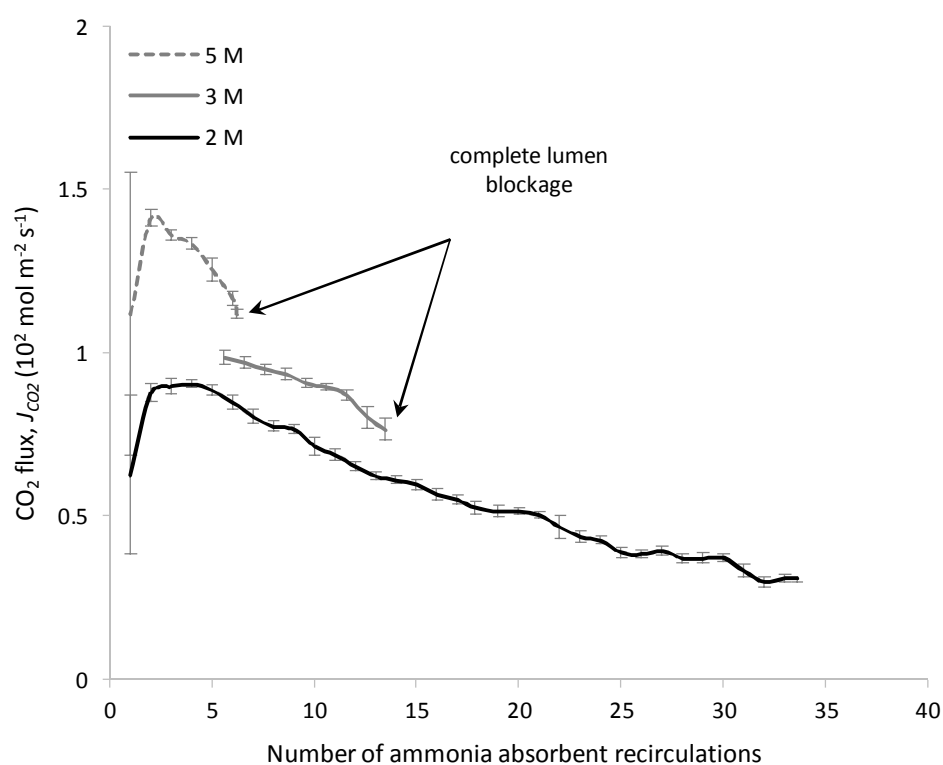


Figure 6. Carbon dioxide flux observed with the PTFE membrane following ammonia absorbent recirculation (2 M, 3 M and 5 M) through the shell-side of the module. Hydrodynamic conditions: G/L 10; V_G 0.93 m s^{-1} ; V_L 0.02 m s^{-1} . Lumen side blockage observed for 3M and 5M solutions. Error bars indicate standard error.

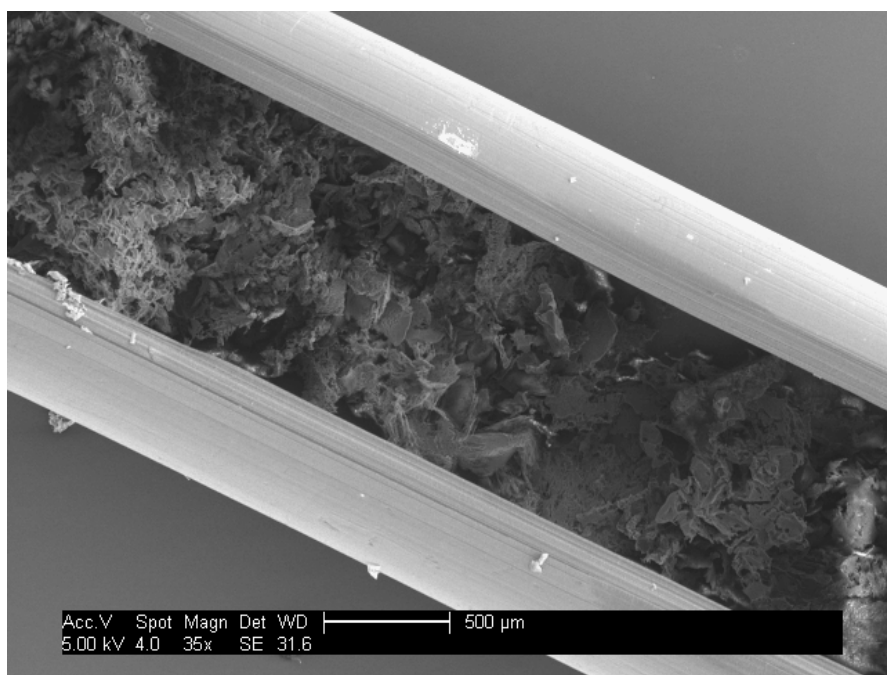


Figure 7. Dissected section of the micro-porous PTFE hollow fibre membrane used for 5M NH_3 absorbent recirculation. The experiment was stopped after 6 recirculations due to gas-side (lumen side) blockage. SEM analysis demonstrates fibre blockage due to formation of NH_4HCO_3 crystals. Hydrodynamic conditions: G/L 10; V_G 0.93 m s^{-1} ; V_L 0.02 m s^{-1} .

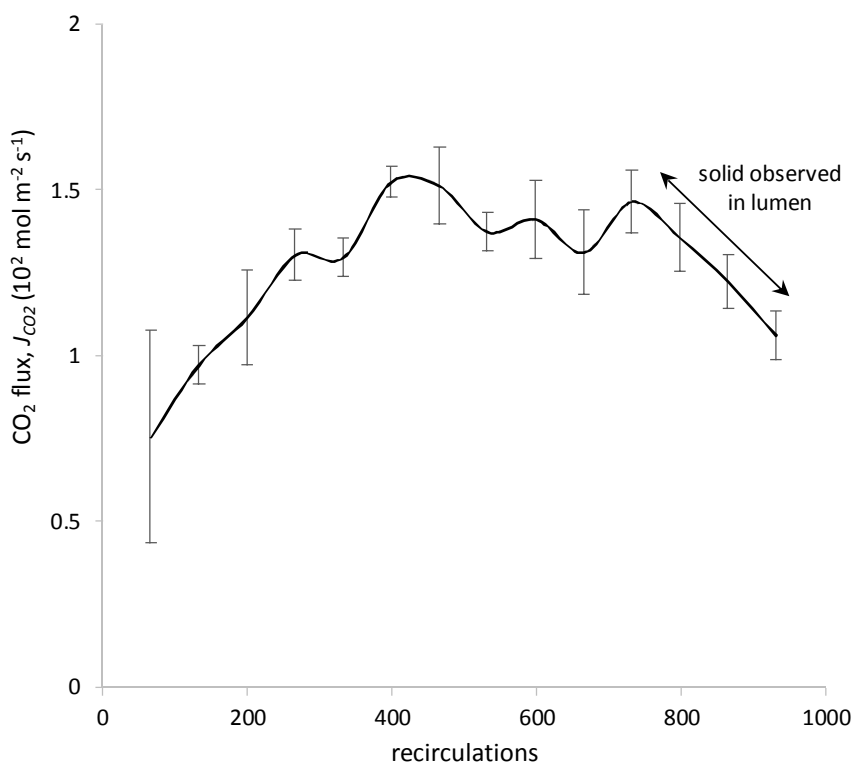


Figure 8. Carbon dioxide flux observed with the nonporous PDMS hollow fibre membrane using 5M NH_3 absorbent recirculated through the module shell-side. Gas-side (lumen side) blockage noted following 800 solvent recirculations. Hydrodynamic conditions: G/L 0.4; V_L 0.1 m s^{-1} . Error bars indicate standard error.

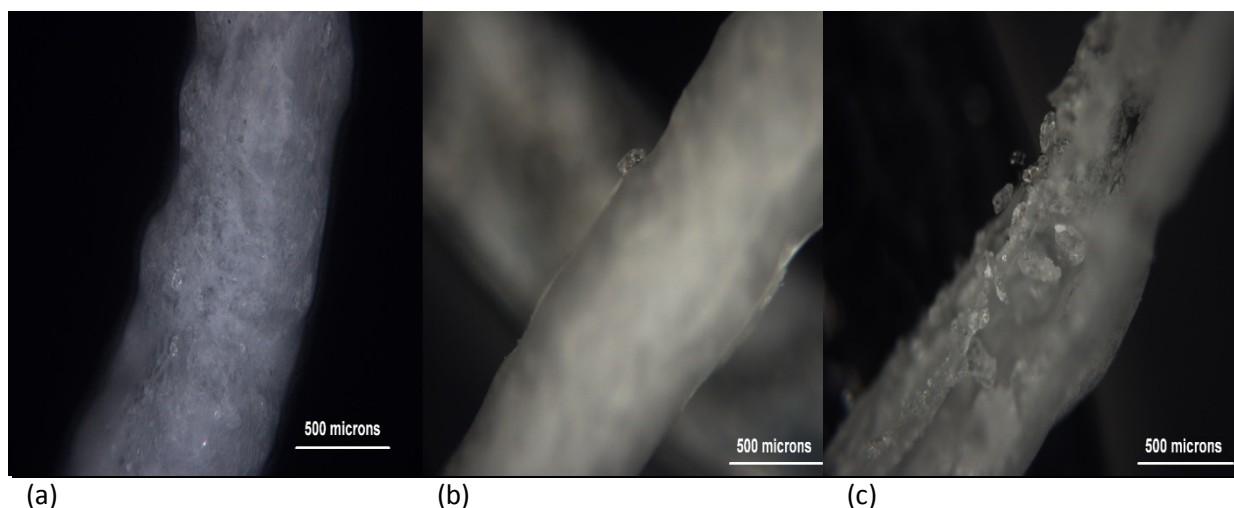


Figure 9. Nonporous PDMS hollow fibre membrane following >800 recirculations of 5M NH_3 absorbent: (a) crystals formed inside the fibre lumen; (b) an example crystal formed on the outside of the fibre; and (c) the PDMS fibre dissected reveals crystals formed within the fibre lumen.

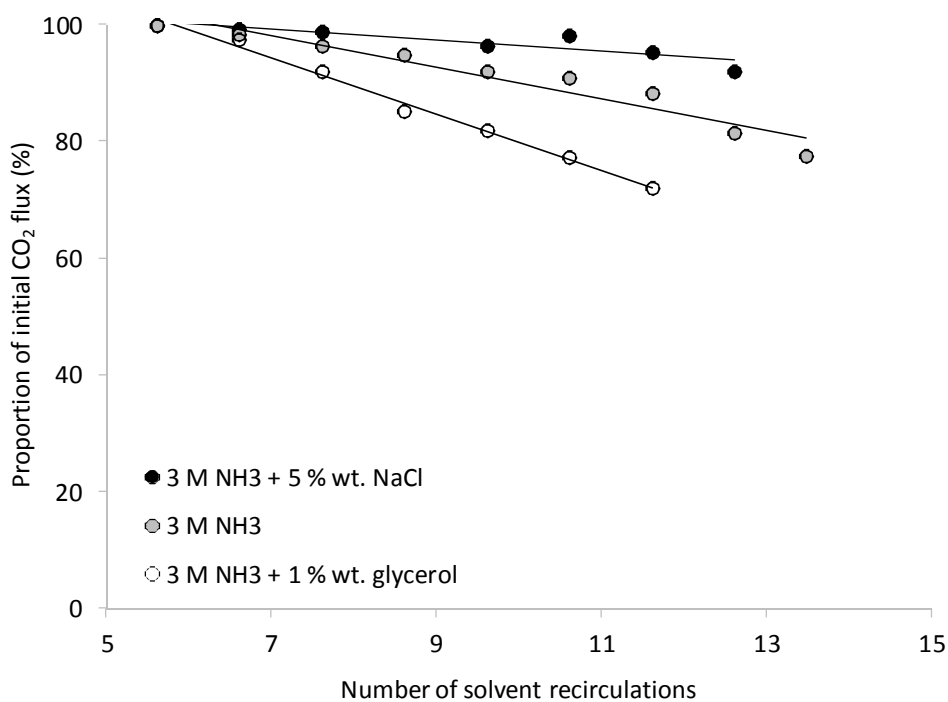


Figure 10. Impact of sodium chloride (5% NaCl) and glycerol (1% $\text{C}_3\text{H}_8\text{O}_3$) on CO_2 flux when used as additives to 3M NH_3 absorbent recirculated through the module shell-side. Hydrodynamic conditions: G/L 10; V_G 0.93 m s^{-1} ; V_L 0.02 m s^{-1} .

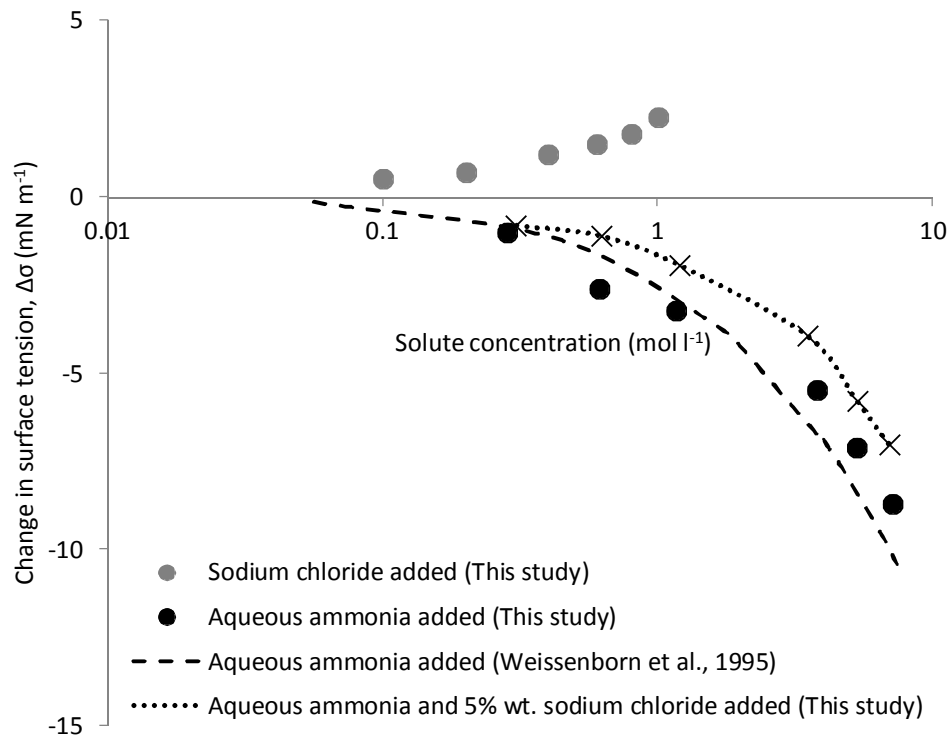


Figure 11. Changes in surface tension relative to deionised water driven by aqueous ammonia and sodium chloride solute concentration within the concentration range examined (NH_3 , 2-7M; NaCl 5% wt. or 0.85 M) (Weissenborn et al., 1995).

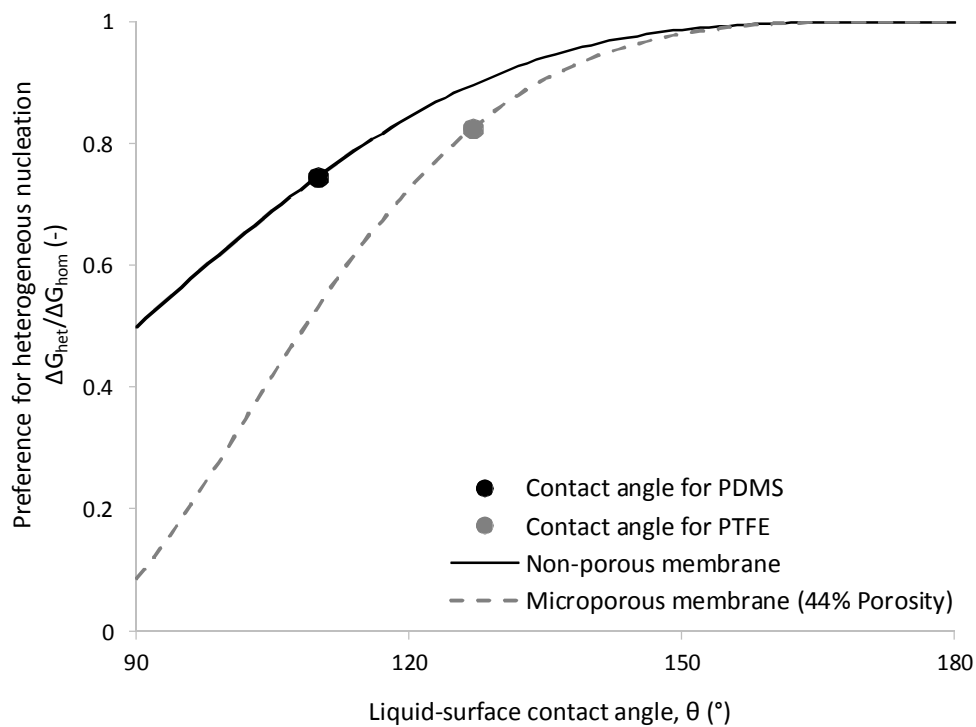


Figure 12. Impact of liquid-surface contact angle on the thermodynamic favourability of heterogeneous vs. homogeneous nucleation calculated for the non-porous PDMS membrane and PTFE micro-porous membrane used (Appendix, Eq. A1).

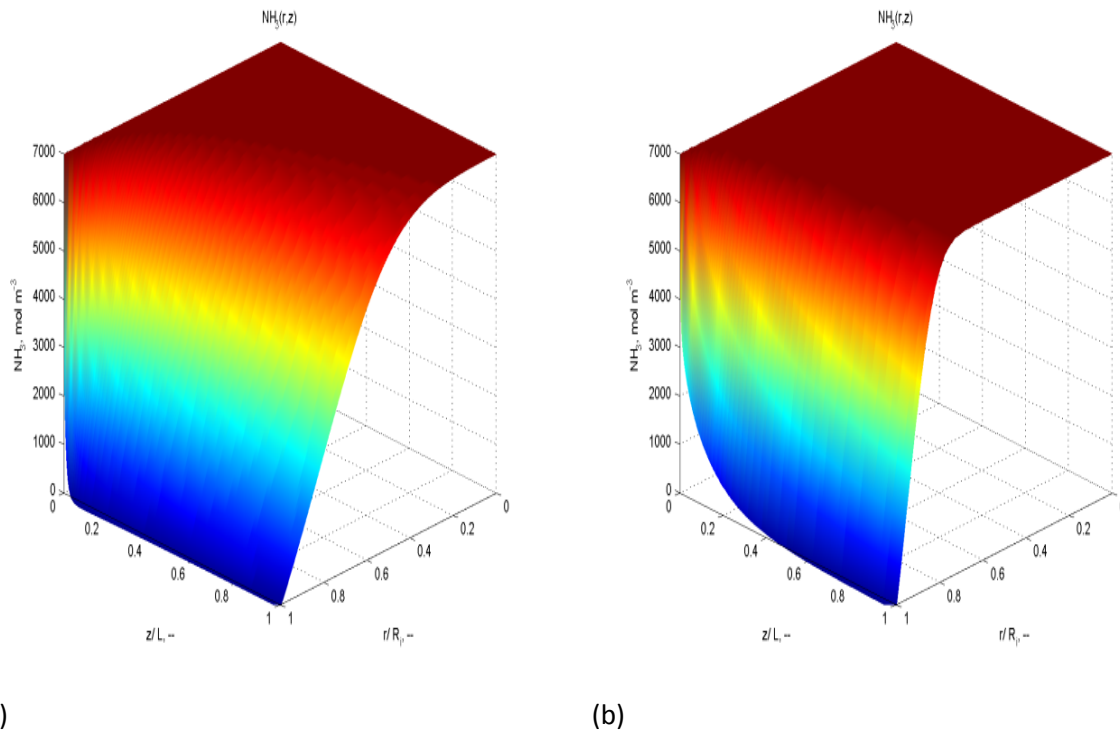


Figure 13. An illustration of NH_3 depletion by chemical reaction with CO_2 : (a) extending into the liquid bulk at low V_L ; and (b) confined to the liquid boundary layer at high V_L . For supporting calculations, see Appendix.

Table 1. Dimensions and surface characteristics of the single membrane fibres

		PDMS ^b	PTFE ^b
Fibre characteristics			
Inner diameter	mm	0.18	1.51
Outer diameter	mm	0.31	1.91
Wall thickness	μm	65	200
Active length	m	0.1	0.1
Surface area ^a	m^2	0.97×10^{-4}	6×10^{-4}
Porosity	%	-	44
Mean pore radius	μm	-	0.16
Average surface roughness ^c	nm	76.6	82.2
Lumen cross sectional area	m^2	2.54×10^{-8}	1.79×10^{-6}
Shell-side characteristics			
Inner diameter	mm	6	6
Outer diameter	mm	4	4
Shell cross sectional area	m^2	2.82×10^{-5}	2.54×10^{-5}
Priming volume	ml	2.82	2.54
Operational Characteristics			
Flow regime		Co-current	Co-current
Shell-side		5 M NH_3 (aq.)	2,3,5,7 M NH_3 (aq.)
Lumen-side		50:50 CO_2 : CH_4	50:50 CO_2 : CH_4

^aBased on fibre outer diameter. ^bData provided by manufacturer. ^cMeasured using AFM.

Table 2. SEM images and EDX analyses of ammonium bicarbonate crystals grown on the PTFE membrane at the membrane-absorbent interface (shell-side) during recirculation of aqueous ammonia absorbents ranging 2 to 5 mol l⁻¹ in concentration.

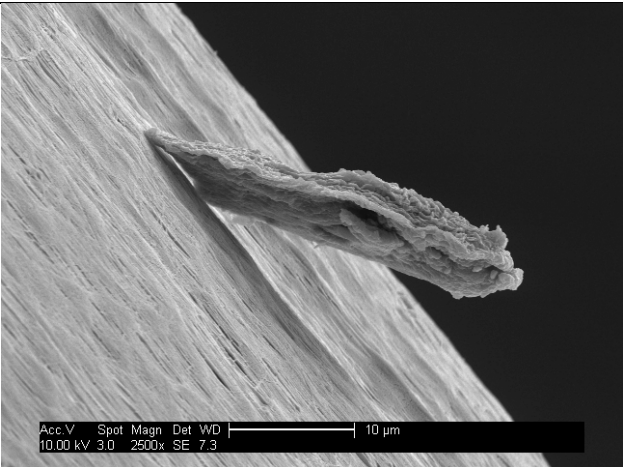
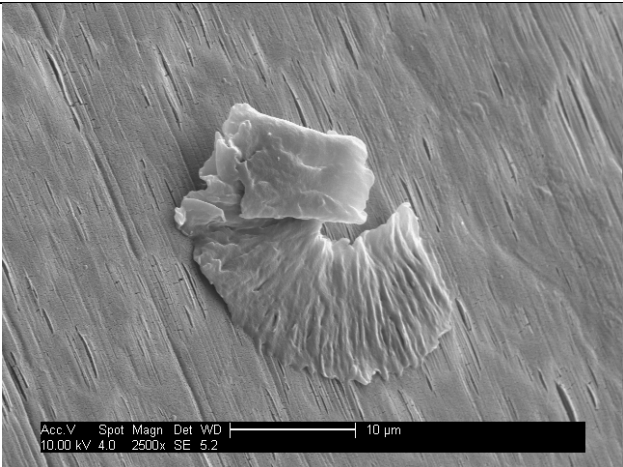
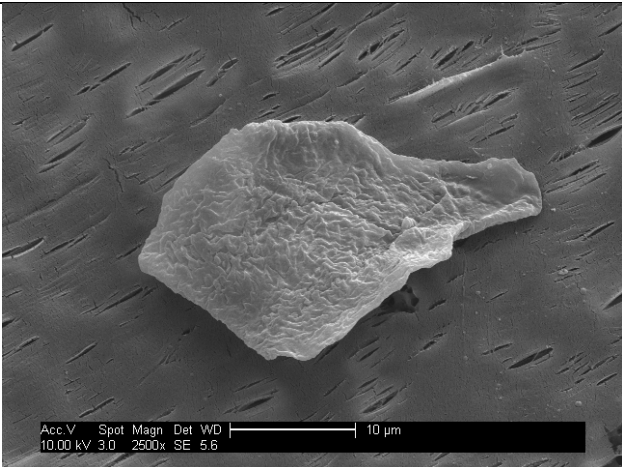
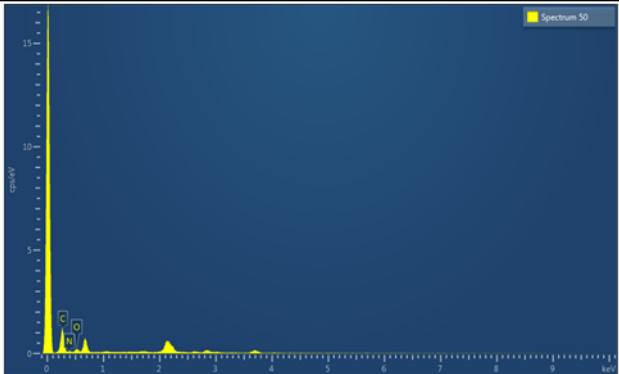
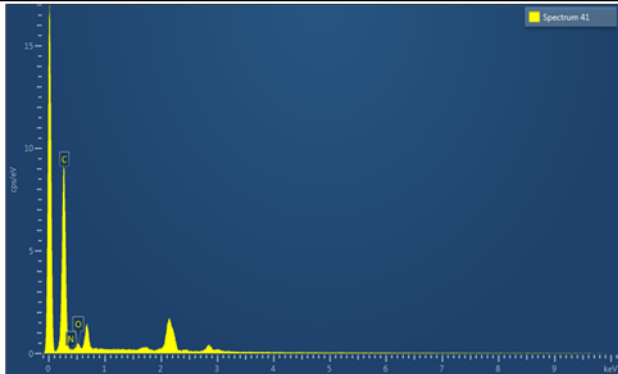
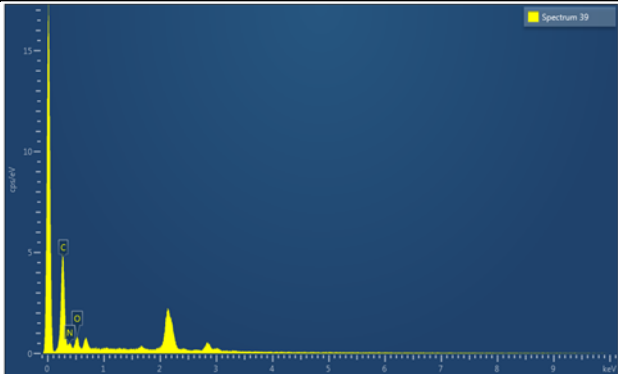
	2 mol l ⁻¹	3 mol l ⁻¹	5 mol l ⁻¹
SEM/ SFEG			
EDX			

Table B1. Parameters determined for modelling of CO₂ absorption in NH₃ solutions of concentrations relevant to the present study adjusted for a system at 25 °C

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Controlling shell-side crystal nucleation in a gas-liquid membrane contactor for simultaneous ammonium bicarbonate recovery and biogas upgrading

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