



BENJAMIN A. LUQMANI

Ammonia recovery and utilisation for biogas upgrading in
membrane contactors

SCHOOL OF WATER, ENERGY AND ENVIRONMENT
Cranfield Water Science Institute

EngD
Academic Year: 2018 - 2023

Supervisor: Professor Ewan McAdam
Associate Supervisor: Dr Marc Pidou

July 2023



SCHOOL OF WATER, ENERGY AND ENVIRONMENT
Cranfield Water Science Institute

EngD

Academic Year 2018 - 2023

BENJAMIN A. LUQMANI

Ammonia recovery and utilisation for biogas upgrading in
membrane contactors

Supervisor: Professor Ewan McAdam
Associate Supervisor: Dr Marc Pidou

July 2023

This thesis is submitted in partial fulfilment of the requirements for
the degree of EngD

© Cranfield University 2023. All rights reserved. No part of this
publication may be reproduced without the written permission of the
copyright owner.

Abstract

This thesis has developed an innovative system for biogas upgrading using hollow fibre membrane contactors (HFMC) whilst recovering ammonia from wastewater as a reactive solvent to intensify CO₂ absorption. An expanded two-phase region for ammonia-water separation was identified and exploited to foster selective, low energy recovery of concentrated gas-phase ammonia from wastewater by vacuum thermal stripping. Selective stripping was translated to a gas-liquid contacting column which demonstrated mass transfer rates analogous to commercially established stripping processes. Investment in selective ammonia recovery from anaerobic digester centrate represents a cost saving over a 20-year economic lifetime relative to biological nitrogen removal. During physical CO₂ absorption in HFMC, solvent chilling and gas pressurisation were observed to increase flux and selectivity, thereby reducing membrane area and path length for biogas upgrading. Chilled conditions will promote wetting resilience to favour the application of microporous membranes, which are low-cost and technologically mature. Translation to recovered ammonia solvents will further intensify CO₂ absorption, but can result in gas-side reactions within the ternary CO₂-NH₃-H₂O system which reduce process stability. In a positive synergy, chilled, pressurised conditions could limit ammonia 'slip' and maintain the system below a critical threshold to prevent gas-side reactions and improve process resilience. Pressurised, reactive crystallisation in HFMC during CO₂ absorption by ammonia solvents was demonstrated for the first time, and observed to occur at a consistent supersaturation level. Consequently, ammonium bicarbonate crystals exhibited consistent characteristics independent of pressure which supports simplified online control and solids recovery for scale-up. The integrated system proposed in this thesis presents a cost effective, circular economy solution for ammonia recovery and biogas upgrading which is closely aligned to net zero ambitions within the water sector and wider society.

Keywords: *ammonia recovery, ammonia to energy, HFMC, biogas upgrading, CAP, reactive crystallisation, net zero, circular economy.*

Acknowledgements

This doctorate has been a tough, rewarding and transformational experience. I'd like to sincerely thank Ewan McAdam for his guidance, support and patience over the past four years, and Marc Pidou for providing insight and perspective throughout.

Thank you to Northumbrian Water, Anglian Water, Severn Trent and the Engineering and Physical Sciences Research Council for the provision of financial and practical support which made this project possible. I'd particularly like to thank Andrew Moore, Adam Brookes and Pete Vale for their enthusiasm and engagement with my project which helped me to contextualise it within the water sector.

Many thanks to my friends within the STREAM and WiRE Industrial Doctorate Centres who are scattered across the UK, particularly Cohort X with whom I started this journey four years ago. Going through this together has been hugely motivating and has helped me to navigate many challenges on the way.

One week before I started this doctorate, Libby and I got married. Back then, we didn't know what I was getting us into. There is no way that I could have completed this without her. And finally, thanks to my daughter Sophie, who has effortlessly brightened every day since she arrived in this world.

It's been an adventure.

Table of Contents

Abstract.....	i
Acknowledgements	iii
List of Figures.....	vii
List of Tables.....	xiii
Nomenclature.....	xiv
Abbreviations.....	xiv
Chemical formulae.....	xv
Notations	xv
Greek symbols.....	xvii
1 Introduction	1
1.1 Biomethane and ammonia recovery to support a net zero water sector	2
1.2 Intensification of biogas upgrading in membrane contactors	7
1.3 Intensification of biogas upgrading using wastewater-derived $\text{NH}_3(\text{aq})$	9
1.4 Crystallisation limits energy demand and creates sustainable products	13
1.5 Thesis aim, objectives and structure.....	15
References	17
2 Transitioning through the vapour-liquid equilibrium for low energy thermal stripping of ammonia from wastewater: Enabling transformation of NH_3 as a zero carbon fuel	29
Abstract	30
2.1 Introduction.....	31
2.2 Materials and methods	38
2.2.1 Experimental set-up	38
2.2.2 Wastewater preparation and analysis	39
2.2.3 Experimental analysis	40
2.3 Results and discussion	42
2.3.1 Validation of empirical dew point as the upper limit for two-phase region	42
2.3.2 Expanded two-phase region determined for selective ammonia separation	46
2.3.3 Stripping within two-phase region supports ammonia to energy strategies.....	50
2.3.4 Predictable ammonia-water separation behaviour for wastewater	52
2.3.5 In-situ decarbonisation facilitates chemical-free vacuum thermal stripping.....	55
2.4 Conclusion.....	57

Appendix A	59
References	62
3 The role of solvent temperature and gas pressure on CO ₂ mass transfer during biogas upgrading within porous and dense-skin hollow fibre membrane contactors.....	71
Abstract	72
3.1 Introduction.....	73
3.2 Materials and methods	77
3.2.1 Experimental set-up	77
3.2.2 Experimental analysis	79
3.3 Results and discussion	82
3.3.1 Microporous and nonporous HFMC influenced strongly by temperature.....	82
3.3.2 Plasticisation and pore wetting do not limit CO ₂ separation under pressure	87
3.3.3 Pressurisation enhances CO ₂ selectivity during biogas upgrading	92
3.4 Conclusion.....	97
Appendix B	99
References	103
4 Examining disruptive gas-phase reactions during CO ₂ capture in membrane contactors: CO ₂ -NH ₃ -H ₂ O as a model ternary system.....	111
Abstract	112
4.1 Introduction.....	113
4.2 Methodology	116
4.3 Results and discussion	117
4.3.1 NH _{3(aq)} associated with chemical enhancement and process instability	117
4.3.2 Condensate formation and composition evidences gas-phase reactions.....	120
4.3.3 High CO ₂ capture can trigger gas-phase reactions in the ternary system.....	123
4.4 Proposed mitigation strategies	127
Appendix C	128
References	132
5 CO ₂ capture and reactive crystallisation using membrane contactors: Impact of pressurisation on process intensification and nucleation kinetics ...	137
Abstract	138
5.1 Introduction.....	139
5.2 Materials and methods	142
5.2.1 Experimental set-up	142
5.2.2 Experimental analysis	144

5.2.3 Solution chemistry within the CO ₂ -NH ₃ -H ₂ O system	146
5.2.4 Crystallisation analysis.....	147
5.3 Results and discussion	149
5.3.1 Process intensification by pressurisation was limited by solvent reactivity	149
5.3.2 High rates of CO ₂ loading under pressure will minimise NH ₃ ‘slip’	151
5.3.3 Reactive membrane crystallisation demonstrated under pressure	153
5.3.4 Nucleation kinetics were independent of pressure	155
5.4 Conclusion	162
Appendix D	163
References	167
6 The recovery of ammonia and its utilisation within a net zero water sector – a techno-economic analysis	175
Abstract	176
6.1 Introduction.....	177
6.2 Selective NH ₃ stripping translated to a gas-liquid contacting column	182
6.3 Techno-economic evaluation for vacuum thermal stripping	185
6.4 Wastewater-derived ammonia as a zero carbon energy resource....	192
6.5 Wastewater-derived ammonia as a solvent for biogas upgrading	196
6.6 Conclusion	198
Appendix E	200
References	210
7 Discussion.....	225
7.1 Discussion	226
7.1.1 Could HFMC offer a competitive alternative to absorption columns?.....	226
7.1.2 What are the synergies and opportunities for reactive biogas upgrading?	229
7.1.3 Does vacuum stripping present a disruptive solution for nitrogen removal?	230
7.1.4 What are the systems level opportunities for wastewater treatment?	233
References	236
8 Conclusions and further work.....	245
8.1 Conclusions	246
8.2 Further work	248

List of Figures

Figure 1.1 Overview of wastewater treatment works with biogas upgrading by conventional PWA process.....	6
Figure 1.2 Layout for the transverse-flow hollow fibre membrane contactors used in this thesis (3M Industrial Group, Charlotte, USA)	7
Figure 1.3 Schematic representation of mass transfer resistances for the absorption of CO ₂ across (a) a microporous membrane with gas-filled pores; (b) a microporous membrane with partially wetted pores; (c) a nonporous membrane with a dense polymer skin; and (d) a microporous membrane using a volatile ammonia solvent. $1/k_l$, $1/k_m$, $1/k_{m(w)}$, $1/k_{m(d)}$ and $1/k_g$ represent resistances in the liquid, dry membrane, wetted membrane, dense polymer skin and gas, respectively. C_{CO_2} is the liquid-phase CO ₂ concentration, p_{CO_2} is the gas-phase CO ₂ partial pressure; and b and i represent bulk and interface conditions respectively.	9
Figure 1.4 Integrated wastewater treatment works where reactive biogas upgrading and crystallisation in HFMC is achieved using wastewater-derived ammonia solvents.....	12
Figure 1.5 Summary of thesis objectives and corresponding chapters.....	16
Figure 2.1 VLE for NH ₃ -H ₂ O at 0.25 bar defined using empirical method (Eq. 2.11-2.12)	36
Figure 2.2: Operating points for vacuum thermal stripping of real and synthetic wastewater at 0.25-0.27 bar in previous work, placed within the context of the NH ₃ -H ₂ O VLE (Eq. 2.11-2.12).....	37
Figure 2.3. Schematic of the vacuum thermal stripping experiment. TT and PT represent temperature and pressure transmitters, respectively.	39
Figure 2.4 Operating points for vacuum thermal stripping in previous work, placed within the context of the pure water boiling curve from 0-1 bar.	44
Figure 2.5 Vacuum thermal stripping of synthetic wastewater at 65°C and 0.25 bar. Operational conditions: $C_{NH_3,0}$, 1.5 g L ⁻¹ ; initial feed mass, 0.5 kg; pH, 11; condenser temperature, 3-5°C.	44
Figure 2.6 Influence of temperature on the vapour pressure of water determined by Raoult's Law and of ammonia determined by Henry's Law for a 1.5 g L ⁻¹ ammonia solution (Appendix A2).....	46
Figure 2.7 Influence of temperature during vacuum thermal stripping of synthetic wastewater at 0.25 bar on (a) ammonia removal from the feed and (b) the water vapourisation rate. Operational conditions: initial C_{NH_3} , 1.5 g L ⁻¹ ; initial feed mass, 0.5 kg; pH, 11; condenser temperature, 3-5°C.....	48
Figure 2.8 Ammonia selectivity during vacuum thermal stripping of synthetic wastewater at 65, 63 and 61°C and 0.25 bar. Operational conditions: initial C_{NH_3} , 1.5 g L ⁻¹ ; initial feed mass, 0.5 kg; pH, 11; condenser temperature, 3-5°C.	49
Figure 2.9 Experimental ammonia vapour quality during transition through two-phase region plotted on VLE for NH ₃ -H ₂ O at 0.25 bar.....	49
Figure 2.10 Influence of temperature during vacuum thermal stripping of synthetic wastewater at 0.25 bar on (a) the mass fraction of ammonia in the vapour phase and (b) the specific thermal demand for ammonia stripping.	

Operational conditions: initial C_{NH_3} , 1.5 g L ⁻¹ ; initial feed mass, 0.5 kg; pH, 11; condenser temperature, 3-5°C.	51
Figure 2.11 (a) Ammonia removal and (b) ammonia selectivity over time during vacuum thermal stripping of synthetic wastewater, Centrate A and Centrate B at 65°C and 0.25 bar. Operational conditions: initial feed mass, 0.5 kg; pH, 11; condenser temperature, 3-5°C.	54
Figure 2.12 Vacuum thermal stripping of Centrate A and Centrate B at their natural pH at 65°C and 0.25 bar. Centrate A: initial C_{NH_3} , 1.0 g L ⁻¹ and initial pH, 7.8. Centrate B: initial C_{NH_3} , 2.0 g L ⁻¹ and initial pH, 8. Operational conditions: initial feed mass, 0.5 kg; pH measurements conducted at 21°C.	56
Figure 3.1: Experimental set-up for gas-liquid absorption in HFMC	79
Figure 3.2: Impact of solvent temperature on CO ₂ flux across microporous (PP) and nonporous (PMP) membranes. Conditions: Pure CO ₂ gas feed; v_g , 0.07-0.08 m s ⁻¹ ; P(gas), 1.1 bar; gas temperature in, 21 °C.....	83
Figure 3.3: Impact of solvent temperature on membrane mass transfer resistance for CO ₂ within microporous (PP) and nonporous (PMP) membranes. Membrane mass transfer resistances determined using Wilson plot method (example inset for nonporous membrane at 10°C) Conditions: Pure CO ₂ gas feed; v_g , 0.07-0.08 m s ⁻¹ ; P(gas), 1.1 bar; gas temperature in, 21°C. Estimated pore wetting annotated (Eq. 3.6). Dotted lines added to guide the eye.	83
Figure 3.4: Influence of water temperature on determined pore wetting and the vapour pressure for pure water. Conditions: pure CO ₂ gas feed; v_g , 0.07-0.08 m s ⁻¹ ; P(gas), 1.1 bar; gas temperature in, 21°C. Solvent temperature annotated.....	85
Figure 3.5: Influence of dense-skin permeability on membrane resistance for nonporous membrane (inset: graphical method for determining dense-skin activation energy, E_a). Conditions: pure CO ₂ gas feed; v_g , 0.07-0.08 m s ⁻¹ ; P(gas), 1.1 bar; gas temperature in, 21°C. Solvent temperature annotated.	85
Figure 3.6: Impact of gas pressure on (a) overall mass transfer resistance, and (b) CO ₂ flux enhancement across microporous (PP) and nonporous (PMP) membranes. Conditions: Pure CO ₂ gas feed; v_l , 3.2x10 ⁻³ m s ⁻¹ ; v_g , 0.07-0.08 m s ⁻¹ ; solvent temperature, 5-10°C; gas temperature in, 21°C. Flux enhancement: $J_{\text{CO}_2}/(J_{\text{CO}_2} \text{ at } 1.1 \text{ bar})$. Dotted line at $J_{\text{CO}_2} \propto P_{\text{CO}_2}$	88
Figure 3.7: Impact of gas pressure on mass transfer resistance within: (a) the microporous membrane, and (b) the nonporous membrane. Membrane resistances previously determined (Figure 3.3) and liquid-phase resistance estimated using Graetz-Leveque solution (Eq. 3.5). Conditions: 50:50 CO ₂ /CH ₄ gas feed; v_g , 0.02 m s ⁻¹ ; v_l , 1.7x10 ⁻³ m s ⁻¹ ; Gz number, 15; solvent temperature, 5-10°C; gas temperature in=21°C.....	90
Figure 3.8: Impact of gas pressure on methane outlet concentration during binary gas separation within: (a) the microporous membrane, and (b) the nonporous membrane. Conditions: 50:50 CO ₂ /CH ₄ gas feed; solvent temperature, 5-10°C; gas temperature in, 21°C. Dotted line represents 98%vol methane concentration in outlet gas. Absolute pressure values provided.	91

- Figure 3.9:** Influence of pressure on the selectivity of CO₂ transport within the microporous membrane. Conditions: 50:50 CO₂/CH₄ gas feed; v_g , 0.02 m s⁻¹; v_l , 1.7x10⁻³ m s⁻¹; solvent temperature, 5-10°C; gas temperature in, 21°C. 93
- Figure 3.10:** Impact of gas pressure on outlet gas quality, methane slip and methane losses from the system in the microporous module. Conditions: 50:50 CO₂/CH₄ gas feed; v_g , 0.02 m s⁻¹; v_l , 1.7x10⁻³ m s⁻¹; solvent temperature, 5-10°C; gas temperature in, 21°C. Ideal dissolved methane recovery estimated for solvent depressurisation to 1.5 bar in a flash vessel. 93
- Figure 3.11:** Methane slip into liquid-phase within: (a) the microporous membrane (m³_{liquid} Nm⁻³_{gas}), (b) the microporous membrane normalised to pressure (m³_{liquid} m⁻³_{gas}), and (c) the nonporous membrane normalised to pressure (m³_{liquid} m⁻³_{gas}). Conditions: 50:50 CO₂/CH₄ gas feed; v_g , 0.02 m s⁻¹; solvent temperature, 5-10°C; gas temperature in, 21°C. Dotted line represents projected slip. Dashed line indicates the L/G ratio at peak outlet gas quality for a specific condition (Figure 3.8). 96
- Figure 4.1:** Ternary vapour-liquid-equilibrium for CO₂-NH₃-H₂O based on the output of the extended UNIQUAC model at 10°C developed by Thomsen and Rasmussen (1999). S – solid; L – liquid; V – vapour; BC – ammonium bicarbonate; SC – ammonium sesqui-carbonate; CB – ammonium carbonate; CM – ammonium carbamate. Annotations added using orange boxes and an orange arrow. Red-white shaded region could not be resolved within the model. Republished from Sutter et al. (2015) with permission from Elsevier Ltd. 117
- Figure 4.2:** CO₂ capture ratio and gas-side pressure drop using: (a) DI water; (b) 1 mol_{NH3} L⁻¹; and (c) 3 mol_{NH3} L⁻¹ solvents. Operating conditions: liquid flowrate, 0.25 L min⁻¹; liquid temperature, 6.5±0.5°C; CO₂ in feed gas, 8%vol; feed gas flowrate, 1.1 L min⁻¹; gas temperature, 21°C. 119
- Figure 4.3:** Temporal analysis of ammonia transfer into the gas-side during experimentation with: (a) 1 mol_{NH3} L⁻¹; and (b) 3 mol_{NH3} L⁻¹ solvents. Ammonia was recovered from the lumen (via acid elution), condensate (collected in a gas-liquid separator), and the outlet gas (captured using an acid trap). Operating conditions: liquid flowrate, 0.25 L min⁻¹; liquid temperature, 6.5±0.5°C; CO₂ in feed gas, 8%vol; feed gas flowrate, 1.1 L min⁻¹; gas temperature, 21°C. 121
- Figure 4.4:** Composition of condensate collected at the gas-outlet using a gas-liquid separator for: (a) 1 mol_{NH3} L⁻¹; and (b) 3 mol_{NH3} L⁻¹. Operating conditions: liquid flowrate, 0.25 L min⁻¹; liquid temperature, 6.5±0.5°C; CO₂ in feed gas, 8%vol; feed gas flowrate, 1.1 L min⁻¹; gas temperature, 21°C. Dotted lines indicated NH₄HCO₃ solubility at 21°C (O’Neil, 2006; Perry and Green, 2007). 122
- Figure 4.5:** Ammonia transfer at the gas outlet (captured using an acid trap) over time when using aqueous ammonia solvents. Operating conditions: liquid flowrate, 0.25 L min⁻¹; liquid temperature, 6.5±0.5°C; CO₂ in feed gas, 8%vol; feed gas flowrate, 1.1 L min⁻¹; gas temperature, 21°C. Dotted lines represent ammonia slip over time at gas-liquid equilibrium estimated using Henry’s Law (Appendix C2). 123

Figure 4.6: Projected ternary system composition based upon gas-liquid equilibrium vapour pressures for ammonia and water and the influence of CO ₂ capture ratio for: (a) 1 mol _{NH₃} L ⁻¹ ; and (b) 3 mol _{NH₃} L ⁻¹ solvents. Based on the output from the extended UNIQUAC model at 10°C (Sutter et al., 2015; Thomsen and Rasmussen, 1999) and equilibrium vapour pressures for NH ₃ and H ₂ O (Appendix C2).	125
Figure 4.7: Experimental ternary system composition based upon the CO ₂ capture ratio when using: (a) 1 mol _{NH₃} L ⁻¹ ; and (b) 3 mol _{NH₃} L ⁻¹ solvents. Relevant regions based on the output from the extended UNIQUAC model at 10°C (Sutter et al., 2015; Thomsen and Rasmussen, 1999) and equilibrium vapour pressures for NH ₃ and H ₂ O (Appendix C2).	126
Figure 4.8: Influence of pressurisation on ammonia slip into the treated gas (pure N ₂). Operational conditions: liquid flowrate, 0.25 L min ⁻¹ ; liquid temperature, 6.5±0.5°C; gas flowrate, 1.1 L min ⁻¹ ; gas temperature, 21°C. Dotted lines represent ammonia slip over time at gas-liquid equilibrium estimated using Henry's Law (Appendix C2).	128
Figure 5.1: Schematic for reactive CO ₂ absorption by aqueous ammonia and membrane facilitated crystallisation of ammonium bicarbonate.	140
Figure 5.2: Experimental setup for reactive CO ₂ absorption and crystallisation	143
Figure 5.3: Influence of gas pressure on the rate of CO ₂ absorption using 3.4 M aqueous ammonia in HFMC over time. Operational conditions: solvent flowrate, 1.5 L min ⁻¹ ; solvent temperature, 7 ±0.5°C; initial solvent pH, 11; gas flowrate, 1.34 L min ⁻¹ ; CO ₂ in feed gas, 90%vol. Gas flowrate, composition and pressure were established gradually over a 30 minute start-up period.	150
Figure 5.4: CO ₂ flux enhancement with pressurisation during reactive absorption in HFMC. Operational conditions: solvent flowrate, 1.5 L min ⁻¹ ; solvent temperature, 7 ±0.5°C; initial solvent pH, 11; initial solvent concentration, 3.4 mol _{NH₃} L ⁻¹ ; gas flowrate, 1.34 L min ⁻¹ ; CO ₂ in feed gas,	150
Figure 5.5: Influence of pressure on (a) ammonia 'slip' and gas condensate composition, and (b) rate of pH decline. Operational conditions: solvent flowrate, 1.5 L min ⁻¹ ; solvent temperature, 7 ±0.5°C; initial solvent pH, 11; initial solvent concentration, 3.4 mol _{NH₃} L ⁻¹ ; gas flowrate, 1.34 L min ⁻¹ ; CO ₂ in feed gas, 90%vol.	152
Figure 5.6: Species concentration and CO ₂ loading during reactive absorption in HFMC at (a) 1.5 bar, (b) 2.0 bar, and (c) 2.5 bar. Operational conditions: solvent flowrate, 1.5 L min ⁻¹ ; solvent temperature, 7 ±0.5°C; initial solvent pH, 11; initial solvent concentration, 3.4 mol _{NH₃} L ⁻¹ ; gas flowrate, 1.34 L min ⁻¹ ; CO ₂ in feed gas, 90%vol. Dotted line represents the solubility limit for ammonium bicarbonate and dashed line represents CO ₂ loading threshold for ammonium bicarbonate formation at solvent temperature.	154
Figure 5.7: Application of online turbidimetry to determine the onset of bulk nucleation during reactive CO ₂ absorption by 3.4 M aqueous ammonia in HFMC. Dotted lines represent the bulk nucleation time.	155
Figure 5.8: Solubility of ammonium bicarbonate in the bulk and interfacial boundary layer. Based upon specific temperatures measured for bulk and estimated for boundary layer by a heat balance (Appendix D1).	156

Figure 5.9: Influence of gas pressure on (a) concentration of HCO_3^- in solvent at nucleation, and (b) supersaturation level in solvent at nucleation. Operational conditions: solvent flowrate, 1.5 L min^{-1} ; solvent temperature, $7 \pm 0.5^\circ\text{C}$; initial solvent pH, 11; initial solvent concentration, $3.4 \text{ mol}_{\text{NH}_3} \text{ L}^{-1}$; gas flowrate, 1.34 L min^{-1} ; CO_2 in feed gas, 90%vol.	157
Figure 5.10: Influence of gas pressure on absolute time to nucleation and crystal induction time. Operational conditions: solvent flowrate, 1.5 L min^{-1} ; solvent temperature, $7 \pm 0.5^\circ\text{C}$; initial solvent pH, 11; initial solvent concentration, $3.4 \text{ mol}_{\text{NH}_3} \text{ L}^{-1}$; gas flowrate, 1.34 L min^{-1} ; CO_2 in feed gas, 90%vol.	159
Figure 5.11: Power law relationship between supersaturation level at nucleation and (a) concentrating rate (Eq. 5.23), and (b) induction time to characterise nucleation kinetics and mechanism (Eq. 5.24) (Sangwal, 2009).	160
Figure 5.12: Analysis of ammonium bicarbonate crystals: (a) XRD analysis for crystals harvested from solvent and from gas condensate, (b) SEM imaging for crystals harvested from bulk solvent at 1.5 bar ($S_{\text{int}} = 1.06$) at 1000x magnification (example crystals identified by white boxes), and (c) SEM imaging for crystals harvested from gas condensate solvent ($S = 1.7\text{-}1.9$) at 150x magnification. SEM imaging for crystals formed at 2.0 and 2.5 bar available in Appendix D3.	161
Figure 6.1: Example wastewater treatment works with 1.2 million P.E. design capacity treating domestic and industrial wastewater alongside imported sludge from smaller works in the region (Ndam, 2017).	180
Figure 6.2: Variance of ammonia selectivity and k_{La} under stripping temperatures $40\text{-}70^\circ\text{C}$ for synthetic feeds and real centrate. Operational conditions: pressure, 0.25 bar; pH >10; feed rate, 0.5 L min^{-1}	183
Figure 6.3: Influence of ammonia selectivity on gas-phase ammonia concentration and specific latent heat for separation for synthetic feeds. Operational conditions: pressure, 0.25 bar; pH >10; feed rate, 0.5 L min^{-1}	184
Figure 6.4: Stripping at $40\text{-}50^\circ\text{C}$ and 0.25 bar to recover a gas-phase ammonia product.	186
Figure 6.5: Stripping at $60\text{-}70^\circ\text{C}$ and 0.25 bar to recover an aqueous ammonia product.	187
Figure 6.6: Influence of stripping temperature on (a) capital costs and energy and chemical costs, and (b) cost of CO_2e emissions under the Emissions Trading Scheme. Equivalent to 90% removal from centrate ($2 \text{ kg}_{\text{NH}_3} \text{ m}^{-3}$) from a centralised works with a design capacity of 1.2 million population equivalent (Ndam, 2017). Dotted lines indicate costs for equivalent ammonia loading in biological nitrogen removal processes. Full methodology for equipment sizing and capital and operating costs determination provided in Appendix E3-E5.	189
Figure 6.7: Levelised cost of ammonia recovery for a full-scale vacuum thermal stripping system which extracts $2340 \text{ kg}_{\text{NH}_3} \text{ d}^{-1}$, relative to a base case where an equivalent ammonia loading is treated in a pre-existing biological nitrogen removal process. Full methodology for LCOA determination provided in Appendix E6.	191
Figure 6.8: Biogas upgrading and ammonium bicarbonate recovery using wastewater-derived ammonia solvents.	197

Figure 7.1: Key scientific outputs in this thesis towards the development of reactive biogas upgrading and crystallisation in HFMC using wastewater-derived ammonia solvents.	228
Figure 7.2: Influence of temperature during air and steam stripping on (a) G/L ratio and (b) gas-phase ammonia concentration in stripped vapour (based on mean reported $C_{\text{NH}_3} = 1.6 \text{ kg}_{\text{NH}_3} \text{ m}^{-3}$). Ideal G/L ratio determined for theoretical 100% ammonia removal (Huang and Shang, 2006). Dotted lines represent approximate boundaries for technology classification. Experimental data sampled across 12 studies (Alitalo et al., 2012; Boardman and McVeigh, 1998; Bonmati and Flotats, 2003; Gopalakrishnan et al., 2000; Guštin and Marinšek-Logar, 2011; Jiang, 2009; Katehis et al., 1998; Kim et al., 2021; O'Farrell et al., 1973; Teichgraber and Stein, 1994; Wickramanayake et al., 1992; Zeng et al., 2006).	232

List of Tables

Table 2.1: Technologies for energy and hydrogen generation using ammonia	33
Table 2.2: Characterisation of centrate used in this work, produced from full-scale AD facilities treating municipal wastewater sludge	40
Table 2.3: Literature comparison for vacuum stripping ammoniacal wastes at 0.25-0.27 bar close to the dew point of the feed.....	45
Table 2.4: Outcomes for vacuum thermal stripping synthetic and real wastewater for 1.5 h at 65°C and 0.25 bar	53
Table 3.1: Material and structural properties of hollow fibre membrane contactors	78
Table 3.2: Pure water properties from 5 to 35°C	82
Table 3.3: Comparison of dense-skin properties	87
Table 3.4: Performance comparison for binary separation at 4.5 bar, for conditions facilitating 98-99%vol CH ₄ product quality in microporous HFMC at different gas loading rates.	95
Table 4.1: Literature summary for CO ₂ absorption using NH _{3(aq)} in HFMC	115
Table 5.1: Material and structural properties of polypropylene hollow fibre membrane contactor.....	143
Table 6.1: Ammonia to energy technology overview.....	185
Table 6.2: Comparison of levelised cost for ammonia (LCOA) for different strategies for wastewater ammonia recovery and ammonia production plants.....	191
Table 6.3: Direct value pathways for wastewater-derived ammonia, based upon the recovery of 2340 kg _{NH3} d ⁻¹	195
Table 6.4: Indirect value pathways for wastewater-derived ammonia use as a solvent for biogas upgrading, based upon the recovery of 2340 kg _{NH3} d ⁻¹	195
Table 7.1: Summary of schemes proposed to recover waste ammonia for utilisation as a zero carbon energy resource	235

Nomenclature

Abbreviations

AAD	Advanced anaerobic digestion
AD	Anaerobic digestion
AFC	Alkaline fuel cell
ANOVA	Analysis of variance
CAP	Chilled ammonia process
CCS	Carbon capture and storage
CHP	Combined heat and power
COD	Chemical oxygen demand
sCOD	Soluble chemical oxygen demand
DI	Deionised (water)
ETS	Emissions Trading Scheme
EU	European Union
GHG	Greenhouse gas
HFMC	Hollow fibre membrane contactor
LCOA	Levelised cost of ammonia
LHV	Lower heating value
MEA	Monoethanolamine
P.E.	Population equivalent
PMP	Poly(4-methyl-1-pentene)
PP	Polypropylene
PSA	Pressure swing absorption
PTFE	Polytetrafluoroethylene
PTMSP	Poly(1-trimethylsilyl-1-propyne)
PWA	Pressurised water absorption
RPS	Regulatory positioning statement
SOFC	Solid oxide fuel cells
TIC	Total inorganic carbon
TOC	Total organic carbon
UK	United Kingdom
USA	United States of America
VOC	Volatile organic compounds
VLE	Vapour-liquid equilibrium
WGS	Water gas shift
XRD	X-ray diffraction

Chemical formulae

N_2	Nitrogen gas
H_2	Hydrogen gas
NH_3	Ammonia gas
CO_2	Carbon dioxide gas
CH_4	Methane gas
N_2O	Nitrous oxide gas
NO_x	Nitrogen oxide or nitrogen dioxide gas
H_2S	Hydrogen sulphide gas
NH_4^+	Ammonium
$NH_4^{+}-N$	Ammoniacal nitrogen
NH_4HCO_3	Ammonium bicarbonate (BC)
NH_2COONH_4	Ammonium carbamate (CM)
$(NH_4)_2CO_3 \cdot H_2O$	Ammonium carbonate (CB)
$(NH_4)_2SO_4$	Ammonium sulphate
NH_2COOH	Carbamic acid
H_2CO_3	Carbonic acid
HCl	Hydrochloric acid
H_2SO_4	Sulphuric acid
$NaOH$	Sodium hydroxide
H_2O	Water
$CaCO_3$	Calcium carbonate
HCO_3^-	Bicarbonate
CO_3^{2-}	Carbonate
NH_2COO^-	Carbamate
OH^-	Hydroxide
H^+	Hydron

Notations

A	Specific interfacial surface area	$m^2 \cdot m^{-3}$
A	Total internal surface area	m^2
a_i, m_i, n_i	Empirical coefficients for NH_3 - H_2O VLE	-
C_g	Gas-phase CO_2 concentration	$mol \cdot m^{-3}$
C_l	Liquid-phase CO_2 concentration	$mol \cdot m^{-3}$
C_H^*	Equilibrium concentration for CO_2	$mol \cdot L^{-1}$
$C_{NH_3}^*$	Equilibrium concentration for ammonia	$g \cdot L^{-1}$ or $mol \cdot L^{-1}$
C_{NH_3}	Dissolved concentration for ammonia	$g \cdot L^{-1}$ or $mol \cdot L^{-1}$

C_x ; $x = \text{bulk, int}$	HCO_3^- concentration in bulk or interface	mol L^{-1}
C_x^* ; $x = \text{bulk, int}$	Solubility limit for NH_4HCO_3 in bulk or interface	mol L^{-1}
$D_{\text{CO}_2,\text{l}}$	Diffusivity of CO_2 in liquid-phase	$\text{m}^2 \text{s}^{-1}$
$D_{\text{CO}_2,\text{g}}$	Diffusivity of CO_2 in gas-phase	$\text{m}^2 \text{s}^{-1}$
dP/dt	Variation in pressure drop over time	mbar min^{-1}
d_h	Hydraulic diameter	m
E_a	Dense polymer activation energy	kJ mol^{-1}
G/L	Gas-liquid ratio	$\text{m}^3_{\text{gas}} \text{m}^{-3}_{\text{liquid}}$
HRT	Hydraulic residence time	h
H	Dimensionless Henry's Law constant	-
ID	Internal diameter	m
J_i	Flux for component i	$\text{mol m}^{-2} \text{s}^{-1}$
$J_{\text{chem}}/J_{\text{phys}}$	Chemical enhancement factor for CO_2	-
k_H	Henry's Law constant	$\text{mol L}^{-1} \text{bar}^{-1}$
$k_L a$	Volumetric mass transfer coefficient for NH_3	h^{-1}
k_L	Liquid-phase mass transfer coefficient for NH_3	m h^{-1}
K_{ov}	Overall mass transfer coefficient	m s^{-1}
$1/K_{ov}$	Overall mass transfer resistance	s m^{-1}
$1/k_g$	Gas-phase mass transfer resistance	s m^{-1}
$1/k_l$	Liquid-phase mass transfer resistance	s m^{-1}
$1/k_m$	Membrane mass transfer resistance	s m^{-1}
$1/k_{m,p}$	$1/k_m$ for microporous HFMC	s m^{-1}
$1/k_{m,d}$	$1/k_m$ for nonporous HFMC	s m^{-1}
L/G	Liquid-gas ratio	$\text{m}^3_{\text{liquid}} \text{m}^{-3}_{\text{gas}}$
M	Mass	g
n_{con}	Number of moles of CO_2 in gas condensate	moles
P	Pressure (absolute)	bar
P_i°	Pure vapour pressure of component i	bar
p_i	Partial pressure for component i	bar
$P_{d(\text{SI})}$	Permeability (SI units)	$10^5 \text{ m}^3 \text{ m bar}^{-1} \text{ s}^{-1} \text{ m}^{-2}$
P_d	Permeability	Barrer
$\text{pK}_{a,T}^{\text{S}}$	Negative logarithm of acid dissociation constant	-
Q_l	Liquid flowrate	$\text{m}^3 \text{s}^{-1} / \text{L min}^{-1}$
Q_g	Gas flowrate	$\text{m}^3 \text{s}^{-1} / \text{L min}^{-1}$
R'	Concentrating rate at nucleation	$\text{g } 100\text{g}^{-1} \text{min}^{-1}$
R	Molar gas constant	$\text{J K}^{-1} \text{mol}^{-1}$
S_x ; $x = \text{bulk, int}$	Supersaturation level in bulk or interface	-
T	Time	hours / minutes

T	Temperature	$^{\circ}\text{C} / \text{K}$
T_b	Bubble point temperature	$^{\circ}\text{C}$
T_d	Dew point temperature	$^{\circ}\text{C}$
T_m	Membrane temperature	K
V	Volume	L
V_m	Molar volume	$\text{m}^3 \text{mol}^{-1}$
V_g	Gas velocity	m s^{-1}
V_l	Liquid velocity	m s^{-1}
x_{NH_3}	Liquid-phase ammonia mole fraction	-
y_{NH_3}	Gas-phase ammonia mole fraction	-
$y_{\text{NH}_3, \text{wt}}$	Gas-phase ammonia mass fraction	$\%\text{wt}$
y_{CO_2}	Volume fraction of CO_2 in gas-phase	$\%\text{vol}$
Gz	Graetz number	-
Ha	Hatta number	-
Re	Reynolds number	-
Sh	Sherwood number	-
Sc	Schmidt number	-

Greek symbols

α_i	Selectivity for component i	-
B	Relative fraction of dissolved CO_2 as HCO_3^-	-
Σ	Solid-liquid interfacial tension	N m^{-1}
ϵ_m	Membrane porosity	-
μ	Dynamic viscosity	Nm^{-1}
Φ	Relative fraction of free ammonia	-
P	Density	kg m^{-3}
η_{NH_3}	Ammonia removal	$\%\text{wt}$
η_{CO_2}	CO_2 capture ratio	$\%\text{vol}$
τ_m	Membrane tortuosity	-
δ_w	Porous fibre wall thickness	M
δ_d	Dense layer thickness	M
γ	Liquid surface tension	N m^{-1}

1 Introduction

1.1 Biomethane and ammonia recovery to support a net zero water sector

To limit anthropogenic climate change and avoid global temperatures rising 1.5°C above pre-industrial levels, major European nations are committed to achieving net zero carbon emissions by 2050 (Department for Business, Energy and Industrial Strategy, 2021a; European Commission, 2019; IPCC, 2018). To support this objective, legally binding targets have been set out within the Renewable Energy Directive (2018/2001/EU) for at least 32% renewable energy in the European Union (EU) by 2030. Consequently, there has been a successful focus on renewable power generation which grew to represent 37% of total electricity consumption across the EU in 2020 (Eurostat, 2022). However, heating and transport sectors, which account for 66% of final energy consumption, have historically proven more challenging to decarbonise, primarily due to their decentralised distribution and consumption (Connolly et al., 2014; Energy and Climate Change Committee, 2016). There is growing emphasis for the expansion of alternative energy resources to support decarbonisation of the heating grid and long-haul transportation. These include carbon neutral biomethane (Northern Gas Networks, 2020; Pesuit et al., 2017; Ryckebosch et al., 2011) in addition to zero carbon 'green' hydrogen and ammonia-based fuels generated using renewable electricity (European Commission, 2022; IRENA, 2021; Kakoulaki et al., 2021).

Biomethane is of strategic interest since it is a direct substitute for natural gas and therefore presents an immediate sustainable alternative which can be used in existing infrastructure without incurring fuel switching costs (Department for Transport, 2021; European Commission, 2022). Biomethane has a high methane content (CH_4 >98%vol) and is produced by extracting CO_2 and trace gas contaminants (e.g., H_2S , siloxanes) from biogas (50-75%vol CH_4 , 25-50%vol CO_2) (McBean, 2008; Pavicic et al., 2022; Tansel and Surita, 2019). Biogas originates from the anaerobic digestion of organic matter in municipal wastewater sludge, agricultural slurries and industrial feedstocks (Angelidaki et al., 2018; Scarlat et al., 2018). It is projected that up to 1000 TWh of biomethane could be generated across Europe in 2050, replacing 30-40% of natural gas consumption (European Biogas Association, 2021; Pavicic et al., 2022). Early adopters within

the retail and logistics sectors are already transitioning fleets of heavy goods vehicles from diesel to biomethane engines, which is prompting wider investment in refuelling stations and delivery infrastructure (BP, 2021; John Lewis Partnership, 2018). Financial incentivisation schemes have been employed to stimulate investment in biogas upgrading plants which remunerate operators per unit of energy injected in the grid (e.g., Renewable Heating Incentive, Green Gas Support Scheme) or per kg exported as transport fuel (e.g., Renewable Transport Fuel Obligation) (Beerepoot and Marmion, 2012; Department for Business, Energy and Industrial Strategy, 2021b; Department for Transport, 2021). Consequently, the number of biogas upgrading facilities across Europe increased from 187 to 880 from 2010 to 2020, leading to the production of 32 TWh biomethane in 2020 (Pavicic et al., 2022). Continued expansion in biogas upgrading is necessary to deliver net zero ambitions for 2050.

The UK water sector announced the first sector-wide commitment to reach net zero carbon emissions by 2030, and similar commitments of energy and carbon neutrality by 2050 have been echoed across Europe (Water Europe, 2021; Water UK, 2020). Biomethane generation from wastewater sludge represents a critical strategy for decarbonisation. Pressurised water absorption (PWA) in packed columns is the dominant technology for biogas upgrading, and accounted for 70% of installed capacity within the European water sector in 2019 (Figure 1.1) (Angelidaki et al., 2018; IEA Bioenergy, 2019; Northern Gas Networks, 2020). This process exploits the difference in solubility between CO₂ and CH₄ for the selective absorption of CO₂, and is conducted in absorption columns which provide high interfacial area to enhance the rate of mass transfer (Angelidaki et al., 2018). Pressurised water absorption was widely adopted within the sector since it was already established for industrial gas treatment and presented an immediate, low-risk investment option which enabled operators to access financial incentives for biomethane (Bauer et al., 2013; Sun et al., 2015). However, due to dispersive contact between gas and liquid-phases, absorption columns are vulnerable to channelling, flooding, foaming and entrainment which can limit gas loading rates (Hoff and Svendsen, 2013). The media is also vulnerable to organic fouling and inorganic scaling which results in operational

downtime for periodic caustic and acid washing cycles (Bauer et al., 2013; Kapoor et al., 2019a). Consequently, conventional PWA processes are associated with relatively high capital and operational costs which weaken the investment case for biogas upgrading. This has been compounded by a general degression in incentivisation tariffs for biomethane over the past decade (Department for Business, Energy and Industrial Strategy, 2016; Houlker, 2019). Furthermore, the CO₂ absorbed from biogas in PWA is released to atmosphere during solvent regeneration along with trace amounts of CH₄ ‘slip’ (typically 1-2%vol of CH₄ in raw biogas) (Kvist and Aryal, 2019). In total, this is equivalent to biogenic emissions of approximately 1.0 kg_{CO2e} per Nm³ biogas treated (IPCC, 2007). This reduces the sustainability criteria for PWA and creates a business risk since investment in ancillary CO₂ capture processes may be required to mitigate biogenic emissions in the future (International Energy Agency, 2022). Process innovations are now necessary to lower the whole life cost for biomethane so it can become economically viable without incentivisation, whilst lowering emissions related to its production so that it is consistent with ambitions for decarbonisation within the sector and wider society.

The treatment of ammonia within wastewater presents a further challenge to the decarbonisation of the water sector. The biological oxidation of ammonia requires forced aeration (3-5 kWh_e kg_N⁻¹) and accounts for 20% of power demand during wastewater treatment (Garrido et al., 2013; Wett, 2006). During this process, it is estimated that 0.3% of influent nitrogen is emitted as nitrous oxide (N₂O) which has a global warming potential 310-times greater than CO₂ (Campos et al., 2016; de Haas and Andrews, 2022; Winter et al., 2012). In the international Greenhouse Gas Protocol, direct process emissions are categorised under Scope 1 whilst indirect emissions from grid electricity consumption are categorised under Scope 2 (Fong et al., 2021). Biological ammonia removal is therefore associated with Scope 1 and Scope 2 emissions of approximately 3.3 kg_{CO2e} kg_N⁻¹ and 1.0 kg_{CO2e} kg_N⁻¹, respectively (Figure 1.1) (Bulb, 2023). These emissions are likely to increase in the near-term due to an intensification of biological treatment processes in response to the introduction of stricter nitrogen limits for final effluent (10 mg L⁻¹; >0.1 million P.E.) within the Urban Wastewater

Treatment Directive (91/271/EEC) (EEC Council, 1991). Industrially, there is a focus on transitioning towards low carbon ammonia production since it is currently synthesised with fossil-fuel derived hydrogen in the Haber-Bosch process (19 kWh kg_N⁻¹) and is associated with 1% of global CO₂ emissions (Nayak-Luke et al., 2018). A circular economy approach for the recovery of ammonia from wastewater is therefore becoming increasingly attractive. Ammonia recovery in the UK water sector alone could provide a sustainable ammonia supply of up to 400 tonnes d⁻¹ which is equivalent to offsetting 2.8 TWh y⁻¹ fossil fuel consumption for commercial ammonia production (Parliamentary Office of Science and Technology, 2007). Furthermore, ammonia is a zero carbon compound with emerging applications as a hydrogen carrier, a transport fuel, and a feedstock for gas turbines and electrochemical fuel cells (Kobayashi et al., 2019; Lan and Tao, 2014; The Royal Society, 2020). Hence, ammonia recovery strategies could directly support decarbonisation for the water sector alongside a wider transition towards zero carbon energy generation.

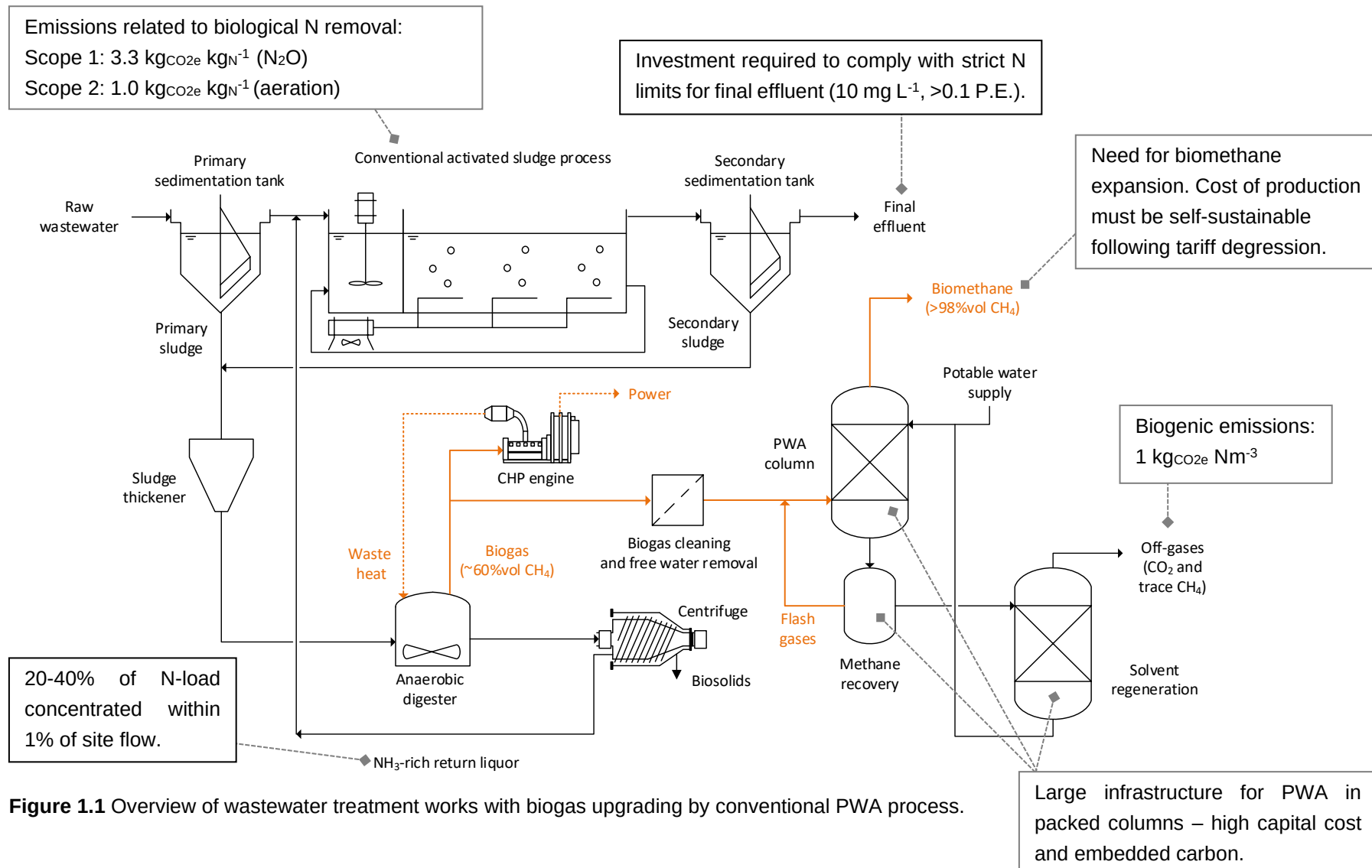


Figure 1.1 Overview of wastewater treatment works with biogas upgrading by conventional PWA process.

1.2 Intensification of biogas upgrading in membrane contactors

Hollow fibre membrane contactors (HFMC) are an emerging alternative to gas-liquid absorption columns which could offer process intensification to reduce capital and operational costs for biogas upgrading (Figure 1.2). Hollow fibre membrane contactors facilitate non-dispersive contact between liquid and gas-phases across a hydrophobic membrane, expanding the operating range for gas loading rates compared to absorption columns (Cui and Demontigny, 2013; Heile et al., 2014). Densely packed HFMC also offer high interfacial area for mass transfer and can enable up to 15-times process intensification versus packed columns (Belaissaoui et al., 2016; Gabelman and Hwang, 1999). Due to their relatively low cost and ease of integration, HFMC can be configured in series to enable cost-effective production of biomethane at industrial quality (>98%vol CH₄) (Houlker, 2019). Consequently, it is projected that the adoption of HFMC for biogas upgrading using physical solvents could lower capital costs by almost 40-times compared to absorption columns (Houlker, 2019). Reduced process size and phase segregation may also support the integration of efficient clean-in-place solutions which will lower chemical costs and equipment outages related to cleaning (Houlker et al., 2021).

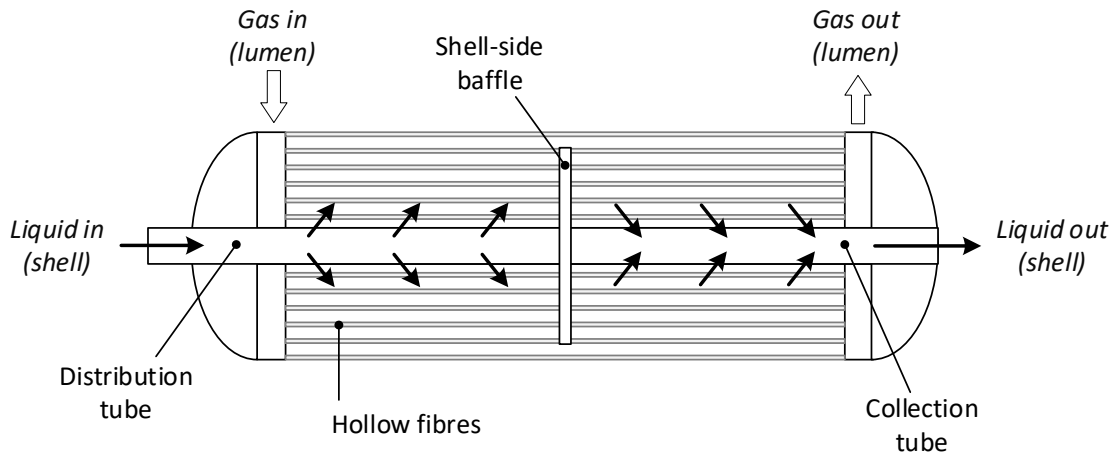


Figure 1.2 Layout for the transverse-flow hollow fibre membrane contactors used in this thesis (3M Industrial Group, Charlotte, USA)

Despite their hydrophobicity, microporous membranes can suffer from the intrusion of solvents into the gas-filled pore structure ('pore wetting') during gas-liquid absorption processes (Figure 1.3) (Gabelman and Hwang, 1999). Due to

the lower diffusivity of CO₂ in liquids, pore wetting will increase mass transfer resistance within the membrane and disrupt CO₂ removal (Dindore et al., 2004; Wang et al., 2005). Resilient nonporous membranes have been developed which rely upon CO₂ permeation through a dense-polymer layer, which adds additional mass transfer resistance, and these have been investigated widely for flue gas CO₂ capture processes (Figure 1.3c) (Heile et al., 2014; Scholes et al., 2015; Villeneuve et al., 2018). However, biogas upgrading is conducted at low-ambient temperatures which may influence wetting characteristics in addition to the gas permeability within the dense-polymer. A direct comparison of microporous and nonporous membranes under conditions relevant for industrial biogas upgrading is necessary for application specific material selection. To compete with established PWA processes, HFMC must also support pressurised biogas upgrading since this will increase solvent absorption capacity, lower methane 'slip' into the liquid-phase and reduce the process footprint and capital cost (Bauer et al., 2013; Kapoor et al., 2019; Sun et al., 2015). This will also generate a biomethane product which is ready for injection into the pressurised gas-grid (2-7 bar) (Northern Gas Networks, 2020). Previous researchers have demonstrated that pressurisation up to 20 bar can intensify mass transfer during physical absorption of CO₂ from flue gases in HFMC (10-25%vol CO₂) (Dindore et al., 2004). A unique element of biogas upgrading is the high initial CO₂ fraction in the gas-phase (25-50%vol) coupled with high CO₂ removal during the separation (>95%vol) (Pavicic et al., 2022). This places a greater emphasis on gas-phase resistance to mass transfer compared to widely studied CO₂ capture applications where mass transfer is dominated by the liquid-phase (Bounaceur et al., 2012; Chabanon et al., 2015; Houlker, 2019). Operating at higher pressures will raise the partial pressure of CO₂ in the gas bulk, which represents the driving force for CO₂ diffusion to the liquid interface (Belaissaoui et al., 2016). Under conditions relevant for biogas upgrading, pressurisation could therefore influence the overall resistance to mass transfer. However, the impact of varying pressure on mass transfer resistances across the liquid, membrane and gas-phases during the production of industrial quality biomethane (<98% CH₄), and the consequent impact on separation efficiency and methane 'slip' has not been explored to date.

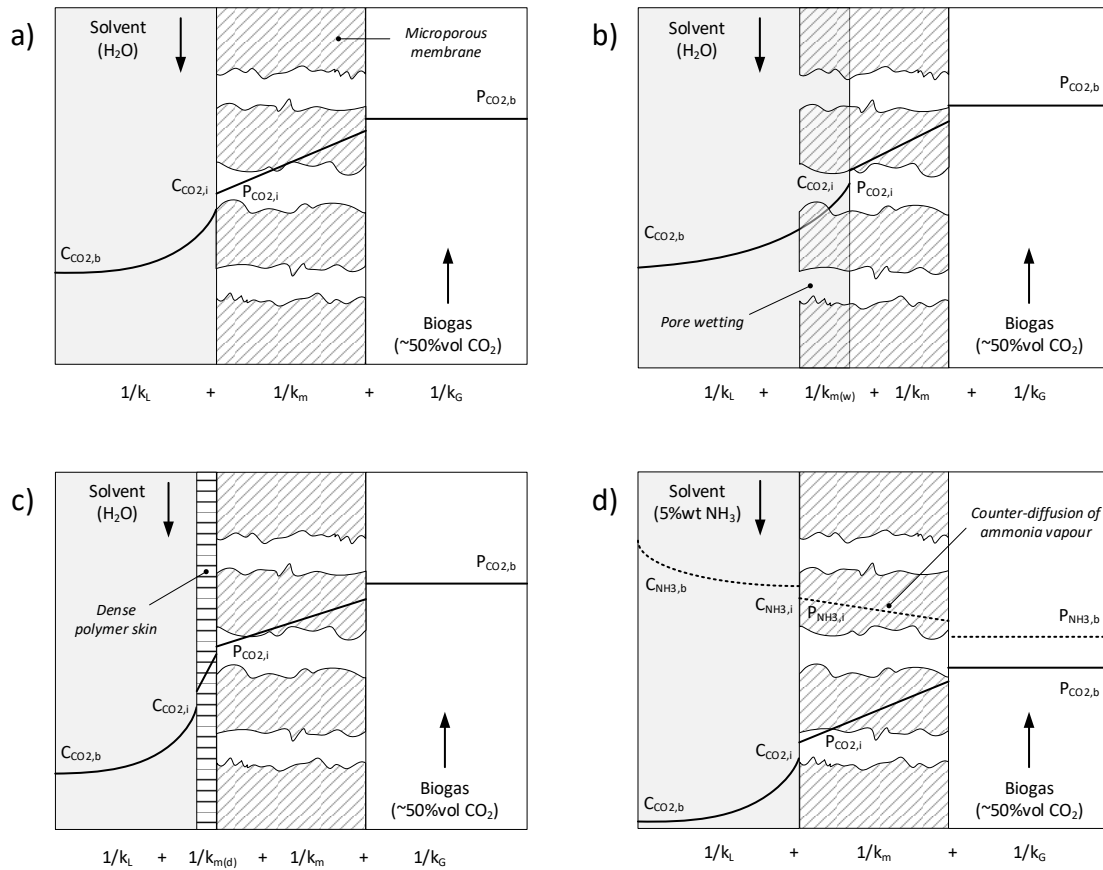


Figure 1.3 Schematic representation of mass transfer resistances for the absorption of CO₂ across (a) a microporous membrane with gas-filled pores; (b) a microporous membrane with partially wetted pores; (c) a nonporous membrane with a dense polymer skin; and (d) a microporous membrane using a volatile ammonia solvent. $1/k_L$, $1/k_m$, $1/k_{m(w)}$, $1/k_{m(d)}$ and $1/k_G$ represent resistances in the liquid, dry membrane, wetted membrane, dense polymer skin and gas, respectively. C_{CO_2} is the liquid-phase CO₂ concentration, p_{CO_2} is the gas-phase CO₂ partial pressure; and b and i represent bulk and interface conditions respectively.

1.3 Intensification of biogas upgrading using wastewater-derived NH_{3(aq)}

Transitioning from physical solvents to chemically reactive solvents can offer further process intensification for biogas upgrading in HFMC (Bauer et al., 2013; Houlker, 2019). There is growing interest in aqueous ammonia as a chemical solvent for CO₂, since it is less corrosive, more thermally stable and requires a lower thermal energy demand for regeneration than established amines (Jilvero et al., 2012; Ochedi et al., 2021). In an innovative approach, McLeod et al. (2014) applied centrate from the anaerobic digestion of wastewater sludge, which had a dissolved ammonia content of 2.3 kg m⁻³, as a chemical solvent to intensify biogas upgrading. A 15-factor enhancement in CO₂ flux was observed relative to deionised water (McLeod et al., 2014). The absorption of CO₂ using synthetic

wastewater containing up to 10 kg m^{-3} ammonia indicated that increasing the concentration will increase reactivity and CO_2 absorption capacity to favour process intensification (McLeod et al., 2014). Mani et al. (2006) identified that the application of aqueous ammonia at approximately 43 kg m^{-3} represented an optimum to support a high CO_2 absorption capacity whilst limiting the loss of volatile ammonia into the gas-phase. Consequently, the prior extraction of ammonia from centrate to create a more concentrated ammonia solvent would support an intensified biogas upgrading strategy. In a typical wastewater treatment works, 20-40% of dissolved ammonia is concentrated within the centrate stream (Mackinnon et al., 2003; Ndam, 2017). Targeted recovery from this source could substantially reduce the ammonia loading into mainstream biological treatment processes. This would lower the Scope 1 and 2 emissions associated with biological ammonia removal, and support the attainment of strict nitrogen discharge limits to protect waterways (91/271/EEC) (Campos et al., 2016; EEC Council, 1991). The recovery of ammonia as a sustainable solvent for biogas upgrading therefore offers strong synergies for the decarbonisation of the water sector and the development of a circular economy (Figure 1.4).

Researchers have recently demonstrated the feasibility of vacuum thermal stripping for the single-stage recovery of concentrated aqueous ammonia up to 39 kg m^{-3} from centrate (Bavarella et al., 2020b; Davey et al., 2022). Thermally driven processes are attractive since they will lower the solubility of ammonia to enhance mass transfer and could incorporate intrinsic heat resources (e.g., biogas, waste heat) available within wastewater treatment works to minimise operating costs (Han et al., 2022; Moore and Auty, 2013). By manipulating the temperature or pressure, there is the potential to exploit differences in volatility between ammonia and water to foster selective ammonia recovery during vacuum thermal stripping (Pátek and Klomfar, 1995). This operating strategy could simultaneously reduce the separation energy and increase the recovered gas-phase ammonia concentration, but has not been investigated to date. Evidence of vacuum thermal stripping for ammonia recovery is currently limited to batch vessels which have low interfacial areas ($<40 \text{ m}^2 \text{ m}^{-3}$) compared to packed column strippers ($200\text{-}400 \text{ m}^2 \text{ m}^{-3}$) (Guida et al., 2022; Han et al., 2022;

Tian et al., 2019). Translation to a gas-liquid contacting column is therefore necessary to lower hydraulic residence times and capital costs for competitive ammonia recovery at scale. Recovered ammonia could have widespread applications beyond biogas upgrading which are also consistent with the strategic direction towards decarbonisation. A suite of technological options have been recently proposed for the recovery of ammonia from wastewater and for its utilisation as a zero carbon energy resource (Davey et al., 2022; Grasham et al., 2019; van Linden et al., 2022). To evaluate this opportunity in the context of wastewater treatment, a systems level analysis is necessary to consider the energy demand for ammonia recovery in addition to the product quality required for exploitation within emerging energy generation technologies.

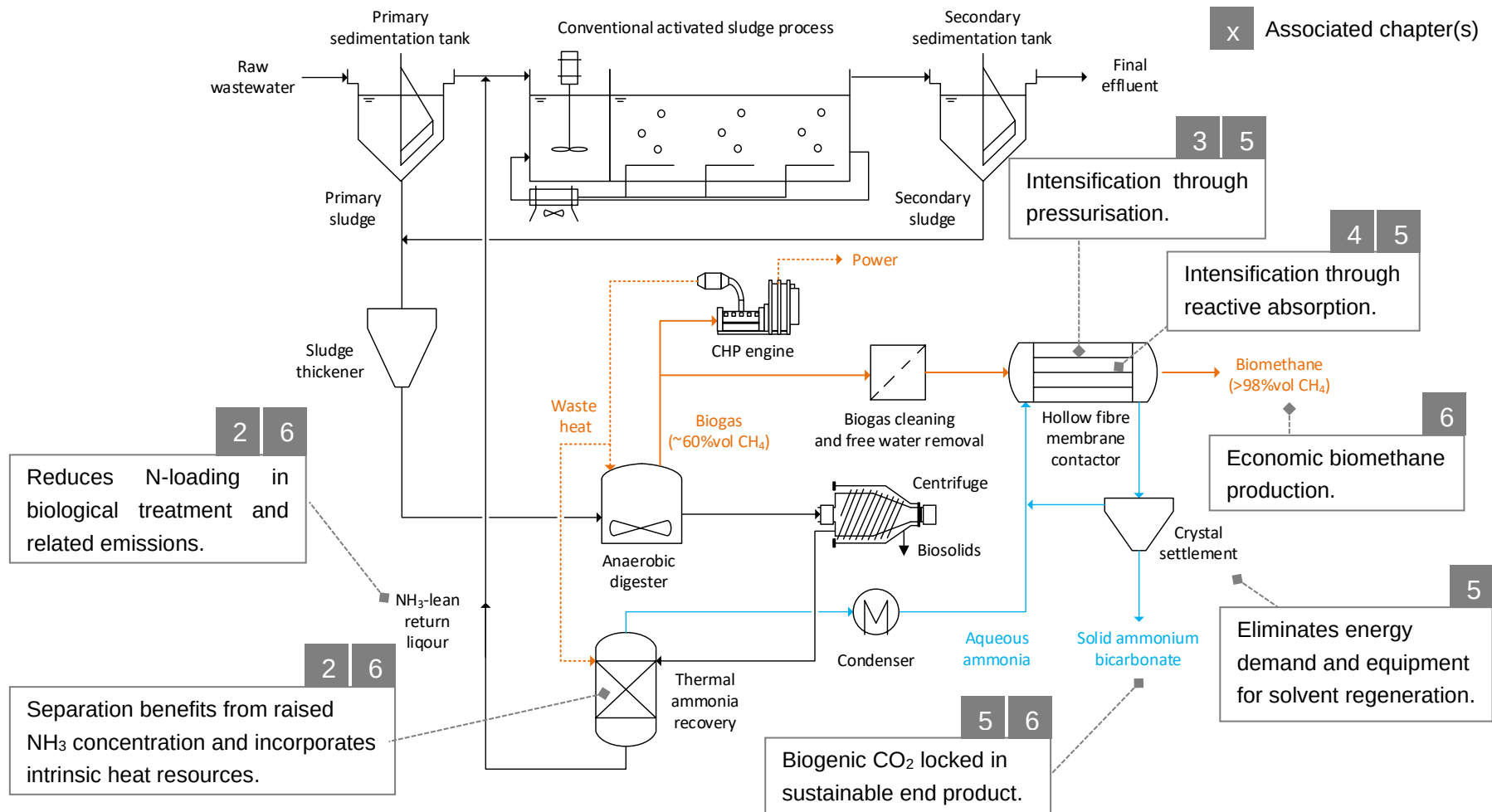


Figure 1.4 Integrated wastewater treatment works where reactive biogas upgrading and crystallisation in HFMC is achieved using wastewater-derived ammonia solvents.

1.4 Crystallisation limits energy demand and creates sustainable products

Chemically reactive solvents such as aqueous ammonia require thermal regeneration to reverse the chemical reaction and desorb CO₂ gas prior to reuse (Darde et al., 2010; Pérez-Calvo et al., 2021). During regeneration, purified CO₂ gas (>99%vol) is released which favours efficient downstream capture processes or upgrading into an industrial CO₂ product (Augustsson et al., 2017; International Energy Agency, 2022). Although aqueous ammonia has a lower thermal demand for regeneration than conventional solvents, this would still require 0.5 kWh_{th} per Nm⁻³ biogas treated (Bauer et al., 2013; Jilvero et al., 2012). This is equivalent to 10% of the energy content for raw biogas (Moore and Auty, 2013). In a positive synergy for the proposed biogas upgrading flowsheet, the energy consumption and infrastructure related to solvent regeneration could be eliminated since a continuous supply of aqueous ammonia is available in wastewater (Figure 1.4). Instead, the solvent could be loaded with CO₂ until it exceeds the thermodynamic threshold for ammonium bicarbonate precipitation (0.63 kg_{CO2} kg_{NH3}⁻¹ at 10°C) (Thomsen and Rasmussen, 1999). Solid ammonium bicarbonate crystals can then be continuously harvested from the solvent loop. The feasibility for high purity ammonium bicarbonate crystallisation has recently been demonstrated using an ammonia solvent (56 kg m⁻³) thermally recovered from concentrated wastewater (Bavarella et al., 2020b). Crystallisation would lock the extracted CO₂ in a solid form to facilitate carbon negative biogas upgrading (International Energy Agency, 2022). Recovered ammonium bicarbonate could provide a new source of revenue as a sustainable fertiliser which has a market value of 112 EUR tonne⁻¹ (McLeod et al., 2014). Further opportunities for its valorisation, such as thermal decomposition under mild heat (>30°C) to release ammonia and CO₂ gas (Villeneuve et al., 2018), could be explored within the context of a low carbon water sector.

Reactive crystallisation within HFMC could therefore enable biogas upgrading using wastewater-derived ammonia solvents and simultaneous ammonium bicarbonate recovery (Bavarella et al., 2020a; McLeod et al., 2015). Hollow fibre membrane contactors present an ideal crystallisation reactor since the development of a concentration boundary layer adjacent to the membrane will

lower the energy barrier for crystallisation and promote heterogeneous nucleation at the interface (Horseman et al., 2021; Jiang et al., 2016). Controlled liquid-side crystallisation and continuous harvesting of ammonium bicarbonate during uninterrupted biogas upgrading in HFMC has been demonstrated by previous researchers (Houlker, 2019; McLeod et al., 2015). This is in stark contrast to packed columns where homogenous nucleation of ammonium bicarbonate can lead to process blockages and instability (Augustsson et al., 2017; Houlker, 2019). Notably, the high volatility of ammonia can lead to ammonia ‘slip’ into the gas-phase during reactive absorption (Figure 1.3d) (Darde et al., 2010; Kozak et al., 2009). In HFMC, this has been linked to unstable pressures and poor separation efficiency due to the formation of liquid and solid products in the gas-phase (Bavarella et al., 2022; Villeneuve et al., 2018). The underpinning mechanism for gas-phase reactions within the $\text{CO}_2\text{-NH}_3\text{-H}_2\text{O}$ system, which must be understood to enable successful mitigation strategies, has not been described.

Conducting reactive absorption under pressurised conditions is required to realise the full intensification potential of this technology. Since pressurisation will change the relative concentration of reactants in the gas-phase, this also has the potential to disrupt or prevent gas-phase reactions. However, chemically reactive membrane crystallisation in HFMC has not been demonstrated under pressurised conditions to date. During absorption in aqueous ammonia, the CO_2 mass transfer rate is governed primarily by reactivity in the solvent boundary layer (Kim et al., 2014). The influence of pressurisation on reactive CO_2 mass transfer therefore requires an application specific investigation (Dindore et al., 2004; Fang et al., 2015). According to classical nucleation theory, the rate of CO_2 absorption into the solvent will directly influence the crystallisation kinetics at the membrane interface, which govern the purity, size and shape of the crystalline product (Horseman et al., 2021; Ulrich and Strege, 2002). These characteristics may be critical to the controllability of the crystallisation process at scale. The association between pressure, CO_2 mass transfer and crystallisation kinetics consequently requires direct exploration under pressurised conditions applicable for biogas upgrading (McDonald et al., 2021).

1.5 Thesis aim, objectives and structure

The aim of this thesis is to develop hollow fibre membrane contactor technology as a disruptive solution for biogas upgrading that can reduce economic dependency on incentives and incorporates the recovery of ammonia from wastewater to reduce energy consumption and emissions, presenting a circular economy solution to support the water sectors transition to net zero (Figure 1.4). The following objectives were developed to address the thesis aim:

1. Develop a technological approach to facilitate low energy recovery of sustainable ammonia solvents from wastewater for use in biogas upgrading.
2. Characterise CO₂ mass transfer within HFMC under industrially relevant pressurised conditions to support translation to full-scale biogas upgrading.
3. Elucidate gas-phase reaction mechanisms in HFMC during CO₂ absorption with NH₃ and identify mitigation strategies.
4. Examine pressurised CO₂ absorption and crystallisation in HFMC using ammonia, to establish intensification potential, and controllability for reactive biogas upgrading and ammonia recovery.
5. Develop a techno-economic analysis for ammonia recovery and utilisation as a zero carbon energy resource and novel biogas upgrading solvent to support decarbonisation and generate revenue within wastewater treatment.

Chapters within this thesis have been formatted as individual journal papers which correspond to the research objectives (Figure 1.5). This thesis is comprised of 4 technical papers (Chapter 2, 3, 4 and 5) and a techno-economic analysis (Chapter 6). A discussion of the overall thesis is then presented in Chapter 7, whilst the conclusions and opportunities for future research are summarised in Chapter 8. Benjamin Luqmani was the lead author on all chapters and was supported through supervision and editing by Professor Ewan McAdam and Dr Marc Pidou.

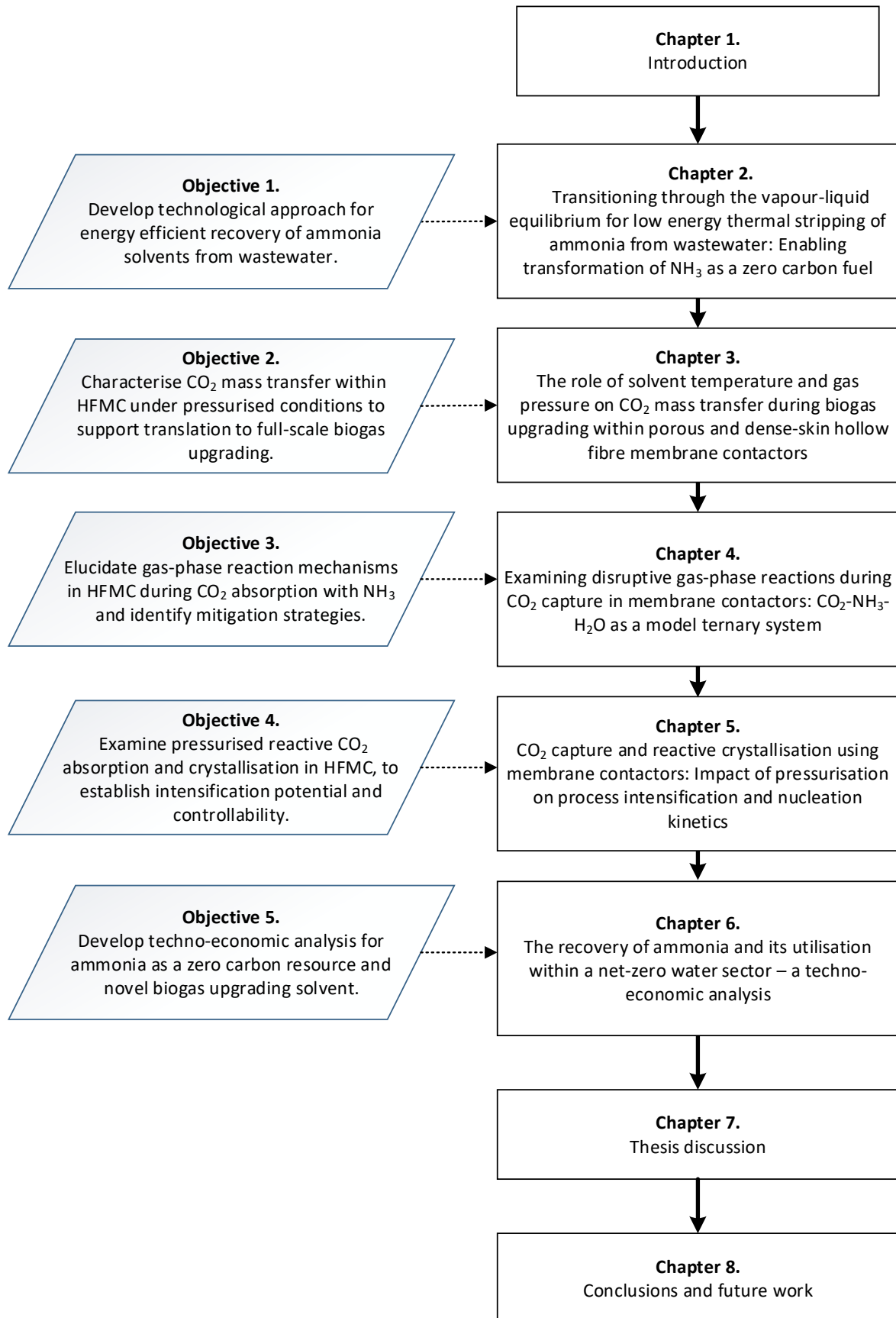


Figure 1.5 Summary of thesis objectives and corresponding chapters.

References

- Angelidaki, I., Treu, L., Tsapekos, P., Luo, G., Campanaro, S., Wenzel, H., and Kougias, P. G. (2018). Biogas upgrading and utilization: Current status and perspectives. *Biotechnology Advances*, 36, 452–466.
- Augustsson, O., Baburao, B., Dube, S., Bedell, S., Strunz, P., Balfe, M., and Stallmann, O. (2017). Chilled Ammonia Process Scale-up and Lessons Learned. 13th International Conference on Greenhouse Gas Control Technologies, Lausanne, Switzerland.
- Bauer, F., Hulteberg, C., Persson, T., and Tamm, D. (2013). Biogas upgrading – Review of commercial technologies. SGC. http://vav.griffel.net/filer/C_SGC2013-270.pdf (accessed 31/03/2023).
- Bavarella, S., Brookes, A., Moore, A., Vale, P., Di Profio, G., Curcio, E., Hart, P., Pidou, M., and McAdam, E. J. (2020a). Chemically reactive membrane crystallisation reactor for CO₂–NH₃ absorption and ammonium bicarbonate crystallisation: Kinetics of heterogeneous crystal growth. *Journal of Membrane Science*, 599, 117682.
- Bavarella, S., Hermassi, M., Brookes, A., Moore, A., Vale, P., Moon, I. S., Pidou, M., and McAdam, E. J. (2020b). Recovery and concentration of ammonia from return liquor to promote enhanced CO₂ absorption and simultaneous ammonium bicarbonate crystallisation during biogas upgrading in a hollow fibre membrane contactor. *Separation and Purification Technology*, 241, 116631.
- Bavarella, S., Luqmani, B., Thomas, N., Brookes, A., Moore, A., Vale, P., Pidou, M., and McAdam, E. J. (2022). CO₂ absorption into aqueous ammonia using membrane contactors: Role of solvent chemistry and pore size on solids formation for low energy solvent regeneration. *Separation and Purification Technology*, 290, 120786.
- Beerepoot, M., and Marmion, A. (2012). Policies for Renewable Heat: An Integrated Approach. International Energy Agency. <https://www.oecd-ilibrary.org/docserver/5k3wb8gtfjhf-en.pdf?expires=1679590377&id=id&accname=guest&checksum=584EC797F4C34A05A56E1551BBA9A064> (accessed 31/03/2023).

- Belaissaoui, B., Claveria-Baro, J., Lorenzo-Hernando, A., Albarracin Zaidiza, D., Chabanon, E., Castel, C., Rode, S., Roizard, D., and Favre, E. (2016). Potentialities of a dense skin hollow fiber membrane contactor for biogas purification by pressurized water absorption. *Journal of Membrane Science*, 513, 236–249.
- Bounaceur, R., Castel, C., Rode, S., Roizard, D., and Favre, E. (2012). Membrane contactors for intensified post combustion carbon dioxide capture by gas-liquid absorption in MEA: A parametric study. *Chemical Engineering Research and Design*, 90, 2325–2337.
- BP. (2021). bp acquires stake in major UK provider of biomethane for HGVs. https://www.bp.com/en_gb/united-kingdom/home/news/press-releases/bp-acquires--stake-in-major-uk-provider-of-biomethane-for-hgvs.html (accessed 01/04/2023).
- Bulb. (2023). Carbon tracker. <https://bulb.co.uk/carbon-tracker/#:~:text=With Bulb%2C annual CO2 emissions for the energy,0.00 kg of CO2 per kWh of gas.> (accessed 01/04/2023).
- Campos, J. L., Valenzuela-Heredia, D., Pedrouso, A., Val Del Río, A., Belmonte, M., and Mosquera-Corral, A. (2016). Greenhouse Gases Emissions from Wastewater Treatment Plants: Minimization, Treatment, and Prevention. *Journal of Chemistry*, 379635.
- Chabanon, E., Bounaceur, R., Castel, C., Rode, S., Roizard, D., and Favre, E. (2015). Pushing the limits of intensified CO₂ post-combustion capture by gas-liquid absorption through a membrane contactor. *Chemical Engineering and Processing: Process Intensification*, 91, 7–22.
- Connolly, D., Lund, H., Mathiesen, B. V., Werner, S., Möller, B., Persson, U., Boermans, T., Trier, D., Østergaard, P. A., and Nielsen, S. (2014). Heat roadmap Europe: Combining district heating with heat savings to decarbonise the EU energy system. *Energy Policy*, 65, 475–489.
- Cui, Z., and Demontigny, D. (2013). Part 7: A review of CO₂ capture using hollow fiber membrane contactors. *Carbon Management*, 4, 69–89.

- Darde, V., Thomsen, K., van Well, W. J. M., and Stenby, E. H. (2010). Chilled ammonia process for CO₂ capture. *International Journal of Greenhouse Gas Control*, 4, 131–136.
- Davey, C. J., Luqmani, B., Thomas, N., and McAdam, E. J. (2022). Transforming wastewater ammonia to carbon free energy: Integrating fuel cell technology with ammonia stripping for direct power production. *Separation and Purification Technology*, 289, 120755.
- de Haas, D., and Andrews, J. (2022). Nitrous oxide emissions from wastewater treatment - Revisiting the IPCC 2019 refinement guidelines. *Environmental Challenges*, 8, 100557.
- Department for Business Energy and Industrial Strategy. (2016). The Renewable Heat Incentive, A reformed and refocused scheme. https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/505132/Consultation_Stage_Impact_Assessment_-_The_RHI_-_a_reformed_and_refocussed_scheme.pdf (accessed 01/04/2023).
- Department for Business Energy and Industrial Strategy. (2021a). Build Back Greener: Net Zero Strategy. <https://www.gov.uk/government/publications/net-zero-strategy> (accessed 01/04/2023).
- Department for Business Energy and Industrial Strategy. (2021b). Future Support for Low Carbon Heat and the Green Gas Levy: government response to consultation. https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/970565/green-gas-levy-future-support-low-carbon-heat-govt-response.pdf (accessed 01/04/2023).
- Department for Transport. (2021). Targeting net zero - Next steps for the Renewable Transport Fuels Obligation. <https://www.gov.uk/government/consultations/amending-the-renewable-transport-fuels-obligation-rfto-to-increase-carbon-savings-on-land-air-and-at-sea> (accessed 01/04/2023).
- Dindore, V. Y., Brilman, D. W. F., Feron, P. H. M., and Versteeg, G. F. (2004). CO₂ absorption at elevated pressures using a hollow fiber membrane contactor. *Journal of Membrane Science*, 235, 99–109.

- EEC Council. (1991). 91/271/EEC of 21 May 1991 concerning urban waste-water treatment. Official Journal of the European Communities, 40–52. <http://eur-lex.europa.eu/legal-content/en/ALL/?uri=CELEX:31991L0271> (accessed 31/03/2023).
- Energy and Climate Change Committee. (2016). 2020 Renewable Heat and Transport Targets. House of Commons. <https://publications.parliament.uk/pa/cm201617/cmselect/cmenergy/173/173.pdf> (accessed 01/04/2023).
- European Biogas Association. (2021). EBA Statistical Report. <https://www.europeanbiogas.eu/wp-content/uploads/2021/11/EBA-STATISTICAL-REPORT-2021-SHORT-VERSION.pdf> (accessed 24/04/2023).
- European Commission. (2019). A European Green Deal. https://commission.europa.eu/strategy-and-policy/priorities-2019-2024/european-green-deal_en (accessed 01/04/2023).
- European Commission. (2022). RePowerEU: Joint European action for more affordable, secure and sustainable energy. <https://ec.europa.eu/commission/presscorner/api/files/attachment/871871/Factsheet - REPowerEU.pdf> (accessed 01/04/2023).
- Eurostat. (2022). Renewable energy on the rise: 37% of EU's electricity. <https://ec.europa.eu/eurostat/web/products-eurostat-news/-/ddn-20220126-1> (accessed 01/04/2023).
- Fang, M., Xiang, Q., Yu, C., Xia, Z., Zhou, X., Cai, D., and Wang, Z. (2015). Experimental study on CO₂ absorption by aqueous ammonia solution at elevated pressure to enhance CO₂ absorption and suppress ammonia vaporization. *Greenhouse Gases: Science and Technology*, 5, 210–221.
- Fong, W. K., Sotos, M., Doust, M., Shultz, S., Marques, A., and Deng-beck, C. (2021). Global Protocol for Gas Emission Inventories An Accounting and Reporting Standard for Cities (Version 1.1). *Greenhouse Gas Protocol*. https://ghgprotocol.org/sites/default/files/standards/GPC_Full_MASTER_RW_v7.pdf (accessed 01/04/2023).

- Gabelman, A., and Hwang, S. (1999). Hollow fiber membrane contactors. *Journal of Membrane Science*, 159, 61–106.
- Garrido, J. M., Fdz-Polanco, M., and Fdz-Polanco, F. (2013). Working with energy and mass balances: A conceptual framework to understand the limits of municipal wastewater treatment. *Water Science and Technology*, 67, 2294–2301.
- Grasham, O., Dupont, V., Camargo-Valero, M. A., García-Gutiérrez, P., and Cockerill, T. (2019). Combined ammonia recovery and solid oxide fuel cell use at wastewater treatment plants for energy and greenhouse gas emission improvements. *Applied Energy*, 240, 698–708.
- Guida, S., Van Peteghem, L., Luqmani, B., Sakarika, M., McLeod, A., McAdam, E. J., Jefferson, B., Rabaey, K., and Soares, A. (2022). Ammonia recovery from brines originating from a municipal wastewater ion exchange process and valorization of recovered nitrogen into microbial protein. *Chemical Engineering Journal*, 427, 130896.
- Han, Y., Agyeman, F., Green, H., and Tao, W. (2022). Stable, high-rate anaerobic digestion through vacuum stripping of digestate. *Bioresource Technology*, 343, 126133.
- Heile, S., Rosenberger, S., Parker, A., Jefferson, B., and McAdam, E. J. (2014). Establishing the suitability of symmetric ultrathin wall polydimethylsiloxane hollow-fibre membrane contactors for enhanced CO₂ separation during biogas upgrading. *Journal of Membrane Science*, 452, 37–45.
- Hoff, K. A., and Svendsen, H. F. (2013). CO₂ absorption with membrane contactors vs. packed absorbers- Challenges and opportunities in post combustion capture and natural gas sweetening. *Energy Procedia*, 37, 952–960.
- Horseman, T., Yin, Y., Christie, K. S., Wang, Z., Tong, T., and Lin, S. (2021). Wetting, Scaling, and Fouling in Membrane Distillation: State-of-the-Art Insights on Fundamental Mechanisms and Mitigation Strategies. *ACS EST Engineering*, 1, 117–140.
- Houlker, S. (2019). Scale up of hollow fibre membrane contactors for biogas upgrading. EngD thesis. Cranfield University.

- Houlker, S., Rutherford, T., Herron, D., Brookes, A., Moore, A., Vale, P., Pidou, M., and McAdam, E. (2021). Demonstrating commercial hollow fibre membrane contactor performance at industrial scale for biogas upgrading at a sewage treatment works. *Water (Switzerland)*, 13, 172.
- IEA Bioenergy. (2019). Task 37: Energy from Biogas Upgrading Plant List 2019. International Energy Agency. <https://task37.ieabioenergy.com/plant-lists/> (accessed 01/04/2023).
- Intergovernmental Panel on Climate Change (IPCC). (2007). Changes in Atmospheric Constituents and in Radiative Forcing. http://www.ipcc.ch/publications_and_data/ar4/wg1/en/ch2s2-10-2.html (accessed 31/03/2023).
- Intergovernmental Panel on Climate Change (IPCC). (2018). Global Warming of 1.5°C. An IPCC Special Report on the impacts of global warming of 1.5°C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change,. <https://www.ipcc.ch/sr15/chapter/summary-for-policy-makers/> (accessed 01/04/2023).
- International Energy Agency. (2022). Bioenergy with Carbon Capture and Storage. <https://www.iea.org/reports/bioenergy-with-carbon-capture-and-storage> (accessed 01/04/2023).
- IRENA. (2021). A pathway to decarbonise the shipping sector by 2050. International Renewable Energy Agency. https://www.irena.org/-/media/Files/IRENA/Agency/Publication/2021/Oct/IRENA_Decarbonising_Shipping_2021.pdf?rev=b5dfda5f69e741a4970680a5ced1ac1e (accessed 01/04/2023).
- Jiang, X., Lu, D., Xiao, W., Ruan, X., Fang, J., and He, G. (2016). Membrane assisted cooling crystallization: Process model, nucleation, metastable zone, and crystal size distribution. *AIChE Journal*, 62, 829–841.
- Jilvero, H., Normann, F., Andersson, K., and Johnsson, F. (2012). Heat requirement for regeneration of aqueous ammonia in post-combustion carbon dioxide capture. *International Journal of Greenhouse Gas Control*, 11, 181–187.

- John Lewis Partnership. (2018). John Lewis Partnership steps up net zero carbon commitment with biomethane gas filling station. <https://www.johnlewispartnership.co.uk/media/press/y2020/jlp-steps-up-net-zero-carbon-commitment.html> (accessed 01/04/2023).
- Kakoulaki, G., Kougias, I., Taylor, N., Dolci, F., Moya, J., and Jäger-Waldau, A. (2021). Green hydrogen in Europe – A regional assessment: Substituting existing production with electrolysis powered by renewables. *Energy Conversion and Management*, 228, 113649.
- Kapoor, R., Ghosh, P., Kumar, M., and Vijay, V. K. (2019a). Evaluation of biogas upgrading technologies and future perspectives: a review. *Environmental Science and Pollution Research*, 26, 11631–11661.
- Kapoor, R., Subbarao, P. M. V., and Vijay, V. K. (2019b). Integration of flash vessel in water scrubbing biogas upgrading system for maximum methane recovery. *Bioresource Technology Reports*, 7, 100251.
- Kim, G. H., Park, S. Y., You, J. K., Hong, W. H., Kim, J. N., and Kim, J. D. (2014). CO₂ absorption kinetics in a CO₂-free and partially loaded aqueous ammonia solution. *Chemical Engineering Journal*, 250, 83–90.
- Kobayashi, H., Hayakawa, A., Somarathne, K. D. K. A., and Okafor, E. C. (2019). Science and technology of ammonia combustion. *Proceedings of the Combustion Institute*, 37, 109–133.
- Kozak, F., Petig, A., Morris, E., Rhudy, R., and Thimsen, D. (2009). Chilled ammonia process for CO₂ capture. *Energy Procedia*, 1, 1419–1426.
- Kvist, T., and Aryal, N. (2019). Methane loss from commercially operating biogas upgrading plants. *Waste Management*, 87, 295–300.
- Lan, R., and Tao, S. (2014). Ammonia as a suitable fuel for fuel cells. *Frontiers in Energy Research*, 2, 1–4.
- Mackinnon, I. D. R., Barr, K., Miller, E., Hunter, S., and Pinel, T. (2003). Nutrient removal from wastewaters using high performance materials. *Water Science and Technology*, 47, 101–107.
- Mani, F., Peruzzini, M., and Stoppioni, P. (2006). CO₂ absorption by aqueous NH₃ solutions: Speciation of ammonium carbamate, bicarbonate and carbonate by a ¹³C NMR study. *Green Chemistry*, 8, 995–1000.

- McBean, E. A. (2008). Siloxanes in biogases from landfills and wastewater digesters. *Canadian Journal of Civil Engineering*, 35, 431–436.
- McDonald, M. A., Salami, H., Harris, P. R., Lagerman, C. E., Yang, X., Bommarius, A. S., Grover, M. A., and Rousseau, R. W. (2021). Reactive crystallization: A review. *Reaction Chemistry and Engineering*, 6, 364–400.
- McLeod, A., Buzatu, P., Autin, O., Jefferson, B., and McAdam, E. (2015). Controlling shell-side crystal nucleation in a gas-liquid membrane contactor for simultaneous ammonium bicarbonate recovery and biogas upgrading. *Journal of Membrane Science*, 473, 146–156.
- McLeod, A., Jefferson, B., and McAdam, E. J. (2014). Biogas upgrading by chemical absorption using ammonia rich absorbents derived from wastewater. *Water Research*, 67, 175–186.
- Moore, A., and Auty, D. (2013). Digestion and Greenhouses – Synergistic Resource Recovery. 18th European Biosolids & Organic Resources Conference & Exhibition, Manchester, UK.
- Nayak-Luke, R., Bañares-Alcántara, R., and Wilkinson, I. (2018). “green” Ammonia: Impact of Renewable Energy Intermittency on Plant Sizing and Levelized Cost of Ammonia. *Industrial and Engineering Chemistry Research*, 57, 14607–14616.
- Ndam, N. E. (2017). Treatment technologies for recycle liquors: Nutrient removal, mass balances, and potential recovery at wastewater treatment plants. PhD thesis. Newcastle University.
- Northern Gas Networks. (2020). Biomethane: a producer’s handbook. https://biomethane.northerngasnetworks.co.uk/wp-content/uploads/2020/07/NGN_BiomethaneHandbook_0420_St04A.pdf (accessed 31/03/2023).
- Ochedi, F. O., Yu, J., Yu, H., Liu, Y., and Hussain, A. (2021). Carbon dioxide capture using liquid absorption methods: a review. *Environmental Chemistry Letters*, 19, 77–109.
- Parliamentary Office of Science and Technology. (2007). Energy and Sewage, Postnote number 282,.

<http://www.parliament.uk/documents/post/postpn282.pdf> (accessed 31/03/2023).

- Pátek, J., and Klomfar, J. (1995). Simple functions for fast calculations of selected thermodynamic properties of the ammonia-water system. *International Journal of Refrigeration*, 18, 228–234.
- Pavicic, J., Mavar, K. N., Brkic, V., and Simon, K. (2022). Biogas and Biomethane Production and Usage: Technology Development, Advantages and Challenges in Europe. *Energies*, 15, 2940.
- Pérez-Calvo, J. F., Sutter, D., Gazzani, M., and Mazzotti, M. (2021). Advanced configurations for post-combustion CO₂ capture processes using an aqueous ammonia solution as absorbent. *Separation and Purification Technology*, 274, 118959.
- Pesuit, M., Proietti, S., and Paolucci, L. P. (2017). Fuelling the use of Biomethane for Grid Injection and as Transport Fuel. *Biosurf.* <https://www.europeanbiogas.eu/wp-content/uploads/2021/02/BIOSURF-D8-7-digital-EN.pdf> (accessed 01/04/2023).
- Ryckebosch, E., Drouillon, M., and Vervaeren, H. (2011). Techniques for transformation of biogas to biomethane. *Biomass and Bioenergy*, 35, 1633–1645.
- Scarlat, N., Dallemand, J. F., and Fahl, F. (2018). Biogas: Developments and perspectives in Europe. *Renewable Energy*, 129, 457–472.
- Scholes, C. A., Kentish, S. E., Stevens, G. W., and DeMontigny, D. (2015). Comparison of thin film composite and microporous membrane contactors for CO₂ absorption into monoethanolamine. *International Journal of Greenhouse Gas Control*, 42, 66–74.
- Sun, Q., Li, H., Yan, J., Liu, L., Yu, Z., and Yu, X. (2015). Selection of appropriate biogas upgrading technology-a review of biogas cleaning, upgrading and utilisation. *Renewable and Sustainable Energy Reviews*, 51, 521–532.
- Tansel, B., and Surita, S. C. (2019). Managing siloxanes in biogas-to-energy facilities: Economic comparison of pre- vs post-combustion practices. *Waste Management*, 96, 121–127.

- The Royal Society. (2020). Ammonia: zero-carbon fertiliser, fuel and energy store. Policy Briefing. <https://royalsociety.org/topics-policy/projects/low-carbon-energy-programme/green-ammonia/> (accessed 31/03/2023).
- Thomsen, K., and Rasmussen, P. (1999). Modeling of vapor-liquid-solid equilibrium in gas-aqueous electrolyte systems. *Chemical Engineering Science*, 54, 1787–1802.
- Tian, X., Gao, Z., Feng, H., Zhang, Z., Li, J., and Wang, A. (2019). Efficient nutrient recovery/removal from real source-separated urine by coupling vacuum thermal stripping with activated sludge processes. *Journal of Cleaner Production*, 220, 965–973.
- Ulrich, J., and Strege, C. (2002). Some aspects of the importance of metastable zone width and nucleation in industrial crystallizers. *Journal of Crystal Growth*, 237–239, 2130–2135.
- van Linden, N., Spanjers, H., and van Lier, J. B. (2022). Fuelling a solid oxide fuel cell with ammonia recovered from water by vacuum membrane stripping. *Chemical Engineering Journal*, 428, 131081.
- Villeneuve, K., Roizard, D., Remigy, J. C., Iacono, M., and Rode, S. (2018). CO₂ capture by aqueous ammonia with hollow fiber membrane contactors: Gas phase reactions and performance stability. *Separation and Purification Technology*, 199, 189–197.
- Wang, R., Zhang, H. Y., Feron, P. H. M., and Liang, D. T. (2005). Influence of membrane wetting on CO₂ capture in microporous hollow fiber membrane contactors. *Separation and Purification Technology*, 46, 33–40.
- Water Europe. (2021). Unleash the Potential of the Water-Energy Nexus in the Energy Efficiency Directive Joint Declaration. <https://watereurope.eu/wp-content/uploads/Joint-Declaration-EU-ASE-.WE-2.pdf> (accessed 31/03/2023).
- Water UK. (2020). Net Zero 2030 Routemap. <https://www.water.org.uk/routemap2030> (accessed 31/03/2023).
- Wett, B. (2006). Solved upscaling problems for implementing deammonification of rejection water. *Water Science and Technology*, 53, 121–128.

Winter, P., Pearce, P., and Colquhoun, K. (2012). Contribution of nitrous oxide emissions from wastewater treatment to carbon accounting. *Journal of Water and Climate Change*, 3, 95–109.

2 Transitioning through the vapour-liquid equilibrium for low energy thermal stripping of ammonia from wastewater: Enabling transformation of NH_3 as a zero carbon fuel

Transitioning through the vapour-liquid equilibrium for low energy thermal stripping of ammonia from wastewater: Enabling transformation of NH₃ as a zero carbon fuel

B. Luqmani^a, A. Brookes^b, A. Moore^c, P. Vale^d, M. Pidou^a, E.J. McAdam^{a,*}

^aCranfield Water Science Institute, Vincent Building, Cranfield University, Bedfordshire, MK43 0AL, UK

^bAnglian Water, Block C-Western House, Peterborough Business Park, Peterborough PE2 6FZ, UK

^cNorthumbrian Water, Boldon House, Wheatlands Way, Durham DH1 5FA, UK

^dSevern Trent Water, 2 St. Johns Street, Coventry CV1 2LZ, UK

*Corresponding Author: e.mcadam@cranfield.ac.uk

Abstract

Vacuum thermal stripping permits the recovery of ammonia from wastewater in a concentrated form, which is key to its exploitation in the circular economy, but the latent heat demand for thermal separation remains a critical barrier to exploitation. In this study, we investigate the vapour-liquid equilibrium (VLE) for ammonia-water as a mechanism to enhance recovered ammonia quality and minimise the thermal energy required for ammonia separation. Below the dew point (65°C at 0.25 bar) a two-phase region of the VLE exists where 48%wt gas-phase ammonia could be produced (61°C) compared to only 2%wt within the stripping region adopted widely in the literature. This was complemented by a 98% reduction in thermal separation energy, since limited water vapourisation can occur when the feed is maintained below the activation energy threshold for bulk evaporation. Operation within this practically unexplored region of the ammonia-water VLE fosters a gas-phase product suitable for energy generation in gas turbines or solid oxide fuel cells. Comparable product quality was achieved using concentrated wastewater, which validated the VLE for design in the presence of a broad range of dissolved gases and volatile inorganic compounds. Rapid desorption of CO₂ occurred during vacuum stripping, subsequently increasing pH >9 without the requirement for alkali addition to shift the ammonia-ammonium equilibrium in favour of gaseous ammonia. Consequently, the two-phase region of the VLE defined for vacuum thermal stripping provides a synergistic strategy to mitigate chemical demand, minimise separation energy and recover gas-phase ammonia for zero carbon energy generation, constituting a significant advancement toward the net zero ambitions of the water sector.

Keywords: *Ammonia to energy, vacuum stripping, net zero, resource recovery, wastewater*

2.1 Introduction

Ammonia in municipal wastewater is removed by biological oxidation in the activated sludge process. Ammonia oxidation consumes 3-5 kWh_e kg_N⁻¹ for forced aeration and can represent 20% of the total energy demand for wastewater treatment (Garrido et al., 2013; Wett, 2006). During ammonia oxidation, 0.3% of the nitrogen is transformed into nitrous oxide (N₂O) which has a global warming potential 310-times greater than CO₂ (Campos et al., 2016; Winter et al., 2012). Consequently, ammonia removal is associated with almost half of greenhouse gas (GHG) emissions in wastewater treatment (Campos et al., 2016). To improve environmental standards and public health, nitrogen limits for treated wastewater in Europe are reducing to 10 mg L⁻¹ (for works serving >0.1 million P.E.) within the Urban Wastewater Treatment Directive 91/271/EEC (EEC Council, 1991). The new discharge standards will require higher nitrogen removal from existing wastewater treatment processes, or prompt investment to expand treatment capacity, which will increase energy demand and GHG emissions associated with ammonia removal.

Ammonia recovery from wastewater is an opportunity to advance sustainability within the water sector. Currently, approximately 185 Mtonnes y⁻¹ of ammonia is synthesised in the energy intensive Haber-Bosch process (19 kWh_{th} kg_N⁻¹) to meet agricultural and industrial demands (Mission Possible Partnership, 2022; Morgan, 2013). Ammonia synthesis is presently 95% reliant on fossil-fuel derived hydrogen feedstocks and is consequently associated with 1.3% of global CO₂ emissions (International Energy Agency, 2021; Nayak-Luke et al., 2018). The demand for ammonia is projected to expand to at least 255 Mtonnes y⁻¹ by 2050 due to the rising global population and this has stimulated interest in decarbonising its production (International Energy Agency, 2021; Mission Possible Partnership, 2022). This could be achieved by incorporating carbon capture and storage for 'blue' ammonia production, or a transition to electrified plants powered by renewable energy sources for 'green' ammonia production (Cesaro et al., 2021; Morgan, 2013). Across the UK water sector alone, there is an opportunity to recover up to 400 tonnes of sustainable ammonia per day which could offset commercial ammonia production and therefore align directly with

existing objectives for industrial decarbonisation (Henze and Comeua, 2008; Parliamentary Office of Science and Technology, 2007).

Many researchers have focussed on ammonia recovery from wastewater to produce agricultural fertilisers (i.e., ammonium sulphate, struvite) (Vaneeckhaute et al., 2017). There are complex barriers to the sale of fertiliser produced from wastewater since it is classified as waste under the European Waste Framework Directive 2008/98/EC (EC, 2008). With a lower heating value of 5.3 kWh kg⁻¹ (comparable to biogas, 6.1 kWh kg⁻¹), ammonia is also emerging as a next generation zero carbon fuel (Table 2.1) (Moore and Auty, 2013; The Royal Society, 2020). As the water sector is already strongly focused on renewable energy production, ammonia can therefore provide significant value. For example, biogas turbines used for combined heat and power (CHP) generation are often co-located with ammonia-rich digested sludge liquors. Gas-phase ammonia recovery could support the co-combustion of an ammonia/biogas mixture to increase energy production (Kurata et al., 2017; Okafor et al., 2021a). Gaseous, aqueous or anhydrous liquified ammonia can also be consumed in fuel cells that are not limited to classical Carnot inefficiencies and thus achieve electrical efficiencies greater than those of existing CHP engines (>50%) (Lan and Tao, 2014; The Royal Society, 2020). Ammonia can also be 'cracked' electrolytically or catalytically to produce hydrogen (Jackson et al., 2015; Vitse et al., 2005), directly in line with ongoing investment into hydropowered hydrogen production within the water sector to access an expanding hydrogen economy (Anglian Water, 2021; Department for Business, Energy and Industrial Strategy, 2021). Ammonia to energy could therefore reduce energy importation for water utilities and limit exposure to volatile energy prices or create new revenue streams through the exportation of hydrogen-based zero carbon fuels. The capability to meet stringent nitrogen discharge limits, reductions in GHG emissions and grid based power, while producing a zero carbon fuel creates a holistic strategy for the water sector that resonates with its broader net zero ambitions (Water Europe, 2021; Water UK, 2020). However, the concentration, purity and form (i.e., aqueous or gas) that the ammonia is recovered in will

determine the available routes for its exploitation as a zero carbon fuel (Table 2.1).

Table 2.1: Technologies for energy and hydrogen generation using ammonia

Application	Ammonia state	Ammonia purity %wt	Electrical efficiency %LHV	Heat generation %LHV	Heat quality -
Gas turbine ^a	Gaseous ^b	>20% ^{b,d}	30-40% ^{c,d}	60-70%	>400°C ^{d,l} ; <100°C ^{d,l}
SOFC	Gas ^{d,e}	>5% ^{e,f}	50-70% ^{c,f}	30-50%	>700°C ^g
Low temperature AFC	Aqueous / Gas ^{h,i}	<0.01% ^{h,i}	50-60% ^{c,i}	-	-
Cracking to H ₂	Gas ^j	>5% ^{e,f,j}	-	-	-
Electrolysis to H ₂	Aqueous ^k	<0.01% ^k	-	-	-

LHV – Lower heating value for ammonia (5.3 kWh kg⁻¹); AFC – alkaline fuel cell; SOFC – solid oxide fuel cell.

^a Ammonia-fed or co-fueled with methane

^g (Patel et al., 2012)

^b (Kurata et al., 2017; Okafor et al., 2021a)

^h (Zhang et al., 2020)

^c (The Royal Society, 2020)

ⁱ (Siddiqui and Dincer, 2019a)

^d (Hewlett et al., 2020, 2019)

^j (Jackson et al., 2015)

^e (van Linden et al., 2022)

^k (Cooper and Botte, 2006; Vitse et al., 2005)

^f (Dekker and Rietveld, 2006)

^l ~50% high-grade and ~50% low grade heat

Since ammonia is relatively dilute and contained within the complex wastewater matrix, its separation and purification from wastewater is required to capitalise on ammonia to energy opportunities. In a centralised wastewater treatment works, 20-40%wt of the ammonia load is concentrated within centrifuged liquors originating from anaerobic digestion (centrate) which represent less than 1% of the treatment flow (Ndam, 2017). This low-volume sidestream presents an ideal target for economic ammonia recovery, since the raised concentration will enhance the driving force for ammonia mass transfer during stripping (Bavarella et al., 2020; Ukwuani and Tao, 2016). Air and steam stripping are already commercially established (Organics Group, 2020; RVT, 2015). High gas-liquid ratios (>2500 m³_{gas} m³_{liquid}⁻³) are necessary during air stripping which generates dilute gas-phase ammonia (<0.05%wt NH₃) (Huang and Shang, 2006; Jiang, 2009). Operating at high temperatures will reduce ammonia solubility, and so steam stripping requires lower gas-liquid ratios (<300

$\text{m}^3_{\text{gas}} \text{ m}^{-3}_{\text{liquid}}$) and generates an ammonia vapour at higher purity (0.5-2.0%wt) but the thermal demand increases to $\sim 150 \text{ kWh}_{\text{th}} \text{ kg}_N^{-1}$ primarily due to the latent heat demand for raising steam (Teichgraber and Stein, 1994; Zeng et al., 2006). As existing stripping solutions are primarily used for abatement, gas-phase ammonia is generally oxidised at high temperatures over a catalyst (250-450°C), or captured in sulphuric acid to produce a relatively dilute ammonium sulphate solution that requires disposal (Huang and Shang, 2006; Jamaludin et al., 2018; Wang et al., 2021). To improve the viability of zero carbon energy production from wastewater ammonia, stripping technologies must be able to produce aqueous ammonia or anhydrous liquified ammonia products in sufficient concentration to meet the needs of emergent energy applications. The separation and purification of ammonia must also be achieved with minimal energy input to maximise the potential for this new resource.

Vacuum thermal stripping is an emerging alternative, demonstrated at laboratory scale, in which wastewater is heated to saturation in a partial vacuum (Bavarella et al., 2020; Han et al., 2022). The absolute temperature for boiling reduces with the vacuum pressure applied. Consequently, the thermal energy demand can be reduced, enabling the integration of low-grade waste heat sources (Anwar and Tao, 2016). In a centralised wastewater treatment works, $47 \text{ kWh}_{\text{th}}$ of low-grade waste heat at modest quality (85°C in water) could be recovered from biogas turbines per m^3 of centrate (Moore and Auty, 2013; Ndam, 2017). Ammonia has a higher volatility than water and so the vapours produced during boiling will be relatively rich in ammonia compared to the liquid-phase (Pátek and Klomfar, 1995; Ukwuani and Tao, 2016). These vapours are continuously extracted by the vacuum pump, which enhances the volumetric mass transfer coefficient and maintains the driving force for ammonia mass transfer across the gas-liquid interface (Han et al., 2022). While several studies on vacuum stripping are reported, there is limited data on the composition of the vapour product. Bavarella et al. (2020) applied vacuum thermal stripping to a 7.5 kg m^{-3} aqueous ammonia feed and condensed the vapours to produce a 101 kg m^{-3} aqueous ammonia product. While the concentration factor compares favourably to air and steam stripping, the product is below the specification

generally required for energy production, implying that further purification stages are required (e.g., distillation). The product quality also indicates substantial evaporation of water from the feed during stripping. This will incur a high latent heat penalty which can represent over 90% of the total energy consumption for ammonia removal (Davey et al., 2022). Consequently, further selectivity toward ammonia must be fostered during the separation to improve the economic and environmental viability for vacuum thermal stripping in wastewater treatment.

Fundamentally, vacuum thermal stripping is a distillation process since it exploits the difference in volatility between ammonia and water (Ukwuani and Tao, 2016; van Linden et al., 2022). In a binary ammonia-water mixture, the fraction of ammonia in the liquid and vapour phase at a specific temperature are related by the vapour-liquid equilibrium (VLE). A model has been developed for estimation of the ammonia-water VLE based on regression analysis of meta-data for absorption refrigeration from 0.5-20 bar (Figure 2.1) (Pátek and Klomfar, 1995). Separation of ammonia and water will occur in the two-phase region bounded by the bubble and dew point curves. When the liquid-phase (x_f) is heated close to its dew point (T_1), a substantial fraction of ammonia will be released into the gas-phase at equilibrium to leave a dilute final solution (x_1). However, this will be associated with a high fraction of water vapourisation and so will produce a vapour phase which has only a slightly higher ammonia content than the initial feed (y_1). In contrast, when the liquid-phase is heated close to its bubble point (T_2), a smaller amount of ammonia is released into the gas-phase which has only a minor impact on the feed concentration (x_2). Under this condition, the selectivity of ammonia (the more volatile component) is enhanced and so water vapourisation is minimal and the resultant vapour is of a much greater ammonia concentration (y_2). Based on the existing boundaries which have been theoretically derived for the VLE, we can postulate that the extraction of the vapour phase during vacuum thermal stripping will continuously reset this equilibrium and cause the liquid-phase ammonia concentration to decline over time. Hence, a stripping process at T_1 will achieve rapid ammonia mass transfer, whilst operating at T_2 will produce high purity vapour but at a limited mass transfer rate. A purer vapour phase could be directly applied for energy generation,

obviating the capital cost and energy requirements related to the downstream purification of ammonia. Further, it would be associated with a lower fraction of water vapourisation from the feed, thereby minimising latent heat demand for the process and increasing the energy efficiency for ammonia recovery. Controlling temperature and pressure to achieve a setpoint within the two-phase region may therefore introduce a disruptive breakthrough for thermal stripping, by delivering an ammonia product at maximum concentration and with minimum separation energy.

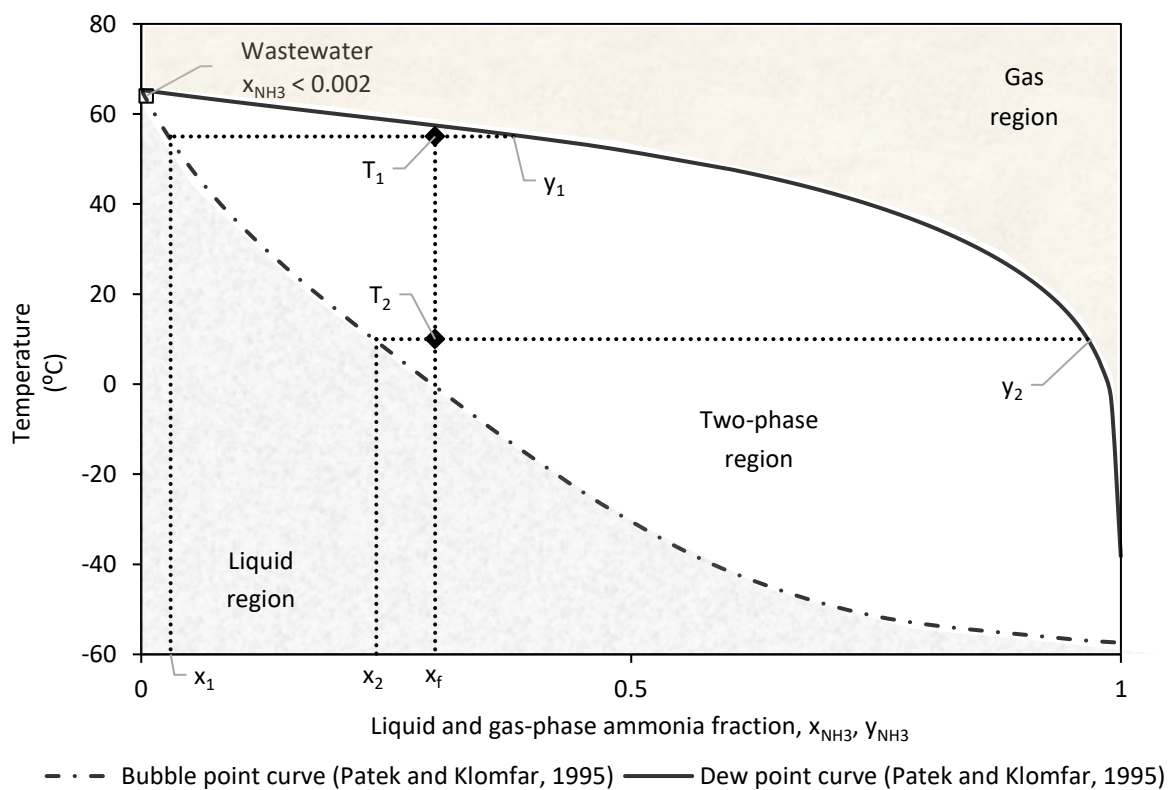


Figure 2.1 VLE for $\text{NH}_3\text{-H}_2\text{O}$ at 0.25 bar defined using empirical method (Eq. 2.11-2.12)

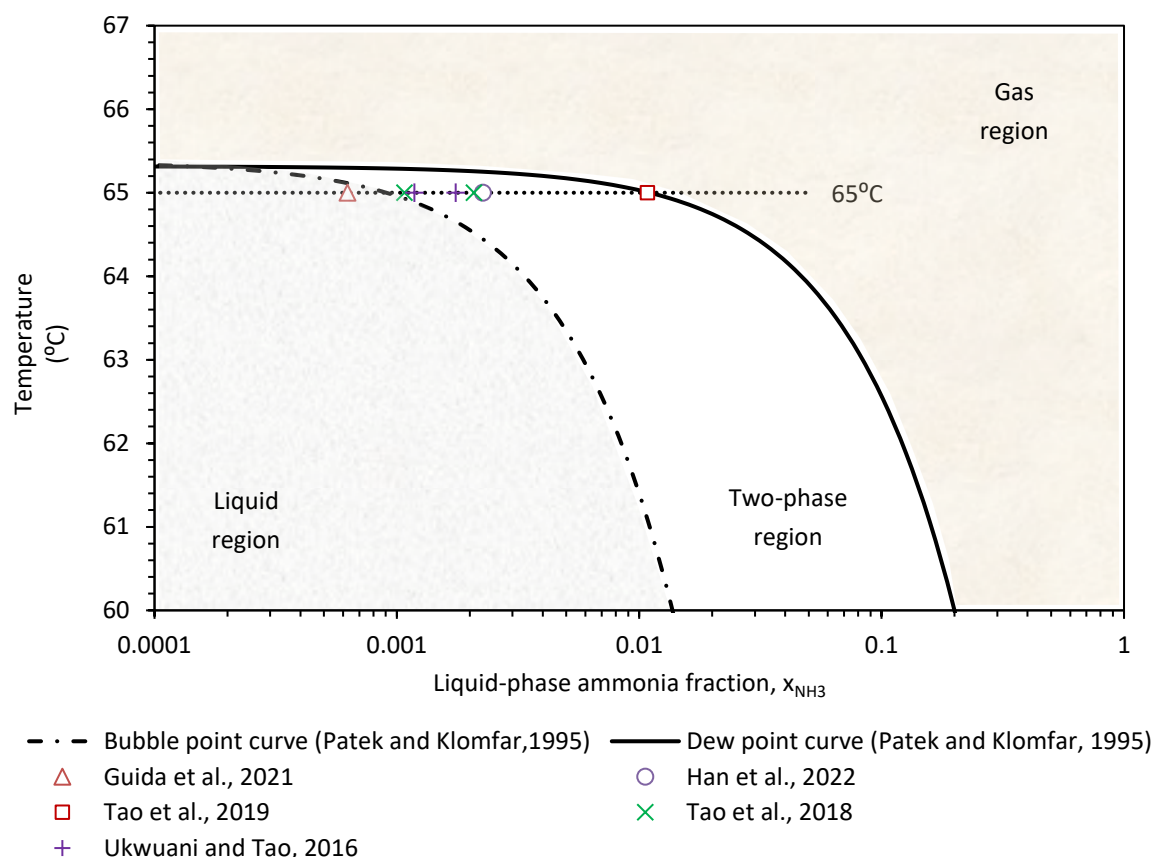


Figure 2.2: Operating points for vacuum thermal stripping of real and synthetic wastewater at 0.25-0.27 bar in previous work, placed within the context of the $\text{NH}_3\text{-H}_2\text{O}$ VLE (Eq. 2.11-2.12).

However, in the majority of research published on vacuum thermal stripping of wastewater, a vacuum pressure of 0.25-0.27 bar and a uniform temperature of 65°C has been applied independently of the feed concentration. The experimental conditions were selected to achieve vigorous boiling in the feed, and when overlaid onto the VLE, evidence that the system was operated close to its dew point (65.1-65.3°C) (Figure 2.2). Consequently, despite the prospective benefits to separation energy and product purity, the two-phase region has not been explored to date. Crucially, concentrated wastewater ($x_{\text{NH}_3} < 0.002$) at 0.25 bar exists at the lower limit of the VLE, which has not been well characterised historically within the literature, since the focus has been on ammonia-water refrigeration mixtures (typically $x_{\text{NH}_3} > 0.5$) (Ganesh and Srinivas, 2017; Raghuvanshi and Maheshwari, 2011). Prediction of the two-phase region using extrapolated data may be particularly challenging due to solvent-solute interactions between ammonia and water which can influence the VLE (Tan et

al., 2004). The precise width of the two-phase region relevant for ammonia stripping from wastewater is therefore uncertain, and experimental characterisation is necessary to establish the extent to which ammonia-water selectivity can be controlled during ammonia stripping. The aim of this study was to characterise the ammonia-water separation mechanism during vacuum thermal stripping and investigate the potential to exploit the two-phase region to increase ammonia selectivity and facilitate low-energy, high purity ammonia recovery from wastewater. Specific objectives were to:

- i) benchmark ammonia separation in vacuum thermal stripping through initially characterising selectivity at the dew point to compare against existing literature;
- ii) transition from the dew point through the two-phase region to determine the extent to which ammonia-water selectivity can be manipulated;
- iii) consider the potential for enhanced ammonia selectivity during stripping as an enabler for ammonia to energy strategies in wastewater treatment;
- iv) characterise stripping performance using concentrated wastewater to investigate the impact of dissolved volatile compounds and gases on the ammonia-water separation;
- v) explore the potential for chemical-free vacuum thermal stripping to complement and enhance the prospective energy and cost benefits when operating within the two-phase region.

2.2 Materials and methods

2.2.1 Experimental set-up

Vacuum thermal stripping experiments were conducted in a batch system developed at laboratory scale (Figure 2.3). In each experiment, 0.5 kg of feed was placed in a 1 L jacketed vessel and agitated using a magnetic stirrer at approximately 450 rpm (SB151, Stuart Ltd., Stone, UK). The feed was heated to 61, 63 or 65 $\pm 0.5^\circ\text{C}$ at atmospheric pressure (MPC-K6, Huber, Offenburg, Germany). When the target temperature was achieved, system pressure was reduced to 0.25 bar using a vacuum pump in combination with a vacuum control valve (ME-1C, Vacuubrand, Wertheim, Germany; SS-4MA-MH, Swagelok, Kings

Langley, UK). Stripping temperature and pressure were monitored continuously (Type K, RS Components, Corby, UK; PXM319-010GI, Omega Engineering Ltd, Manchester, UK). Ammonia-rich vapour stripped from the feed was drawn through a condenser operated at 3-5°C with 250 cm² surface area (Quickfit C6/12/SC, Fisher Scientific, Loughborough, UK; LT Ecocool 150, Grant Instruments, Cambridge, UK). Condensate was stored in a chilled, jacketed vessel at 3-5°C to prevent further ammonia stripping. Each primary data point was collected in duplicate or triplicate. Standard deviation is represented by error bars.

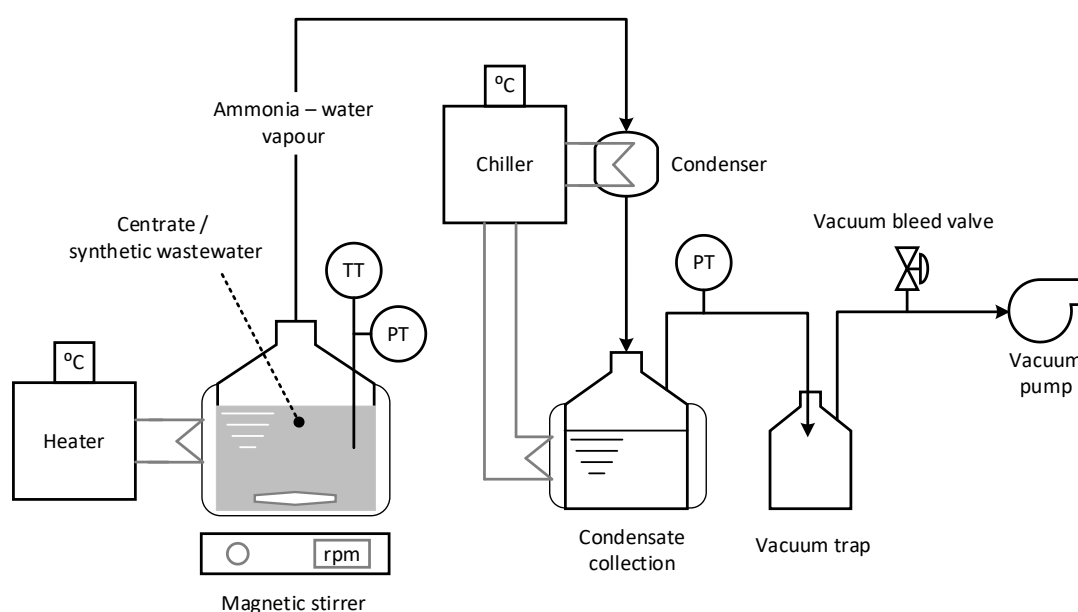


Figure 2.3. Schematic of the vacuum thermal stripping experiment. TT and PT represent temperature and pressure transmitters, respectively.

2.2.2 Wastewater preparation and analysis

Synthetic wastewater containing 1.5 g L⁻¹ ammonia was produced using deionised water (15 MΩ cm) and ammonium hydroxide (35%wt, Fisher Scientific, Loughborough, UK). Centrifuged sludge liquors originating from conventional anaerobic digestion (Centrate A) and advanced anaerobic digestion (Centrate B) were sampled from separately located wastewater treatment works in England (Table 2.2). Sodium hydroxide was added to amend pH as required (97%wt pearl, Fisher Scientific, Loughborough, UK). Ammoniacal nitrogen and chemical oxygen demand (COD) was determined using spectrophotometry with proprietary cell

tests (114558 & 114559 NH₄-N, 11451 COD, Spectroquant cell tests, Merck-Millipore, Darmstadt, Germany). For the centrate and distillate, soluble COD was determined following 0.45 µm syringe filtration (Whatman, Maidstone, UK), whilst pH measurement was conducted in a temperature-controlled environment at 21°C (InPro 3250i/SG/120, Mettler-Toledo Ltd, Leicester, UK). Standard methods 2540B and 2540D were applied to determine total solids, suspended solids and dissolved solids (APHA/AWWA/WEF, 2012). Centrate alkalinity was determined by titration with hydrochloric acid (37%, Fisher Scientific, Loughborough, UK). Total inorganic carbon content (TIC) was analysed using a TOC analyser (Shimadzu, Milton Keynes, UK).

Table 2.2: Characterisation of centrate used in this work, produced from full-scale AD facilities treating municipal wastewater sludge

Parameter	Centrate A	Centrate B ^a
Origin	Conventional AD	Advanced AD ^b
Ammonia concentration, C _{NH3} (g L ⁻¹)	1.0	2.0
pH (-)	7.8	8.0
Total COD (g L ⁻¹)	1.2	5.8
Soluble COD (g L ⁻¹)	0.4	0.3
Total suspended solids (g L ⁻¹)	0.2	0.3
Total dissolved solids (g L ⁻¹)	1.6	4.6
Total inorganic carbon (as C) (g L ⁻¹)	1.0	1.7
Alkalinity (as CaCO ₃) (g L ⁻¹)	3.7	6.9

AD – anaerobic digestion; COD – chemical oxygen demand.

^a Characterisation originally published by Davey et al. (2022)

^b Raw sludge pre-treated by thermal hydrolysis prior to anaerobic digestion

2.2.3 Experimental analysis

Ammonia will partially dissociate in wastewater to form non-volatile ammonium (Eq. 2.1). The fraction of free ammonia in the feed can be estimated from the pH and temperature (Eq. 2.2-2.3; Figure A1) (Bates and Pinching, 1950).



$$\Phi = \frac{1}{1 + 10^{(pK_{a,T}^S - pH)}} \quad (\text{Eq. 2.2})$$

$$pK_{a,T}^s = pK_{a,298}^s + 0.0324 [298.15 - T] \quad (\text{Eq. 2.3})$$

where Φ is the fraction of free ammonia (-); $pK_{a,298}^s$ and $pK_{a,T}^s$ are the negative logarithm of the acid dissociation constant at 298 K and T (K), respectively [-].

Ammonia mass transfer across the gas-liquid interface can be described by the Lewis-Whitman model (Eq. 2.4) (Heile et al., 2017; Tao and Ukwuani, 2015). The equilibrium concentration for dissolved ammonia (C_{NH3}^*) approaches zero under vacuum conditions across all temperatures applied in this work (Salavera et al., 2005; Ukwuani and Tao, 2016). Integration of Eq. 2.4 from time = 0 to time = t provides a straight-line function in which the gradient represents the volumetric mass transfer coefficient ($k_L a$) (Eq. 2.5).

$$\frac{dC_{NH3}}{dt} = k_L a (\Phi C_{NH3} - C_{NH3}^*) \quad (\text{Eq. 2.4})$$

$$-\ln\left(\frac{C_{NH3,t}}{C_{NH3,0}}\right) = k_L a t \quad (\text{Eq. 2.5})$$

where dC_{NH3}/dt is the rate of ammonia transfer across the gas-liquid interface ($g L^{-1} h^{-1}$); k_L is the mass transfer coefficient for ammonia ($m h^{-1}$); a is the specific interfacial area ($m^2 m^{-3}$); C_{NH3} is the dissolved ammonia concentration ($g L^{-1}$); Φ is the fraction of free ammonia (-); t is stripping time (h); and subscripts 0 and t represent time = 0 and time = t .

During vacuum thermal stripping, the concentration of ammonia in the feed and the total condensate mass were recorded over time. This enabled a mass balance to determine ammonia removal from the feed (Eq. 2.6-2.8) and the ammonia mass fraction within the stripped vapour at any time (Eq. 2.9). It was assumed that all stripped water was captured by condensation at 3-5°C and the feed density was equal to that of pure water at the operating temperature due to its dilute nature ($x_{NH3} < 0.002$).

$$V_0 = \frac{m_0}{\rho} \quad (\text{Eq. 2.6})$$

$$V_t = \frac{(m_0 - m_{c,t})}{\rho} \quad (\text{Eq. 2.7})$$

$$\eta_{NH3} = \frac{C_{NH3,0}V_0 - C_{NH3,t}V_t}{C_{NH3,0}V_0} * 100 \quad (\text{Eq. 2.8})$$

$$y_{NH3,wt} = \frac{C_{NH3,0} V_0 - C_{NH3,t} V_t}{m_{c,t}} * 100 \quad (\text{Eq. 2.9})$$

where V is the feed volume (L); m is the feed mass (g); m_c is the condensate mass (g); and ρ is the feed density (g L^{-1}); η_{NH3} is ammonia removal from the feed (%wt); $y_{NH3,wt}$ is the mass fraction of ammonia in the stripped vapour (%wt).

Ammonia selectivity during stripping could be estimated using the equilibrium pressures of ammonia and water in the feed at the stripping condition and could be experimentally measured based on the relative amounts of ammonia and water removed from the feed over time (Eq. 2.10).

$$\alpha_{NH3} = \frac{p_{NH3}}{p_{H2O}} = \frac{\text{mol}_{NH3}}{\text{mol}_{H2O}} \quad (\text{Eq. 2.10})$$

where α_{NH3} is the selectivity for ammonia during stripping ($\text{bar}_{NH3} \text{ bar}_{H2O}^{-1}$ or $\text{mol}_{NH3} \text{ mol}_{H2O}^{-1}$); p_{NH3} and p_{H2O} represent the equilibrium vapour pressures of ammonia and water, respectively (bar); and mol_{NH3} and mol_{H2O} represent the amount of ammonia and water removed from the feed, respectively (moles).

The empirical dew and bubble point curves for the ammonia-water system were computed at 0.25 bar (Eq. 2.11-2.12) (Pátek and Klomfar, 1995):

$$T_b(P, x_{NH3}) = T_0 \sum_i a_i (1 - x_{NH3})^{m_i} \left[\ln \left(\frac{P_0}{P} \right) \right]^{n_i} \quad (\text{Eq. 2.11})$$

$$T_d(P, y_{NH3}) = T_0 \sum_i a_i (1 - y_{NH3})^{\frac{m_i}{4}} \left[\ln \left(\frac{P_0}{P} \right) \right]^{n_i} \quad (\text{Eq. 2.12})$$

where T_b is the bubble temperature (K) of the ammonia-water mixture at the applied pressure P (0.25 bar) for a liquid-phase containing an ammonia mole fraction of x_{NH3} (-); T_d is the dew temperature (K) of the ammonia-water mixture at P for a vapour phase containing an ammonia mole fraction of y_{NH3} (-); T_0 is the reference temperature (100 K); P_0 is the reference pressure (20 bar); a_i , m_i and n_i are empirical coefficients (Pátek and Klomfar, 1995).

2.3 Results and discussion

2.3.1 Validation of empirical dew point as the upper limit for two-phase region

To characterise vacuum thermal stripping close to the empirical dew point and evaluate performance against previous literature, an initial experiment was conducted at 65°C and 0.25 bar. This corresponded to the high mass transfer

region identified along the pure water boiling curve (Figure 2.4) (Ukwuani and Tao, 2016). At this condition, 98%wt ammonia was stripped from the feed after 2.3 h (Figure 2.5). The rate of ammonia removal declined over time, as the driving force for mass transfer became limiting (Eq. 2.4). The volumetric mass transfer coefficient for ammonia was determined as 1.4 h^{-1} (Figure A2). When normalised against the interfacial surface area of the stripping vessel ($16 \text{ m}^2 \text{ m}^{-3}$), this provided a mass transfer coefficient of 88 mm h^{-1} . This is comparable to published data for vacuum thermal stripping of real ammoniacal wastes ($21\text{-}106 \text{ mm h}^{-1}$) at equivalent conditions along the pure water boiling curve (Table 2.3). Ammonia removal had negligible impact on the mass fraction of water in the feed ($x_{\text{H}_2\text{O}} > 0.998$), and therefore on water vapour pressure (Appendix A2). This was evidenced by the stable rate of water vapourisation throughout (2 mol h^{-1}). Consequently, there was a decline in ammonia selectivity as the separation progressed (Figure 2.5). At 65°C , the equilibrium vapour pressures for water and ammonia were estimated to be 0.249 bar and 0.008 bar using Henry's Law, respectively (Figure 2.6). Ammonia selectivity, therefore, is expected to be in the region of 0.03 which is in close agreement with the experimental results (Eq. 2.10). This evidences that the empirical dew point curve predicted for the solution was consistent with the feed saturation curve. Limited data is available for the composition of ammonia products from vacuum thermal stripping, as the vapour is typically delivered into a downstream acid scrubber for ammonia capture (Han et al., 2022; Tao et al., 2019, 2018; Ukwuani and Tao, 2016). In an example of vapour condensation, Guida et al. (2022) recovered 0.4%wt aqueous ammonia after stripping a 0.6 g L^{-1} feed. In this work, a 2.1%wt ammonia vapour was recovered after the same period of stripping. This is consistent with the higher initial feed concentration and therefore the higher ammonia vapour pressure during the separation (Bavarella et al., 2020).

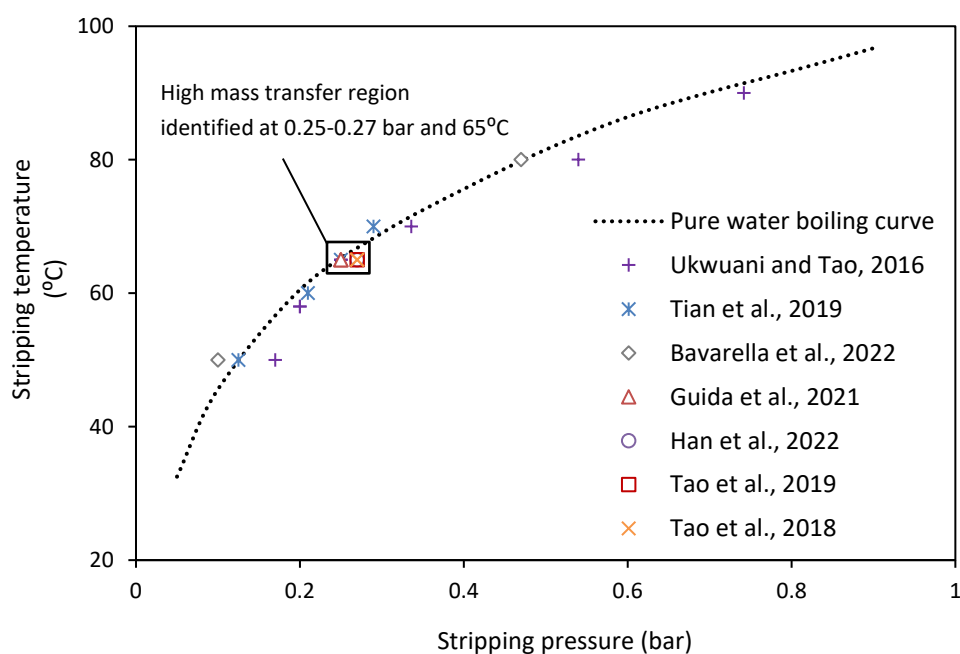


Figure 2.4 Operating points for vacuum thermal stripping in previous work, placed within the context of the pure water boiling curve from 0-1 bar.

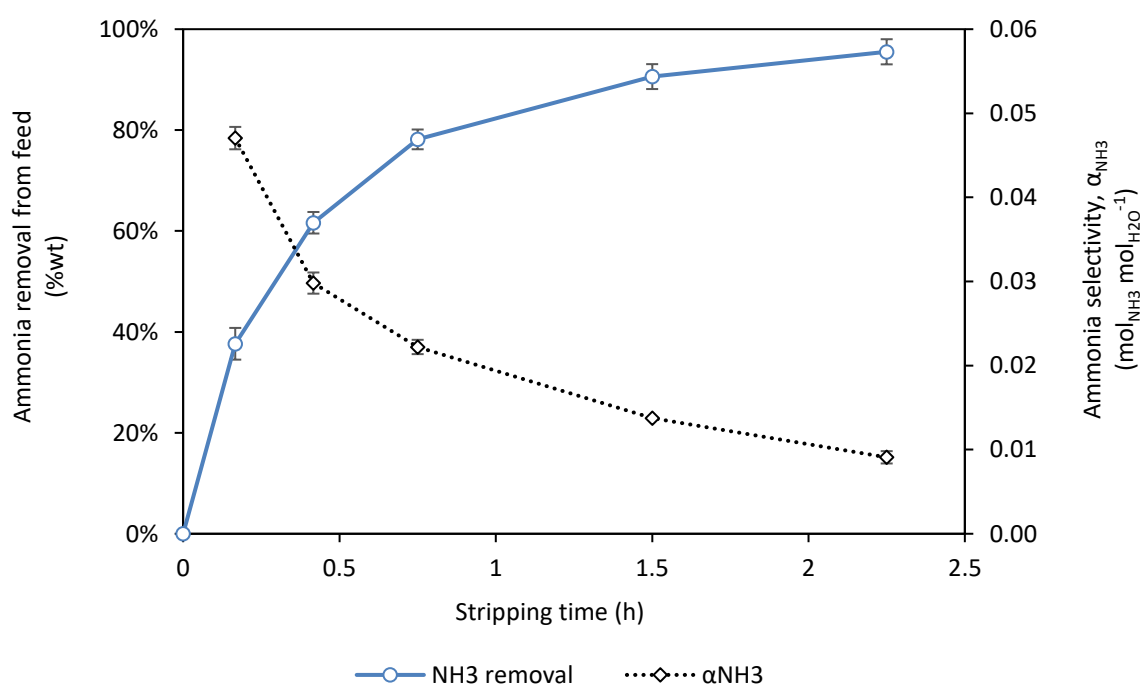


Figure 2.5 Vacuum thermal stripping of synthetic wastewater at 65°C and 0.25 bar. Operational conditions: $C_{\text{NH}_3,0}$, 1.5 g L⁻¹; initial feed mass, 0.5 kg; pH, 11; condenser temperature, 3-5°C.

Table 2.3: Literature comparison for vacuum stripping ammoniacal wastes at 0.25-0.27 bar close to the dew point of the feed.

Feed	C _{NH3,0} g L ⁻¹	η _{NH3} %	pH	P bar	T °C	HRT h	k _{La} h ⁻¹	a m ² m ⁻³	k _L mm h ⁻¹	Product	Reference
Synthetic wastewater	1.5	79%	11.0	0.25	65	0.8	1.4	16.0	88	2.1%wt _(v) ^c	This study
Synthetic wastewater	1.5	98%	11.0	0.25	65	2.3	1.4	16.0	88	0.9%wt _(v) ^c	
Synthetic wastewater	0.6	74%	10.0	0.25	65	0.8	1.7	16.0	106 ^c	0.4%wt _(aq) ^c	Guida et al. (2022)
Ion exchange brine	0.6	44%	10.0	0.25	65	0.8	0.7	16.0	44 ^c	0.4%wt _(aq) ^c	
Co-digestate	2.1	95%	9.5	0.27	65	6.0	0.5 ^a	7.6 ^b	67 ^c	(NH ₄) ₂ SO _{4 (aq)}	Han et al. (2022)
Hydrolysed urine	10.0	72%	9.3	0.27	65	12.0	0.1	5.0 ^b	21 ^c	(NH ₄) ₂ SO _{4 (aq)}	Tao et al. (2019)
Municipal digestate	1.0	93%	9.0	0.27	65	5.0	0.6	5.9 ^b	100 ^c	(NH ₄) ₂ SO _{4 (aq)}	Tao et al. (2018)
Dairy digestate	1.9	63%	9.0	0.27	65	5.0	0.2	5.9 ^b	32 ^c	(NH ₄) ₂ SO _{4 (aq)}	
Dairy digestate	1.6	96%	9.0	0.25	65	1.5	0.6	16.1 ^b	37	(NH ₄) ₂ SO _{4 (aq)}	Ukwuani and Tao, (2016)
Municipal digestate	1.1	28%	9.0	0.25	65	2.0	0.2 ^a	6.6 ^b	24 ^c	(NH ₄) ₂ SO _{4 (aq)}	

T – temperature; P- pressure

^a Calculated based on data provided (Eq. 2.5)^b Calculated based on geometry of stripping reactor and feed volume^c Ammonia concentration in recovered product

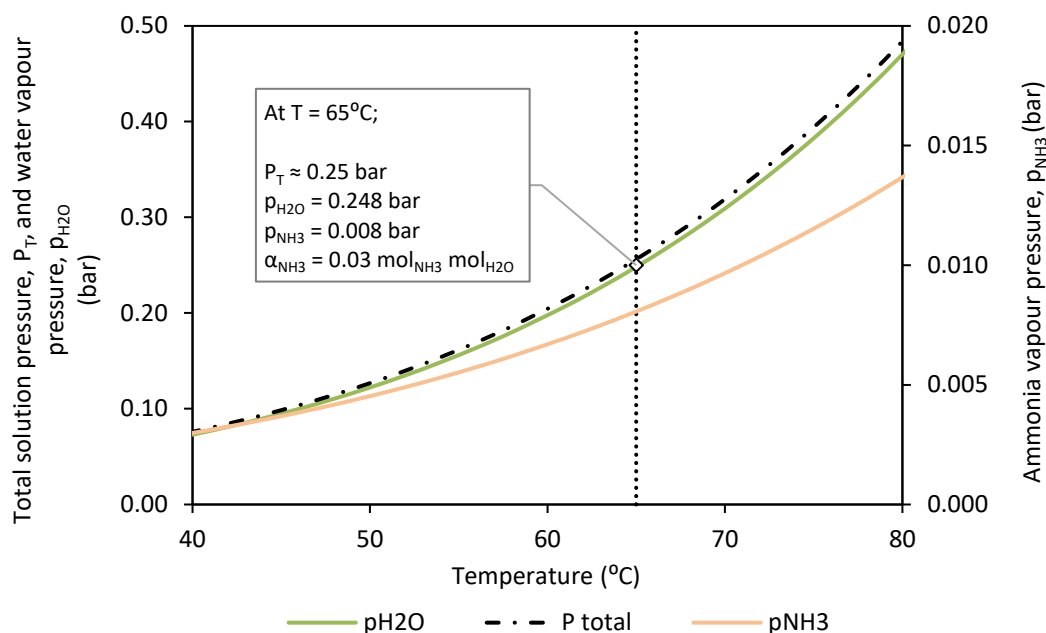


Figure 2.6 Influence of temperature on the vapour pressure of water determined by Raoult's Law and of ammonia determined by Henry's Law for a 1.5 g L^{-1} ammonia solution (Appendix A2).

2.3.2 Expanded two-phase region determined for selective ammonia separation

The stripping temperature was reduced from 65 to 61°C at 0.25 bar to investigate the extent to which ammonia-water selectivity could be modified when transitioning across the two-phase region of the VLE. The rate of ammonia mass transfer was substantially influenced by the stripping temperature across this narrow range (Figure 2.7a). Since the mass transfer driving force and the interfacial area were constant across all experiments, the direct influence of temperature on the ammonia mass transfer coefficient could be calculated (Eq. 2.5) (Salavera et al., 2005; Ukwuani and Tao, 2016). The mass transfer coefficient reduced from 88 mm h^{-1} at 65°C to 40 and 10 mm h^{-1} at 63°C and 61°C , respectively (Figure A2). Consequently, when compared after 1.5 h stripping then 91 , 66 and 23% wt ammonia removal was achieved at 65°C , 63°C and 61°C , respectively. Operating below the pure water boiling temperature (65°C at 0.25 bar), and therefore below the activation energy threshold necessary for bulk evaporation, also greatly restricted water transport during stripping (Figure 2.7b) (Prado and Vyazovkin, 2011). This is consistent with thermal stripping at atmospheric pressures where water vapourisation reduced by an

order of magnitude when temperature was reduced from 102 to 86°C (Tao and Ukwuani, 2015). Since lowering the temperature had a disproportionately greater impact on the vapourisation of water during stripping, it subsequently enhanced the selectivity for ammonia transport (Figure 2.8). When stripping at 63 and 61°C, an enhancement in ammonia selectivity of up to 1 and 2 orders of magnitude was observed, respectively, compared to 65°C. Unlike stripping at 65°C, the results strongly deviate from the theoretical selectivity based on the equilibrium vapour pressures of water and ammonia using Henry's Law ($\alpha_{\text{NH}_3} \approx 0.033\text{-}0.034$). This highlights a discontinuity in the ammonia-water separation behaviour when stripping below the dew point and entering the two-phase region. Interestingly, selective ammonia separation was demonstrated beyond the two-phase region initially proposed within the VLE, as estimated by extrapolation from ammonia-water mixtures across a higher concentration range relevant for absorption refrigeration (Pátek and Klomfar, 1995). In practice, solute-solvent interactions will affect the strength and type of intermolecular forces between ammonia and water, which can introduce uncertainty for individual component volatilities (Atkins and De Paula, 2006; Tan et al., 2004). Further complexity is introduced by the polar contribution of ammonia bonds which will influence interactive forces between molecules (Atkins and De Paula, 2006). These effects may be compounded by the highly dilute nature of the feed, therefore reducing the empirical predictability of the ammonia-water separation. Interestingly, the separation appears to conform more closely to the two-phase region bounded by the bubble point curve derived from Raoult's Law, which considers a mixture of two pure components (Figure 2.9) (Appendix A2). A Raoult's Law approach predicts ammonia selectivity to be an order of magnitude greater due to the higher contribution of ammonia towards the total vapour pressure and is therefore a closer approximation for experimental selectivity measured at 63 and 61°C. Reducing stripping temperature across this experimentally determined two-phase region enhances selectivity for ammonia, while simultaneously lowering the rate of ammonia mass transfer consistent with the principles of distillation. Whilst ammonia selectivity at 61°C appears to have exceeded the theoretical limits of the VLE, the low vapour velocity at this condition may have facilitated partial water

condensation and vapour rectification within the boundary of the reactor, analogous to the installation of a demister at the reactor outlet (Ukwuani and Tao, 2016).

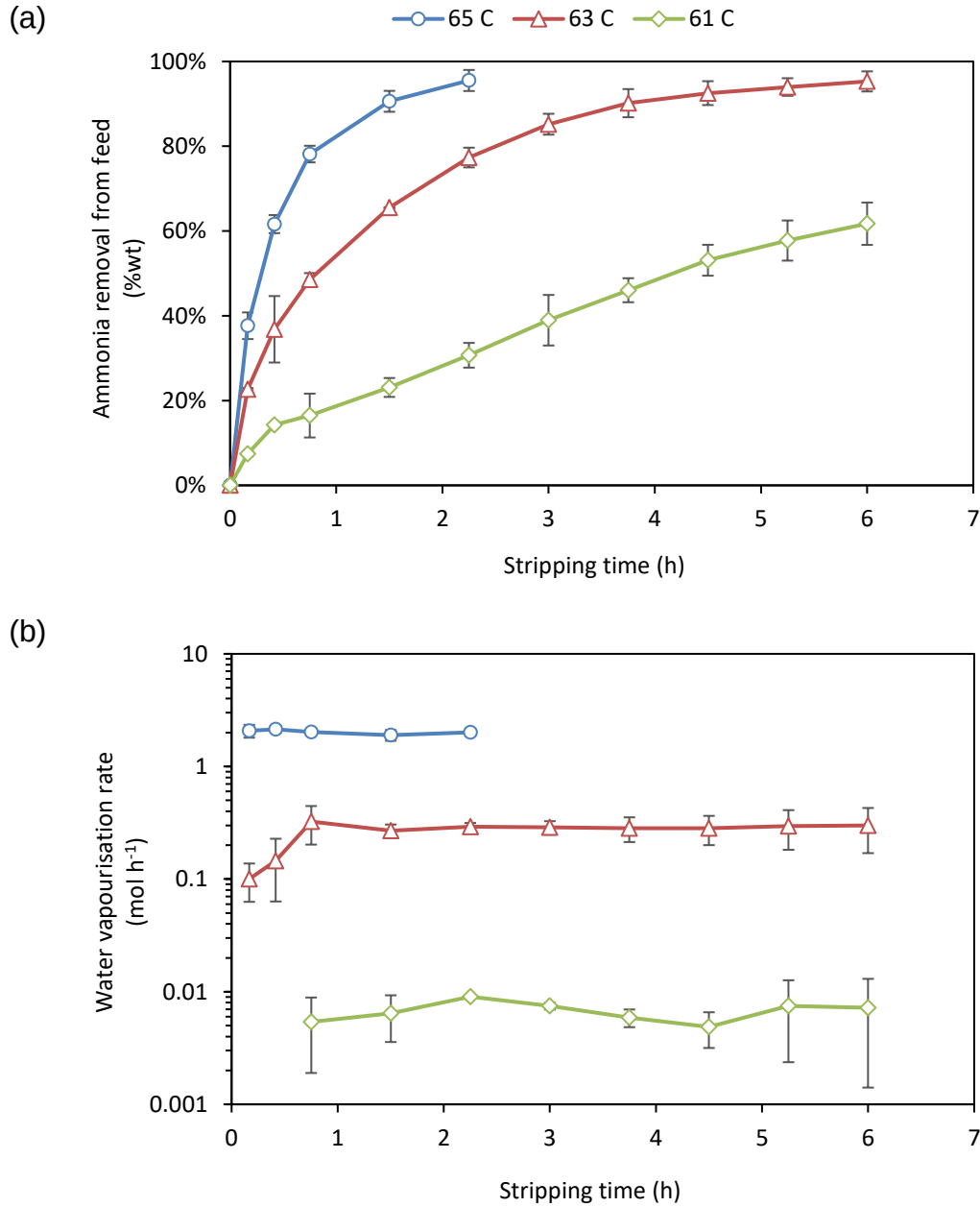


Figure 2.7 Influence of temperature during vacuum thermal stripping of synthetic wastewater at 0.25 bar on (a) ammonia removal from the feed and (b) the water vapourisation rate. Operational conditions: initial C_{NH_3} , 1.5 g L^{-1} ; initial feed mass, 0.5 kg; pH, 11; condenser temperature, 3-5°C.

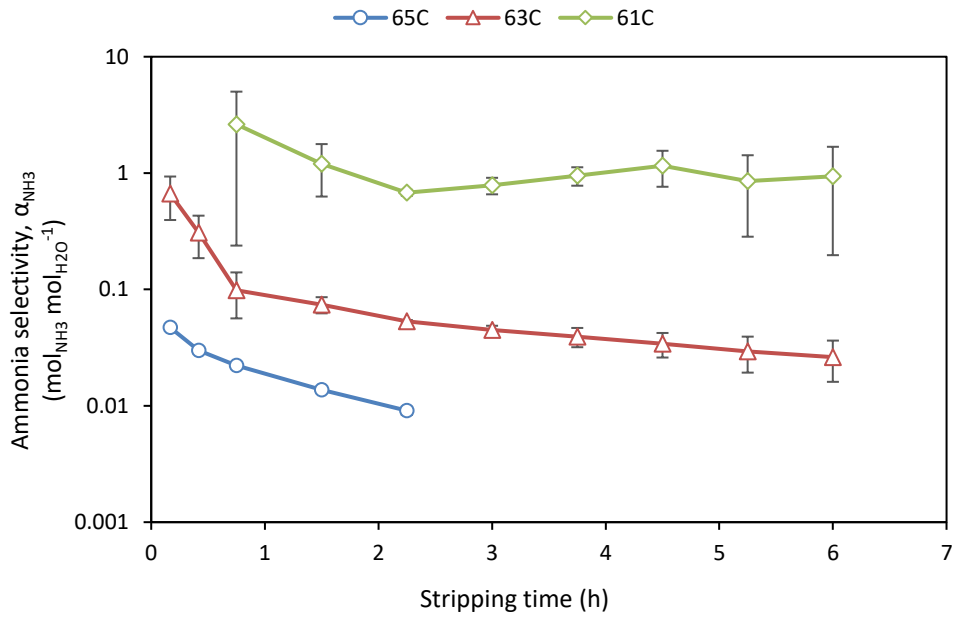


Figure 2.8 Ammonia selectivity during vacuum thermal stripping of synthetic wastewater at 65, 63 and 61°C and 0.25 bar. Operational conditions: initial C_{NH_3} , 1.5 g L⁻¹; initial feed mass, 0.5 kg; pH, 11; condenser temperature, 3-5°C.

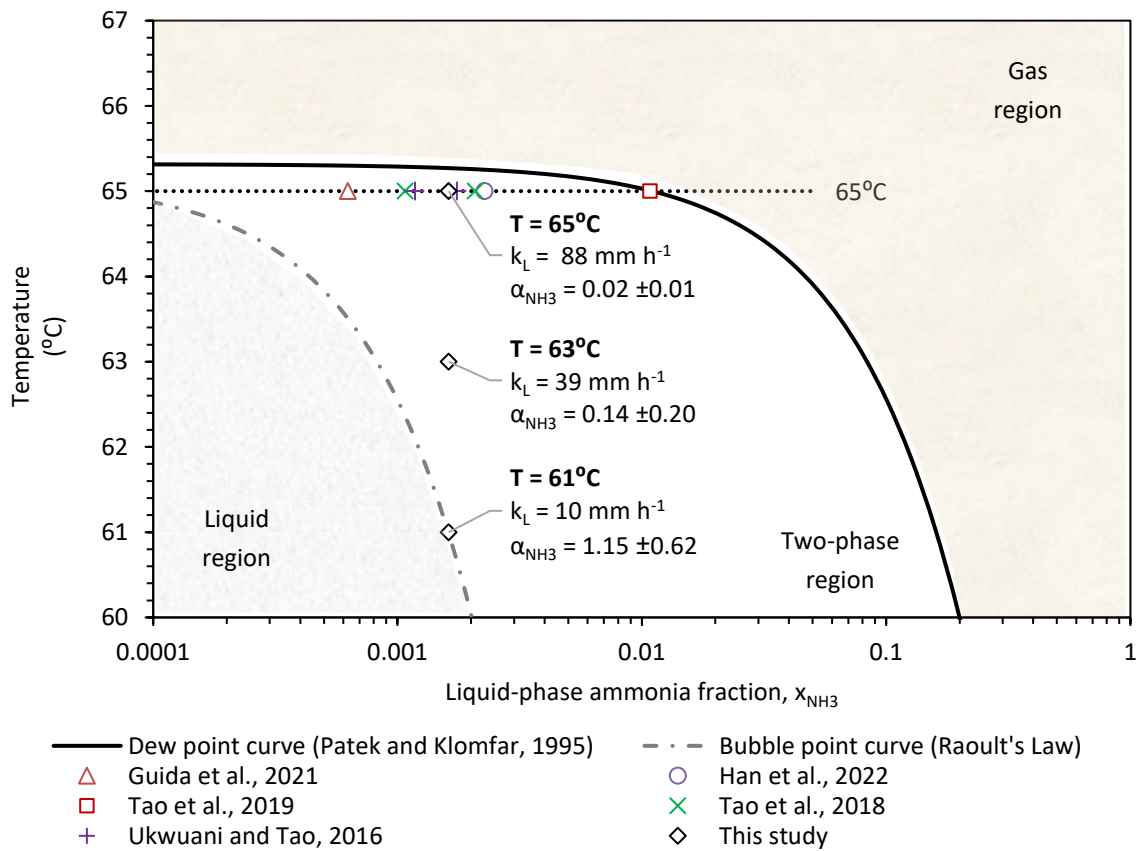


Figure 2.9 Experimental ammonia vapour quality during transition through two-phase region plotted on VLE for NH₃-H₂O at 0.25 bar.

2.3.3 Stripping within two-phase region supports ammonia to energy strategies

Manipulation of the stripping temperature within the two-phase region defined in this work could facilitate low energy, high purity ammonia recovery and has implications for ammonia to energy flowsheets within wastewater treatment. At 65°C, low ammonia selectivity led to the production of vapour containing 1-5%wt ammonia (Figure 2.10a). Substantial water vapourisation incurred a high latent heat penalty of up to 91 kWh_{th} kg_N⁻¹ (Figure 2.10b). The dilute vapour could be directly condensed to produce aqueous ammonia for utilisation in low temperature alkaline fuel cells (AFC) or for electrolytic hydrogen production (Table 2.1) (Davey et al., 2022; Lan and Tao, 2014; Vitse et al., 2005). Increasing the ammonia concentration will significantly enhance fuel cell power density or increase the rate of hydrogen evolution, therefore reducing cell size and cost (Cheddie, 2012; Davey et al., 2022; Zhang et al., 2020). This could be achieved by reducing the stripping temperature to 63°C to generate concentrated ammonia vapour in the range 2-38%wt. This is of sufficient quality to directly fuel a high efficiency solid oxide fuel cell (SOFC) which would avoid an intermediate condensation stage, liquid handling and the associated energy demand and exergy losses (van Linden et al., 2022). Alternatively, the addition of a downstream rectification stage could reduce the water content and increase the gas-phase ammonia concentration to enhance SOFC power density and expand options for energy generation (Teichgraber & Stein, 1994). Reduced water transport at 63°C will limit the latent heat penalty below 35 kWh_{th} kg_N⁻¹. By further reducing the stripping temperature to 61°C, a 43-64% ammonia vapour was generated. Removal of the excess water vapour using a chiller or an advanced dehumidification process (e.g., desiccant coated heat exchanger) could produce a pure ammonia gas product to fuel an SOFC, co-fire a biogas turbine, be cracked into hydrogen or liquified to produce anhydrous ammonia (Venegas et al., 2021). Very high ammonia selectivity at 61°C means that the production of the most energy dense and flexible ammonia product is associated with the lowest latent heat penalty (1 kWh_{th} kg_N⁻¹). To overcome the limited rates of mass transfer observed when operating at higher selectivity, translation from a batch vessel to a continuous stripping column may be necessary. Packed columns will facilitate

intensified rates of ammonia mass transfer by providing a high interfacial area. Vacuum thermal stripping close to the bubble point ($k_L = 10 \text{ mm h}^{-1}$) in a packed column with an interfacial area of $400 \text{ m}^2 \text{ m}^{-3}$ could theoretically provide a volumetric mass transfer coefficient of 3.4 h^{-1} . Mass transfer could then become competitive with thermal air strippers ($3\text{-}5 \text{ h}^{-1}$) employed commercially for ammonia removal from concentrated wastewaters (Guštin and Marinšek-Logar, 2011; Jiang, 2009; RVT, 2015).

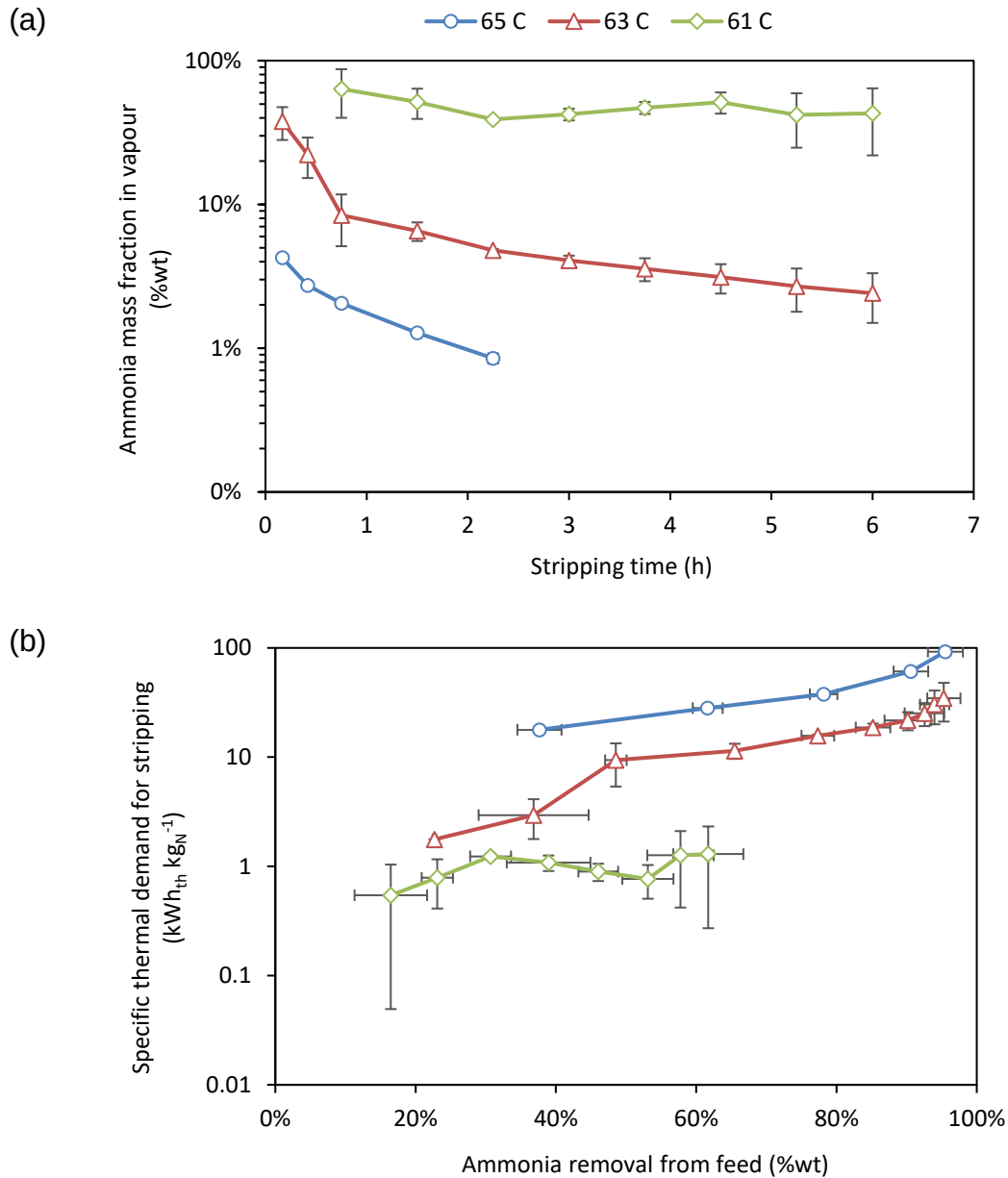


Figure 2.10 Influence of temperature during vacuum thermal stripping of synthetic wastewater at 0.25 bar on (a) the mass fraction of ammonia in the vapour phase and (b) the specific thermal demand for ammonia stripping. Operational conditions: initial C_{NH_3} , 1.5 g L^{-1} ; initial feed mass, 0.5 kg; pH, 11; condenser temperature, $3\text{-}5^\circ\text{C}$.

2.3.4 Predictable ammonia-water separation behaviour for wastewater

Vacuum thermal stripping was conducted using complex wastewaters to compare ammonia-water separation behaviour to that achieved within synthetic wastewater, to validate the industrial relevance of the VLE for product quality control. Vacuum stripping was operated close to the dew point (65°C, 0.25 bar) on two centrates of distinct provenance (Table 2.2). Centrate A was produced from a conventional AD plant and comprised a dissolved ammonia concentration of 1.0 g L⁻¹, whereas Centrate B originated from an advanced AD (AAD) plant and had an ammonia concentration of 2.0 g L⁻¹. The higher ammonia concentration in Centrate B arises from the thermal hydrolysis of raw sludge in AAD. Thermal hydrolysis breaks down organic matter through intracellular lysis to increase the availability of microbial nutrients and enhance biogas yield (Wilson and Novak, 2009). During this process, the dissolved ammonia concentration increases due to the conversion of organic nitrogen and the hydrolysis of proteins in the sludge (Ndam, 2017; Wilson and Novak, 2009). This disruption of cell and floc structure also alters the wider matrix chemistry which can increase the concentration of dissolved organic matter, gases and volatile compounds within the liquid-phase which could interact with the ammonia-water separation (Bougrier et al., 2008; Ndam, 2017). After 1.5 h stripping, 88%wt and 86%wt ammonia was removed from Centrate A and B, respectively (pH 11, Figure 2.11a). Ammonia mass transfer coefficients were 95 and 87 mm h⁻¹ for Centrate A and B, respectively, comparable to that of synthetic wastewater at the same condition (88 mm h⁻¹) (Figure A3). A greater ammonia selectivity was observed for Centrate B, in line with its higher concentration and higher ammonia vapour pressure (Figure 2.11b). Similar to stripping synthetic wastewater close to the dew point, the experimentally derived selectivity was in good agreement with theoretical values predicted by Henry's Law for Centrate A ($\alpha_{\text{NH}_3} \approx 0.02$) and Centrate B ($\alpha_{\text{NH}_3} \approx 0.04$). Consequently, the results indicate that despite the complex characteristics and presence of other dissolved species within real wastewater, the ammonia-water separation behaviour can be described through the binary VLE. After 1.5 h stripping, condensate produced from Centrate A had the lowest concentration (0.8%wt) whilst condensate from Centrate B had the

highest concentration (1.9%wt) (Table 2.4). This reflected the higher initial concentration in Centrate B and therefore the greater driving force for ammonia mass transfer (Eq. 2.4). Both centrates yielded colourless condensate (Figure A4). Interestingly, soluble COD of 0.42 and 0.24 g L⁻¹ was present in condensate from Centrate A and Centrate B, respectively. This indicates that volatile organic compounds (VOCs) were co-transported during stripping. The presence of VOCs may explain why pH values were lower than expected, when compared against synthetic ammonia solutions of equivalent concentration (Davey et al., 2022). While further work is required, it may be possible to reduce VOC transfer by stripping within the two-phase region where water evaporation is limited to subsequently minimise product contamination. Mitigating the co-transport of dissolved compounds during stripping could have particular significance for the efficiency or lifetime for downstream generation technologies. For example, trace amounts of hydrogen sulphide (>1.0 mg m⁻³) and siloxanes (>0.2 mg m⁻³) which are present in wastewater can cause fatal cell degradation in SOFC (Papadias and Ahmed, 2012; Sasaki et al., 2011).

Table 2.4: Outcomes for vacuum thermal stripping synthetic and real wastewater for 1.5 h at 65°C and 0.25 bar

Parameter	Synthetic wastewater	Centrate A	Centrate B
Ammonia removal (%wt)	90%	88%	86%
k _L (mm h ⁻¹)	88	95	87
Ammonia fraction in condensate (%wt)	1.3%	0.8%	1.9%
Condensate pH (-)	12.2	9.8	10.5 ^a
Condensate sCOD (g L ⁻¹)	-	0.42	0.24 ^a

^aValues originally published by Davey et al. (2022)

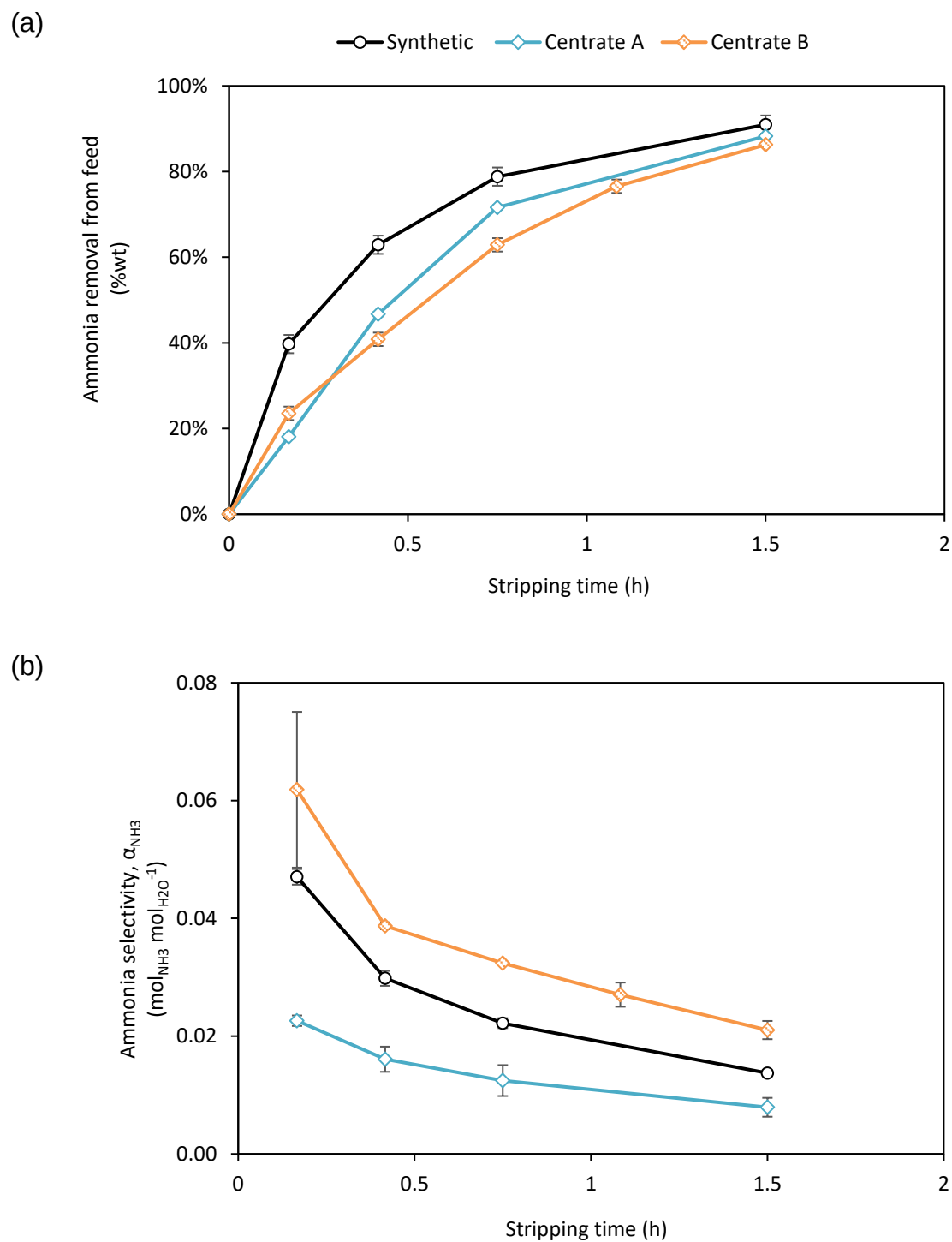


Figure 2.11 (a) Ammonia removal and (b) ammonia selectivity over time during vacuum thermal stripping of synthetic wastewater, Centrate A and Centrate B at 65°C and 0.25 bar. Operational conditions: initial feed mass, 0.5 kg; pH, 11; condenser temperature, 3-5°C.

2.3.5 *In-situ decarbonisation facilitates chemical-free vacuum thermal stripping*

Raising the wastewater pH will increase the fraction of free ammonia and therefore favour mass transfer rate, selectivity and energy demand during vacuum thermal stripping (Figure A1). Increasing Centrate A and B from pH 7.8 and 8.0 up to pH 11 demanded 135 and 275 mol_{NaOH} m⁻³, respectively (Figure A5). The increased chemical demand for Centrate B was consistent with its higher pH buffering capacity as indicated by alkalinity (Table 2.2). To overcome high buffering capacities within concentrated wastewaters, chemical addition for pH amendment will incur a substantive cost to ammonia recovery and is contrary to strategic roadmaps for net zero carbon and low chemical wastewater treatment (Water Europe, 2021; Water UK, 2020). Direct stripping of Centrate A and B without pH amendment was explored as an alternative treatment option (Figure 2.12). Interestingly, both centrates exhibited a rapid increase in pH during vacuum thermal stripping at 65°C and 0.25 bar. After 0.2 h, both feeds had increased above pH 9. After 1.5 h, a 67% and 80% decline in total inorganic carbon was observed for Centrate A and B, respectively, indicating that CO₂ desorption had occurred during stripping. Dissolved CO₂ contributes to wastewater acidity and decarbonisation by air stripping at low gas-liquid ratios has been previously explored for chemical-free pH amendment prior to ammonia stripping (Kang et al., 2017; Cohen & Kirchmann, 2004). In this work, a maximum pH of 9.4 was achieved during stripping. This is consistent with the bicarbonate equilibrium, which indicates that less than 0.01% free CO₂ is available above pH 9.4, limiting further decarbonisation beyond this point (Bavarella et al., 2022; Kang et al., 2017). Thus, the increase in feed pH by CO₂ stripping enabled continuous ammonia stripping without pH amendment. After 1.5 h, 69%wt and 65%wt ammonia had been removed from Centrate A and B, respectively. Based on the stable trajectory of ammonia removal and the final pH (9.2) after 1.5 h, it is likely that ammonia removal would have continued if the experimental stripping period had been extended. However, the fraction of ammonia removal was lower than observed for Centrate A and B at initial pH 11 under the same stripping conditions after 1.5h (Figure 2.11a). A lower rate of ammonia removal indicates that a lower fraction of free ammonia (Φ) was available during stripping, therefore

reducing the mass transfer driving force (Eq. 2.4). This is consistent with the chemistry of ammonia speciation at 65°C, which suggests that operating at pH 11 will release 100% free ammonia whilst operating at pH 9 will release 92% free ammonia (Figure A1). In accordance with Le Châtelier's principle, the continuous removal of ammonia from solution will prompt the breakdown of ammonium and develop a dynamic chemical equilibrium (Eq. 2.1) (Licon Bernal et al., 2016). This enables ammonia removal to progress at a stable rate in systems where less than 100% free ammonia is available at any time. The breakdown of ammonium is associated with the release of protons which can lower the solution pH. This was observed during ammonia extraction from batches of dilute wastewater using membrane contactors where regular addition of alkali was necessary to maintain a high pH and facilitate a consistent rate of mass transfer (Licon Bernal et al., 2016). In this work, pH values for Centrate A and B were relatively consistent despite progressive ammonia removal. This can be attributed to the high buffering capacity of centrate to resist pH change, which supported continuous chemical-free ammonia stripping from the complex wastewater matrix.

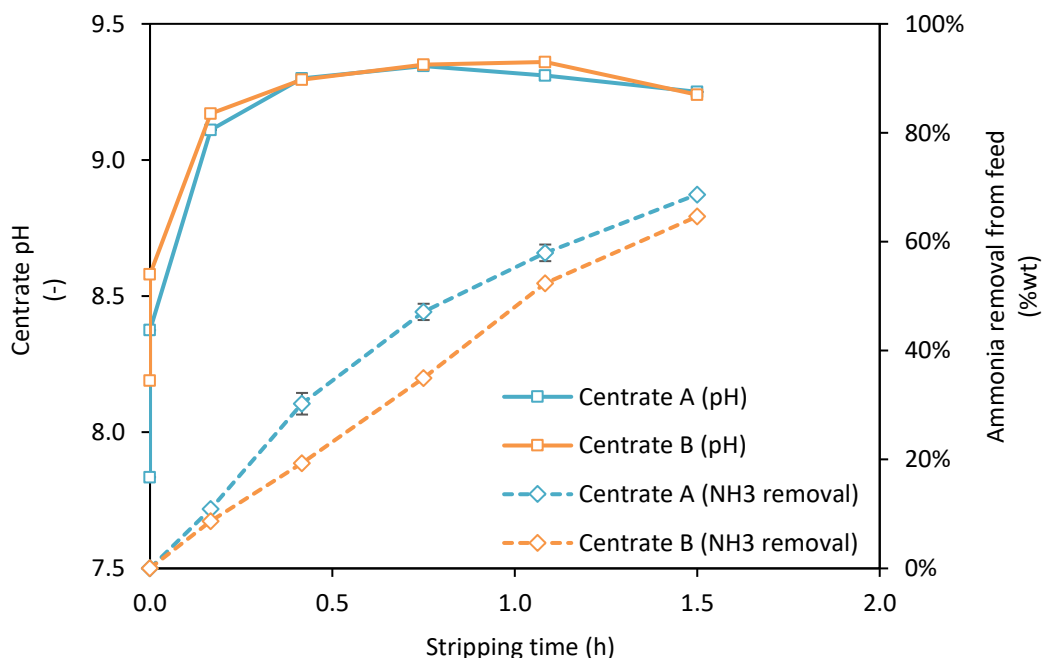


Figure 2.12 Vacuum thermal stripping of Centrate A and Centrate B at their natural pH at 65°C and 0.25 bar. Centrate A: initial C_{NH_3} , 1.0 g L⁻¹ and initial pH, 7.8. Centrate B: initial C_{NH_3} , 2.0 g L⁻¹ and initial pH, 8. Operational conditions: initial feed mass, 0.5 kg; pH measurements conducted at 21°C.

2.4 Conclusion

This is the first study to demonstrate an enhancement in ammonia selectivity during vacuum thermal stripping of wastewater by transitioning through the two-phase region of the VLE. When stripping close to the predicted dew point for the solution at 0.25 bar (65°C), the ammonia mass transfer coefficient was consistent with published data whilst ammonia selectivity agreed closely with both Henry's Law and empirical modelling for the VLE. Lowering the stripping temperature below 65°C into the two-phase region led to a substantial enhancement in ammonia selectivity. Selective ammonia mass transfer was demonstrated to occur below the lower boundary of the two-phase region which had been projected using an existing empirical model. This deviation may have resulted from the highly dilute nature of ammonia in wastewater ($x_{\text{NH}_3} < 0.002$) in combination with complex intermolecular forces arising from both solute-solvent interactions and the polar nature of the ammonia molecule. Consequently, the results indicate that Raoult's Law which considers a mixture of pure components could offer a more accurate description of ammonia vapour pressure in the expanded two-phase region. Lowering the stripping temperature from 65°C to 61°C reduced the thermal demand for ammonia recovery by >98% to 1 kWh_{th} kg_N⁻¹. This compares to 3-5 kWh_e kg_N⁻¹ for mainstream biological nitrogen removal. As a thermally driven process, vacuum thermal stripping could recover sensible heat within the system boundary to reduce external heat demand. In the context of a centralised wastewater treatment works, low-cost intrinsic heat sources may also be available due to onsite biogas combustion. Where extrinsic heating is required, the costs for the importation of 1 unit of heat (kWh_{th}) is historically 4-5 times lower than 1 unit of electricity (kWh_e) (Department for Business, Energy and Industrial Strategy, 2022). Consequently, the recovery of ammonia from concentrated sidestreams by vacuum thermal stripping presents an energetically and economically favourable solution for nitrogen removal. Furthermore, enhancing ammonia selectivity will increase the energy density, flexibility and value of the recovered ammonia product. This could facilitate its utilisation as zero carbon energy resource within the water sector to support wider decarbonisation objectives. Since the increase in selectivity is associated with a

reduction of the ammonia mass transfer coefficient, process intensification will be necessary to support acceptable rates of mass transfer at full-scale. This could be achieved by the translation of vacuum thermal stripping from batch reactors to gas-liquid contacting columns and should be the focus of future work.

When stripping at a fixed condition, comparable ammonia mass transfer coefficients were observed for synthetic ammonia solution and for centrates originating from conventional and advanced anaerobic digestion processes. This indicates that the presence and concentration of dissolved gases, volatile organic compounds and organic matter within the wastewater matrix did not substantively influence the ammonia-water separation or the relative operating position within the VLE. This could enable simple translation for the process across different wastewater feeds. The reliance on pH amendment of wastewater by the addition of alkali could result in high operational costs and poor sustainability criteria for full-scale ammonia recovery. The feasibility for chemical-free stripping of centrate has been demonstrated in this work. This was facilitated by the rapid desorption of dissolved CO₂ during vacuum thermal stripping which raised the centrate pH. It is proposed therefore, that chemical-free vacuum thermal stripping of concentrated wastewaters could be conducted within a single process unit and when operated within the two-phase region, could be complemented by the energy efficient production of a rich ammonia product for use in the emerging ammonia and hydrogen economy.

Acknowledgements

We are grateful for the financial and technical support offered by Anglian Water, Northumbrian Water and Severn Trent Water. We also acknowledge the funding and training resources provided to Benjamin Luqmani from the Engineering and Physical Sciences Research Council through the STREAM Industrial Doctorate Centre. Data underlying this paper can be accessed at: *(DOI to be completed following peer review)*.

Appendix A

A1 Supplementary figures

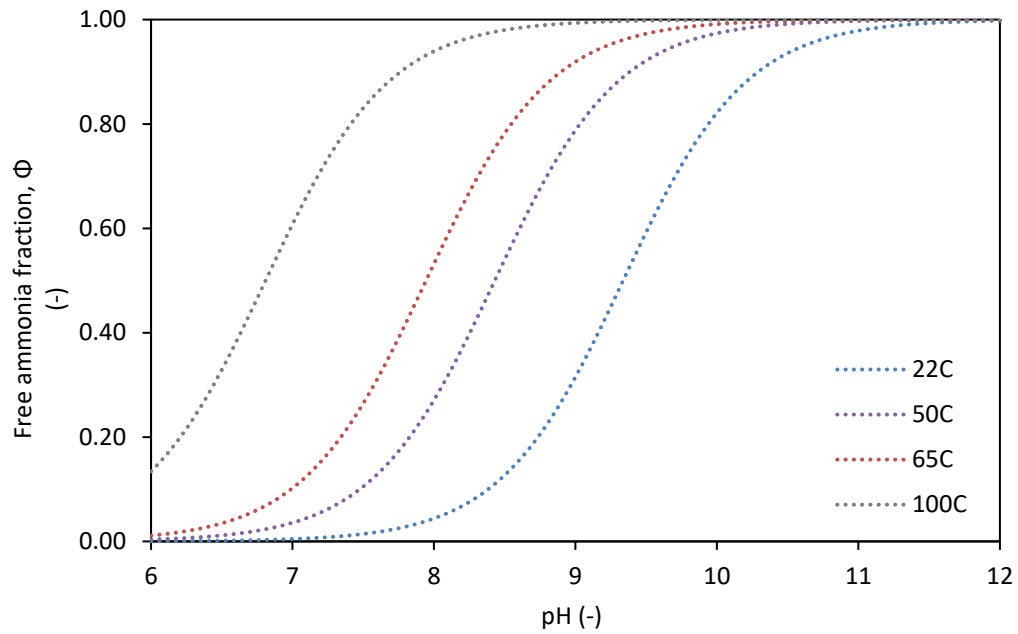


Figure A1 Estimated influence of temperature and pH on free ammonia in solution (Eq. 2.2)

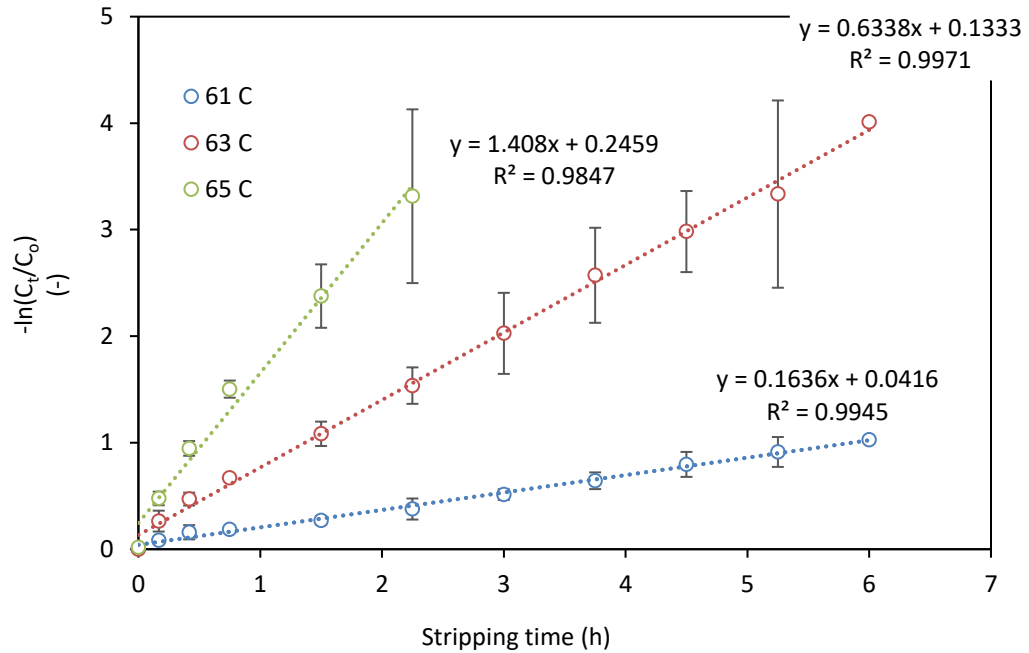


Figure A2 Graphical determination of k_{La} when vacuum thermal stripping synthetic wastewater at 65, 63 and 61°C and 0.25 bar (Eq. 2.5).

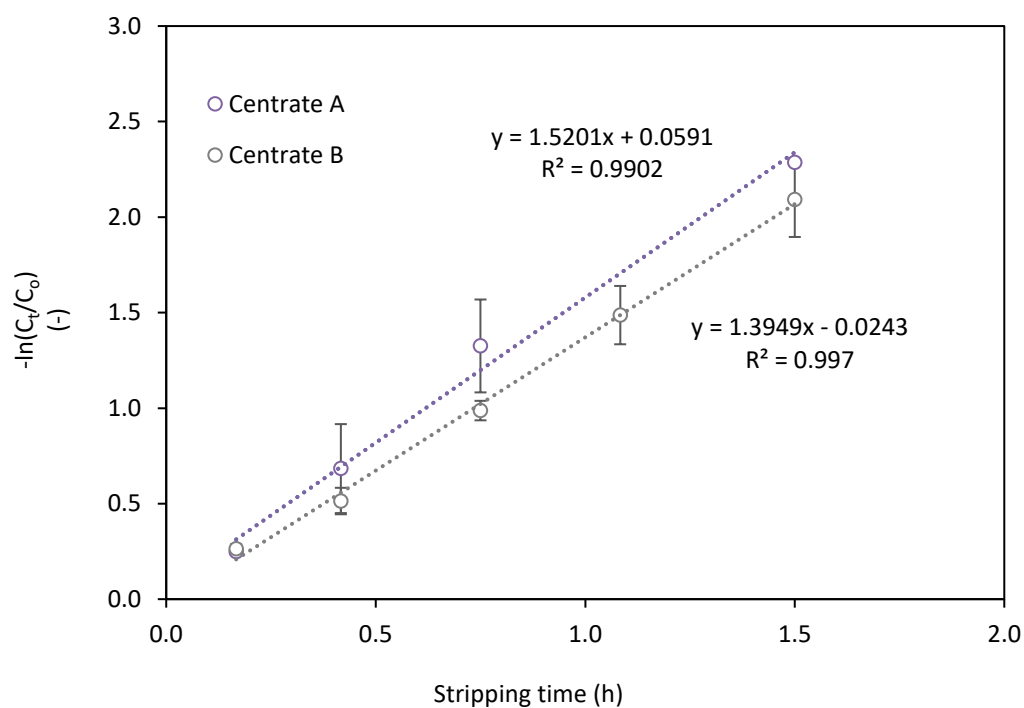


Figure A3: Graphical determination of k_{La} when vacuum thermal stripping Centrate A and Centrate B at 65°C and 0.25 bar (Eq. 2.5).

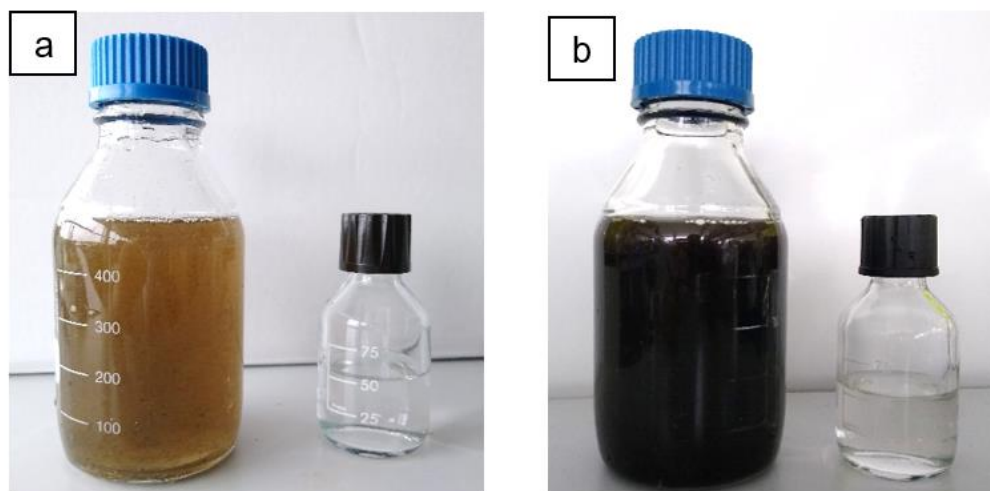


Figure A4: Wastewater centrates with their respective condensates after 1.5 h stripping. (a) Centrate A from conventional AD and condensate; (b) Centrate B from advanced AD and condensate.

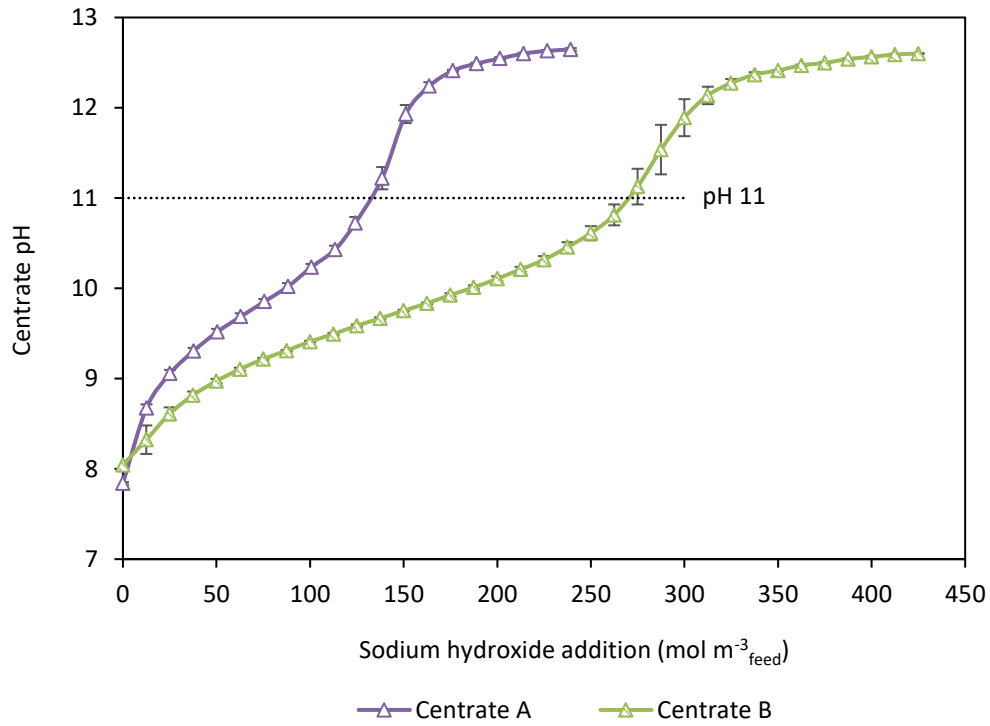


Figure A5 Sodium hydroxide dosing curves for Centrate A and Centrate B. pH measurements conducted at 21°C.

A2 Raoult's Law and Henry's Law for determining vapour pressures

Raoult's Law estimates the vapour-liquid equilibrium for a mixture of pure components (Eq. A1-A2). To generate an associated bubble point curve, Eq. A3 was resolved at 0.25 bar over $x_{NH3} = 0-0.2$.

$$p_{NH3} = x_{NH3} P_{NH3}^{\circ} \quad (\text{Eq. A1})$$

$$p_{H2O} = (1 - x_{NH3}) P_{H2O}^{\circ} \quad (\text{Eq. A2})$$

$$P_T = x_{NH3} P_{NH3}^{\circ} + (1 - x_{NH3}) P_{H2O}^{\circ} \quad (\text{Eq. A3})$$

$$\log_{10}(P_i) = A_i - \frac{B_i}{T_K + C_i} \quad (\text{Eq. A4})$$

where p_{NH3} and p_{H2O} represent the partial pressures of ammonia and water estimated by Raoult's Law respectively (bar); P_T is the total solution pressure (bar); P_{NH3}° and P_{H2O}° are the pure component vapour pressures at the operating temperature T_K (K) determined by the Antoine equation (Eq. A4) (bar); i represents the ammonia or water; and A_i , B_i and C_i represent empirical coefficients (National Institute of Standards and Technology (NIST), 2021a,

2021b). Henry's Law is typically applied for describing the vapour-liquid equilibrium behaviour of highly dilute solutes (i.e., ammonia in wastewater):

$$p_{NH_3} = \frac{C_{NH_3}}{k_{H(T)}} \quad (\text{Eq. A5})$$

$$k_{H(T)} = k_H^0 e^{\left[A_H \left(\frac{1}{T} - \frac{1}{298}\right)\right]} \quad (\text{Eq. A6})$$

where p_{NH_3} is the vapour pressure for ammonia estimated by Henry's Law and $k_{H(T)}$ is the Henry's coefficient for ammonia in water ($\text{mol L}^{-1} \text{ bar}^{-1}$) at the temperature T_K ; k_H^0 is the Henry's coefficient for ammonia in water at 298 K ($59 \text{ mol L}^{-1} \text{ bar}^{-1}$) and A_H is the temperature dependence constant (4200 K) (Sander, 2015).

References

- Anglian Water. (2021). Ofwat Breakthrough Challenge Success. <https://www.anglianwater.co.uk/news/ofwat-breakthrough-challenge-success/> (accessed 31/03/2023).
- Anwar, S. W., and Tao, W. (2016). Cost benefit assessment of a novel thermal stripping – Acid absorption process for ammonia recovery from anaerobically digested dairy manure. *Water Practice and Technology*, 11, 355–364.
- Atkins, P. W., and De Paula, J. (2006). *Atkin's Physical Chemistry* (8th ed., pp. 174–199). Oxford University Press, Oxford, UK.
- Bates, R. G., and Pinching, G. D. (1950). Dissociation Constant of Aqueous Ammonia at 0 to 50° from E. m. f. Studies of the Ammonium Salt of a Weak Acid. *Journal of the American Chemical Society*, 72, 1393–1396.
- Bavarella, S., Hermassi, M., Brookes, A., Moore, A., Vale, P., Moon, I. S., Pidou, M., and McAdam, E. J. (2020). Recovery and concentration of ammonia from return liquor to promote enhanced CO₂ absorption and simultaneous ammonium bicarbonate crystallisation during biogas upgrading in a hollow fibre membrane contactor. *Separation and Purification Technology*, 241, 116631.
- Bavarella, S., Luqmani, B., Thomas, N., Brookes, A., Moore, A., Vale, P., Pidou, M., and McAdam, E. J. (2022). CO₂ absorption into aqueous ammonia using membrane contactors: Role of solvent chemistry and pore size on solids

- formation for low energy solvent regeneration. *Separation and Purification Technology*, 290, 120786.
- Bougrier, C., Delgenès, J. P., and Carrère, H. (2008). Effects of thermal treatments on five different waste activated sludge samples solubilisation, physical properties and anaerobic digestion. *Chemical Engineering Journal*, 139, 236–244.
- Campos, J. L., Valenzuela-Heredia, D., Pedrouso, A., Val Del Río, A., Belmonte, M., and Mosquera-Corral, A. (2016). Greenhouse Gases Emissions from Wastewater Treatment Plants: Minimization, Treatment, and Prevention. *Journal of Chemistry*, 379635.
- Cesaro, Z., Ives, M., Nayak-Luke, R., Mason, M., and Bañares-Alcántara, R. (2021). Ammonia to power: Forecasting the levelized cost of electricity from green ammonia in large-scale power plants. *Applied Energy*, 282, 1–19.
- Cheddie, D. (2012). *Hydrogen Energy - Challenges and Perspectives* (1st ed., pp. 333–362). IntechOpen, London, UK.
- Cooper, M., and Botte, G. G. (2006). Hydrogen Production from the Electro-oxidation of Ammonia Catalyzed by Platinum and Rhodium on Raney Nickel Substrate. *Journal of The Electrochemical Society*, 153, A1894.
- Davey, C. J., Luqmani, B., Thomas, N., and McAdam, E. J. (2022). Transforming wastewater ammonia to carbon free energy: Integrating fuel cell technology with ammonia stripping for direct power production. *Separation and Purification Technology*, 289, 120755.
- Dekker, N. J. J., and Rietveld, G. (2006). Highly efficient conversion of ammonia in electricity by solid oxide fuel cells. *Journal of Fuel Cell Science and Technology*, 3, 499–502.
- Department for Business Energy and Industrial Strategy. (2021). UK Hydrogen Strategy.
https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/1011283/UK-Hydrogen-Strategy_web.pdf (accessed 31/03/2023).
- Department for Business Energy and Industrial Strategy. (2022). Gas and electricity prices in the non-domestic sector.

- <https://www.gov.uk/government/statistical-data-sets/gas-and-electricity-prices-in-the-non-domestic-sector> (accessed 31/03/2023).
- EC (European Community). (2008). 2008/98/EC of 19 November 2008 on waste and repealing certain Directives. Official Journal of the European Union, 3–30. <http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32008L0098&from=EN%3E> (accessed 31/03/2023).
- EEC Council. (1991). 91/271/EEC of 21 May 1991 concerning urban waste-water treatment. Official Journal of the European Communities, 40–52. <http://eur-lex.europa.eu/legal-content/en/ALL/?uri=CELEX:31991L0271> (accessed 31/03/2023).
- Ganesh, N. S., and Srinivas, T. (2017). Development of thermo-physical properties of aqua ammonia for Kalina cycle system. *International Journal of Materials and Product Technology*, 55, 113–141.
- Garrido, J. M., Fdz-Polanco, M., and Fdz-Polanco, F. (2013). Working with energy and mass balances: A conceptual framework to understand the limits of municipal wastewater treatment. *Water Science and Technology*, 67, 2294–2301.
- Guida, S., Van Peteghem, L., Luqmani, B., Sakarika, M., McLeod, A., McAdam, E. J., Jefferson, B., Rabaey, K., and Soares, A. (2022). Ammonia recovery from brines originating from a municipal wastewater ion exchange process and valorization of recovered nitrogen into microbial protein. *Chemical Engineering Journal*, 427, 130896.
- Guštin, S., and Marinšek-Logar, R. (2011). Effect of pH, temperature and air flow rate on the continuous ammonia stripping of the anaerobic digestion effluent. *Process Safety and Environmental Protection*, 89, 61–66.
- Han, Y., Agyeman, F., Green, H., and Tao, W. (2022). Stable, high-rate anaerobic digestion through vacuum stripping of digestate. *Bioresource Technology*, 343, 126133.
- Heile, S., Chernicharo, C. A. L., Brandt, E. M. F., and McAdam, E. J. (2017). Dissolved gas separation for engineered anaerobic wastewater systems. *Separation and Purification Technology*, 189, 405–418.

- Henze, M., and Comeua, Y. (2008). Wastewater Characterisation. In M. Henze, M. C. M. van Loosdrecht, G. A. Ekama, & D. Brdjanovic (Eds.), *Biological Wastewater Treatment: Principles, Modelling and Design* (1st ed., pp. 33–52). IWA Publishing, London, UK.
- Hewlett, S. G., Pugh, D. G., Valera-Medina, A., Giles, A., Runyon, J., Goktepe, B., and Bowen, P. J. (2020). Industrial wastewater as an enabler of green ammonia to power via gas turbine technology. *Proceedings of the ASME Turbo Expo 2020: Turbomachinery Technical Conference and Exposition*, London, UK.
- Hewlett, S. G., Valera-Medina, A., Pugh, D. G., and Bowen, P. J. (2019). Gas turbine co-firing of steelworks ammonia with coke oven gas or methane: A fundamental and cycle analysis. *Proceedings of the ASME Turbo Expo 2019: Turbomachinery Technical Conference and Exposition*, Phoenix, AZ, USA.
- Huang, J., and Shang, C. (2006). Air Stripping. In L. K. Wang, Y. Hung, & N. K. Shamas (Eds.), *Advanced Physicochemical Treatment Processes* (1st ed., pp. 47–79). The Humana Press Inc., Totowa, NJ, USA.
- International Energy Agency. (2021). Ammonia Technology Roadmap. <https://iea.blob.core.windows.net/assets/6ee41bb9-8e81-4b64-8701-2acc064ff6e4/AmmoniaTechnologyRoadmap.pdf> (accessed 31/03/2023).
- Jackson, C., Fothergill, K., Gray, P., Haroon, F., Makhloufi, C., Kezibri, N., Davey, A., Lhote, O., Zarea, M., Davenne, T., Greenwood, S., Huddart, A., Makepeace, J., Wood, T., David, B., and Wilkinson, I. (2015). Ammonia to Green Hydrogen Project. https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/880826/HS420_-_Ecuity_-_Ammonia_to_Green_Hydrogen.pdf (accessed 31/03/2023).
- Jamaludin, Z., Rollings-Scattergood, S., Lutes, K., and Vaneeckhaute, C. (2018). Evaluation of sustainable scrubbing agents for ammonia recovery from anaerobic digestate. *Bioresource Technology*, 270, 596–602.
- Jiang, A. (2009). Ammonia recovery from digested dairy manure as nitrogen fertilizer. PhD thesis. Washington State University.

- Kang, J., Kwon, G., Nam, J. H., Kim, Y. O., and Jahng, D. (2017). Carbon dioxide stripping from anaerobic digestate of food waste using two types of aerators. *International Journal of Environmental Science and Technology*, 14, 1397–1408.
- Kurata, O., Iki, N., Matsunuma, T., Inoue, T., Tsujimura, T., Furutani, H., Kobayashi, H., and Hayakawa, A. (2017). Performances and emission characteristics of NH₃-air and NH₃-CH₄-air combustion gas-turbine power generations. *Proceedings of the Combustion Institute*, 36, 3351–3359.
- Lan, R., and Tao, S. (2014). Ammonia as a suitable fuel for fuel cells. *Frontiers in Energy Research*, 2, 1–4.
- Licon Bernal, E. E., Maya, C., Valderrama, C., and Cortina, J. L. (2016). Valorization of ammonia concentrates from treated urban wastewater using liquid-liquid membrane contactors. *Chemical Engineering Journal*, 302, 641–649.
- Mission Possible Partnership. (2022). Making net-zero ammonia possible. <https://missionpossiblepartnership.org/wp-content/uploads/2022/09/Making-1.5-Aligned-Ammonia-possible.pdf> (accessed 31/03/2023).
- Moore, A., and Auty, D. (2013). Digestion and Greenhouses – Synergistic Resource Recovery. 18th European Biosolids & Organic Resources Conference & Exhibition, Manchester, UK.
- Morgan, E. R. (2013). Techno-economic feasibility study of ammonia plants powered by offshore wind. PhD thesis. University of Massachusetts Amherst.
- National Institute of Standards and Technology (NIST). (2021a). Chemistry WebBook (Ammonia). <https://webbook.nist.gov/cgi/cbook.cgi?ID=C7664417&Mask=10#Solubility> (accessed 06/04/2023).
- National Institute of Standards and Technology (NIST). (2021b). Chemistry WebBook (Water). <https://webbook.nist.gov/cgi/cbook.cgi?Name=water> (accessed 06/04/2023).
- Nayak-Luke, R., Bañares-Alcántara, R., and Wilkinson, I. (2018). “green” Ammonia: Impact of Renewable Energy Intermittency on Plant Sizing and

- Levelized Cost of Ammonia. *Industrial and Engineering Chemistry Research*, 57, 14607–14616.
- Ndam, N. E. (2017). Treatment technologies for recycle liquors: Nutrient removal, mass balances, and potential recovery at wastewater treatment plants. PhD thesis. Newcastle University.
- Okafor, E. C., Kurata, O., Yamashita, H., Inoue, T., Tsujimura, T., Iki, N., Hayakawa, A., Ito, S., Uchida, M., and Kobayashi, H. (2021). Liquid ammonia spray combustion in two-stage micro gas turbine combustors at 0.25 MPa; Relevance of combustion enhancement to flame stability and NO_x control. *Applications in Energy and Combustion Science*, 7, 100038.
- Organics Group. (2020). Removal, Recovery and Re-use of Ammoniacal Nitrogen from Wastewater for Power Generation. <https://organicsgroup.com/recovery-and-re-use-of-of-ammonia/> (accessed 31/03/2023).
- Papadimas, D., and Ahmed, S. (2012). Biogas Impurities and Cleanup for Fuel Cells. Biogas and Fuel Cells Workshop, Golden, CO, USA.
- Parliamentary Office of Science and Technology. (2007). Energy and Sewage, Postnote number 282,. <http://www.parliament.uk/documents/post/postpn282.pdf> (accessed 31/03/2023).
- Pátek, J., and Klomfar, J. (1995). Simple functions for fast calculations of selected thermodynamic properties of the ammonia-water system. *International Journal of Refrigeration*, 18, 228–234.
- Patel, H. C., Woudstra, T., and Aravind, P. V. (2012). Thermodynamic analysis of solid oxide fuel cell gas turbine systems operating with various biofuels. *Fuel Cells*, 12, 1115–1128.
- Prado, J. R., and Vyazovkin, S. (2011). Activation energies of water vaporization from the bulk and from laponite, montmorillonite, and chitosan powders. *Thermochimica Acta*, 524, 197–201.
- Raghuvanshi, S., and Maheshwari, G. (2011). Analysis of Ammonia – Water (NH₃-H₂O) Vapor Absorption Refrigeration System based on First Law of

- Thermodynamics. *International Journal of Scientific & Engineering Research*, 2, 1–7.
- RVT. (2015). Ammonia recovery Removal from liquids and gases. http://www.rvtpe.net/wp-content/uploads/prospekte/RVT_Ammonia_Recovery_120529.pdf (accessed 31/03/2023).
- Salavera, D., Chaudhari, S. K., Esteve, X., and Coronas, A. (2005). Vapor-liquid equilibria of ammonia + water + potassium hydroxide and ammonia + water + sodium hydroxide solutions at temperatures from (293.15 to 353.15) K. *Journal of Chemical and Engineering Data*, 50, 471–476.
- Sander, R. (2015). Compilation of Henry's law constants (version 4.0) for water as solvent. *Atmospheric Chemistry and Physics*, 15, 4399–4981.
- Sasaki, K., Haga, K., Yoshizumi, T., Minematsu, D., Yuki, E., Liu, R.-R., Uryu, C., Oshima, T., Taniguchi, S., Shiratori, Y., and Ito, K. (2011). Impurity Poisoning of SOFCs. *ECS Transactions*, 35, 2805–2814.
- Siddiqui, O., and Dincer, I. (2019). Development and performance evaluation of a direct ammonia fuel cell stack. *Chemical Engineering Science*, 200, 285–293.
- Tan, T. C., Chai, C. M., Tok, A. T., and Ho, K. W. (2004). Prediction and experimental verification of the salt effect on the vapour-liquid equilibrium of water-ethanol-2-propanol mixture. *Fluid Phase Equilibria*, 218, 113–121.
- Tao, W., Bayrakdar, A., Wang, Y., and Agyeman, F. (2019). Three-stage treatment for nitrogen and phosphorus recovery from human urine: Hydrolysis, precipitation and vacuum stripping. *Journal of Environmental Management*, 249, 109435.
- Tao, W., and Ukwuani, A. T. (2015). Coupling thermal stripping and acid absorption for ammonia recovery from dairy manure: Ammonia volatilization kinetics and effects of temperature, pH and dissolved solids content. *Chemical Engineering Journal*, 280, 188–196.
- Tao, W., Ukwuani, A. T., and Agyeman, F. (2018). Recovery of ammonia in anaerobic digestate using vacuum thermal stripping - Acid absorption process: Scale-up considerations. *Water Science and Technology*, 78, 878–885.

- Teichgraber, B., and Stein, A. (1994). Nitrogen elimination from sludge treatment reject water – comparison of the steam-stripping and denitrification processes. *Water Science and Technology*, 30, 41–51.
- The Royal Society. (2020). Ammonia: zero-carbon fertiliser, fuel and energy store. Policy Briefing. <https://royalsociety.org/topics-policy/projects/low-carbon-energy-programme/green-ammonia/> (accessed 31/03/2023).
- Ukwuani, A. T., and Tao, W. (2016). Developing a vacuum thermal stripping – acid absorption process for ammonia recovery from anaerobic digester effluent. *Water Research*, 106, 108–115.
- van Linden, N., Spanjers, H., and van Lier, J. B. (2022). Fuelling a solid oxide fuel cell with ammonia recovered from water by vacuum membrane stripping. *Chemical Engineering Journal*, 428, 131081.
- Vaneeckhaute, C., Lebuf, V., Michels, E., Belia, E., Vanrolleghem, P. A., Tack, F. M. G., and Meers, E. (2017). Nutrient Recovery from Digestate: Systematic Technology Review and Product Classification. *Waste and Biomass Valorization*, 8, 21–40.
- Venegas, T., Qu, M., Nawaz, K., and Wang, L. (2021). Critical review and future prospects for desiccant coated heat exchangers: Materials, design, and manufacturing. *Renewable and Sustainable Energy Reviews*, 151, 111531.
- Vitse, F., Cooper, M., and Botte, G. G. (2005). On the use of ammonia electrolysis for hydrogen production. *Journal of Power Sources*, 142, 18–26.
- Wang, Z., Li, S., Zhang, C., Wang, D., and Li, X. (2021). The Opportunities and Challenges for NH₃ Oxidation with 100% Conversion and Selectivity. *Catalysis Surveys from Asia*, 25, 103–113.
- Water Europe. (2021). Unleash the Potential of the Water-Energy Nexus in the Energy Efficiency Directive Joint Declaration. <https://watereurope.eu/wp-content/uploads/Joint-Declaration-EU-ASE-.WE-2.pdf> (accessed 31/03/2023).
- Water UK. (2020). Net Zero 2030 Routemap. <https://www.water.org.uk/routemap2030> (accessed 31/03/2023).
- Wett, B. (2006). Solved upscaling problems for implementing deammonification of rejection water. *Water Science and Technology*, 53, 121–128.

- Wilson, C. A., and Novak, J. T. (2009). Hydrolysis of macromolecular components of primary and secondary wastewater sludge by thermal hydrolytic pretreatment. *Water Research*, 43, 4489–4498.
- Winter, P., Pearce, P., and Colquhoun, K. (2012). Contribution of nitrous oxide emissions from wastewater treatment to carbon accounting. *Journal of Water and Climate Change*, 3, 95–109.
- Zeng, L., Mangan, C., and Li, X. (2006). Ammonia recovery from anaerobically digested cattle manure by steam stripping. *Water Science and Technology*, 54, 137–145.
- Zhang, M., Zou, P., Jeerh, G., Chen, S., Shields, J., Wang, H., and Tao, S. (2020). Electricity Generation from Ammonia in Landfill Leachate by an Alkaline Membrane Fuel Cell Based on Precious-Metal-Free Electrodes. *ACS Sustainable Chemistry and Engineering*, 8, 12817–12824.

3 The role of solvent temperature and gas pressure on CO₂ mass transfer during biogas upgrading within porous and dense-skin hollow fibre membrane contactors

The role of solvent temperature and gas pressure on CO₂ mass transfer during biogas upgrading within porous and dense-skin hollow fibre membrane contactors

B. Lugmani^a, A. Brookes^b, A. Moore^c, P. Vale^d, M. Pidou^a, E.J. McAdam^{a,*}

^aCranfield Water Science Institute, Vincent Building, Cranfield University, Bedfordshire, MK43 0AL, UK

^bAnglian Water, Block C-Western House, Peterborough Business Park, Peterborough PE2 6FZ, UK

^cNorthumbrian Water, Boldon House, Wheatlands Way, Durham DH1 5FA, UK

^dSevern Trent Water, 2 St. Johns Street, Coventry CV1 2LZ, UK

*Corresponding Author: e.mcadam@cranfield.ac.uk

Abstract

Biogas upgrading uniquely requires pressurisation of hollow fibre membrane contactors (HFMC) to be competitive with classical water absorption, and when complemented with an ambient industrial temperature range, these conditions will determine CO₂ mass transport phenomena that are distinct dependent upon whether microporous or nonporous membranes are used. This study therefore examines the independent and concomitant role of temperature and pressure in determining CO₂ mass transport, and selectivity, within microporous and nonporous HFMC. At low solvent temperatures, higher CO₂ flux was achieved which indicates that solvent solubility is more critical than CO₂ diffusivity to enhancing mass transport. Low temperatures also favoured mass transfer within the microporous membrane, explained by the reduction in solvent vapour pressure which limited pore wetting by condensation. In contrast, the nonporous membrane exhibited poorer mass transfer at low temperatures due to a decline in dense polymer permeability. Crucially in this study, neither wetting of the microporous membrane or plasticisation of the nonporous membrane were observed following pressurisation. Consequently, CO₂ flux increased in proportion to the applied pressure for both membrane types, emphasising the critical role of pressurisation in augmenting process intensification for biogas upgrading which is typically facilitated at pressures of 7-10 bar. Resistance-in-series analysis illustrated how pressurisation reduced gas-phase resistance, and subsequently enhanced selectivity. Consequently, an outlet gas quality of 98% methane could be achieved within a single microporous module at 4.5 bar, meeting the industrial standard for biomethane whilst reducing solvent requirements, separation energy and methane losses. Comparable behaviour was observed during pressurisation of the nonporous membrane, but with a less

significant benefit to CO₂ mass transfer and selectivity, ostensibly due to the resistance imparted by the dense polymer. When considered collectively, low solvent temperature and high gas pressure enhance process intensification subsequently reducing process size (e.g., membrane area) and separation energy, while also advancing selectivity to deliver a gas product at the composition required for biomethane with minimum methane losses, which are critical factors in demonstrating microporous HFMC as an industrially competitive solution for biogas upgrading.

Keywords: *asymmetric; carbon capture (CCS); water; biomethane; selectivity; permeability*

3.1 Introduction

Biogas produced from the anaerobic digestion of organic rich waste can be upgraded into biomethane (>98% CH₄) to decarbonise existing natural gas infrastructure or as a sustainable 'drop-in' transport fuel by replacing fossil derived gasoline and diesel (Bauer et al., 2013; Scarlat et al., 2018). Biomethane is therefore seen as a critical resource for the decarbonisation of heat and transport in Europe (Alberici et al., 2021; Connor et al., 2015). Pressurised water absorption (PWA) is the dominant technology for biomethane production, and uses water to facilitate carbon dioxide (CO₂) absorption from biogas in packed columns (Angelidaki et al., 2018; Northern Gas Networks, 2020). Hollow fibre membrane contactors (HFMC) are an emerging technology that can similarly mediate CO₂ absorption for biogas upgrading. In HFMC, the gas and liquid are separated by a gas permeable membrane to facilitate non-dispersive gas transfer between phases, thus avoiding channelling, flooding, foaming and entrainment that are common challenges for packed columns (Hoff and Svendsen, 2013). This enables higher gas loading rates to be applied resulting in smaller installed capacity, while the superior specific surface area in HFMC can enable process intensification of up to fifteen times versus packed columns (Belaissaoui et al., 2016).

A dry microporous membrane layer will offer negligible resistance to CO₂ mass transfer (Mavroudi et al., 2006). However, many researchers have observed

wetting of the pore structure which can substantially increase membrane resistance due to the lower diffusivity of CO₂ in water (Dindore et al., 2004; Khaisri et al., 2009; Wang et al., 2005). For example, pore wetting in polypropylene (PP) hollow fibres resulted in an increase in membrane resistance up to 143000 s m⁻¹ (43% of the overall mass transfer resistance) (Khaisri et al., 2009). Scholes et al. (2015b) reported total pore wetting of microporous HFMC during CO₂ absorption into 30% MEA at 35 to 65°C. During carbon capture, the elevated flue gas temperature (>50°C) will naturally raise the solvent temperature due to efficient heat transfer across the HFMC (Chan et al., 2020; Villeneuve et al., 2018). Investigation of CO₂ absorption at lower solvent temperatures is relevant for biomethane production (<30°C), since biogas is produced at ambient conditions (Houlker et al., 2021b). Lowering solvent temperature improves gas solubility which can increase CO₂ flux (Cesari et al., 2021; Dai and Deng, 2016; Mansourizadeh, 2012). However, this will also increase methane flux into the solvent (i.e., methane 'slip'). As the increase in solubility is proportionate to temperature, selectivity of the binary gas mixture (CO₂/CH₄) should not be affected but the increase in methane slip will have financial and environmental implications (Belaissaoui et al., 2016). Reduced pore wetting has also been observed at lower temperatures (Dai and Deng, 2016; Lu et al., 2008). This has been related to an increase in solvent surface tension, since this increases the pore pressure required for solvent breakthrough. The reduction in vapour pressure may also mitigate pore wetting, by reducing the probability for capillary condensation (Chan et al., 2020), analogous to the reduction of ammonia slip at lower temperatures during chemical absorption (Bavarella et al., 2022). Since transmembrane pressure is not consistently reported and wetting has been observed well below the theoretical breakthrough pressure, confirmation of the link between temperature and wetting in microporous membranes has yet to be demonstrated (Dai and Deng, 2016; Dindore et al., 2004; Lu et al., 2008).

For hollow fibre membrane contactors to be competitive with packed columns, they must also be capable of pressurisation, as pressure is used to improve absorption capacity, reduce solvent mass flow to regeneration, minimise methane slip and advance the co-absorption of trace gases (e.g., siloxanes,

hydrogen sulphide and ammonia) (Kapoor et al., 2019; Sun et al., 2015). The biomethane product is then also at a pressure compatible for injection into the gas network, which is typically rated at 2-7 bar (Northern Gas Networks, 2020; Yang et al., 2014). Pressurisation of HFMC is therefore needed to achieve competitive process intensification to conventional PWA. However, limited data is available on the influence of pressure on CO₂ absorption within HFMC, particularly for biogas upgrading. Dindore et al. (2004) demonstrated that increasing gas pressures up to 20 bar led to a proportional enhancement in CO₂ flux across a single microporous hollow fibre, due to the increase in volumetric CO₂ concentration. Pressure was not observed to reduce overall mass transfer resistance, while membrane resistance was observed to be constant, indicating that pore wetting was avoided by sustaining a constant transmembrane pressure (Dindore et al. 2004). These experiments were conducted in semi-batch mode, with a continuous flow of solvent used to absorb CO₂ from a reservoir which sustained CO₂ partial pressure leading to a negligible gas-phase mass transfer resistance (<0.5%) (Dindore et al. 2004). During biomethane production, the partial pressure of CO₂ will reduce by 95% and there is evidence that gas-phase resistance can become more significant to mass transfer possibly due to the reduction in partial pressure and decrease in gas velocity across the length of the HFMC, which may have a more significant effect for biogas than flue gas due to the higher initial CO₂ partial pressure (Houlker, 2019). The extent to which pressure governs mass transfer within each phase of a microporous HFMC, and its implications for gas quality in a binary separation have not been explored to date.

To prevent pore wetting and stabilise mass transfer during CO₂ absorption, a thin layer of gas-permeable dense polymer can be incorporated on to the membrane surface to produce a nonporous HFMC (Chabanon et al., 2014; Nguyen et al., 2011). When compared to microporous HFMC, gas transport is more dependent on the thickness and permeability of the polymer layer (Chabanon et al., 2014). This transport mechanism is expected to mitigate methane slip into the solvent since the polymer can introduce an inherent selectivity toward CO₂ (e.g., poly(4-methyl-1-pentene), thus enhancing CO₂/CH₄

selectivity (Belaissaoui et al., 2016; Mohr and Paul, 1991; Nematollahi et al., 2016). While nonporous HFMC offer several advantages, gas permeability is likely to decline at lower temperatures (Scholes et al., 2015b). When in contact with an aqueous solvent, lower polymer permeability (e.g., Teflon AF1600, PTMSP and PIM 1) has been observed than for dry conditions, which may infer the competitive sorption of water vapour within the polymer (Chen et al., 2012; Scholes et al., 2015a, 2015b). Whilst the dense polymer poly(4-methyl-1-pentene) has been explored widely for gas-phase separations due to its high permeability and chemical resistance (Markova et al., 2020), permeability data in the presence of aqueous solvents is unavailable. Permeability can be expected to be independent of pressure, but a decline in CO₂ permeability and selectivity was observed during the pressurisation of ultrathin (0.1-0.2 µm) polyethersulfone-polyimide nonporous hollow fibres due to the suspected plasticisation of the dense polymer (Kapantaidakis et al., 2003). However, when studying a poly(phenylene oxide) nonporous HFMC for the absorption of CO₂ into water at 2.5 bar, a membrane resistance of 1970 s m⁻¹ was reported which is comparable to the mass transfer resistance determined for a microporous HFMC (Belaissaoui et al., 2016; Houlker, 2019). This suggests that pressurisation did not affect polymer permeability, although higher pressures within the range relevant for biogas upgrading were not explored.

The aim of this research is to compare microporous and nonporous HFMC at low temperatures and high pressures which represent critical parameters for biomethane production. Specific objectives are to:

- i) characterise the role of solvent temperature (5-35°C) on membrane resistance and CO₂ transport mechanisms within microporous and nonporous HFMC to aid material selection for biomethane production;
- ii) determine how pressure (1.1-4.5 bar) informs on mass transfer behaviour across the three discrete phases within the system, with emphasis on the susceptibility of microporous and nonporous membranes to the implicit risks of pressurisation on wetting and gas permeability;

- iii) evaluate how temperature and pressure modify selectivity, including gas product quality and methane slip from a binary CO₂/CH₄ gas comprised of a high CO₂ partial pressure.

3.2 Materials and methods

3.2.1 Experimental set-up

The experimental set-up was developed to evaluate CO₂ mass transfer within transverse flow membrane contactors comprising microporous polypropylene hollow fibres with a maximum pore size of 0.1 µm, or nonporous hollow fibres with an asymmetric structure comprising a 1 µm dense poly(4-methyl-1-pentene) layer (3M Industrial Group, Charlotte, USA) (Table 3.1). The microporous module contained 10200 fibres and provided a total internal surface area of 1.2 m². Each fibre had an internal diameter, wall thickness and length of 240 µm, 30 µm and 0.16 m, respectively. The nonporous module contained approximately 8500 fibres and provided a total internal surface area of 0.9 m². Each fibre had an internal diameter, wall thickness and length of 240 µm, 89 µm and 0.16 m, respectively. Pure carbon dioxide or a 50/50 volumetric blend of carbon dioxide and methane (CO₂, 99.7%; CH₄, 99.995%, BOC gases, Ipswich, UK) was introduced into the HFMC lumen (0.01– 5.0 L min⁻¹, Roxspur Measurement and Control Ltd., Sheffield, UK). Deionised water (15 MΩ cm) was pumped counter-currently through the shell-side (AD4/90, Xylem Inc., New York, USA) (Figure 3.1). Gases were supplied at approximately 21°C, and gas and liquid temperatures monitored using k-type thermocouples (±1.5°C, RS Components, Corby, UK). Shell-side water temperature was modified using a thermostatic recirculating water bath (LT Ecocool 150, Grant Instruments, Cambridge, UK) to permit solvent temperatures ranging 5 to 35°C. Gas and liquid pressures were monitored across the system (DPG1001B-100G, ±0.10% full scale, Omega Engineering Ltd., Manchester, UK) and controlled using throttling valves at the lumen and shell-side outlets respectively (SS-4MA-MH, Swagelok, Kings Langley, UK) to ensure gas pressure between 1.1 and 4.5 bar could be used. Gas bubbling was observed when pressure equalised across the membrane and so a liquid-side overpressure was established of between 0.2 and 0.4 bar with

care taken not to exceed the breakthrough pressure at the liquid inlet (Table 3.1) (Dindore et al., 2004). Outlet gas flow was measured at atmospheric pressure using volumetric bubble flowmeters (50 ml, $\pm 2\%$ full scale, Restek, Bellefonte, USA; 1000 ml, Model 311, $\pm 2\%$ full scale, Blandford Forum, UK) and normalised to the gas inlet temperature and pressure (Appendix B1). Gas outlet composition was monitored using an in-line infrared CH₄ analyser (BCP-CH₄, $<0.5\%$ full scale, BlueSens gas sensor GmbH, Herten, Germany). Following each experiment, the lumen underwent a 45-minute drying step with compressed air at 30 L min⁻¹ to restore hydrophobicity (3M, 2023). In this work, mild drying conditions were applied (20°C, 1 bar) and reproducible results throughout experimentation indicated that membrane properties were unaffected by cycles of wetting and drying. Each data point was replicated, and the mean reported with standard deviation represented by the error bars. To discriminate the role of temperature on membrane wetting, solvent exposure during the resistance in series analyses was standardised by allowing the system to stabilise for 2 minutes at each operating condition prior to data collection.

Table 3.1: Material and structural properties of hollow fibre membrane contactors

	Microporous HFMC	Nonporous HFMC
Dense-skin (μm) ^a	N/A	~ 1
Internal fibre diameter (μm) ^a	240	200
Fibre wall thickness (μm) ^a	30	89
Fibre length (m) ^a	0.16	0.16
Tortuosity (-) ^a	0.4	-
Porosity (-) ^a	2.5	-
No. fibres (-) ^b	~ 10200	~ 8500
Total surface area (m ²) ^b	1.2	0.9
Specific surface area (m ² m ⁻³) ^b	1860	1293
Contact angle (°) ^c	122	-
Geometric pore factor (-) ^d	0.56	-
Max. pore size (μm) ^{d,e}	0.1	-
Breakthrough pressure (bar) ^f	8.9 (5°C); 8.4 (35°C)	N/A

^a Data supplied by manufacturer

^d Bavarella. (2018)

^b Based upon internal fibre diameter

^e Heile et al. (2014)

^c Lv et al. (2010)

^f Based upon pure water

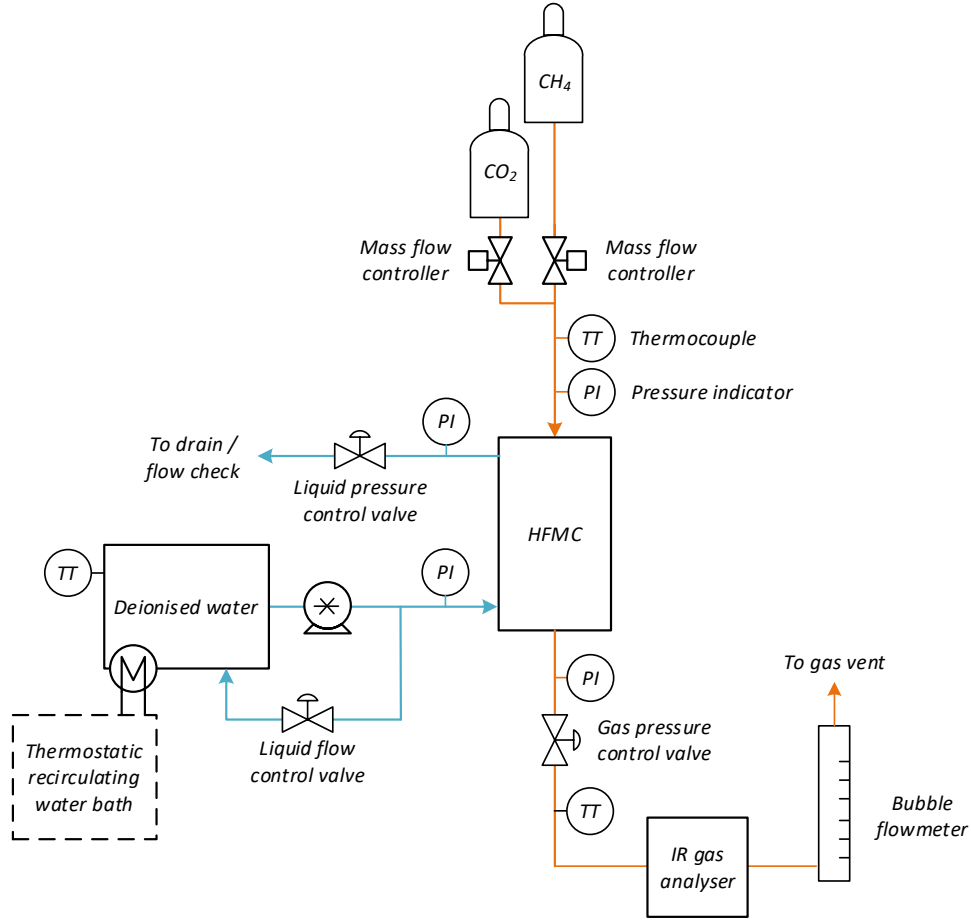


Figure 3.1: Experimental set-up for gas-liquid absorption in HFMC

3.2.2 Experimental analysis

Experimental CO₂ capture ratio (Gabelman and Hwang, 1999) was determined using:

$$\eta_{CO_2} = \frac{Q_{g,in} y_{CO_2,in} - Q_{g,out} y_{CO_2,out}}{Q_{g,in} y_{CO_2,in}} \quad (\text{Eq. 3.1})$$

where η_{CO_2} is the CO₂ capture ratio (-); Q_g is the gas flowrate (m³ s⁻¹); y_{CO_2} is the CO₂ fraction in the gas-phase (%vol); and subscripts 'in' and 'out' refer to conditions at the membrane inlet and outlet respectively. Experimental CO₂ flux and overall mass transfer coefficients (Gabelman and Hwang, 1999) were calculated as:

$$J_{CO_2} = \frac{Q_l C_{l,out}}{A} = K_{ov} \Delta(C_l^* - C_l)_{lm} = K_{ov} \Delta(HC_g - C_l)_{lm} \quad (\text{Eq. 3.2})$$

$$\Delta(HC_g - C_l)_{lm} = \frac{(HC_{g,in} - C_{l,out}) - (HC_{g,out} - C_{l,in})}{\ln \left[\frac{HC_{g,in} - C_{l,out}}{HC_{g,out} - C_{l,in}} \right]} \quad (\text{Eq. 3.3})$$

where J_{CO_2} is the flux ($\text{mol m}^{-2} \text{s}^{-1}$); Q_l is the liquid flowrate in and out of the shell-side ($\text{m}^3 \text{s}^{-1}$); A is the total surface area based upon fibre internal diameter (m^2); K_{ov} is the overall mass transfer coefficient for CO_2 (m s^{-1}); H is the dimensionless Henry's law partition coefficient for CO_2 in water for a given temperature (-) (Table 3.2); C_g is the gas-phase CO_2 concentration for a given pressure and temperature (mol m^{-3}) (Appendix B1); C_l is the liquid-phase CO_2 concentration and C_l^* is the liquid-phase CO_2 concentration at gas-liquid equilibrium (mol m^{-3}).

A resistance-in-series approach was applied to separate the overall mass transfer resistance, $1/K_{ov}$ (s m^{-1}), into three constituent resistances (gas, liquid and membrane) (Eq. 3.4) (Cui and Demontigny, 2013; Gabelman and Hwang, 1999).

$$\frac{1}{K_{ov}} = \frac{1}{k_g} + \frac{1}{k_m} + \frac{1}{k_l} \quad (\text{Eq. 3.4})$$

where $1/k_g$, $1/k_l$, and $1/k_m$ represent mass transfer resistance for the gas-phase, membrane and liquid-phase respectively (s m^{-1}).

Liquid-phase mass transfer resistances were estimated using a shell-side Graetz-Leveque solution for transverse-flow HFMC (Eq. 3.5) first developed for liquid-liquid extraction (Baudot et al., 2001). The Reynolds number, Re (-), and shell-side hydraulic diameter, d_h (m), were calculated assuming parallel flow within the shell-side in accordance with previous literature (Houlker et al., 2021a; Shen et al., 2010). Since both microporous and nonporous modules had the same internal geometry, Re was equivalent across the liquid velocity range. The Graetz-Leveque solution was determined to accurately predict liquid-phase mass transfer resistance, under conditions where the liquid Graetz number was greater than 15 (Appendix B2).

$$Sh = 0.56 Re^{0.62} Sc^{0.33} = \frac{k_l d_h}{D_{CO_2,l}} \quad (\text{Eq. 3.5})$$

where Sh is the Sherwood number (-); Sc is the Schmidt number (-) and $D_{CO_2,l}$ is the diffusivity of CO_2 in the solvent at a given temperature (Table 3.2) ($\text{m}^2 \text{s}^{-1}$).

Membrane mass transfer resistance was estimated from the experimental data using the Wilson plot method (Gabelman and Hwang, 1999). Membrane resistance for the microporous HFMC, $1/k_{m,p}$ ($s\ m^{-1}$), enabled estimation of wetted pore fraction, x (-), for each condition (Eq. 3.6) (Chabanon et al., 2013). This approach is based upon the principle that the diffusivity of CO_2 in gas-filled pores is 3-4 orders of magnitude greater than in water-filled pores at 5-35°C and so the membrane resistance will decline as water progresses along the pore length. Notably, this assumes all pores are uniformly wetted across the contactor, which is unlikely in practice due to pore size distribution, but this does provide useful approximation for comparing the magnitude of wetting across different conditions (Chabanon et al., 2013).

$$\frac{1}{k_{m,p}} = (1 - x) \frac{\tau_m \delta_w}{D_{CO_2,g} \epsilon_m} + x \frac{\tau_m \delta_w}{H D_{CO_2,l} \epsilon_m} \quad (\text{Eq. 3.6})$$

where τ_m is membrane tortuosity (-); δ_w is the porous wall thickness (m); $D_{CO_2,g}$ is the diffusivity of CO_2 in the gas-phase ($m^2\ s^{-1}$); ϵ_m is the membrane porosity (-).

Membrane resistance for the nonporous HFMC, $1/k_{m,d}$ ($s\ m^{-1}$), permits estimation of the permeability for the dense polymer (Eq. 3.7-3.8). This was in direct contact with the liquid-phase and so it was assumed to approach the solvent temperature via rapid conductive heat transfer (Villeneuve et al., 2018).

$$\frac{1}{k_{m,d}} = \frac{\tau_m \delta_w}{D_{CO_2,g} \epsilon_m} + \frac{v_m \delta_d}{P_{d(SI)} R T_m} \quad (\text{Eq. 3.7})$$

$$P_d = \frac{1}{3.35 * 10^{-11}} \left(\frac{P_{d(SI)}}{v_m} \right) \quad (\text{Eq. 3.8})$$

where v_m is the gas molar volume ($m^3\ mol^{-1}$); δ_d is the dense polymer layer thickness (m); $P_{d(SI)}$ and P_d represent the CO_2 permeability of the polymer in SI units ($10^5\ m^3\ m\ bar^{-1}\ s^{-1}\ m^{-2}$) and Barrer respectively; R is the molar gas constant ($8.314 * 10^{-5}\ m^3\ bar\ K^{-1}\ mol^{-1}$) and T_m is the membrane temperature (K).

Table 3.2: Pure water properties from 5 to 35°C

	5°C	10°C	20°C	35°C
Density (kg m^{-3}) ^a	999.9	999.6	998.1	994.0
Dynamic viscosity ($10^{-3} \text{ N s m}^{-2}$) ^a	1.5	1.3	1.0	0.7
Vapour pressure (kPa) ^a	0.9	1.2	2.3	5.6
CO ₂ diffusivity ($10^{-9} \text{ m}^2 \text{ s}^{-1}$) ^b	1.1	1.3	1.7	2.5
Schmidt number (-) ^c	1375	1032	600	293
Henry's constant for CO ₂ , C_i^*/C_g (-) ^{c,d}	1.5	1.3	1.0	0.7
Henry's constant for CH ₄ , C_i^*/C_g (-) ^{c,d}	4.8×10^{-2}	4.4×10^{-2}	3.7×10^{-2}	3.0×10^{-2}

^a Perry and Green, (2007)^c Calculated values^b Frank et al., (1996)^d Sander, (2015)

3.3 Results and discussion

3.3.1 Microporous and nonporous HFMC influenced strongly by temperature

To simplify mass transfer analysis, initial experiments were undertaken using a pure CO₂ feed gas (99.7%) as this will set gas-phase resistance to near zero, leaving only the membrane and liquid-phase resistances to be determined (Gabelman and Hwang, 1999). Increasing liquid velocity improved CO₂ flux (Figure 3.2), due to a higher rate of solvent renewal at the membrane interface (Heile et al., 2017). For each condition, a plateau was approached which represents a reduction in boundary layer thickness and implies that liquid-phase resistance was tending toward a minimum (Appendix B2) (Gabelman and Hwang, 1999). In both microporous and nonporous membranes, CO₂ flux decreased following an increase in water temperature which modified the solubility constant to restrict the solvent CO₂ capacity (Table 3.2). Flux across the microporous membrane exhibited a greater sensitivity to temperature, indicating a lower overall resistance to mass transfer (Equation 3.2).

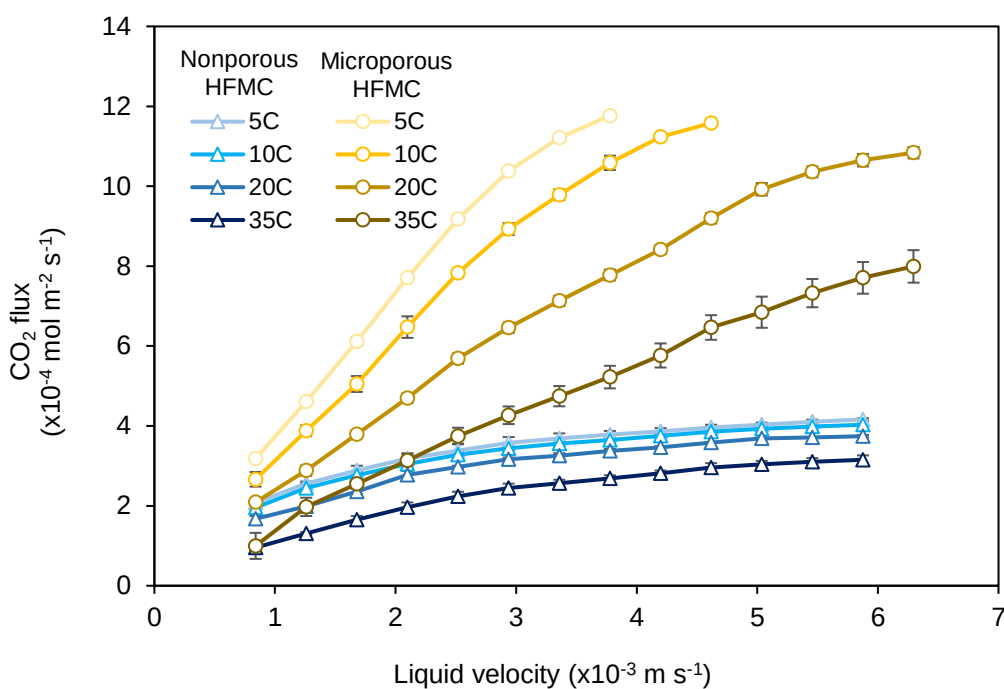


Figure 3.2: Impact of solvent temperature on CO₂ flux across microporous (PP) and nonporous (PMP) membranes. Conditions: Pure CO₂ gas feed; v_g , 0.07-0.08 m s⁻¹; P(gas), 1.1 bar; gas temperature in, 21 °C.

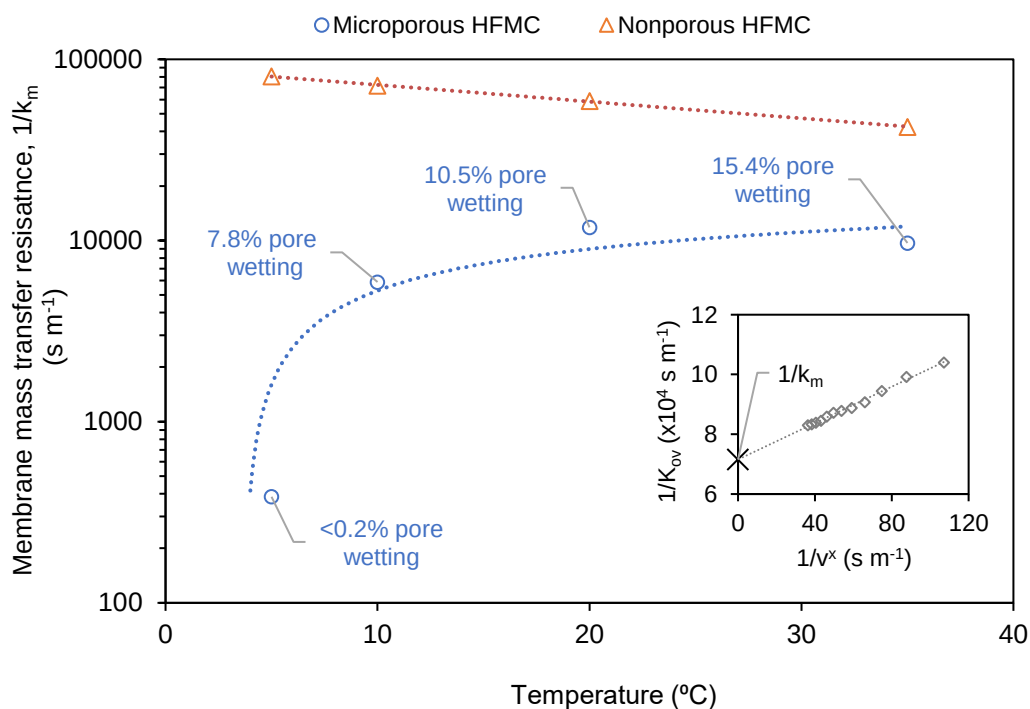


Figure 3.3: Impact of solvent temperature on membrane mass transfer resistance for CO₂ within microporous (PP) and nonporous (PMP) membranes. Membrane mass transfer resistances determined using Wilson plot method (example inset for nonporous membrane at 10°C). Conditions: Pure CO₂ gas feed; v_g , 0.07-0.08 m s⁻¹; P(gas), 1.1 bar; gas temperature in, 21°C. Estimated pore wetting annotated (Eq. 3.6). Dotted lines added to guide the eye.

Mass transfer resistance of the microporous membrane was 385 s m^{-1} at 5°C , around two orders of magnitude lower than the nonporous membrane (80700 s m^{-1}) (Figure 3.3). As solvent temperature was increased, mass transfer resistance in the microporous membrane increased and was correlated to wetting (Eq. 3.6). At 5°C , $<0.2\%$ of the pore structure was presumed to be wetted which increased to 7.8% at 10°C , and 15.4% at 35°C . Observations of pore wetting at increased temperatures have been attributed to the reduction in solvent surface tension, since this will reduce the pore breakthrough pressure (Dai and Deng, 2016; Lu et al., 2008). However, the variation in solvent surface tension is minor across the temperature range studied. Consequently, transmembrane pressure ($0.2\text{-}0.4 \text{ bar}$) represented less than 5% of the pore breakthrough pressure at the highest temperature tested (8.4 bar , based on maximum pore size $\sim 0.1 \mu\text{m}$), and so liquid entry was not expected to be the primary mechanism for pore wetting (Table 3.1). Instead, the exponential increase in water vapour pressure that occurs with an increase in temperature is more likely to have led to partial wetting by the condensation of water vapour in the pore structure (Figure 3.4). Capillary condensation will occur when the saturated vapour pressure exceeds the equilibrium vapour pressure for condensed water within the pores (Chan et al., 2020). While the probability of wetting is lower within hydrophobic membranes (Appendix B1), pore wetting by condensation has been previously reported (Atchariyawut et al., 2006; Khaisri et al., 2009; Mahmud et al., 2000). Chan et al. (2020) proposed this occurred through minor transients in flowrate and temperature which create local conditions conducive to condensation since the equilibrium vapour pressure responds more quickly than the saturated vapour pressure as sufficient time is required for water vapour to diffuse out of the pores. Notably, a dry gas feed was used in this work in contrast to real biogas which is typically saturated with water vapour (Houlker et al., 2021b). Introduction of a saturated gas-phase would limit the vapour pressure gradient across the HFMC and is expected to reduce the probability and extent of wetting by condensation, leading to more favourable mass transfer characteristics in practice.

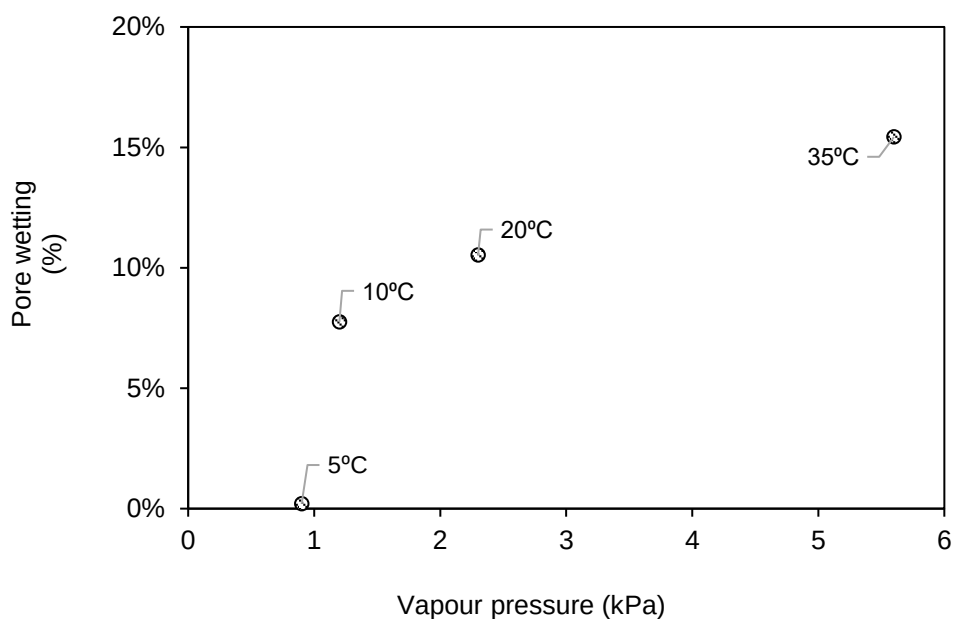


Figure 3.4: Influence of water temperature on determined pore wetting and the vapour pressure for pure water. Conditions: pure CO₂ gas feed; v_g , 0.07-0.08 m s⁻¹; P(gas), 1.1 bar; gas temperature in, 21°C. Solvent temperature annotated.

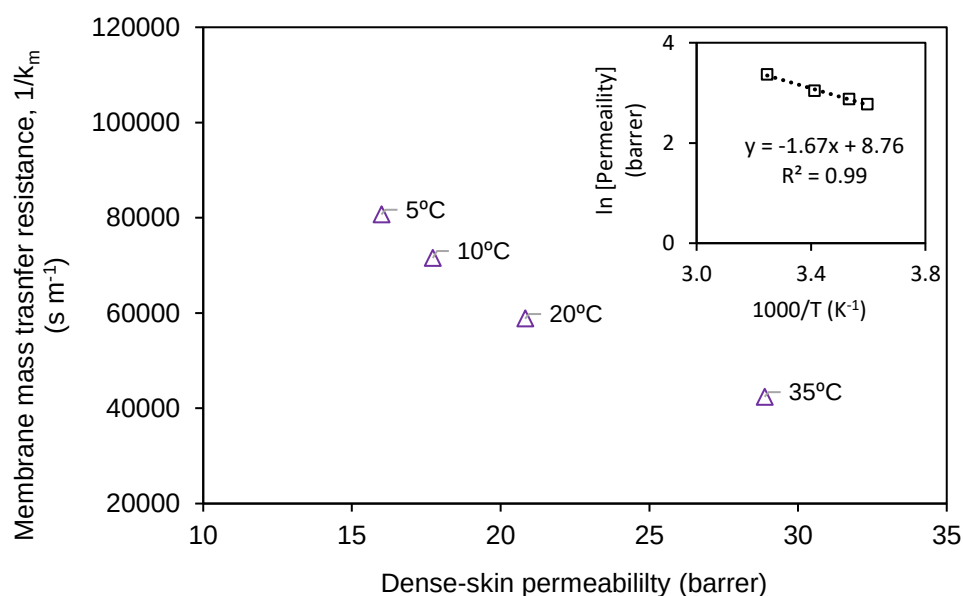


Figure 3.5: Influence of dense-skin permeability on membrane resistance for nonporous membrane (inset: graphical method for determining dense-skin activation energy, E_a). Conditions: pure CO₂ gas feed; v_g , 0.07-0.08 m s⁻¹; P(gas), 1.1 bar; gas temperature in, 21°C. Solvent temperature annotated.

Mass transfer resistance in the nonporous membrane progressively declined from 80700 s m⁻¹ at 5°C to 42400 s m⁻¹ when water temperature was increased to 35°C (Figure 3.3). The decline in membrane resistance was associated with an increase in CO₂ permeability for the dense polymer (Figure 3.5) (Scholes et al., 2015b). In this study, permeability of the polymer was estimated to be 28.8 barrer at 35°C, which is substantially lower than has been reported for poly(4-methyl-1-pentene) in dry conditions (Table 3.3) (Makhloufi et al., 2013; Mohamad et al., 2019; Yasuda and Rosengren, 1970). This supports previous observations for dense polymers where permeability is reduced when exposed to water vapour (Scholes et al., 2015a, 2015b). Temperature and permeability can be related using an Arrhenius expression, in which the activation energy is a compound parameter used to characterise the overall temperature dependence for the polymer (Feng and Huang, 1996) (Appendix B1). An activation energy of 13.9 kJ mol⁻¹ was determined from the experimental data which compares closely to literature for poly(4-methyl-1-pentene) (15.2 kJ mol⁻¹) (Makhloufi et al., 2013). This indicates that the impact of competitive sorption on permeability was consistent across the temperature range, despite variation in water vapour pressure. Therefore, in contrast to the microporous membrane, operating at low temperatures where water vapour transport is limited does not offer any advantage to mass transfer within the nonporous membrane. Distinct gas transport properties have therefore been demonstrated for microporous and nonporous membranes. At low temperatures, the microporous membrane resistance is comparable to a dry membrane and offers negligible mass transfer resistance. For higher temperatures more relevant for carbon capture, the dense polymer permeability increases while wetting begins to dominate within the micropores. Consequently, microporous membranes may favour ambient temperature applications such as biogas upgrading, whereas nonporous membranes may represent the best available technology for carbon capture. Microporous membranes have also demonstrated resilience during exposure to real biogas containing volatile organic compounds (320 mg m⁻³) such as siloxanes, which could be simultaneously absorbed into the liquid-phase under sufficient pressure to overcome their inherent low solubility (Houlker et al., 2021b;

Tansel and Surita, 2019). Permeability data for poly(4-methyl-1-pentene) suggests that the separation layer must be reduced from 1.0 to 0.1 μm for the nonporous membrane to achieve comparable mass transfer (Appendix B3). Notably, incorporation of a sub-micron polymer layer requires the addition of a gutter layer which can modify permeability and selectivity and increases complexity for commercial fabrication (Kattula et al., 2015). Gas pressurisation represents an alternative strategy to enhance mass transfer, that may compensate for high membrane resistances.

Table 3.3: Comparison of dense-skin properties

Polymer	Solvent	Dense-skin μm	CO ₂ permeability ^a barrer	Reference
PMP	DI water	$\sim 1.0^b$	29	This study
PMP	None	0.1	61	Mohamad et al. (2019)
PMP	None	0.1-0.2	99	Makhloufi et al. (2013)
PMP	None	0.1	93-128	Yasuda & Rosengren (1970)
Teflon AF1600	30% MEA	12	290	Scholes et al. (2015b)
Teflon AF1600	None	12	512	
PTMSP	30% MEA	2	31100	
PTMSP	None	2	632	

^a Reported at 35°C

^b Provided by manufacturer

3.3.2 Plasticisation and pore wetting do not limit CO₂ separation under pressure

To determine the effect of pressure on CO₂ mass transfer in HFMC, the gas inlet was initially fixed to pure CO₂ (>99.7%) to provide a consistent gas-phase resistance. Consistent overall mass transfer resistance was observed for the microporous and nonporous membranes for pressures up to 4.5 bar (Figure 3.6a). This is in agreement with the work of Dindore et al. (2004). This infers that pore wetting of the microporous membrane was successfully avoided by employing a constant transmembrane pressure of 0.2-0.4 bar across the liquid inlet - gas outlet (Dindore et al., 2004). Consistent overall mass transfer resistance for the nonporous membrane up to 4.5 bar indicated that the dense polymer did not undergo plasticisation as has been observed for other polymers

previously (Figure 3.6a) (Kapantaidakis et al., 2003). Notably, the relatively thick polymer layer (1 μm) may have provided the mechanical strength to withstand deformation during pressurisation. The density of CO_2 (and its concentration, C_g) will increase in direct proportion with gas pressure (Appendix B1). Consequently, an enhancement in CO_2 flux was observed in proportion to the extent of pressurisation (Figure 3.6b; Appendix B1). Pressurised gas-liquid absorption can therefore enable increased gas loading ($\text{mol m}^{-2} \text{s}^{-1}$) at the same solvent flowrate which reduces normalised pumping costs, regeneration load and cooling demand.

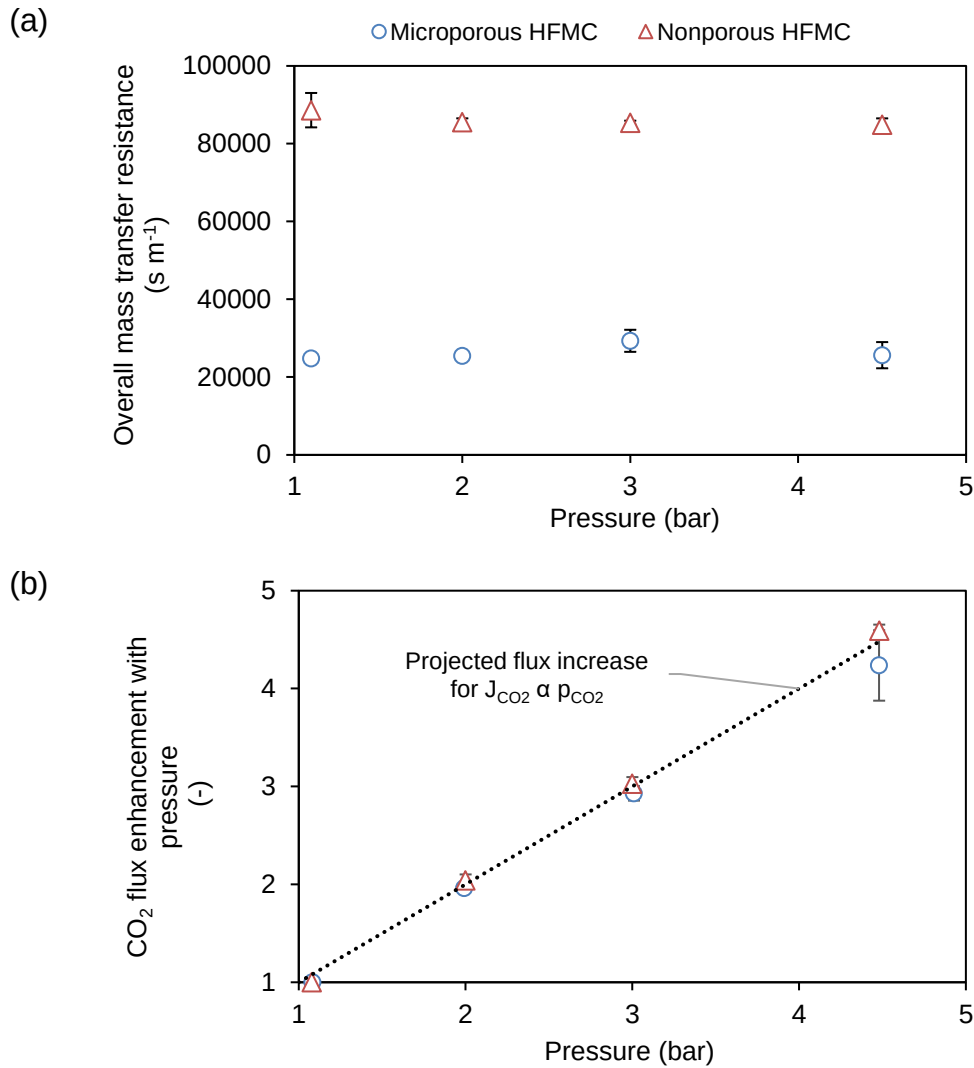
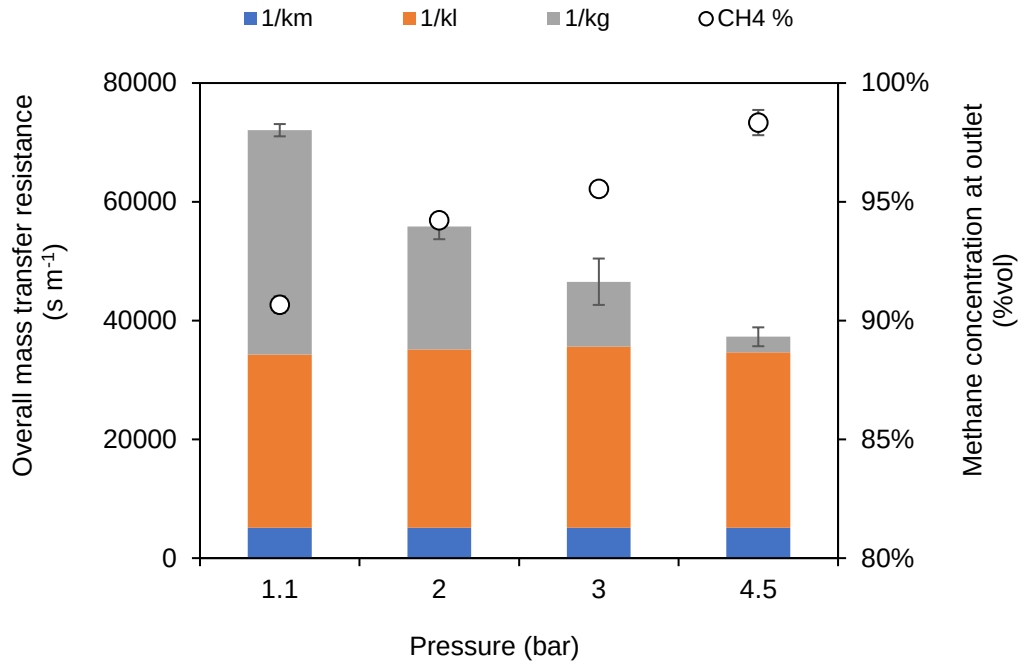


Figure 3.6: Impact of gas pressure on (a) overall mass transfer resistance, and (b) CO_2 flux enhancement across microporous (PP) and nonporous (PMP) membranes. Conditions: Pure CO_2 gas feed; v_l , $3.2 \times 10^{-3} \text{ m s}^{-1}$; v_g , $0.07\text{-}0.08 \text{ m s}^{-1}$; solvent temperature, $5\text{-}10^\circ\text{C}$; gas temperature in, 21°C . Flux enhancement: $J_{\text{CO}_2}/(J_{\text{CO}_2} \text{ at } 1.1 \text{ bar})$. Dotted line at $J_{\text{CO}_2} \propto P_{\text{CO}_2}$.

Gas pressurisation was subsequently investigated using a 50:50 CO₂-CH₄ gas feed to introduce the gas-phase resistance component to CO₂ transport (Figure 3.7). Resistance-in-series analysis was based upon consistent membrane resistance observed for the microporous and nonporous membrane following pressurisation. Membrane resistance of the dense polymer is inversely proportional to the pressure dependent permeability parameter (Eq. 3.7) (Villeneuve et al., 2018). Consequently, membrane resistance is a constant that is independent of pressure and so it can be inferred that the sorption of water vapour did not obviously increase with applied pressure. Liquid-phase resistance was also consistent across the pressure range studied for both membranes since the solubility of CO₂ increased in proportion to the pressure applied (Cesari et al., 2021). However, gas-phase resistance reduced following an increase in pressure. This can be explained by the increase in volumetric concentration of CO₂ with pressure which increases the driving force for mass transfer while sustaining the same residence time for separation. For example, in the microporous membrane, $1/k_g$ decreased from 37800 s m⁻¹ at 1.1 bar to 2650 s m⁻¹ at 4.5 bar. Consequently, the increased rate of mass transfer complemented by the higher CO₂ solubility in solution, led to a higher methane gas composition at the outlet, which increased from 91 to 98% CH₄ following pressurisation. Comparable behaviour was demonstrated with the nonporous membrane. However, methane concentration at the gas outlet did not increase significantly following pressurisation to 2 bar. This pressure is coincident with the region where $1/k_m$ becomes the dominant resistance to mass transfer (57%). Under these conditions, CO₂ flux is therefore more closely controlled by permeability of the dense polymer layer, and since permeability is proportionate to pressure ($\approx 1/k_m$), a comparable methane outlet concentration was determined above 2 bar. This analysis suggests that the selectivity provided by the dense polymer layer is not beneficial under pressure as has been previously proposed. Instead, it may negate the selectivity advantage that can be imparted when the liquid-phase controls mass transfer, as is the case for the non-wetted microporous membrane.

(a)



(b)

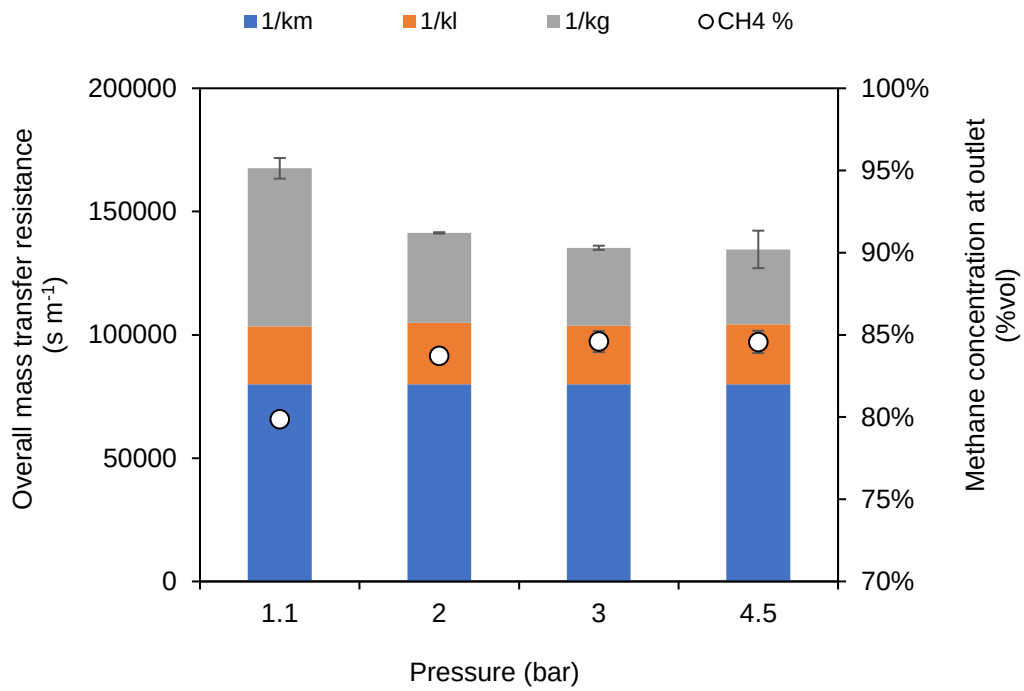


Figure 3.7: Impact of gas pressure on mass transfer resistance within: (a) the microporous membrane, and (b) the nonporous membrane. Membrane resistances previously determined (Figure 3.3) and liquid-phase resistance estimated using Graetz-Leveque solution (Eq. 3.5). Conditions: 50:50 CO_2/CH_4 gas feed; v_g , $0.02\ \text{m}\ \text{s}^{-1}$; v_l , $1.7 \times 10^{-3}\ \text{m}\ \text{s}^{-1}$; Gz number, 15; solvent temperature, $5\text{--}10^\circ\text{C}$; gas temperature $\text{in}=21^\circ\text{C}$.

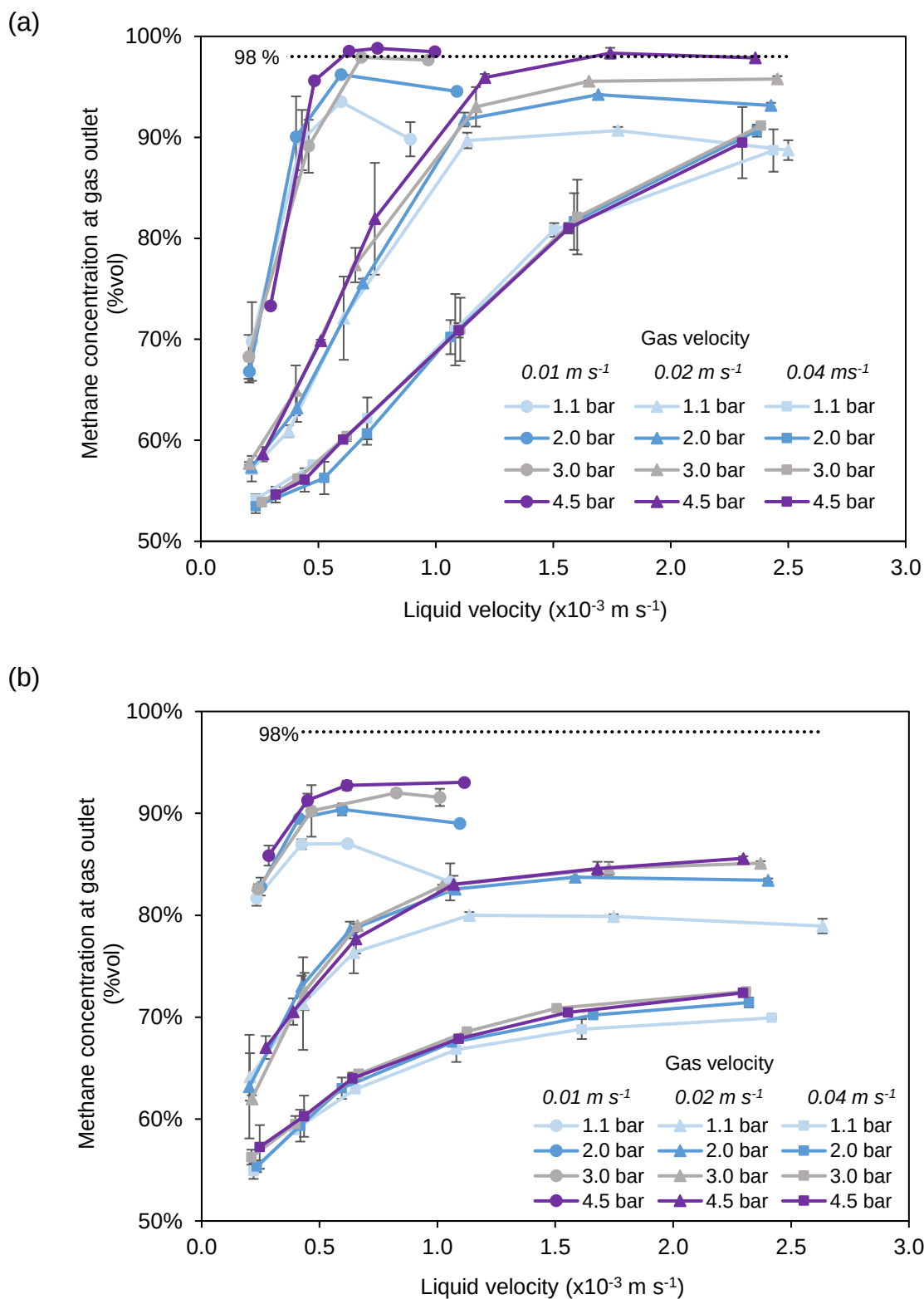


Figure 3.8: Impact of gas pressure on methane outlet concentration during binary gas separation within: (a) the microporous membrane, and (b) the nonporous membrane. Conditions: 50:50 CO₂/CH₄ gas feed; solvent temperature, 5-10°C; gas temperature in, 21°C. Dotted line represents 98%vol methane concentration in outlet gas. Absolute pressure values provided.

3.3.3 Pressurisation enhances CO₂ selectivity during biogas upgrading

To characterise how high gas pressures and low solvent temperatures can enhance selectivity, transitions in liquid and gas-phase velocity were undertaken to vary mass transfer resistance while modifying gas and solvent loading (Figure 3.8). The CO₂ partial pressure declined across the length of the HFMC as indicated by an increase in outlet methane concentration. At a gas velocity of 0.01 m s⁻¹ and 1.1 bar pressure, an increase in liquid velocity within the microporous HFMC enabled a peak outlet gas quality of 94%vol at v_L 0.6x10⁻³ m s⁻¹. The enhancement in gas product quality is due to the reduction in liquid-phase resistance at higher liquid velocity, which increased CO₂ mass transfer into the solvent (Houlker et al., 2021a). When increasing pressure to 4.5 bar, a higher outlet gas quality could be achieved at a lower liquid velocity than at 1.1 bar. A final product quality of >98% methane was achieved. This conforms with industrial standards for biomethane (Bauer et al., 2013), and demonstrates that pressure is not only advantageous for the rate of mass transfer but can also enhance product quality within the same process scale. While increasing gas velocity to 0.02 m s⁻¹ raised gas loading and shortened residence time, comparable gas-phase quality could be achieved at the highest pressure studied (4.5 bar). However, at lower pressures, the same product quality could not be achieved. The observed enhancement in gas quality with pressurisation is reflected by an increase in selectivity for CO₂ (Figure 3.9). Whilst both CO₂ and methane fluxes are enhanced by pressure, there is a greater relative increase for CO₂ due to the associated reduction in gas-phase resistance (Figure 3.7). As methane is the majority component in the gas-phase, $1/k_g$ will be less significant and thus CO₂ mass transfer will be less affected by pressurisation (Houlker, 2019). In the nonporous module, higher liquid velocities and lower gas loading also increased methane purity of the product gas due to an increased surface renewal within the solvent, and a longer residence time in the gas-phase (Figure 3.8). Pressure was also demonstrated to increase gas product quality but could not achieve the target concentration specified for biomethane. Pressurisation is therefore not sufficient to offset the reduction in permeability introduced by low temperature. Since $1/k_m$ will primarily control mass transfer at high v_L , where the

plateau is approached, the resistance is too high to take advantage of the enhanced selectivity provided by the polymer that must be compensated for either by a reduction in gas flow rate or a reduction in membrane resistance by incorporation of a thinner separation layer, and/or the application of a polymer which exhibits a higher gas permeability.

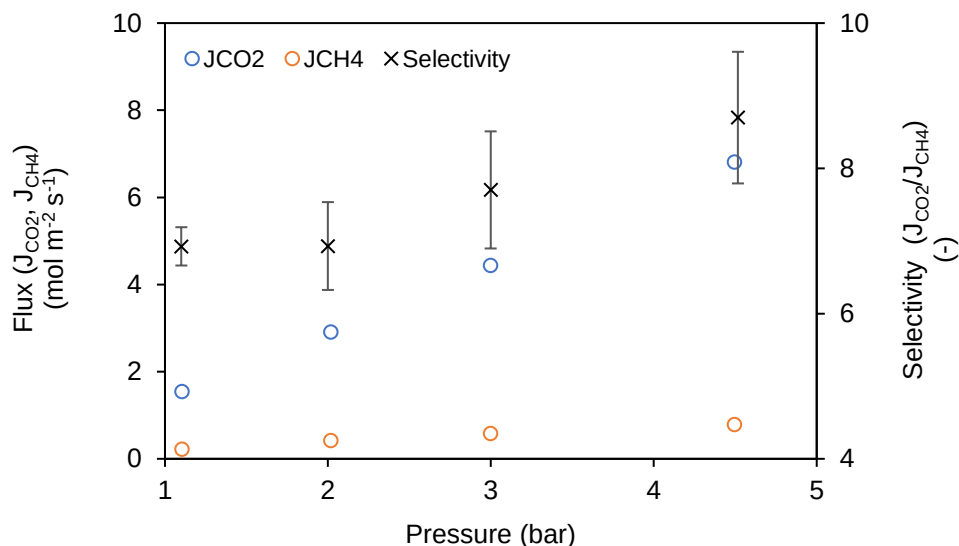


Figure 3.9: Influence of pressure on the selectivity of CO₂ transport within the microporous membrane. Conditions: 50:50 CO₂/CH₄ gas feed; v_g , 0.02 m s⁻¹; v_l , 1.7x10⁻³ m s⁻¹; solvent temperature, 5-10°C; gas temperature in, 21°C.

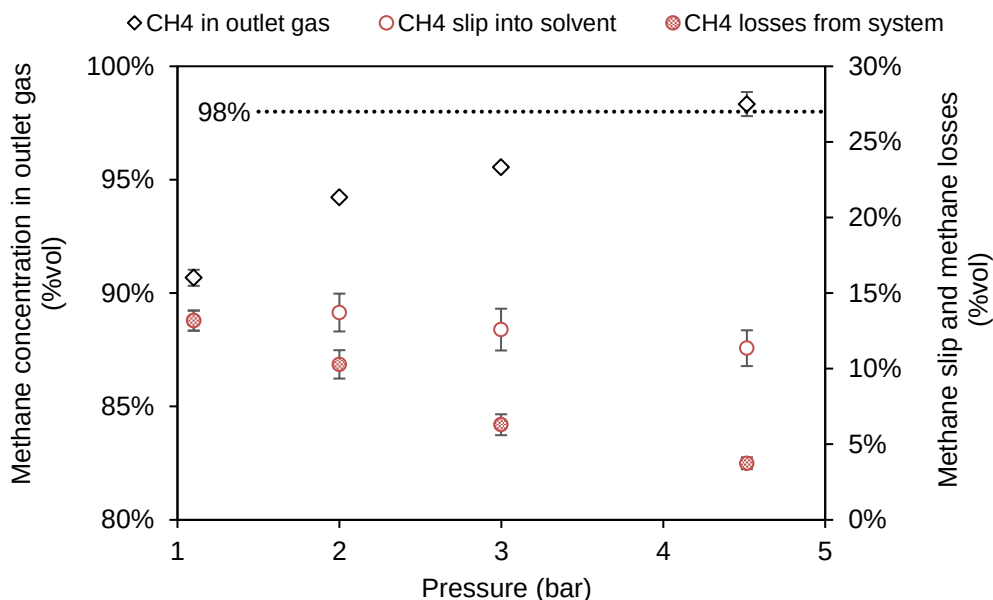


Figure 3.10: Impact of gas pressure on outlet gas quality, methane slip and methane losses from the system in the microporous module. Conditions: 50:50 CO₂/CH₄ gas feed; v_g , 0.02 m s⁻¹; v_l , 1.7x10⁻³ m s⁻¹; solvent temperature, 5-10°C; gas temperature in, 21°C. Ideal dissolved methane recovery estimated for solvent depressurisation to 1.5 bar in a flash vessel.

While methane flux into the solvent is less significant than for CO₂, the ‘slip’ of methane into the solvent is critically important to biogas upgrading, due to methane constituting a global warming potential 21-times greater than CO₂ (IPCC, 2007). As such, the carbon benefit of biomethane is fully negated when methane losses exceed 13%vol. By increasing pressure, gas quality can be improved at a fixed liquid velocity through the higher CO₂ gas-phase partial pressure which enhances CO₂/CH₄ selectivity (Figure 3.10). This lowers the energy demand for biogas upgrading, since the liquid velocity will determine the energy consumption required for the compression, chilling and regeneration of the solvent. Methane mass transfer is liquid-phase controlled and so ‘slip’, as a volume fraction of methane in the raw biogas feed, was relatively consistent across pressures (McLeod et al., 2013). However, operating at higher pressures will allow recovery of a greater fraction of the slipped methane once the solvent is depressurised ahead of solvent regeneration (so called ‘flash’) which will lower overall methane losses (Bucklin and Schendel, 1985; Kapoor et al., 2019). As such, whilst 11%vol methane slip occurred during biomethane production in the microporous membrane at 4.5 bar, this can be reduced to 4%vol methane losses from the system through downstream recovery. In practice, losses below 1-2%vol are necessary to compete with commercial PWA biogas upgrading plants (Kvist and Aryal, 2019), whilst losses below 0.5%vol are necessary to qualify for financial incentivisation under the German tariff system (EEG 2009) (Patterson et al., 2011). A further increase in pressure into the range utilised by commercial PWA plants (7-10 bar) may be necessary to lower methane losses to satisfy this incentivisation threshold (Angelidaki et al., 2018). This pressure range was evidenced to be feasible for microporous HFMC by Dindore et al. (2004) for pure CO₂, and it can be inferred from this study that methane losses will progressively reduce with increasing pressure. However, demonstration of this reduction in slip at higher pressures must be validated for CO₂/CH₄ binary gas separation. This may be complemented by increasing gas loading into the HFMC (Figure 3.8), where the increased rate of mass transfer can further enhance CO₂/CH₄ selectivity to sustain product quality (>98%vol) while minimising slip (Table 3.4).

Table 3.4: Performance comparison for binary separation at 4.5 bar, for conditions facilitating 98-99%vol CH₄ product quality in microporous HFMC at different gas loading rates.

V_g m s ⁻¹	V_l x10 ⁻³ m s ⁻¹	$1/K_{ov}$ s m ⁻¹	Selectivity J_{CO_2} / J_{CH_4}	CH ₄ slip %vol
0.01	0.6	37300	7.4	13%
0.02	1.7	50500	8.7	11%

Volumetric analysis demonstrates the increased gas loading that can be achieved under pressure using considerably less absorption solvent (Figure 3.10) and delivering a higher gas quality. However, the volumetric methane ‘slip’ (rather than losses) is within a comparable range across the pressures tested. This can be explained by the normalisation of L/G for pressure ($m^3_{liquid} m^{-3}_{gas}$) which creates a volumetric equivalency for the gas-phase, but with a higher molar concentration as pressure is increased (Figure 3.11). Consequently, methane slip into the liquid-phase is in proportion to the gas-phase partial pressure, where the dotted line evidences that an equilibrium is achieved between gas and solvent such that ‘slip’ can be estimated based on Henry’s law for microporous HFMC (Figure 3.11b; Appendix B.1). The equilibrium line also confirms that methane mass transport was not hindered by the microporous membrane (McLeod et al., 2013). In the nonporous module, methane ‘slip’ similarly followed equilibrium in proportion with the pressure normalised L/G ratio up to a value of 2-3, after which methane slip was seemingly mitigated (Figure 3.11c). This point of transition is consistent with the permeance of methane across the polymer layer approaching 1.5 GPU, close to the limit for poly(4-methyl-1-pentene) (2 GPU) (Mohr and Paul, 1991; Nematollahi et al., 2016). We therefore propose that within this operating region, methane transport is limited by the permeance of the polymer whose properties then determine CO₂/CH₄ selectivity. However, due to the material resistance, higher L/G ratios were required to achieve peak outlet gas quality in the nonporous membrane (~3.6 versus ~1.5 for microporous), increasing slip sufficiently to offset the advantage of the CO₂/CH₄ selectivity provided by the polymer layer. On this basis, microporous membranes may be preferential for producing biomethane to industrial standards, where low temperatures provide resilience to wetting and high pressures can benefit CO₂/CH₄ selectivity to improve product quality, while minimising methane losses.

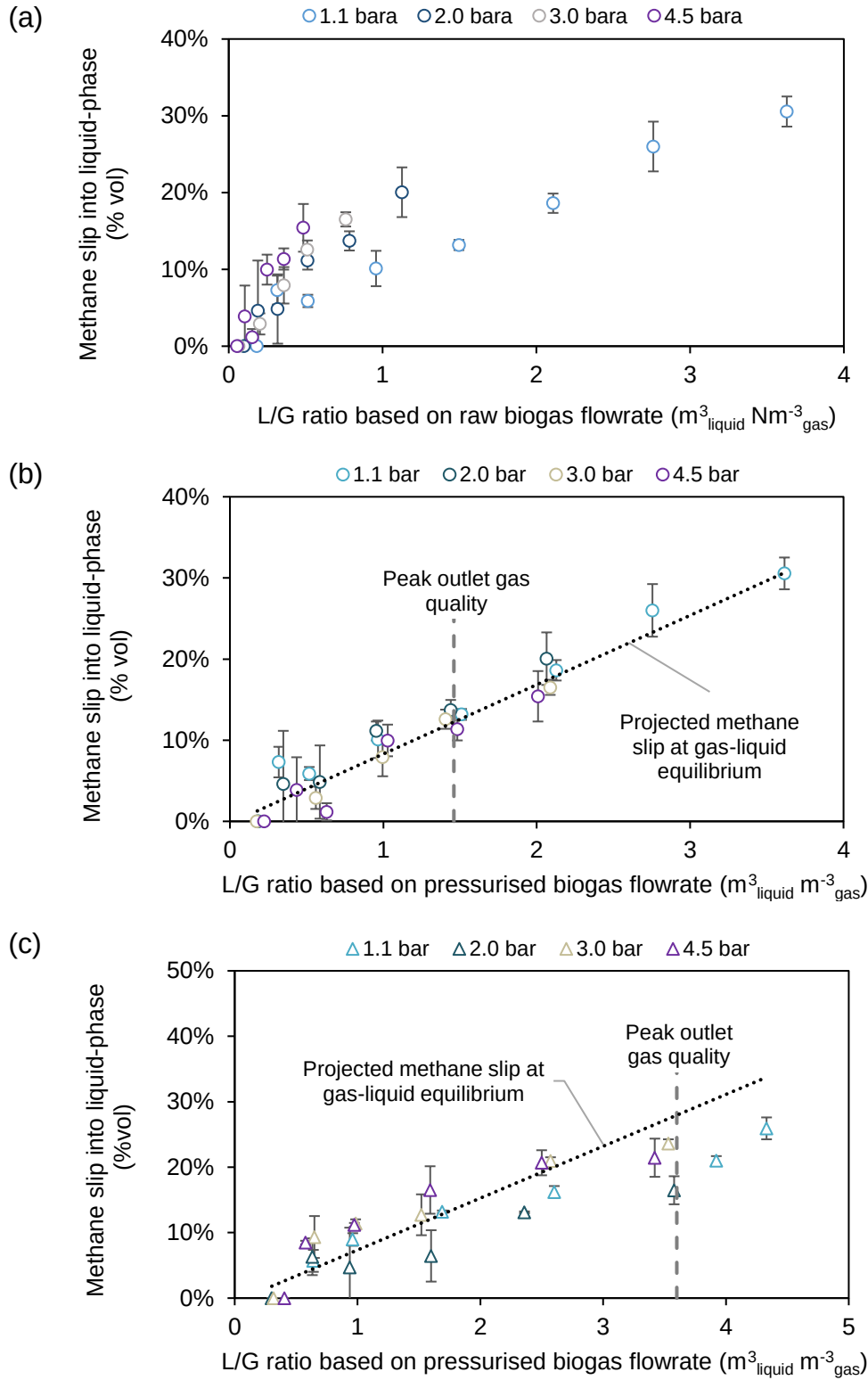


Figure 3.11: Methane slip into liquid-phase within: (a) the microporous membrane ($\text{m}^3_{\text{liquid}} \text{Nm}^{-3}_{\text{gas}}$), (b) the microporous membrane normalised to pressure ($\text{m}^3_{\text{liquid}} \text{m}^{-3}_{\text{gas}}$), and (c) the nonporous membrane normalised to pressure ($\text{m}^3_{\text{liquid}} \text{m}^{-3}_{\text{gas}}$). Conditions: 50:50 CO_2/CH_4 gas feed; v_g , 0.02 m s^{-1} ; solvent temperature, $5\text{-}10^\circ\text{C}$; gas temperature in, 21°C . Dotted line represents projected slip. Dashed line indicates the L/G ratio at peak outlet gas quality for a specific condition (Figure 3.8).

3.4 Conclusion

This study has investigated the concomitant role of pressure and temperature on CO₂ mass transfer and selectivity within microporous and nonporous membranes for the first time, which is critical to advancing HFMC as a next-generation biogas upgrading technology. Based on a systematic examination of temperature, the reduction in wetting observed at lower temperatures is not due to an increase in surface tension, but the reduction in vapour pressure of the solvent which mitigates capillary condensation within the pore structure. The presence of water vapour in real biogas will reduce the vapour pressure gradient across the membrane and is likely to further mitigate the probability and extent of wetting by condensation. Consequently, microporous membranes may be more robust for biogas upgrading than for flue gas carbon capture due to the lower temperature of the gas-phase. Inline chillers are commonly present in biogas pipelines to modify relative humidity of biogas before gas treatment, and so an engineered approach to temperature control may be practically achievable to further enhance separation robustness.

This is the first study to examine pressurisation of a non-stationary binary gas-phase within a microporous HFMC and illustrates that despite the significant pressure and velocity transient across the gas-side of the membrane when under pressure, wetting was not instigated when transmembrane pressure was regulated to below the breakthrough pressure. Henry's solubility constant increased in proportion to pressure and as such liquid-phase resistance was independent of pressure. Conversely, resistance within the gas film is reduced by increasing pressure due to the increased volumetric concentration which enhances the driving force for mass transfer in proportion to the pressure applied. This mechanism is comparable between microporous and nonporous HFMC, despite mass transfer being primarily controlled by membrane resistance within the poly(4-methyl-1-pentene) separation layer which was constant due to its inverse relationship to the pressure dependent polymer permeability. Although CO₂ permeability within poly(4-methyl-1-pentene) was ostensibly below that reported for dry conditions, membrane resistance was consistent as pressure

was increased, suggesting that water vapour sorption and plasticisation behaviour do not significantly inhibit CO₂ permeation.

Pressurisation can enhance CO₂ selectivity to improve gas product quality and levelised cost of production (capital and operational savings) while also minimising methane losses through 'slip' and enhancing methane recovery which is of practical significance to the viability of HFMC for biogas upgrading. Future work could include a detailed economic evaluation examining interactions between membrane material and operational conditions to enable direct comparison for biogas upgrading in HFMC and absorption columns. While pressurisation is shown to reduce the cost of nonporous membranes through an increase in flux, microporous HFMC have been demonstrated as an effective solution for low temperature, high pressure applications within this study, and as such poly(4-methyl-1-pentene) based membranes are unlikely to compete economically unless they can be manufactured with an ultrathin dense layer that offers comparable mass transfer without compromising mechanical strength and plasticisation behaviour. Existing nonporous membranes may still prove competitive for high temperature, high pressure CO₂ applications due to the enhancement in permeability, and comparative increased risk of wetting in microporous membranes.

Acknowledgements

We are grateful for the financial and technical support offered by Anglian Water, Northumbrian Water and Severn Trent Water. We also acknowledge the funding and training resources provided to Benjamin Luqmani from the Engineering and Physical Sciences Research Council through the STREAM Industrial Doctorate Centre. Data underlying this paper can be accessed at <https://doi.org/10.17862/cranfield.rd.22634158.v1>.

Appendix B

B1 Supporting equations

Gas flow measurements were corrected based on the temperature and pressure:

$$Q_{g,out} = Q_{g,bubble} \left(\frac{P_{g,out}}{P_{g,in}} \right) \left(\frac{T_{g,in}}{T_{g,out}} \right) \quad (\text{Eq. B1})$$

where $Q_{g,bubble}$ is the gas flowrate measured using the bubble flowmeter [$\text{m}^3 \text{s}^{-1}$]; $P_{g,out}$ is the gas pressure at the point of measurement [1 bar]; $T_{g,out}$ is the gas outlet temperature at the point of measurement [K] and $T_{g,in}$ is the gas inlet temperature [K].

Gas-phase CO_2 concentrations were determined using the ideal gas law:

$$C_g = \frac{n}{V} = \frac{P_g}{z R T_g} \quad (\text{Eq. B2})$$

where n/V is the amount of CO_2 per unit volume [mol m^{-3}]; P_g is the total gas pressure [bar]; z is the compressibility factor for CO_2 [-] and T_g is the gas temperature [K].

The probability for capillary condensation is described by the Kelvin equation:

$$\ln \left(\frac{P_{eq}}{P_{sat}} \right) = - \left(\frac{2 \gamma v_l}{R T x_{crit}} \right) \cos \theta \quad (\text{Eq. B3})$$

where P_{eq} is the equilibrium vapour pressure (bar); P_{sat} is the saturated vapour pressure (bar); γ is the liquid surface tension (N m^{-1}); v_L is this liquid molar volume ($\text{m}^3 \text{mol}^{-1}$); and x_{crit} is the average pore diameter (m).

Polymer permeability is related to temperature through an Arrhenius relationship:

$$P_d = P_{d,0} e^{\frac{-E_a}{RT}} \quad (\text{Eq. B4})$$

where P_d is polymer permeability (barrer) $P_{d,0}$ is a constant (-) and E_a is the polymer activation energy (J mol^{-1}).

Methane slip could be projected based upon gas-liquid equilibrium at the HFMC outlet:

$$CH_4 \text{ slip} = \frac{Q_l C_{CH_4,l,out}^*}{Q_{g,in} C_{CH_4,g,in}} \quad (\text{Eq. B5})$$

$$C_{CH_4,l}^* = P_{CH_4,out} \rho_l k_H^o e^{\left[c \left(\frac{1}{T_l} - \frac{1}{298.15} \right) \right]} \quad (\text{Eq. B6})$$

where $C_{CH_4,l}^*$ is the equilibrium concentration of methane in the liquid-phase [mol m⁻³]; ρ_l is density of pure water at the liquid temperature [kg m⁻³]; $p_{CH_4,out}$ is the partial pressure of methane in the gas outlet [bar]; k_H^0 and c are the Henry's Law constant for methane in pure water at 298 K [0.0013 mol kg⁻¹ bar⁻¹] and its temperature dependence constant [K] respectively (Sander, 2015); T_l is the liquid-phase temperature [K].

B2 Evaluation of Graetz-Leveque solution accuracy

Liquid-phase resistances from the Graetz-Leveque solution (Eq. 3.5) were projected over a range of liquid velocities at 5, 10, 20 and 35 °C (Figure B1). The error between the projected values and the experimental values was calculated and compared (Figure B2). A convergence between projected and experimental values to within ± 5000 s m⁻¹ was observed above $Gz = 15$, providing an acceptable degree of accuracy. Application of the Graetz-Leveque solution under these conditions supported the deduction of gas-phase mass transfer resistances during binary gas experiments.

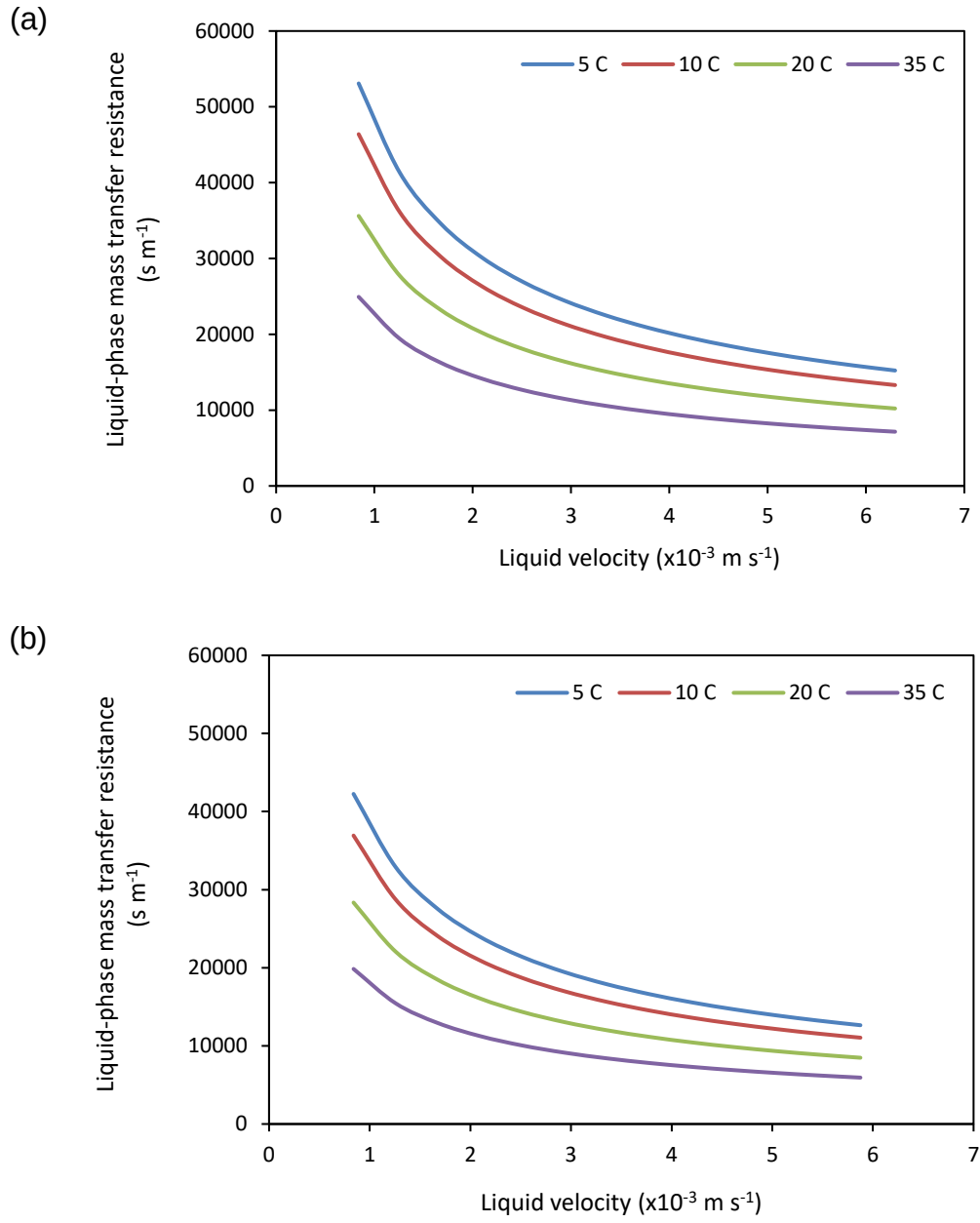


Figure B1: Projected impact of temperature on liquid-phase mass transfer resistance for CO_2 transport from the liquid-membrane interface to the liquid bulk for the (a) microporous, and (b) nonporous membranes (Eq. 3.5).

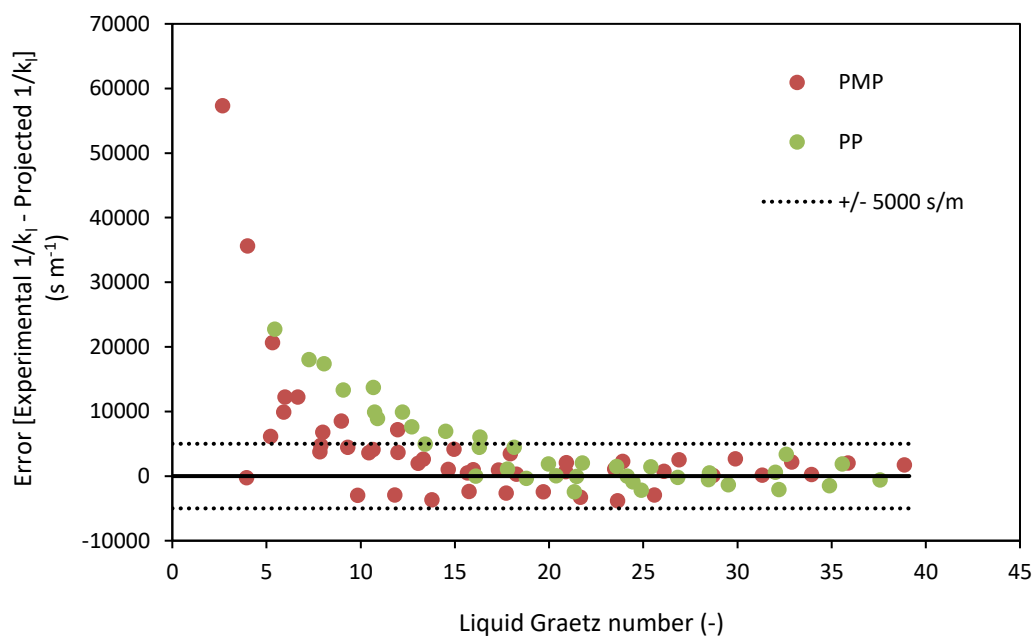


Figure B2: Evaluation of Graetz-Leveque solution accuracy in the microporous (PP) and nonporous (PMP) membranes. Conditions: Pure CO_2 gas feed; v_G , 0.07-0.08 m s^{-1} ; P_g , 1.1 bar; gas temperature in, 21°C. Dotted lines at 5000 and -5000 s m^{-1} to represent typical error.

B3 - Impact of thinning dense-skin for nonporous module

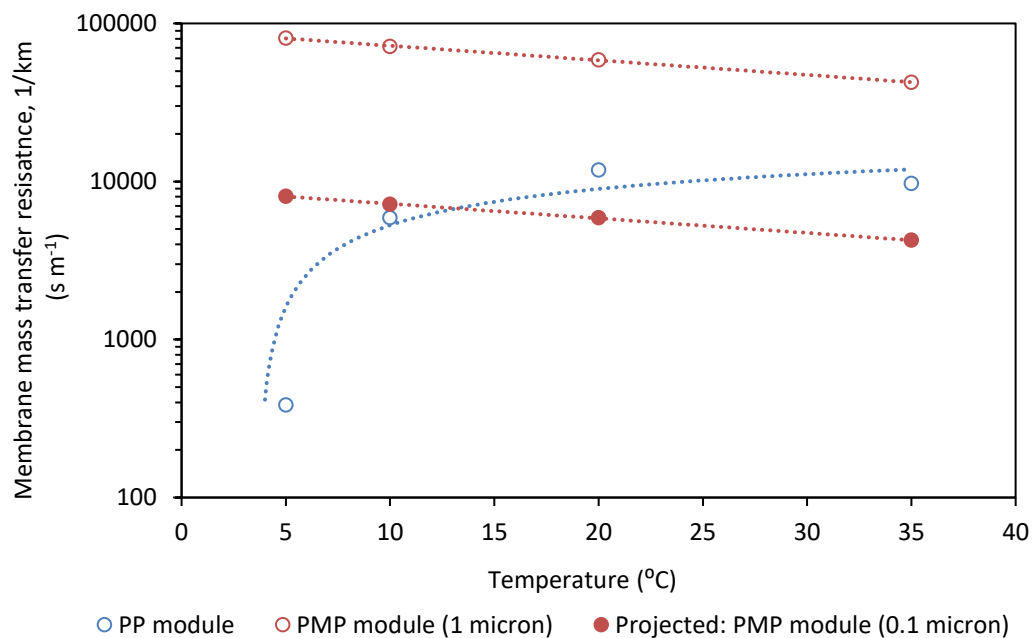


Figure B3: Impact of reducing dense-skin thickness on membrane mass transfer resistance for the nonporous (PMP) module. Resistance at 0.1 μm dense-skin thickness projected based upon experimental permeability data (Eq. 3.7). Dotted lines added to guide the eye.

References

- 3M. (2023). Liqui-Cel EXF Series Membrane Contactors - Cleaning and Storage Guidelines. <https://multimedia.3m.com/mws/media/2282742O/pdf-of-the-cleaning-and-storage-guidelines-for-the-3m-liqui-cel-exf-membrane-contactors.pdf> (accessed 24/04/2023).
- Alberici, S., Moultaq, M., and Peters, J. (2021). The future role of biomethane. https://www.europeanbiogas.eu/wp-content/uploads/2022/01/The_future_role_of_biomethane-December_2021.pdf (accessed 31/03/2023).
- Angelidaki, I., Treu, L., Tsapekos, P., Luo, G., Campanaro, S., Wenzel, H., and Kougias, P. G. (2018). Biogas upgrading and utilization: Current status and perspectives. *Biotechnology Advances*, 36, 452–466.
- Atchariyawut, S., Feng, C., Wang, R., Jiratananon, R., and Liang, D. T. (2006). Effect of membrane structure on mass-transfer in the membrane gas–liquid contacting process using microporous PVDF hollow fibers. *Journal of Membrane Science*, 285, 272–281.
- Baudot, A., Flourey, J., and Smorenburg, H. E. (2001). Liquid-Liquid Extraction of Aroma Compounds with Hollow Fiber Contactor. *AIChE Journal*, 47, 1780–1793.
- Bauer, F., Hulteberg, C., Persson, T., and Tamm, D. (2013). Biogas upgrading – Review of commercial technologies. SGC. http://vav.griffel.net/filer/C_SGC2013-270.pdf (accessed 31/03/2023).
- Bavarella, S. (2018). Chemically reactive membrane crystallisation reactor for CO₂ separation and ammonia recovery. PhD thesis. Cranfield University.
- Bavarella, S., Luqmani, B., Thomas, N., Brookes, A., Moore, A., Vale, P., Pidou, M., and McAdam, E. J. (2022). CO₂ absorption into aqueous ammonia using membrane contactors: Role of solvent chemistry and pore size on solids formation for low energy solvent regeneration. *Separation and Purification Technology*, 290, 120786.
- Belaissaoui, B., Claveria-Baro, J., Lorenzo-Hernando, A., Albarracin Zaidiza, D., Chabanon, E., Castel, C., Rode, S., Roizard, D., and Favre, E. (2016). Potentialities of a dense skin hollow fiber membrane contactor for biogas

- purification by pressurized water absorption. *Journal of Membrane Science*, 513, 236–249.
- Bucklin, R. W., and Schendel, R. L. (1985). Comparison of Physical Solvents Used for Gas Processing. In S. A. Newman (Ed.), *Acid and Sour Gas Treating Processes* (pp. 42–48). Gulf Publishing Company, Houston, TX, USA.
- Cesari, L., Castel, C., and Favre, E. (2021). Membrane contactors for intensified gas-liquid absorption processes with physical solvents: A critical parametric study. *Journal of Membrane Science*, 635, 119377.
- Chabanon, E., Belaisaoui, B., and Favre, E. (2014). Gas-liquid separation processes based on physical solvents: Opportunities for membranes. *Journal of Membrane Science*, 459, 52–61.
- Chabanon, E., Roizard, D., and Favre, E. (2013). Modeling strategies of membrane contactors for post-combustion carbon capture: A critical comparative study. *Chemical Engineering Science*, 87, 393–407.
- Chan, Z. P., Li, L., Kang, G., Manan, N. A., Cao, Y., and Wang, T. (2020). Discussion on Water Condensation in Membrane Pores during CO₂ Absorption at High Temperature. *Membranes*, 10, 407.
- Chen, G. Q., Scholes, C. A., Doherty, C. M., Hill, A. J., Qiao, G. G., and Kentish, S. E. (2012). Modeling of the sorption and transport properties of water vapor in polyimide membranes. *Journal of Membrane Science*, 409–410, 96–104.
- Connor, P. M., Xie, L., Lowes, R., Britton, J., and Richardson, T. (2015). The development of renewable heating policy in the United Kingdom. *Renewable Energy*, 75, 733–744.
- Cui, Z., and Demontigny, D. (2013). Part 7: A review of CO₂ capture using hollow fiber membrane contactors. *Carbon Management*, 4, 69–89.
- Dai, Z., and Deng, L. (2016). Membrane absorption using ionic liquid for pre-combustion CO₂ capture at elevated pressure and temperature. *International Journal of Greenhouse Gas Control*, 54, 59–69.
- Dindore, V. Y., Brilman, D. W. F., Feron, P. H. M., and Versteeg, G. F. (2004). CO₂ absorption at elevated pressures using a hollow fiber membrane contactor. *Journal of Membrane Science*, 235, 99–109.

- Feng, X., and Huang, R. Y. M. (1996). Estimation of activation energy for permeation in pervaporation processes. *Journal of Membrane Science*, 118, 127–131.
- Frank, M. J. W., Kuipers, J. A. M., and van Swaaij, W. P. M. (1996). Diffusion Coefficients and Viscosities of CO₂ + H₂O, CO₂ + CH₃OH, NH₃ + H₂O, and NH₃ + CH₃OH Liquid Mixtures. *Journal of Chemical Engineering Data*, 41, 297–302.
- Gabelman, A., and Hwang, S. (1999). Hollow fiber membrane contactors. *Journal of Membrane Science*, 159, 61–106.
- Heile, S., Chernicharo, C. A. L., Brandt, E. M. F., and McAdam, E. J. (2017). Dissolved gas separation for engineered anaerobic wastewater systems. *Separation and Purification Technology*, 189, 405–418.
- Heile, S., Rosenberger, S., Parker, A., Jefferson, B., and McAdam, E. J. (2014). Establishing the suitability of symmetric ultrathin wall polydimethylsiloxane hollow-fibre membrane contactors for enhanced CO₂ separation during biogas upgrading. *Journal of Membrane Science*, 452, 37–45.
- Hoff, K. A., and Svendsen, H. F. (2013). CO₂ absorption with membrane contactors vs. packed absorbers- Challenges and opportunities in post combustion capture and natural gas sweetening. *Energy Procedia*, 37, 952–960.
- Houlker, S. (2019). Scale up of hollow fibre membrane contactors for biogas upgrading. EngD thesis. Cranfield University.
- Houlker, S., Davey, C. J., Allemand, A., Brookes, A., Moore, A., Vale, P., Pidou, M., and McAdam, E. J. (2021a). Reconciliation of gas to liquid mass transfer in parallel and transverse flow (cross-flow) hollow fiber membrane contactors (HFMC) for CO₂ absorption. *Separation Science and Technology*, 56, 129–140.
- Houlker, S., Rutherford, T., Herron, D., Brookes, A., Moore, A., Vale, P., Pidou, M., and McAdam, E. (2021b). Demonstrating commercial hollow fibre membrane contactor performance at industrial scale for biogas upgrading at a sewage treatment works. *Water (Switzerland)*, 13, 172.

- Intergovernmental Panel on Climate Change (IPCC). (2007). Changes in Atmospheric Constituents and in Radiative Forcing. http://www.ipcc.ch/publications_and_data/ar4/wg1/en/ch2s2-10-2.html (accessed 31/03/2023).
- Kapantaidakis, G. C., Koops, G. H., Wessling, M., Kaldis, S. P., and Sakellariopoulos, G. P. (2003). CO₂ Plasticization of Polyethersulfone / Polyimide Gas-Separation Membranes. *AIChE Journal*, 49, 1702–1711.
- Kapoor, R., Subbarao, P. M. V., and Vijay, V. K. (2019). Integration of flash vessel in water scrubbing biogas upgrading system for maximum methane recovery. *Bioresource Technology Reports*, 7, 100251.
- Kattula, M., Ponnuru, K., Zhu, L., Jia, W., Lin, H., and Furlani, E. P. (2015). Designing ultrathin film composite membranes: the impact of a gutter layer. *Nature Scientific Reports*, 5, 15016.
- Khaisri, S., DeMontigny, D., Tontiwachwuthikul, P., and Jiraratananon, R. (2009). Comparing membrane resistance and absorption performance of three different membranes in a gas absorption membrane contactor. *Separation and Purification Technology*, 65, 290–297.
- Kvist, T., and Aryal, N. (2019). Methane loss from commercially operating biogas upgrading plants. *Waste Management*, 87, 295–300.
- Lu, J. G., Zheng, Y. F., and Cheng, M. D. (2008). Wetting mechanism in mass transfer process of hydrophobic membrane gas absorption. *Journal of Membrane Science*, 308, 180–190.
- Lv, Y., Yu, X., Tu, S. T., Yan, J., and Dahlquist, E. (2010). Wetting of polypropylene hollow fiber membrane contactors. *Journal of Membrane Science*, 362, 444–452.
- Mahmud, H., Kumar, A., Narbaitz, R. M., and Matsuura, T. (2000). A study of mass transfer in the membrane air-stripping process using microporous polypropylene hollow fibers. *Journal of Membrane Science*, 179, 29–41.
- Makhloufi, C., Roizard, D., and Favre, E. (2013). Reverse selective NH₃/CO₂ permeation in fluorinated polymers using membrane gas separation. *Journal of Membrane Science*, 441, 63–72.

- Mansourizadeh, A. (2012). Experimental study of CO₂ absorption/stripping via PVDF hollow fiber membrane contactor. *Chemical Engineering Research and Design*, 90, 555–562.
- Markova, S., Shalygin, M., Pelzer, M., Gries, T., and Teplyakov, V. (2020). Application prospects of dense gas separation hollow fibers based on poly (4-methyl-1-pentene). *Chemical Papers*, 74, 1917–1921.
- Mavroudi, M., Kaldis, S. P., and Sakellaropoulos, G. P. (2006). A study of mass transfer resistance in membrane gas – liquid contacting processes. *Journal of Membrane Science*, 272, 103–115.
- McLeod, A., Jefferson, B., and McAdam, E. J. (2013). Quantifying the loss of methane through secondary gas mass transport (or 'slip') from a micro-porous membrane contactor applied to biogas upgrading. *Water Research*, 47, 3688–3695.
- Mohamad, Z., Mohd, H., Ahmad, A. L., Rode, S., Belaisaoui, B., Roizard, D., Low, S. C., Cnrs, U. D. L., Bp, G., and Cedex, N. (2019). Prospect of Oxyplus Hollow Fibre Membrane with Dense Polymethylpentene (PMP) Skin as Support-gutter Layer of Thin Film Composite (TFC) for Biogas Upgrading. *Journal of Physical Science*, 30, 179–189.
- Mohr, J. M., and Paul, D. R. (1991). Effect of casting solvent on the permeability of poly (4-methyl-1-pentene). *Polymer*, 32, 1236–1243.
- Nematollahi, M. H., Dehaghani, A. H. S., and Abedini, R. (2016). CO₂/CH₄ separation with poly(4-methyl-1-pentyne) (TPX) based mixed matrix membrane filled with Al₂O₃ nanoparticles. *Korean Journal of Chemical Engineering*, 33, 657–665.
- Nguyen, P. T., Lasseuguette, E., Medina-Gonzalez, Y., Remigy, J. C., Roizard, D., and Favre, E. (2011). A dense membrane contactor for intensified CO₂ gas/liquid absorption in post-combustion capture. *Journal of Membrane Science*, 377, 261–272.
- Northern Gas Networks. (2020). Biomethane: a producer's handbook. https://biomethane.northerngasnetworks.co.uk/wp-content/uploads/2020/07/NGN_BiomethaneHandbook_0420_St04A.pdf (accessed 31/03/2023).

- Patterson, T., Esteves, S., Dinsdale, R., and Guwy, A. (2011). An evaluation of the policy and techno-economic factors affecting the potential for biogas upgrading for transport fuel use in the UK. *Energy Policy*, 39, 1806–1816.
- Perry, R. H., & Green, D. W. (Eds.). (2007). *Perry's Chemical Engineers' Handbook* (8th ed.). McGraw-Hill, New York, NY, USA.
- Sander, R. (2015). Compilation of Henry's law constants (version 4.0) for water as solvent. *Atmospheric Chemistry and Physics*, 15, 4399–4981.
- Scarlat, N., Dallemand, J. F., and Fahl, F. (2018). Biogas: Developments and perspectives in Europe. *Renewable Energy*, 129, 457–472.
- Scholes, C. A., Kanehashi, S., Stevens, G. W., and Kentish, S. E. (2015a). Water permeability and competitive permeation with CO₂ and CH₄ in perfluorinated polymeric membranes. *Separation and Purification Technology*, 147, 203–209.
- Scholes, C. A., Kentish, S. E., Stevens, G. W., and DeMontigny, D. (2015b). Comparison of thin film composite and microporous membrane contactors for CO₂ absorption into monoethanolamine. *International Journal of Greenhouse Gas Control*, 42, 66–74.
- Shen, S., Kentish, S. E., and Stevens, G. W. (2010). Shell-side mass-transfer performance in hollow-fiber membrane contactors. *Solvent Extraction and Ion Exchange*, 28, 817–844.
- Sun, Q., Li, H., Yan, J., Liu, L., Yu, Z., and Yu, X. (2015). Selection of appropriate biogas upgrading technology-a review of biogas cleaning, upgrading and utilisation. *Renewable and Sustainable Energy Reviews*, 51, 521–532.
- Tansel, B., and Surita, S. C. (2019). Managing siloxanes in biogas-to-energy facilities: Economic comparison of pre- vs post-combustion practices. *Waste Management*, 96, 121–127.
- Villeneuve, K., Torres Hernandez, A. A., Albarracin Zaidiza, D., Roizard, D., and Rode, S. (2018). Effects of water condensation on hollow fiber membrane contactor performance for CO₂ capture by absorption into a chemical solvent. *Journal of Membrane Science*, 556, 365–373.

- Wang, R., Zhang, H. Y., Feron, P. H. M., and Liang, D. T. (2005). Influence of membrane wetting on CO₂ capture in microporous hollow fiber membrane contactors. *Separation and Purification Technology*, 46, 33–40.
- Yang, L., Ge, X., Wan, C., Yu, F., and Li, Y. (2014). Progress and perspectives in converting biogas to transportation fuels. *Renewable and Sustainable Energy Reviews*, 40, 1133–1152.
- Yasuda, H., and Rosengren, K. (1970). Isobaric measurement of gas permeability of polymers. *Journal of Applied Polymer Science*, 14, 2839–2877.

4 Examining disruptive gas-phase reactions during CO₂ capture in membrane contactors: CO₂-NH₃-H₂O as a model ternary system

Examining disruptive gas-phase reactions during CO₂ capture in membrane contactors: CO₂-NH₃-H₂O as a model ternary system

B. Luqmani^a, A. Brookes^b, A. Moore^c, P. Vale^d, M. Pidou^a, E.J. McAdam^{a,*}

^aCranfield Water Science Institute, Vincent Building, Cranfield University, Bedfordshire, MK43 0AL, UK

^bAnglian Water, Block C-Western House, Peterborough Business Park, Lynch Wood, Peterborough PE2 6FZ, UK

^cNorthumbrian Water, Boldon House, Wheatlands Way, Durham DH1 5FA, UK

^dSevern Trent Water, 2 St. Johns Street, Coventry CV1 2LZ, UK

*Corresponding Author: e.mcadam@cranfield.ac.uk

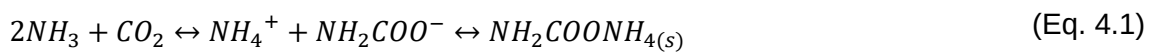
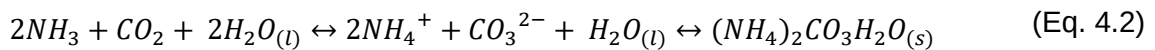
Abstract

Liquid and solid products can form in the gas-side of membrane contactors following reactive absorption of CO₂ in ternary systems, which is a critical barrier to adoption for carbon capture applications. While it is acknowledged that these products form due to ‘slip’ of reactants from the solvent, the precise mechanism is unclear. This study therefore sought to systematically characterise CO₂ absorption in distinct regions of the ternary vapour-liquid equilibrium (VLE) to provide a framework on which to develop mitigation strategies for gas-phase reactions. The CO₂-NH₃-H₂O system was used for illustration. Instability in CO₂ absorption indicated the onset of gas-phase reactions, which coincided with an increase in pressure drop due to formation of liquid products once high CO₂ capture ratios (>89%vol) were achieved. Analysis of the temporal gas-phase composition suggests liquid products form due to a critical shift in the relative composition of reactants within the ternary system. This is consistent with compositional analysis of gas-side ammonia collected in independent fractions across the system. Our study confirmed that product formation correlated to relevant regions of the VLE, implying that these mechanisms can be mitigated by identifying coordinates within the VLE where liquid and solid reaction products are less likely to form. Pressurisation was proposed as a strategy that can modify the relative gas-phase ammonia composition to more favourable coordinates within the VLE. An increase in CO₂ transfer into the solvent through pressurisation will also shift the ammonia-ammonium equilibrium toward ammonium to indirectly reduce vapour pressure. This synergistic strategy provides evidence for the operation of membrane contactors for sustained CO₂ separation in ternary systems, and is of importance to a range of prospective reactive solvents which are critical to delivering carbon capture at scale.

Keywords: HFMC, CO₂ capture, CCS, chilled ammonia process, crystallisation

4.1 Introduction

Hollow fibre membrane contactors (HFMC) are an emerging alternative to packed columns for CO₂ absorption due to their higher interfacial area which lowers installed capacity (capital cost) and solvent requirements (separation energy) (Belaissaoui et al., 2016; Houlker et al., 2021). Chemical solvents have been studied in HFMC to facilitate higher CO₂ absorption capacities and enhanced mass transfer (Khaisri et al., 2011, 2009; Scholes et al., 2015). Aqueous ammonia (NH_{3(aq)}) has a CO₂ capacity which is three times greater than amines, whilst also being cheaper, less corrosive and requiring less energy for regeneration (Chin Yeh and Hsunling, 1999; Jilvero et al., 2012; Mani et al., 2006). However, its higher volatility leads to greater 'slip' into the treated gas which has been linked to difficulties with achieving stable CO₂ separation in HFMC (Table 4.1) (Bavarella et al., 2022; Cui and DeMontigny, 2017; Villeneuve et al., 2018a). Makhloufi et al. (2014) reported a decline in CO₂ capture from 94 to 20%vol during absorption using NH_{3(aq)}. The authors associated this with the visible precipitation of solids in the gas-side of the membrane, and this phenomenon has since been observed by others (Cui and DeMontigny, 2017; Makhloufi et al., 2014). The mechanism of solids formation was postulated to arise from a gas-phase CO₂-NH₃ reaction followed by deposition onto the membrane surface which modified the hydrophobicity sufficiently to initiate liquid breakthrough into the pore structure, as indicated by an increase in the membrane mass transfer resistance (Cui and deMontigny, 2017). The crystalline solid formed within the gas-phase was presumed to be ammonium bicarbonate using compositional analysis (Bavarella et al., 2022). However, there is recognition that the reaction pathways are dependent on the conditions employed, leading to the possible formation of several solid products which include ammonium carbamate (NH₂COONH₄) (Eq. 4.1), ammonium carbonate ((NH₄)₂CO₃H₂O) (Eq. 4.2) and ammonium bicarbonate (NH₄HCO₃) (Eq. 4.3) (Mani et al., 2006):





Gas-phase precipitation could be mitigated by lowering the ammonia vapour pressure through solvent chilling (Bavarella et al., 2022). Increasing CO₂ loading of the solvent also reduced NH₃ slip by shifting the ammonia-ammonium equilibrium toward non-volatile ammonium (Bavarella et al., 2022; Darde et al., 2010; Houlker, 2019). Villeneuve et al. (2018a) observed that raising humidity within the gas feed (comparable to industrial flue gases) diminished gas-phase precipitation but a concentrated ammonia solution was formed in the gas-phase. Stable CO₂ capture was nevertheless observed, and the liquid could be continuously drained from the lumen without contributing to pore wetting or introducing an increased resistance to mass transfer (Villeneuve et al., 2018a, 2018b). The authors proposed that solids formation occurred through gas-phase reactions between CO₂, NH₃ and water, which then dissociate to release gaseous components when the CO₂ partial pressure lowers along the HFMC length (Villeneuve et al., 2018a). The liquid product was suggested to be formed by oversaturation of the gas-phase, leading to the condensation of a concentrated salt solution which exhibits an osmotic pressure sufficient to drive water from the solvent across the membrane into the gas-phase (Villeneuve et al., 2018a).

Table 4.1: Literature summary for CO₂ absorption using NH_{3(aq)} in HFMC

Membrane	C _{NH3} mol _{NH3} L ⁻¹	pH	T °C	p _{NH3} mbar	p _{H2O} mbar	CO ₂ in %vol	Process instability	Observations	Source
PP	0.6-3.0	>11 ^b	21	8-42	23-24	15%	Yes	Gas-side solids formation	(Makhloufi et al., 2014)
PTFE	3-5	11	25	51-85	29-30	50%	Yes	Gas-side solids formation	(McLeod et al., 2015)
PTFE	1.0-2.0	>11 ^b	21	14-28	24	15%	Yes	Gas-side solids formation and pore wetting	(Cui and DeMontigny, 2017)
PMP/PP ^a	3	>11 ^b	10-40	23-101	12-69	15%	Yes	Gas-side solids and liquid formation	(Villeneuve et al., 2018a)
PP	3.3	13	20	45	21	50%	Yes	Suspected pore wetting	(Houlker, 2019)
PP	3.3	9-13 ^c	6	3-22	8	50%	No	-	
PTFE	2.3-3.0	10	20	25-32	22	100%	Yes	Gas-side solids and liquid formation	(Bavarella et al., 2022)
PTFE	0.6	10	20	6	23	100%	No	-	
PTFE	2.3	7.5-10 ^c	20	1-25	22	100%	No	-	
PTFE	3.0	7.5-10 ^c	5	1-11	8	100%	No	-	

C_{NH3} – solvent concentration; T – solvent temperature; p_{NH3} and p_{H2O} – ammonia and water partial pressures in the gas-phase at equilibrium (Appendix C); PP – polypropylene; PMP – polymethylpentene; PTFE – polytetrafluoroethylene.

^a Nonporous polymethylpentene skin (0.1 micron) on polypropylene matrix

^b Solvent pH not reported - presumed to exceed pH 11 based on ammonia concentration

^c Solvent pH declined over time due to recirculation and increased CO₂ loading (Darde et al., 2010)

While a causal link has been established between the presence of an elevated ammonia vapour concentration and the development of both solid and liquid ammonia products within the gas-phase (Table 4.1), a method to predict the reaction mechanisms is yet unclear (Bavarella et al., 2022; Villeneuve et al., 2018a). Capture of CO₂ by ammonia is illustrative of a ternary system comprising CO₂-NH₃-H₂O, which is common to many current and emerging solvents for CO₂ capture (Zhao et al., 2023). In ternary systems, the relative fractions of the three components in the gas-phase will determine reaction kinetics and products (Sutter et al., 2015). The ternary vapour-liquid equilibrium (VLE) for CO₂-NH₃-H₂O (Darde, 2010; Thomsen and Rasmussen, 1999) has been resolved to accurately describe interaction between phases, and enables specific regions to be isolated where solid, liquid and vapour products could most likely form (Figure 4.1) (Sutter et al., 2015). Since gas and liquid-phases are freely mixed in conventional contacting columns, the formation of solid and liquid products is less critical to robust operation. However, in HFMC the phases are separated by the membrane, which increases the likelihood and significance of isolated gas-phase reactions. Consequently, the aim of this study is to evidence the mechanisms that underpin gas-phase reactions in the CO₂-NH₃-H₂O system by using the VLE for diagnostic characterisation. The outcome is intended to explain previous literature observations and provide a foundation on which to develop mitigation strategies for stable CO₂ absorption in HFMC which has wider relevance for reactive ternary systems.

4.2 Methodology

This study employed a similar experimental set-up to previous work (Cui and deMontigny, 2017). An 8%vol CO₂ gas was fed counter-current into the HFMC lumen, with deionised (DI) water (15 MΩ cm) or aqueous ammonia (1-3 mol_{NH3} L⁻¹) in the shell-side (6.5±0.5°C). The system was operated at a fixed volumetric gas-liquid (G/L) ratio of 4.4. At the end of each experiment, a mass balance was conducted to determine ammonia transfer into the gas-phase. Four fractions were characterised: (i) the solvent; (ii) the liquid condensate (collected in a gas-liquid separator) (Villeneuve et al., 2018a); (iii) the gas-phase outlet (captured in

an acid trap); and (iv) the residual ammonia in the HFMC lumen (using an acid rinse). Full details of the methodology are available in Appendix C.

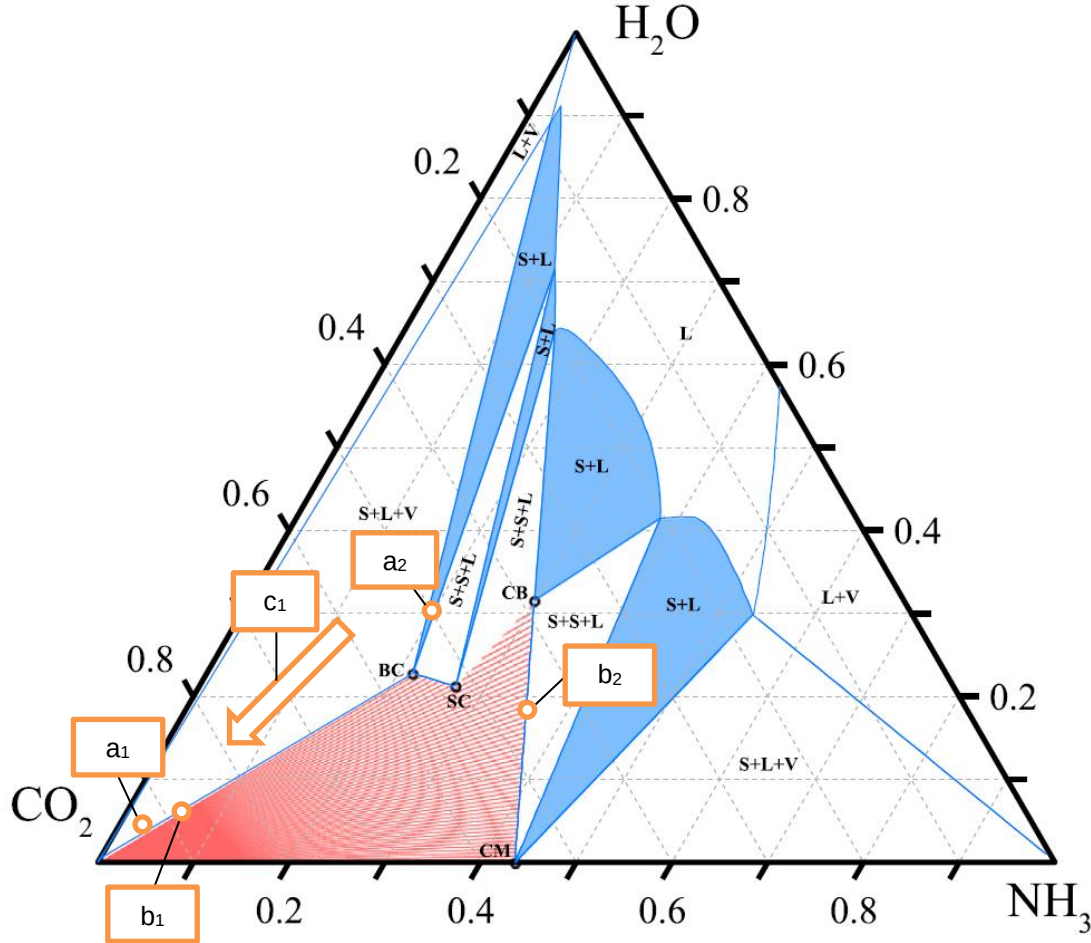


Figure 4.1: Ternary vapour-liquid-equilibrium for CO₂-NH₃-H₂O based on the output of the extended UNIQUAC model at 10°C developed by Thomsen and Rasmussen (1999). S – solid; L – liquid; V – vapour; BC – ammonium bicarbonate; SC – ammonium sesqui-carbonate; CB – ammonium carbonate; CM – ammonium carbamate. Annotations added using orange boxes and an orange arrow. Red-white shaded region could not be resolved within the model. Republished from Sutter et al. (2015) with permission from Elsevier Ltd.

4.3 Results and discussion

4.3.1 NH_{3(aq)} associated with chemical enhancement and process instability

The absorption of CO₂ by NH_{3(aq)} was compared directly to DI water to evaluate the potential for chemical enhancement. When using DI water, a consistent CO₂ capture ratio of 35%vol was established (Figure 4.2). An NH_{3(aq)} solvent (1 mol_{NH3} L⁻¹) initially increased the CO₂ capture ratio up to 92%vol but was unstable,

gradually achieving a pseudo steady-state value of 58%vol toward 60 minutes, equivalent to chemical enhancement ($J_{\text{chem}}/J_{\text{phys}}$) of 1.7 (Appendix C2). A similar trend was observed for 3 mol_{NH₃} L⁻¹, where following an initial peak in CO₂ capture ratio of 89%vol, CO₂ capture became unstable, eventually reaching a pseudo steady-state value of 83%vol ($J_{\text{chem}}/J_{\text{phys}}$, 2.4). The CO₂ enhancement increased with solvent reactivity but the initial peak in CO₂ capture ratio observed for both NH_{3(aq)} solvents correlated to an increased pressure drop in the fibre of between 45 and 85 mbar and was coincident with liquid droplets at the gas-outlet (collected as condensate in the gas-liquid separator). Formation of solid or liquid products within the lumen will reduce the effective diameter, thereby increasing the pressure drop (Chan et al., 2020; Villeneuve et al., 2018a). Since the gas flowrate was fixed throughout, a reduction in the effective diameter will also increase the superficial gas velocity. This will restrict the time for CO₂ to diffuse from the gas bulk to the liquid interface, and is consistent with the observed reduction and instability in mass transfer (Houlker, 2019; Makhoulfi et al., 2014).

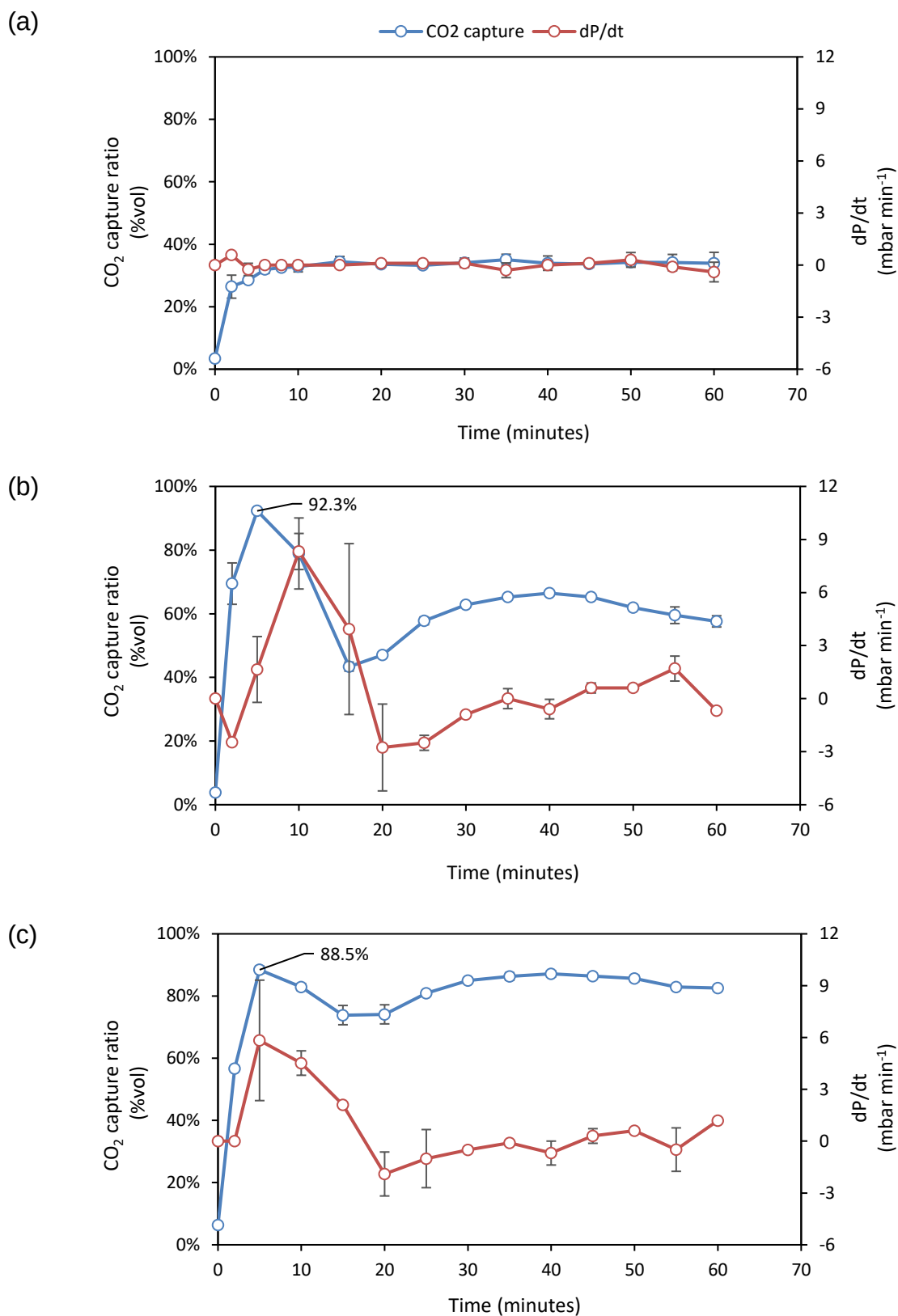


Figure 4.2: CO₂ capture ratio and gas-side pressure drop using: (a) DI water; (b) 1 mol_{NH3} L⁻¹; and (c) 3 mol_{NH3} L⁻¹ solvents. Operating conditions: liquid flowrate, 0.25 L min⁻¹; liquid temperature, 6.5±0.5°C; CO₂ in feed gas, 8%vol; feed gas flowrate, 1.1 L min⁻¹; gas temperature, 21°C.

4.3.2 Condensate formation and composition evidences gas-phase reactions

Over 60 minutes, a total of 2.5 and 7.9 g ammonia was transferred to the gas-phase from the 1 and 3 mol_{NH₃} L⁻¹ solvents respectively (Figure 4.3). The increase in ammonia transfer from the 3 mol_{NH₃} L⁻¹ solvent is due to the higher ammonia vapour pressure (7 versus 21 mbar) (Appendix C2). Through sacrificial sampling, the ammonia identified within the lumen through acid extraction of the hollow-fibre indicated early formation of solid ammonium salts as evidenced in previous work (Bavarella et al., 2022; Villeneuve et al., 2018a). However, the amount of ammonia located within the lumen did not change markedly over time. This reduced as a relative fraction of the total ammonia products as the system migrated toward the preferential formation of an ammonia-rich condensate. The final condensate produced from the 3 mol_{NH₃} L⁻¹ solvent was 63.7 ml, around 80% higher than recorded at 1 mol_{NH₃} L⁻¹, despite comparable water vapour pressures for both solvents (~10 mbar). We therefore propose that the intensification in water vapour mass transfer was driven by the increase in the solvent concentration and volatility, consistent with reaction pathways for ammonium salt formation (Eq. 4.1-4.3) (Sutter et al., 2015). The sustained salt concentration may therefore arise from the condensate partially dissolving solid products as suggested by previous researchers (Villeneuve et al., 2018a), or from the reaction favouring condensate formation.

Ammonia concentration within the condensate was two to three times greater than in the solvent (Figure 4.4). This is inconsistent with previous proposals that liquid is present in the gas-side due to breakthrough following pore wetting (Bavarella et al., 2022; Cui and DeMontigny, 2017) or water transfer promoted by an osmotic gradient (Villeneuve et al., 2018a) since both propositions would result in condensate concentrations less than or equal to the solvent. It is also incompatible with physical condensation driven by the binary ammonia-water mixture, since the vapour composition (40-66%wt ammonia) and gas-side conditions (21°C, 1.1 bar) are insufficient to facilitate a phase-change (Pátek and Klomfar, 1995) (Appendix C2). For both solvents, ammonium concentration in the liquid did not consistently exceed 1.7 mol_{NH₄⁺} L⁻¹ required to precipitate NH₄HCO₃, which is the least soluble of the ammonium salts under these conditions (Eq. 4.3)

(Bates and Pinching, 1950; Mani et al., 2006). This confirmed that the liquid would have the capacity to dissolve crystallised salts and capture ammonia from the lumen over time as observed in this study (Figure 4.3). Ammonia collected from the gas outlet (using an acid-trap) was in close agreement with the 'slip' expected at equilibrium (Figure 4.5). Consequently, this indicates that despite considerable ammonia fractionation into the solid and liquid products within the lumen, equilibrium was re-established along the fibre length according to Le Châtelier's principle. Hence, ammonia and water vapour will be continuously drawn across the membrane to sustain gas-phase reactions, the rate of which will be dependent on the solvent ammonia vapour pressure.

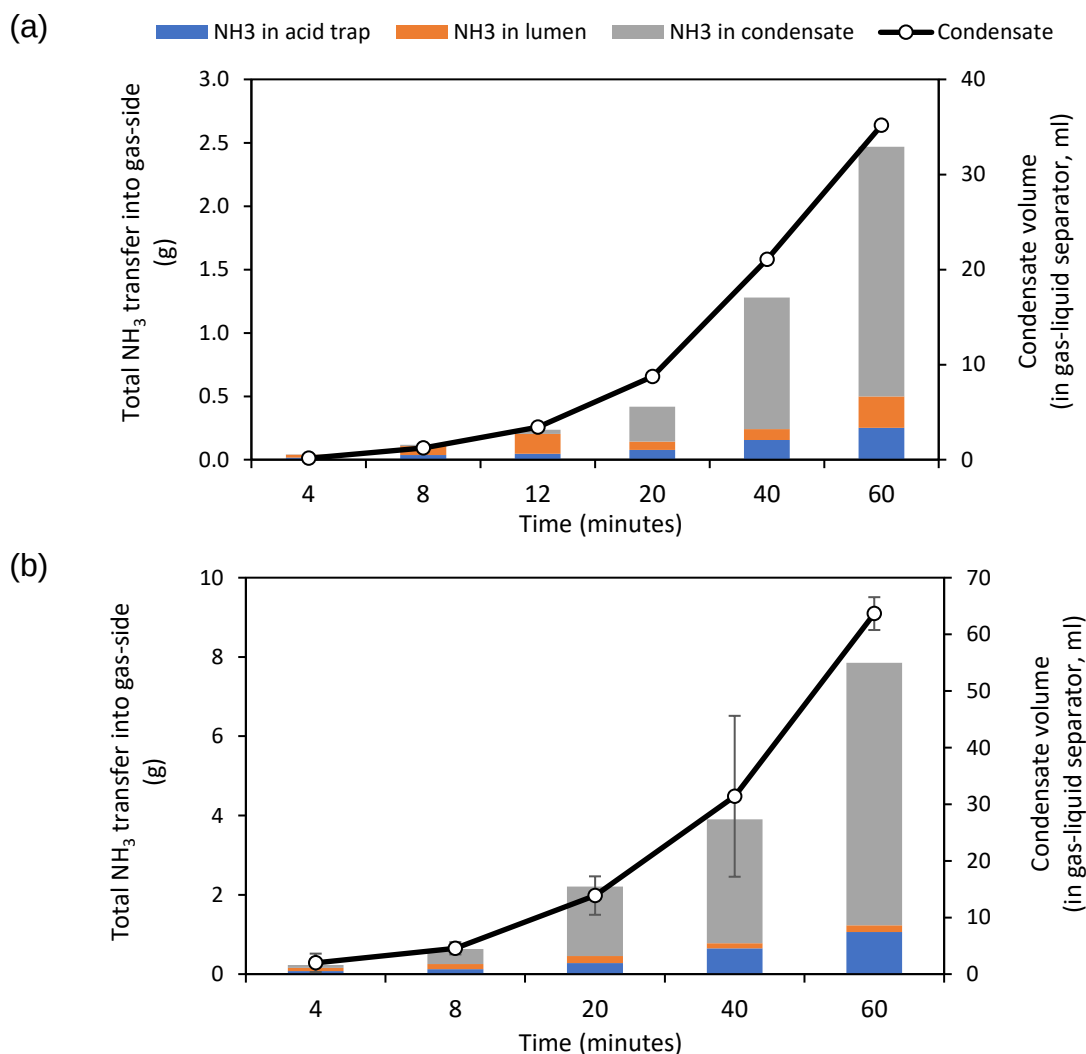


Figure 4.3: Temporal analysis of ammonia transfer into the gas-side during experimentation with: (a) 1 mol_{NH₃} L⁻¹; and (b) 3 mol_{NH₃} L⁻¹ solvents. Ammonia was recovered from the lumen (via acid elution), condensate (collected in a gas-liquid separator), and the outlet gas (captured using an acid trap). Operating conditions: liquid flowrate, 0.25 L min⁻¹; liquid temperature, 6.5±0.5°C; CO₂ in feed gas, 8%vol; feed gas flowrate, 1.1 L min⁻¹; gas temperature, 21°C.

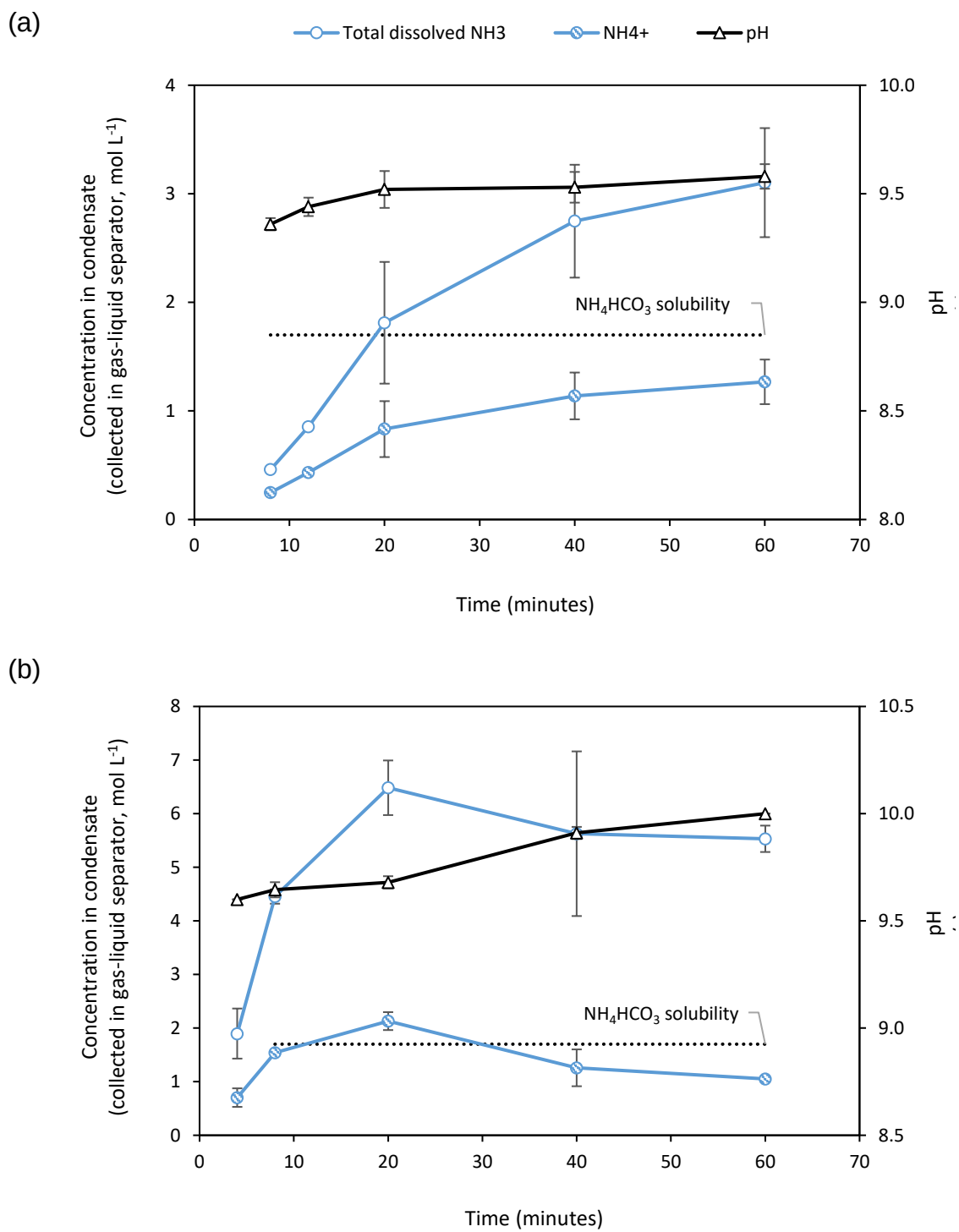


Figure 4.4: Composition of condensate collected at the gas-outlet using a gas-liquid separator for: (a) 1 mol_{NH₃} L⁻¹; and (b) 3 mol_{NH₃} L⁻¹. Operating conditions: liquid flowrate, 0.25 L min⁻¹; liquid temperature, 6.5±0.5°C; CO₂ in feed gas, 8%vol; feed gas flowrate, 1.1 L min⁻¹; gas temperature, 21°C. Dotted lines indicated NH₄HCO₃ solubility at 21°C (O'Neil, 2006; Perry and Green, 2007).

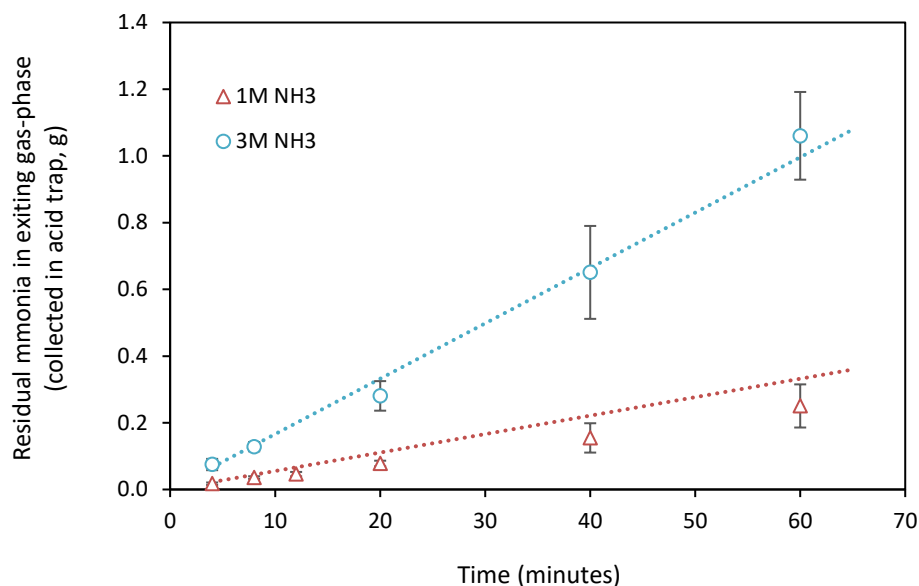


Figure 4.5: Ammonia transfer at the gas outlet (captured using an acid trap) over time when using aqueous ammonia solvents. Operating conditions: liquid flowrate, 0.25 L min^{-1} ; liquid temperature, $6.5 \pm 0.5^\circ\text{C}$; CO_2 in feed gas, 8%vol; feed gas flowrate, 1.1 L min^{-1} ; gas temperature, 21°C . Dotted lines represent ammonia slip over time at gas-liquid equilibrium estimated using Henry's Law (Appendix C2).

4.3.3 High CO_2 capture can trigger gas-phase reactions in the ternary system

During experimentation, equilibrium between gas and liquid-phases will establish at the membrane inlet due to the low gas velocity (0.04 m s^{-1}) (Chan et al., 2020; Gabelman and Hwang, 1999). Therefore, ammonia and water vapour were present in predictable quantities alongside CO_2 in the gas-phase. Absorption of CO_2 across the fibre length reduced the CO_2 fraction and lowered the overall gas volume (Figure 4.6), shifting the gas-phase composition within the ternary system. This will impact the fugacity of each gaseous component and the activity coefficients associated with each of the potential aqueous species, therefore determining the preferential reaction sequence as described by the VLE (Darde et al., 2010; Sutter et al., 2015). This is the basis of urea production, which fosters the conditions for the gas-phase interaction of CO_2 and NH_3 in the presence of water to form a highly concentrated aqueous solution based upon $\text{NH}_3\text{COONH}_4$ (Verbrugge, 1979). When using $1 \text{ mol}_{\text{NH}_3} \text{ L}^{-1}$, the initial gas-phase composition (prior to CO_2 separation) is in a region of the VLE where components can exist in

vapour, liquid or solid phases (Figure 4.1: a₁). Without the external energy required to initiate a phase-change, the components can be expected to transit through the lumen as a vapour mixture. However, the early peak in CO₂ capture (92%vol) reduced the CO₂ mass fraction, shifting the system into a thermodynamic region where only liquid and solid reaction products (NH₄HCO₃) are viable (Figure 4.1: a₂; Figure 4.7). This corresponded with the sudden increase in pressure drop and the observation of liquid at the outlet. Since the relative water fraction in the gas-phase at this condition ($x_{\text{H}_2\text{O}}=0.3$) was slightly greater than required for solid NH₄HCO₃ precipitation, the VLE predicts a concentrated aqueous solution to be the primary reaction product which is consistent with analysis of the liquid composition (Figure 4.4). The 3 mol_{NH₃} L⁻¹ solvent exhibited a higher ammonia vapour pressure, leading to an initial gas-side composition which was richer in ammonia (Figure 4.7b). Consequently, a lower CO₂ capture threshold (86%vol) was necessary to transition the system into a region of the VLE where liquid and solid reaction products are predicted to form (Figure 4.1: b₂). This is corroborated by the lower peak in CO₂ capture (88%vol) for this solvent, despite its higher reactivity, prior to observation of liquid at the gas outlet (Figure 4.2c). The associated salts were (NH₄)₂CO₃·H₂O and NH₂COONH₄ which are highly soluble (>32 g L⁻¹), and so minimal deposition in the lumen was expected as observed throughout the experiment (Figure 4.3b) (Mani et al., 2006).

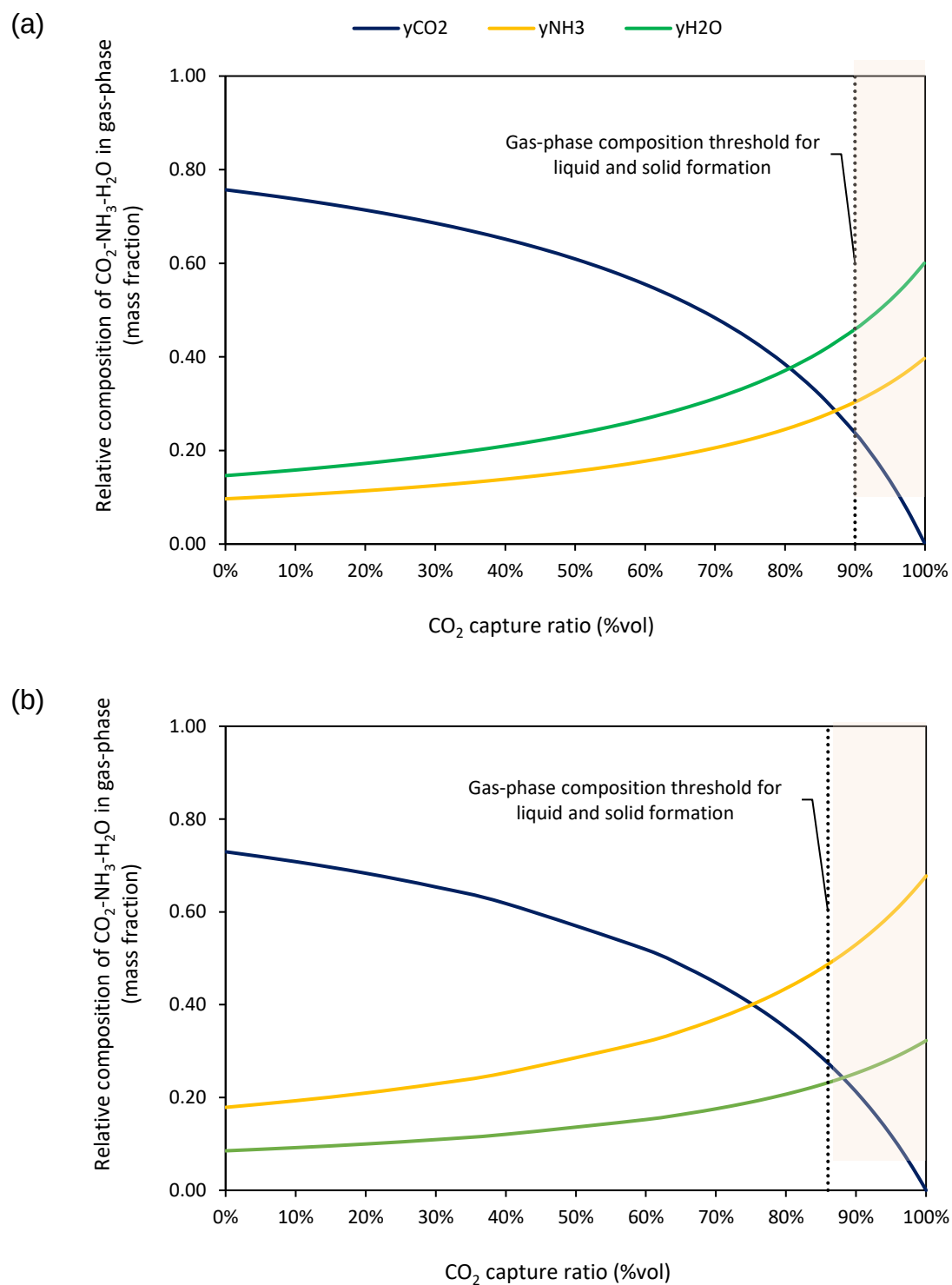


Figure 4.6: Projected ternary system composition based upon gas-liquid equilibrium vapour pressures for ammonia and water and the influence of CO_2 capture ratio for: (a) $1 \text{ mol}_{\text{NH}_3} \text{ L}^{-1}$; and (b) $3 \text{ mol}_{\text{NH}_3} \text{ L}^{-1}$ solvents. Based on the output from the extended UNIQUAC model at 10°C (Sutter et al., 2015; Thomsen and Rasmussen, 1999) and equilibrium vapour pressures for NH_3 and H_2O (Appendix C2).

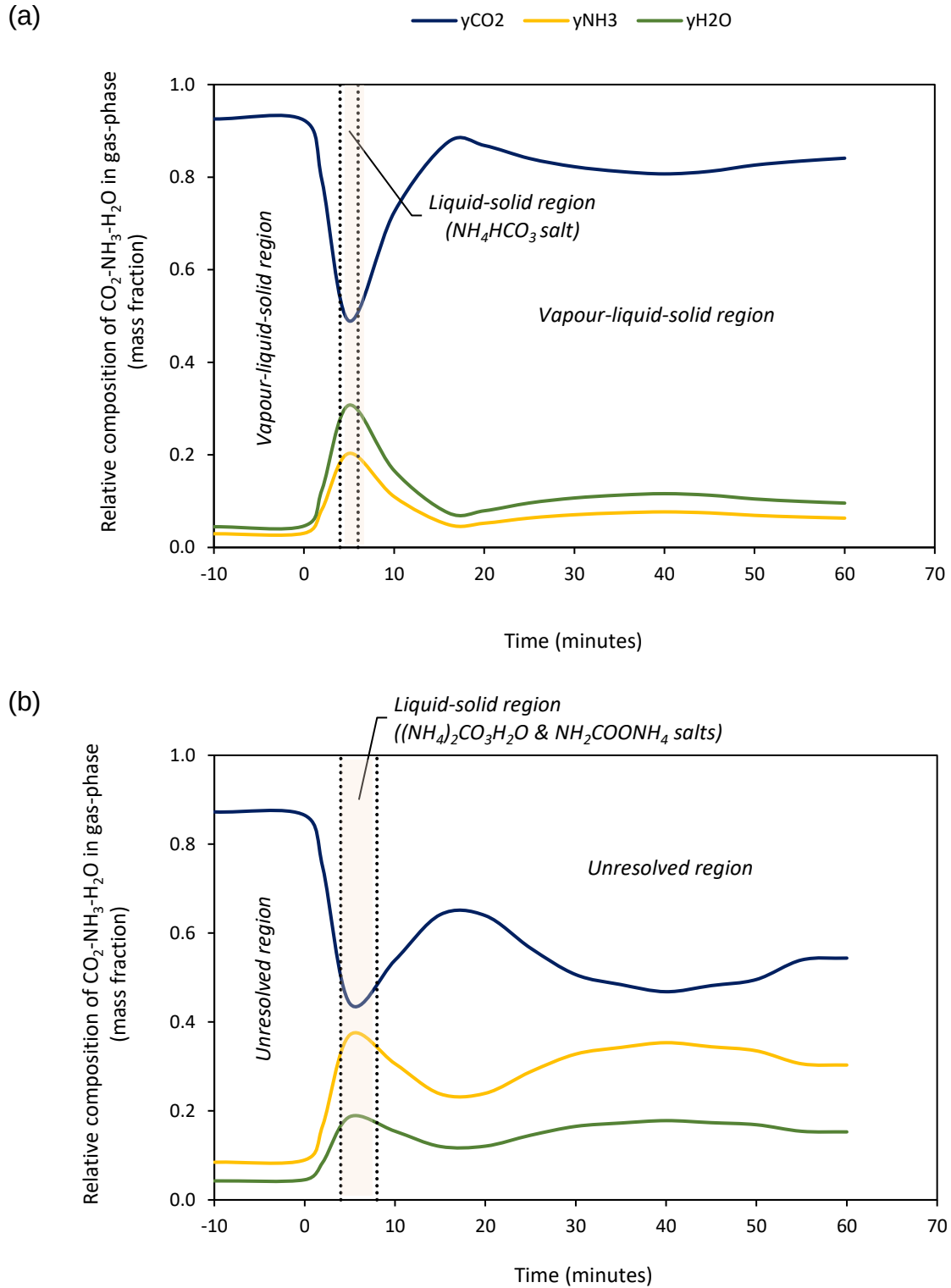


Figure 4.7: Experimental ternary system composition based upon the CO_2 capture ratio when using: (a) $1 \text{ mol}_{\text{NH}_3} \text{ L}^{-1}$; and (b) $3 \text{ mol}_{\text{NH}_3} \text{ L}^{-1}$ solvents. Relevant regions based on the output from the extended UNIQUAC model at 10°C (Sutter et al., 2015; Thomsen and Rasmussen, 1999) and equilibrium vapour pressures for NH_3 and H_2O (Appendix C2).

4.4 Proposed mitigation strategies

This study has identified the probable mechanism underpinning disruptive gas-phase reactions during CO₂ absorption by NH_{3(aq)} in HFMC. It is proposed that two pre-conditions must be met to initiate reactions: (i) ammonia and water vapour must be present alongside CO₂ in the gas-phase, and (ii) the gas-phase composition must exceed a system specific threshold necessary to promote the formation of liquid and solid reaction products (Figure 4.1). Previous researchers have targeted the first pre-condition by lowering ammonia vapour pressure to reduce the extent of gas-phase reactions (Table 4.1) (Bavarella et al., 2022; Houlker, 2019). This can be achieved by solvent chilling and high CO₂ loading (Bavarella et al., 2022; Darde et al., 2010) both of which are complimentary to the chilled ammonia process where NH₄HCO₃ precipitation is mediated within the solvent to reduce the equipment size and energy demand related to regeneration (Milella et al., 2018; Sutter et al., 2017). However, some ‘slip’ is inevitable in practice, particularly since highly reactive, concentrated solvents are necessary to favour process intensification and economics (Augustsson et al., 2017). This work highlights the relevant role of the ternary VLE phase diagram in determining conditions which set the second pre-condition for gas-phase reactions and can therefore better inform mitigation strategies. For example, pressurisation will increase CO₂ concentration in the gas-phase and since ‘slip’ is independent of pressure, this will lower the relative amount of ammonia (and water) in the gas-phase at equilibrium (Figure 4.8) (Fang et al., 2015). Pressurisation will therefore shift the system towards the CO₂-rich region in the ternary VLE (Figure 4.1: c₁) where formation of gas and liquid products cannot proceed via gas-phase reactions even under high CO₂ capture ratios. Since commercial CO₂ absorption columns operate under pressurised conditions (4-10 bar) for process intensification (Angelidaki et al., 2018), pressurisation offers a strategy to improve stability whilst intensifying mass transfer and increasing the commercial competitiveness of HFMC for reactive CO₂ absorption in ternary systems.

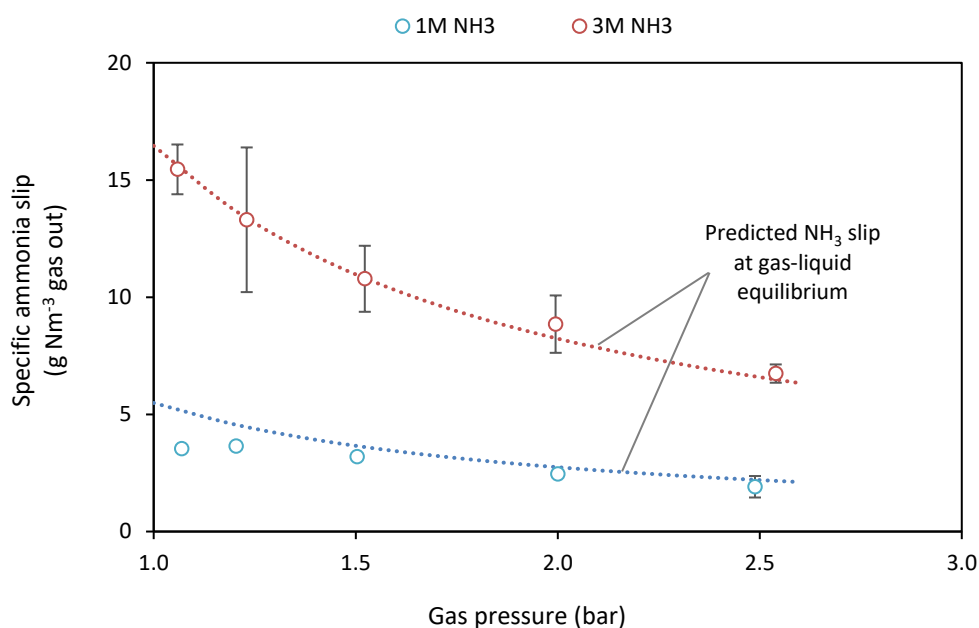


Figure 4.8: Influence of pressurisation on ammonia slip into the treated gas (pure N₂). Operational conditions: liquid flowrate, 0.25 L min⁻¹; liquid temperature, 6.5±0.5°C; gas flowrate, 1.1 L min⁻¹; gas temperature, 21°C. Dotted lines represent ammonia slip over time at gas-liquid equilibrium estimated using Henry's Law (Appendix C2).

Acknowledgements

We are grateful for the financial and technical support offered by Anglian Water, Northumbrian Water and Severn Trent Water. We also acknowledge the funding and training resources provided to Benjamin Luqmani from the Engineering and Physical Sciences Research Council through the STREAM Industrial Doctorate Centre.

Appendix C

C1 Experimental set-up

An experimental set-up was developed to investigate gas-phase reactions during CO₂ capture with ammonia within a transverse-flow HFMC (Figure C1). The HFMC contained 10200 polypropylene hollow fibres, each with a length of 0.16 m (EXF-2.5x8"; 3M Industrial Group, Charlotte, USA). The fibres had internal diameters and wall thicknesses of 240 µm and 30 µm, to provide a total internal surface area of 1.2 m² for the HFMC. Aqueous ammonia solvents (1 or 3 mol L⁻¹), prepared by mixing concentrated aqueous ammonia (35% Fisher Chemicals,

Loughborough, UK) and de-ionised water (15 M Ω cm), were pumped into the HFMC shell-side (AD550, Xylem, New York, USA). Solvent flowrate was controlled at 0.25 L min⁻¹ using a throttling valve (Double acting inline control valve, F.lli Tognella Spa, Rome, Italy). Solvent temperature was maintained at 6.5 $\pm$ 0.5 $^{\circ}$ C using a thermostatic recirculating water bath (LT Ecocool 150, Grant Instruments, Cambridge, UK). A gas blend comprised of 8%vol CO₂ and 92%vol N₂, analogous to an industrial flue gas (Kozak et al., 2009; Makhloufi et al., 2014; Scholes et al., 2015), flowed through the HFMC lumen in countercurrent with the solvent (99.8% CO₂; 99.9% N₂, BOC gases, Ipswich, UK). The total gas flow was set at 1.1 L min⁻¹ using mass flow controllers (0.01– 5.0 L min⁻¹, Roxspur Measurement and Control Ltd., Sheffield, UK). Gases were supplied to the lumen at a temperature of 21 $\pm$ 0.5 $^{\circ}$ C and a pressure of 1.1 bar (DPG1001B-15G, $\pm$ 0.1% full scale, Omega Engineering Ltd., Manchester, UK). An overpressure of 0.2-0.4 bar was maintained on the liquid-side to prevent gas bubbling or liquid breakthrough using throttling valves at the HFMC outlet (Dindore et al., 2004) (SS-4MA-MH, Swagelok, Kings Langley, UK; Double acting inline control valve, F.lli Tognella Spa, Rome, Italy). A gas-liquid separator was positioned at the gas outlet to collect condensate. The outlet gas was bubbled through dilute sulphuric acid (0.5 mol L⁻¹) in two 1 L gas-tight aspirator bottles to capture gas-phase ammonia (Schott Duran, VWR, NL). Outlet gas composition was monitored continuously using an infrared CO₂ analyser (BCP-CO₂, <0.5% full scale, BlueSens gas sensor GmbH, Herten, Germany). Outlet gas flow was measured using volumetric bubble flowmeters (50 ml, $\pm$ 2% full scale, Restek, Bellefonte, USA; 1000 ml, Model 311, $\pm$ 2% full scale, Blandford Forum, UK). At end of each experiment, the HFMC lumen was flushed with compressed air at 40 L min⁻¹ for 2 minutes to purge condensate into the gas-liquid separator. Dilute sulphuric acid (0.5 L; 0.5 mol L⁻¹) was then recirculated through the lumen for 15 minutes to capture any remaining ammonia. Finally, the lumen was rinsed with 10 L of de-ionised water and flushed for 45-minutes with compressed air at 40 L min⁻¹ to restore hydrophobicity. Ammoniacal nitrogen concentrations within the condensate, the acid rinse solution and the acid traps were determined by spectrophotometry using proprietary cell tests (114558 NH₄-N, Spectroquant cell

tests, Merck-Millipore, Darmstadt, Germany). Condensate pH measurements were conducted in a temperature-controlled environment at 21 ± 0.5 °C (InPro 3250i/SG/120, Mettler-Toledo Ltd, Leicester, UK). Each primary data point was collected in duplicate or triplicate and standard deviation is represented by error bars.

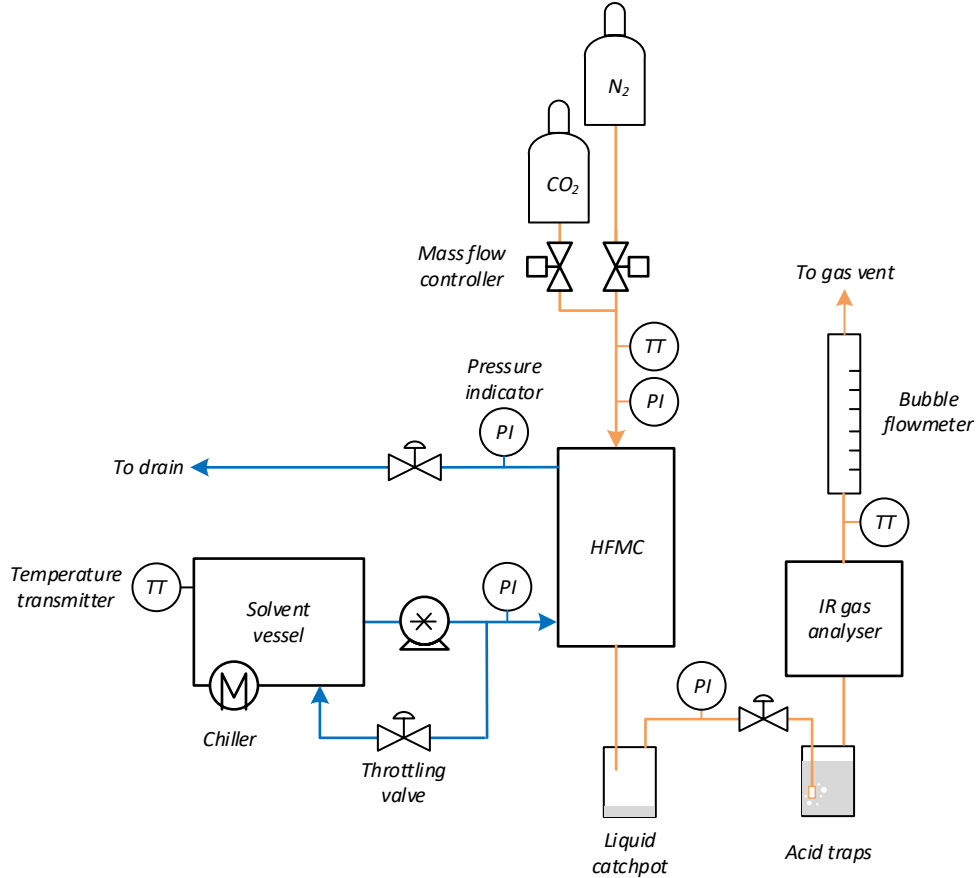


Figure C1: Experimental layout

C2 Experimental Analysis

The experimental CO₂ flux across the HFMC was determined as:

$$J_{CO_2} = \frac{C_g (Q_{g,in} y_{CO_2,in} - Q_{g,out} y_{CO_2,out})}{a} \quad (\text{Eq. C1})$$

where J_{CO_2} is CO₂ flux ($\text{mol m}^{-2} \text{min}^{-1}$); Q_g is the gas flowrate (L min^{-1}); y_{CO_2} is the fraction of CO₂ in the gas-phase (%vol); C_g is the concentration of pure CO₂ at the inlet gas temperature and pressure (0.045 mol L^{-1}) (Air Liquide, 2023b); a is the HFMC surface area (1.23 m^2); and subscripts *in* and *out* refer to the inlet and

outlet of the HFMC respectively. The corresponding CO₂ capture ratio (%vol) was calculated as (Gabelman and Hwang, 1999):

$$\eta_{CO_2} = \frac{Q_{g,in} y_{CO_2,in} - Q_{g,out} y_{CO_2,out}}{Q_{g,in} y_{CO_2,in}} \quad (\text{Eq. C2})$$

A dimensionless chemical enhancement factor was applied to compare CO₂ fluxes for chemical absorption in NH_{3(aq)} relative to physical absorption in DI water:

$$E = \frac{J_{chem}}{J_{phy}} \quad (\text{Eq. C3})$$

Ammonia vapour pressure at gas-liquid equilibrium was determined using Henry's Law:

$$P_{NH_3} = \frac{C_{NH_3}}{k_{H(T)}} \quad (\text{Eq. C4})$$

$$k_{H(T)} = k_H^0 e^{\left[A_H \left(\frac{1}{T+273.15} - \frac{1}{298} \right) \right]} \quad (\text{Eq. C5})$$

where P_{NH_3} is ammonia vapour pressure (bar), $k_{H(T)}$ is the Henry's coefficient for ammonia in water (mol L⁻¹ bar⁻¹) at the solvent temperature T (°C); k_H^0 is the Henry's coefficient for ammonia in water at 25°C (59 mol L⁻¹ bar⁻¹; Sander, 2015); C_{NH_3} is the ammonia concentration in the solvent (mol L⁻¹); and A_H is the temperature dependence constant (4200°C; Sander, 2015). Water vapour pressure at gas-liquid equilibrium was determined Raoult's Law:

$$P_{H_2O} = x_{H_2O} P_{H_2O}^\circ \quad (\text{Eq. C6})$$

$$\log_{10}(P_{H_2O}^\circ) = A - \frac{B}{(T + 273.15) + C} \quad (\text{Eq. C7})$$

where P_{H_2O} is water vapour pressure (bar); x_{H_2O} is mole fraction of water in the solvent (0.018-0.054 for 1-3 mol L⁻¹ aqueous ammonia); $P_{H_2O}^\circ$ is the vapour pressure of pure water (bar) determined by the Antoine equation using empirical constants A, B and C (National Institute of Standards and Technology (NIST), 2021b).

Ammonia and water 'slip' from the solvent at gas-liquid equilibrium were estimated based on their equilibrium vapour pressures and the gas pressure and flowrate:

$$m_i = \rho_i \left(\frac{P_i}{P_T} Q_{g,out} t \right) \quad i = H_2O, NH_3 \quad (\text{Eq. C8})$$

where m_i is the component slip (g) at gas-liquid equilibrium over the experimental duration t (minutes); P_T is the total pressure of the gas-phase (bar); ρ_i is the density of the component as a vapour at the operating temperature and pressure (Air Liquide, 2023a).

References

- Air Liquide. (2023a). Gas Encyclopedia - Ammonia. <https://encyclopedia.airliquide.com/ammonia#properties> (accessed 06/04/2023).
- Air Liquide. (2023b). Gas Encyclopedia - Carbon Dioxide. <https://encyclopedia.airliquide.com/carbon-dioxide> (accessed 06/04/2023).
- Angelidaki, I., Treu, L., Tsapekos, P., Luo, G., Campanaro, S., Wenzel, H., and Kougias, P. G. (2018). Biogas upgrading and utilization: Current status and perspectives. *Biotechnology Advances*, 36, 452–466.
- Augustsson, O., Baburao, B., Dube, S., Bedell, S., Strunz, P., Balfe, M., and Stallmann, O. (2017). Chilled Ammonia Process Scale-up and Lessons Learned. 13th International Conference on Greenhouse Gas Control Technologies, Lausanne, Switzerland.
- Bates, R. G., and Pinching, G. D. (1950). Dissociation Constant of Aqueous Ammonia at 0 to 50° from E. m. f. Studies of the Ammonium Salt of a Weak Acid. *Journal of the American Chemical Society*, 72, 1393–1396.
- Bavarella, S., Luqmani, B., Thomas, N., Brookes, A., Moore, A., Vale, P., Pidou, M., and McAdam, E. J. (2022). CO₂ absorption into aqueous ammonia using membrane contactors: Role of solvent chemistry and pore size on solids formation for low energy solvent regeneration. *Separation and Purification Technology*, 290, 120786.
- Belaissaoui, B., Claveria-Baro, J., Lorenzo-Hernando, A., Albarracin Zaidiza, D., Chabanon, E., Castel, C., Rode, S., Roizard, D., and Favre, E. (2016). Potentialities of a dense skin hollow fiber membrane contactor for biogas purification by pressurized water absorption. *Journal of Membrane Science*, 513, 236–249.

- Chan, Z. P., Li, L., Kang, G., Manan, N. A., Cao, Y., and Wang, T. (2020). Discussion on Water Condensation in Membrane Pores during CO₂ Absorption at High Temperature. *Membranes*, 10, 407.
- Chin Yeh, A., and Hsunling, B. (1999). Comparison of ammonia and monoethanolamine solvents to reduce CO greenhouse gas emissions. *The Science of the Total Environment*, 228, 279–284.
- Cui, Z., and DeMontigny, D. (2017). Experimental study of carbon dioxide absorption into aqueous ammonia with a hollow fiber membrane contactor. *Journal of Membrane Science*, 540, 297–306.
- Darde, V., Thomsen, K., van Well, W. J. M., and Stenby, E. H. (2010). Chilled ammonia process for CO₂ capture. *International Journal of Greenhouse Gas Control*, 4, 131–136.
- Dindore, V. Y., Brillman, D. W. F., Feron, P. H. M., and Versteeg, G. F. (2004). CO₂ absorption at elevated pressures using a hollow fiber membrane contactor. *Journal of Membrane Science*, 235, 99–109.
- Fang, M., Xiang, Q., Yu, C., Xia, Z., Zhou, X., Cai, D., and Wang, Z. (2015). Experimental study on CO₂ absorption by aqueous ammonia solution at elevated pressure to enhance CO₂ absorption and suppress ammonia vaporization. *Greenhouse Gases: Science and Technology*, 5, 210–221.
- Gabelman, A., and Hwang, S. (1999). Hollow fiber membrane contactors. *Journal of Membrane Science*, 159, 61–106.
- Houlker, S. (2019). Scale up of hollow fibre membrane contactors for biogas upgrading. EngD thesis. Cranfield University.
- Houlker, S., Rutherford, T., Herron, D., Brookes, A., Moore, A., Vale, P., Pidou, M., and McAdam, E. (2021). Demonstrating commercial hollow fibre membrane contactor performance at industrial scale for biogas upgrading at a sewage treatment works. *Water (Switzerland)*, 13, 172.
- Jilvero, H., Normann, F., Andersson, K., and Johnsson, F. (2012). Heat requirement for regeneration of aqueous ammonia in post-combustion carbon dioxide capture. *International Journal of Greenhouse Gas Control*, 11, 181–187.

- Khaisri, S., DeMontigny, D., Tontiwachwuthikul, P., and Jiraratananon, R. (2009). Comparing membrane resistance and absorption performance of three different membranes in a gas absorption membrane contactor. *Separation and Purification Technology*, 65, 290–297.
- Khaisri, S., DeMontigny, D., Tontiwachwuthikul, P., and Jiraratananon, R. (2011). Membrane contacting process for CO₂ desorption. *Energy Procedia*, 4, 688–692.
- Kozak, F., Petig, A., Morris, E., Rhudy, R., and Thimsen, D. (2009). Chilled ammonia process for CO₂ capture. *Energy Procedia*, 1, 1419–1426.
- Makhloufi, C., Lasseuguette, E., Remigy, J. C., Belaisaoui, B., Roizard, D., and Favre, E. (2014). Ammonia based CO₂ capture process using hollow fiber membrane contactors. *Journal of Membrane Science*, 455, 236–246.
- Mani, F., Peruzzini, M., and Stoppioni, P. (2006). CO₂ absorption by aqueous NH₃ solutions: Speciation of ammonium carbamate, bicarbonate and carbonate by a ¹³C NMR study. *Green Chemistry*, 8, 995–1000.
- McLeod, A., Buzatu, P., Autin, O., Jefferson, B., and McAdam, E. (2015). Controlling shell-side crystal nucleation in a gas-liquid membrane contactor for simultaneous ammonium bicarbonate recovery and biogas upgrading. *Journal of Membrane Science*, 473, 146–156.
- Milella, F., Gazzani, M., Sutter, D., and Mazzotti, M. (2018). Process synthesis, modeling and optimization of continuous cooling crystallization with heat integration - application to the chilled ammonia CO₂ Capture Process. *Industrial and Engineering Chemistry Research*, 57, 11712–11727.
- National Institute of Standards and Technology (NIST). (2021). Chemistry WebBook (Water). <https://webbook.nist.gov/cgi/cbook.cgi?Name=water> (accessed 06/04/2023).
- O'Neil, M. J. (Ed.). (2006). *The Merck Index - An Encyclopedia of Chemicals, Drugs, and Biologicals*. (1st ed., pp. 88–100). Merck & Co., Inc., Rahway, NJ, USA.
- Pátek, J., and Klomfar, J. (1995). Simple functions for fast calculations of selected thermodynamic properties of the ammonia-water system. *International Journal of Refrigeration*, 18, 228–234.

- Perry, R. H., & Green, D. W. (Eds.). (2007). *Perry's Chemical Engineers' Handbook* (8th ed., pp. 2–126). McGraw-Hill, New York, NY, USA.
- Sander, R. (2015). Compilation of Henry's law constants (version 4.0) for water as solvent. *Atmospheric Chemistry and Physics*, 15, 4399–4981.
- Scholes, C. A., Kentish, S. E., Stevens, G. W., and DeMontigny, D. (2015). Comparison of thin film composite and microporous membrane contactors for CO₂ absorption into monoethanolamine. *International Journal of Greenhouse Gas Control*, 42, 66–74.
- Sutter, D., Gazzani, M., and Mazzotti, M. (2015). Formation of solids in ammonia-based CO₂ capture processes — Identification of criticalities through thermodynamic analysis of the CO₂–NH₃–H₂O system. *Chemical Engineering Science*, 133, 170–180.
- Sutter, D., Gazzani, M., Pérez-Calvo, J. F., Leopold, C., Milella, F., and Mazzotti, M. (2017). Solid Formation in Ammonia-based Processes for CO₂ Capture - Turning a Challenge into an Opportunity. 13th International Conference on Greenhouse Gas Control Technologies, Lausanne, Switzerland.
- Thomsen, K., and Rasmussen, P. (1999). Modeling of vapor-liquid-solid equilibrium in gas-aqueous electrolyte systems. *Chemical Engineering Science*, 54, 1787–1802.
- Verbrugge, P. (1979). Vapour-liquid Equilibria of the Ammonia-Carbon dioxide-Water System. PhD thesis. Delft University.
- Villeneuve, K., Roizard, D., Remigy, J. C., Iacono, M., and Rode, S. (2018a). CO₂ capture by aqueous ammonia with hollow fiber membrane contactors: Gas phase reactions and performance stability. *Separation and Purification Technology*, 199, 189–197.
- Villeneuve, K., Torres Hernandez, A. A., Albarracin Zaidiza, D., Roizard, D., and Rode, S. (2018b). Effects of water condensation on hollow fiber membrane contactor performance for CO₂ capture by absorption into a chemical solvent. *Journal of Membrane Science*, 556, 365–373.
- Zhao, D., Dong, S., Bai, L., Li, D., and Liu, H. (2023). Experimental method and mathematical method for VLE plots in 3DMA1P-CO₂-H₂O system. *Separation and Purification Technology*, 307, 122800.

5 CO₂ capture and reactive crystallisation using membrane contactors: Impact of pressurisation on process intensification and nucleation kinetics

CO₂ capture and reactive crystallisation using membrane contactors: Impact of pressurisation on process intensification and nucleation kinetics

B. Luqmani^a, A. Brookes^b, A. Moore^c, P. Vale^d, M. Pidou^a, E.J. McAdam^{a,*}

^aCranfield Water Science Institute, Vincent Building, Cranfield University, Bedfordshire, MK43 0AL, UK

^bAnglian Water, Block C-Western House, Peterborough Business Park, Peterborough PE2 6FZ, UK

^cNorthumbrian Water, Boldon House, Wheatlands Way, Durham DH1 5FA, UK

^dSevern Trent Water, 2 St. Johns Street, Coventry CV1 2LZ, UK

*Corresponding Author: e.mcadam@cranfield.ac.uk

Abstract

Membrane contactors could be employed for post-combustion CO₂ capture using ammonia solvents to promote solids formation and lower the energy penalty for regeneration, which is a critical barrier to industrial adoption. This study has explored gas pressurisation (up to 2.5 bar) as a process intensification strategy to reduce membrane area and has examined the interaction of pressure with nucleation kinetics for ammonium bicarbonate. Increasing gas pressure enhanced the rate of CO₂ loading in the solvent and reduced the time to nucleation, due to the raised driving force for CO₂ mass transfer to the liquid interface. However, a weaker relative enhancement in CO₂ flux was observed for reactive absorption than for physical absorption, due to declining reactivity in the liquid film as CO₂ loading progressed. Pressurisation also reduced ammonia 'slip', due to the rapid acidification of the solvent, thereby maximising ammonium availability at nucleation. Despite variation in the CO₂ loading rate with pressure, a consistent supersaturation level (i.e., metastable zone width), induction time and crystal morphology was observed, which is contrary to classical nucleation theory. It is proposed that limited solvent reactivity under fixed hydrodynamic conditions enabled an excess of CO₂ to accumulate in the film before being transformed to HCO₃⁻, resulting in the nucleation energy barrier being exceeded at the same supersaturation level for all conditions. Pressurisation therefore offers an effective process intensification strategy which could lower ammonia 'slip', whilst predictable nucleation behaviour under pressure could enable simplified process control to reduce the regeneration energy penalty and support an expansion of post-combustion CO₂ capture.

Keywords: *CO₂ capture, CCS, chilled ammonia process, CAP, membrane crystallisation, membrane contactors.*

5.1 Introduction

Electricity generation is associated with 40% of global CO₂ emissions (IEA, 2022). An expansion of post-combustion CO₂ capture using chemical solvents could therefore play a central role in global decarbonisation. Aqueous ammonia is three times more efficient than amines for CO₂ absorption, whilst also being cheaper and less corrosive (Chin Yeh and Hsunling, 1999; Mani et al., 2006). However, the high volatility of aqueous ammonia is a key challenge as the 'slipped' ammonia must be separated downstream from the gas product to avoid fugitive emissions and solvent losses (Pérez-Calvo et al., 2021b). This has led to the development of chilled ammonia processes (CAP) which operate at low solvent temperatures (<10°C) to suppress ammonia vapour pressure and limit 'slip' (Augustsson et al., 2017; Darde et al., 2010). Reduced solvent temperatures also adjust the solubility limit to favour ammonium bicarbonate precipitation. This lowers the energy penalty for solvent regeneration as the precipitated slurry can be readily separated (e.g., by hydrocyclones) to reduce the solvent mass flow to regeneration (Milella et al., 2018; Sutter et al., 2017). Furthermore, aqueous ammonia also requires 30% less heat for CO₂ desorption than amines (Jilvero et al., 2012). Therefore, the chilled ammonia process can substantially reduce the thermal energy demand for regeneration, which is the critical technical barrier for widescale adoption of post-combustion CO₂ capture (Jilvero et al., 2012).

Since CAP has been developed for the treatment of flue gases which are close to atmospheric pressure, the CO₂ absorber is typically operated at 1.1 bar to minimise energy usage (Augustsson et al., 2017; Fang et al., 2015). To reduce the membrane area and lower operational costs required for the separation, gas pressurisation could be employed to raise the CO₂ partial pressure and increase the driving force for mass transfer from the bulk gas to the liquid interface (Dindore et al., 2004). Pressurisation has proven critical for delivering cost effective biomethane production, which uses physical absorption to facilitate CO₂/CH₄ separation (Angelidaki et al., 2018; Belaïssaoui et al., 2016). It is proposed that increasing the gas throughput by pressurisation could also lower ammonia 'slip' during absorption ($g_{\text{NH}_3} \text{ Nm}^{-3}$), since it is equilibrium controlled and will not scale with pressure. Hence, adoption of pressurised conditions during

reactive absorption has the potential to enhance mass transfer and limit ammonia ‘slip’, thereby improving the investment case for this technology.

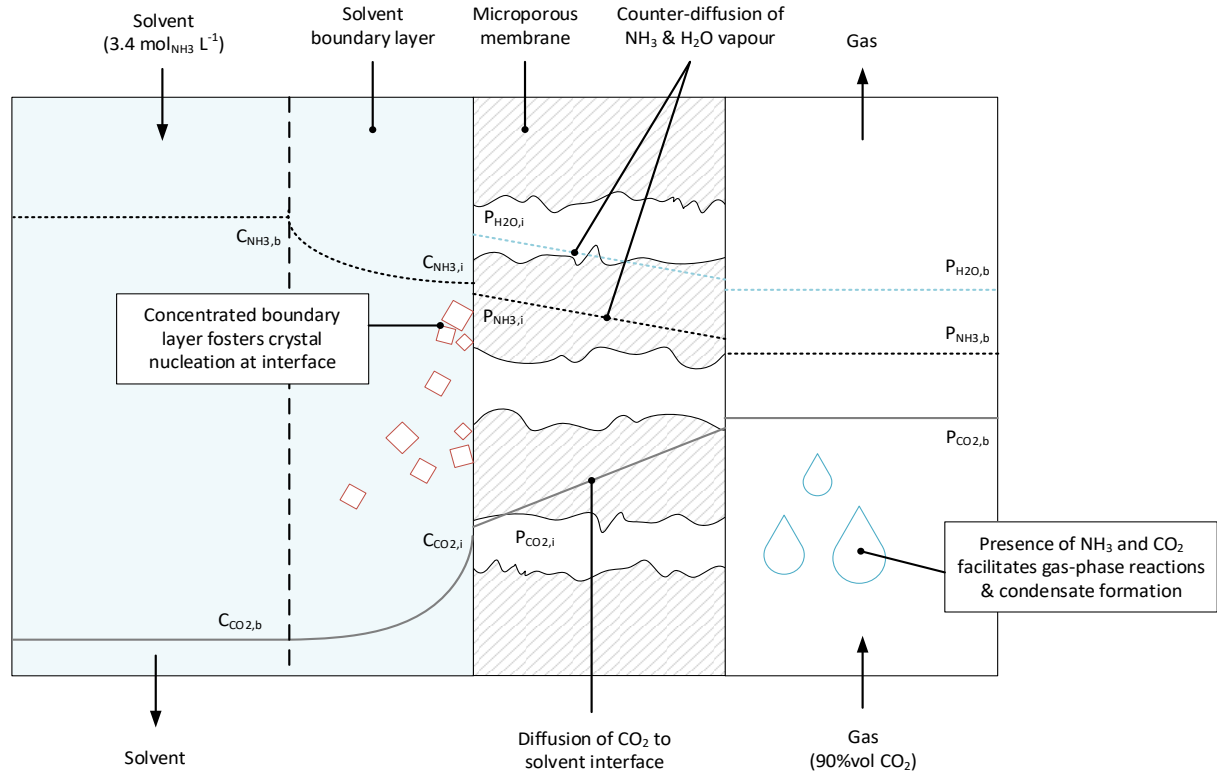


Figure 5.1: Schematic for reactive CO_2 absorption by aqueous ammonia and membrane facilitated crystallisation of ammonium bicarbonate.

To achieve further process intensification, pressurised CAP could be conducted within hollow fibre membrane contactors (HFMC). The hydrophobic membrane facilitates non-dispersive contact between gas and liquid-phases (Bavarella et al., 2020a; Gabelman and Hwang, 1999), offering fifteen times greater interfacial area and higher gas loading rates, thereby reducing process size (capital cost) and solvent requirements (separation energy) without incurring channelling, flooding, foaming or entrainment (Belaissaoui et al., 2016; Hoff and Svendsen, 2013). The fixed interfacial area and well-defined hydrodynamics can also provide greater control over the primary nucleation kinetics which influence crystal growth, where the consistency and quality of the product is important in managing regeneration conditions (Horseman et al., 2021; Jiang et al., 2016). To evidence this, controlled shell-side nucleation of ammonium bicarbonate has

been demonstrated in HFMC during uninterrupted CO₂ absorption (Figure 5.1) (Houlker, 2019; McLeod et al., 2015). In situ crystallisation presents operational challenges for conventional scrubbers, where homogeneous nucleation leads to clogging of media and subsequent flooding of the column (Augustsson et al., 2017; Houlker, 2019). However, evidence for reactive crystallisation in HFMC is also limited to operation at atmospheric pressures (Bavarella et al., 2020b; McDonald et al., 2021; McLeod et al., 2015). Any enhancement in the rate of CO₂ loading provided by pressurisation will increase the rate of pH decline (Bavarella et al., 2022). This will influence the chemical equilibria for dissolved ammonia and CO₂ species, with lower pH values favouring the production of ammonium and bicarbonate in the solvent (Bates and Pinching, 1950; Darde et al., 2010). In classical nucleation theory, increasing the concentrating rate for reactants will raise the supersaturation level, an indicator of metastable zone width, and reduce the crystal induction time (Jiang et al., 2021; McDonald et al., 2021). This will influence the crystallisation kinetics and the size and morphology of the solid product (Ulrich and Strege, 2002). In CAP, these properties are critical for process design as they will inform the dissolution kinetics and therefore the heat demand and rate of the regeneration process (Augustsson et al., 2017; Sutter et al., 2017). Compared to conventional crystallisation by cooling or evaporation, complexity is introduced by multiple interacting species within a reactive CO₂-NH₃-H₂O system which can also form highly soluble ammonium salts (ammonium carbonate, ammonium carbamate) depending on the extent of CO₂ loading within the solvent (McDonald et al., 2021; Sutter et al., 2015). This study therefore aims to translate reactive absorption and membrane facilitated crystallisation in HFMC to pressurised conditions which may be critical to lowering the cost barrier for industrial adoption of CO₂ capture. Specific objectives are to:

- i) apply pressurisation for process intensification during reactive absorption in HFMC, to enhance the rate of solvent CO₂ loading and reduce absolute time to nucleation;
- ii) investigate pressurisation as a strategy to reduce countercurrent ammonia 'slip' during CO₂ absorption and maximise the availability of reactants in the solvent at nucleation;

- iii) characterise the dynamic solvent chemistry for the reactive $\text{CO}_2\text{-NH}_3\text{-H}_2\text{O}$ system during CO_2 loading under pressurised conditions, to determine the rate of reactant accumulation and concentrations at nucleation;
- iv) determine the extent to which pressurisation can broaden the metastable zone width for ammonium bicarbonate by evaluating the supersaturation level at nucleation and relating supersaturation level to the nucleation rate using power law analyses.

5.2 Materials and methods

5.2.1 Experimental set-up

The absorption of CO_2 in aqueous ammonia was conducted within a transverse-flow HFMC (Figure 5.2). The HFMC contained 10200 polypropylene hollow fibres each with internal diameter of 240 μm , wall thickness of 30 μm and length of 0.16 m, to provide a total internal surface area of 1.23 m^2 (Table 5.1) (EXF-2.5x8"; 3M Industrial Group, Charlotte, USA). Aqueous ammonia ($3.4 \pm 0.1 \text{ mol L}^{-1}$, pH 11) with initial volume 1.1 L was loaded into a jacketed feed vessel and chilled to $7 \pm 0.5^\circ\text{C}$ (LT Ecocool 150, Grant Instruments, Cambridge, UK). The solvent was recirculated through the HFMC shell-side at $1.5 \pm 0.2 \text{ L min}^{-1}$ using a pump and throttling valve (AD550, Xylem, New York, USA; Double acting inline control valve, F.lli Tognella Spa, Rome, Italy). A gas blend comprising of 90%vol CO_2 and 10%vol N_2 (99.8% CO_2 ; 99.9% N_2 , BOC gases, Ipswich, UK) was supplied to the lumen in countercurrent at 1.34 L min^{-1} using mass flow controllers ($0.01\text{--}5.0 \text{ L min}^{-1}$, Roxspur Measurement and Control Ltd., Sheffield, UK). During each experiment, the gas inlet conditions were achieved over a 30 minute start-up period by gradually increasing the CO_2 flowrate to avoid sudden pressure instability due to gas-phase reactions (Villeneuve et al., 2018a).

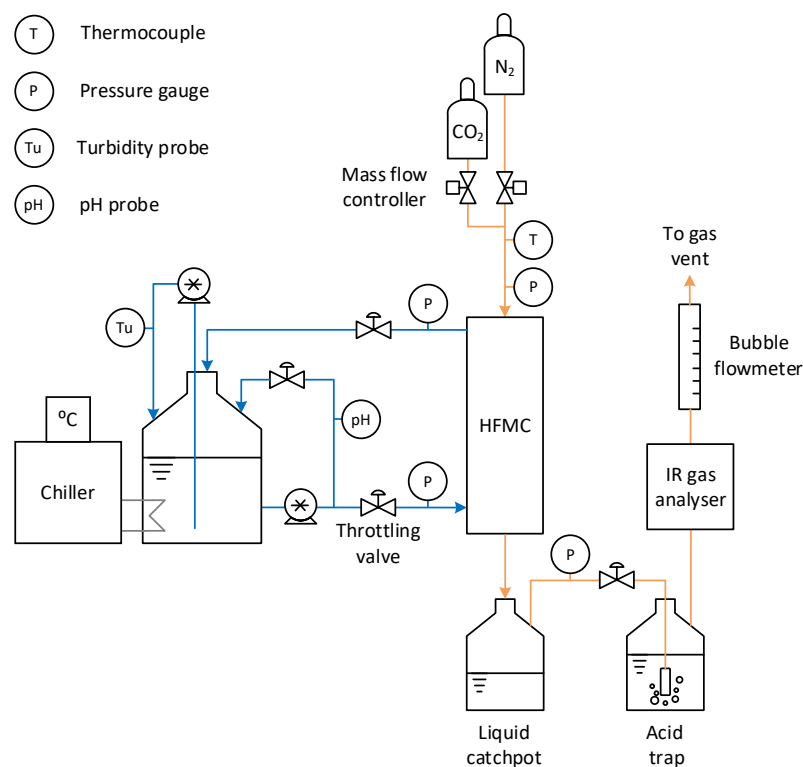


Figure 5.2: Experimental setup for reactive CO₂ absorption and crystallisation

Table 5.1: Material and structural properties of polypropylene hollow fibre membrane contactor

Parameter	Value
Internal fibre diameter ^a (μm)	240
Fibre wall thickness ^a (μm)	30
Fibre length ^a (m)	0.16
Tortuosity ^a (-)	0.4
Porosity ^a (-)	2.5
No. fibres ^b (-)	10200
Total surface area ^b (m ²)	1.2
Specific surface area ^b (m ² m ⁻³)	1860
Contact angle ^c (°)	122
Geometric pore factor ^d (-)	0.56
Max. pore size (μm) ^{d,e}	0.1
Breakthrough pressure ^f (bar)	8.0

^a Data supplied by manufacturer ^e (Heile et al., 2014)

^b Based on internal diameter

^f Based on 3.4 M NH₃ at 20°C

^c (Lv et al., 2010)

(King et al., 1930)

^d (Bavarella, 2018)

A liquid-side overpressure was established (0.2-0.4 bar) to prevent gas bubbling and pore wetting (Dindore et al., 2004). Gas and liquid pressures were measured across the system (DPG1001B-100G, $\pm 0.10\%$ full scale, Omega Engineering Ltd., Manchester, UK) and controlled using throttling valves at the HFMC outlets (SS-4MA-MH, Swagelok, Kings Langley, UK; Double acting inline control valve, F.lli Tognella Spa, Rome, Italy). Solvent pH and temperature were measured continuously using an inline probe which was installed on a mixing loop to promote homogeneity (InPro3250i/SG/120; Mettler-Toledo Ltd, Leicester, UK). A heat balance was applied to estimate the solvent temperature within the boundary layer, based upon the measured value in the bulk (Appendix D1). Solvent turbidity was monitored continuously to detect the presence of particles (i.e., nucleation) through light backscatter (Kashchiev and Van Rosmalen, 2003) (InPro 8200/S/Epoxy/120, Mettler-Toledo Ltd, Leicester, UK). A gas-liquid separator was installed at the gas outlet to collect condensate, followed by an acid trap ($0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$) to capture gas-phase ammonia (Schott Duran, VWR, NL). This enabled the amount of ammonia 'slip' into the gas-phase to be quantified for each experimental condition. The HFMC was rinsed with 10 L of de-ionised water at 40°C after each experiment to remove traces of ammonia. Subsequently, the membrane underwent drying with compressed air (30 L min^{-1}) for 45-minutes to restore hydrophobicity (3M, 2023). Mild drying conditions were applied (20°C , 1 bar) and reproducible results indicated that membrane properties were unaffected by cycles of cleaning and drying. Experiments were performed in triplicate, with mean values reported, and standard deviation is represented by error bars.

5.2.2 Experimental analysis

Solvent was prepared by mixing deionised water ($15 \text{ M}\Omega \text{ cm}$), ammonium hydroxide (35%, Fisher Scientific, Loughborough, UK) and hydrochloric acid (37%, Fisher Scientific, Loughborough, UK). Samples were extracted periodically to determine ammoniacal nitrogen content using spectrophotometry with proprietary cell tests (114559 $\text{NH}_4\text{-N}$, Spectroquant cell tests, Merck-Millipore, Darmstadt, Germany). Condensate collected within the gas-liquid separator was

analysed at the end of each experiment to determine its volume, pH, ammoniacal nitrogen content, and bicarbonate content based on UV absorbance at 215 nm (Jenway 6715, Cole-Parmer, Stone, UK) (Bavarella et al., 2022; Birkmann et al., 2018). Solvent samples were extracted 5 minutes after nucleation and subjected to vacuum filtration using 8 µm cellulose filter paper to recover the crystal fraction (Whatman Grade 2, Cytiva, Maidstone, UK). Crystals were recovered from condensate collected at the gas outlet by the same method. Crystals were dried at 22°C for 48 hours prior to imaging using scanning electron microscopy (SEM) (Tescan VEGA 4, Tescan Orsay Holding, a.s., Czech Republic) and compared against pure ammonium bicarbonate using X-ray diffraction (XRD) to evaluate their crystallinity (D5005, Siemens, Munich, Germany).

Based upon outlet gas composition, flowrate and the accumulation of CO₂ within the condensate, the instantaneous CO₂ flux into the solvent could be determined:

$$J_{CO_2} = \frac{C_g(Q_{g,in} y_{in} - Q_{g,out} y_{out}) - \frac{dn_{con}}{dt}}{A} \quad (\text{Eq. 5.1})$$

where J_{CO_2} is the CO₂ flux into the solvent (mol m⁻² min⁻¹); C_g is the concentration of pure CO₂ gas at the operating temperature and pressure (mol L⁻¹); Q_g is the total gas flowrate (L min⁻¹); y is the CO₂ fraction in the gas-phase (%vol); A is the HFMC surface area (1.23 m²); dn_{con}/dt is the rate of CO₂ accumulation in the gas condensate determined by mass balance at the end of each experiment (mol min⁻¹); subscripts *in* and *out* refer to the inlet and outlet of the HFMC, respectively. The CO₂ loading (mol_{CO2} mol_{NH3}⁻¹) at any time could also be determined:

$$CO_2 \text{ loading} = \frac{C_{CO_2,t}}{C_{NH_3,t}} = \frac{\left(\frac{n_{CO_2,t}}{V_t}\right)}{C_{NH_3,t}} \quad (\text{Eq. 5.2})$$

$$V_t = V_0 - V_{con,t} - V_{sample,t} \quad (\text{Eq. 5.3})$$

where C_{NH_3} and C_{CO_2} represent the total dissolved concentrations of ammonia (mol L⁻¹) and CO₂ (mol L⁻¹) in the solvent respectively; n_{CO_2} is the amount of CO₂ in the solvent (moles); V is the solvent volume (L); V_{sample} is the sample volume (L); V_{con} is the gas condensate volume (L); and subscripts 0 and t refer to time = 0 and time = t respectively.

The extent of chemical enhancement during CO₂ absorption is determined by the relative rates of reaction and diffusion in the liquid film. This can be expressed by the Hatta number (Ha), defined as (Rongwong et al., 2013):

$$Ha = \frac{\sqrt{k_{2,NH3} D_{CO2,l} C_{NH3}}}{k_l} \quad (\text{Eq. 5.4})$$

where $k_{2,NH3}$ is the second-order reaction rate constant ($0.55 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$) (Liu et al., 2011); $D_{CO2,l}$ is the diffusivity of CO₂ in the solvent ($1.33 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) (Seo et al., 2011). The liquid phase mass transfer coefficient, k_l (m s^{-1}), was determined using the Graetz-Leveque solution developed for transverse-flow HFMC (Baudot et al., 2001):

$$Sh = 0.56 Re^{0.62} Sc^{0.33} = \frac{k_l d_h}{D_{CO2,l}} \quad (\text{Eq. 5.5})$$

where Sh is the Sherwood number (-); Re is the Reynolds number (Shen et al., 2010) and Sc is the Schmidt number ($\mu/\rho D_{CO2,l}$) determined using solvent density (ρ) and dynamic viscosity (μ) of 1020 kg m^{-3} and $1.63 \times 10^{-3} \text{ N s m}^{-1}$, respectively (Pérez-Calvo et al., 2021a).

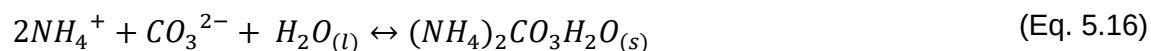
5.2.3 Solution chemistry within the CO₂-NH₃-H₂O system

Previous authors have described the solution chemistry within the CO₂-NH₃-H₂O system (Thomsen and Rasmussen, 1999; Wang et al., 2011). Solvent temperature and pH will determine the extent of ammonia dissociation to ammonium (NH₄⁺), and the speciation of dissolved CO₂ within the bicarbonate equilibrium (Appendix D2) (Eq. 5.8-5.12). The system can also form carbamic acid (NH₂COOH) and the intermediate reaction product carbamate (Eq. 5.13-5.14).





Three ammonium salts can form in the CO₂-NH₃-H₂O system under the conditions employed (7.2 ±0.3°C). Low CO₂ loading in the solvent, where ammonia is in large excess, will favour reaction pathways for ammonium carbamate (Eq. 5.15) and ammonium carbonate (Eq. 5.16) (Mani et al., 2006). However, precipitation of these salts is unlikely due to their high solubility in water (Darde et al., 2010; Mani et al., 2006). As CO₂ loading increases towards comparable amounts CO₂ and ammonia in solution, the reaction pathway for ammonium bicarbonate formation is prevalent (Eq. 5.17). This salt has the lowest solubility, and so its precipitation is thermodynamically favoured (Mani et al., 2006).



5.2.4 Crystallisation analysis

The supersaturation level (S_x) for ammonium bicarbonate in the solvent bulk and the interfacial boundary layer could be determined by:

$$S_x = \frac{C_x}{C_x^*} \quad x = \text{bulk, int} \quad (\text{Eq. 5.18})$$

where C_x is the dissolved concentration of bicarbonate (HCO_3^-) which was the limiting species for nucleation (mol L^{-1}); C_x^* is the solubility limit for ammonium bicarbonate (mol L^{-1}) and is a function of temperature (Appendix D1) (O'Neil, 2006; Perry and Green, 2007); and subscript x can refer to conditions at the bulk or interfacial boundary layer (int), respectively. The manifestation of a concentration boundary layer during radial liquid flow across tightly packed bundles such as HFMC is highly complex and poorly defined. In this study, it was assumed that the dissolved HCO_3^- concentration at the interfacial boundary layer

(C_{int}) was equivalent to the log mean of the HCO_3^- concentration in bulk and the gas-liquid interface at equilibrium (Eq. 5.19-5.20).

$$C_H^* = k_{H(T)} p_{CO_2} \quad (\text{Eq. 5.19})$$

$$C_{int} = \beta \left(\frac{(C_{CO_2} + C_H^*) - C_{CO_2}}{\ln \left(\frac{C_{CO_2} + C_H^*}{C_{CO_2}} \right)} \right) \quad (\text{Eq. 5.20})$$

where C_H^* is the equilibrium concentration for dissolved CO_2 at the gas-liquid interface (mol L^{-1}); $k_{H(T)}$ is the Henry's Law constant for CO_2 ($\text{mol L}^{-1} \text{ bar}^{-1}$) computed from empirical data using solvent temperature and ammonia concentration (Kim et al., 2014; Seo et al., 2011); p_{CO_2} is the CO_2 partial pressure in the gas-phase (bar); β is the relative fraction of dissolved CO_2 which will dissociate to HCO_3^- at the solvent temperature and pH (Appendix D2) (-).

Crystal nucleation was assumed to be controlled in the interfacial boundary layer, analogous to membrane distillation crystallisation (Jiang et al., 2015). Crystallisation behaviour can be compared against classical nucleation theory using the method developed by Sangwal (2009), where the nucleation rate is equivalent to the concentrating rate (R') (Eq. 5.21-5.22). The nucleation constants (k , m) can then be determined graphically from the linear trend exhibited when plotting $\ln(R')$ versus $\ln^2(S_{int})$ (Eq. 5.23) (Kulkarni et al., 2013; Sangwal, 2009).

$$R' = k(\ln S_{int})^m \quad (\text{Eq. 5.21})$$

$$R' = \frac{d(\Delta C_{int})}{dt} \quad \Delta C_{int} = C_{int} - C_{int}^* \quad (\text{Eq. 5.22})$$

$$\ln(R') = m \ln^2(S_{int}) + \ln(k) \quad (\text{Eq. 5.23})$$

The nucleation rate is typically inversely proportional to induction time, which is defined as the time between saturation being exceeded in the boundary layer and the occurrence of nucleation in the bulk, and so a plot of $\ln(t_{ind})$ versus $\ln^2(S_{int})$ should also provide information on the primary nucleation mechanism (Eq. 5.24) (Guo et al., 2017; Kashchiev and Van Rosmalen, 2003)

$$\ln(t_{ind}) = m \ln^{-2}(S_{int}) + \ln(k) \quad (\text{Eq. 5.24})$$

5.3 Results and discussion

5.3.1 Process intensification by pressurisation was limited by solvent reactivity

Increasing the gas pressure during reactive absorption led to a higher rate of CO₂ loading into the solvent (Figure 5.3). For example, comparable amounts of CO₂ absorption were achieved after 120, 103 and 82 minutes at 1.5, 2.0 and 2.5 bar, respectively. Pressurisation is expected to enhance mass transfer since it raises CO₂ partial pressure, increasing the driving force for diffusion from the bulk gas to the solvent interface (Dindore et al., 2004). Although reactive solvents facilitate greater CO₂ flux than physical solvents, pressurisation led to a weaker relative enhancement in flux than water absorption in HFMC (Figure 5.4) (Scholes et al., 2015). A similar response to pressurisation was observed for reactive absorption in a wetted wall column (CO₂ in 3 M NH₃) (Fang et al., 2015). The accumulation of CO₂ within the boundary layer can lower reactivity at the interface (Kim et al., 2014). Mass transfer could then become reaction limited in the film, with the physical driving force having a lesser impact on the rate of CO₂ absorption. Whilst reactive and physical absorption will occur simultaneously within the film, the extent of each is influenced by the hydrodynamics. In this study, fixed conditions were employed (liquid-gas ratio of 1.1 m³_{liquid} m⁻³_{gas}). The liquid Graetz number (Gz) was 41, which is in excess of the threshold (>20) required for the development of a thin concentration boundary layer at the interface (Wang et al., 2017). Lowering the liquid velocity to reduce Gz below this threshold will increase the solvent residence time relative to the time for CO₂ to diffuse across the film, therefore extending the reaction zone and favouring reactive absorption at the interface (Dindore et al., 2005). The Hatta number (Ha) describes the ratio of the reaction rate and the CO₂ diffusion rate through the film, and will determine the extent of chemical enhancement at the interface (Eq. 5.4) (Rongwong et al., 2013). At the initial condition (1.5 bar), Ha was 32. When pressure was increased to 2.0 and 2.5 bar, greater CO₂ flux across the reaction front enhanced the reaction rate and therefore increased the relative ratio of Ha/Gz. Lowering the liquid velocity under increasing pressures to reduce Gz, maintain Ha/Gz and maximise reactivity within the film could counteract the influence of CO₂ loading at the interface and support greater mass transfer enhancement with

pressurisation. Alongside optimisation of hydrodynamics, pressurisation could therefore offer an effective process intensification strategy to lower membrane area (i.e., capital cost), solvent consumption and reduce the time to nucleation.

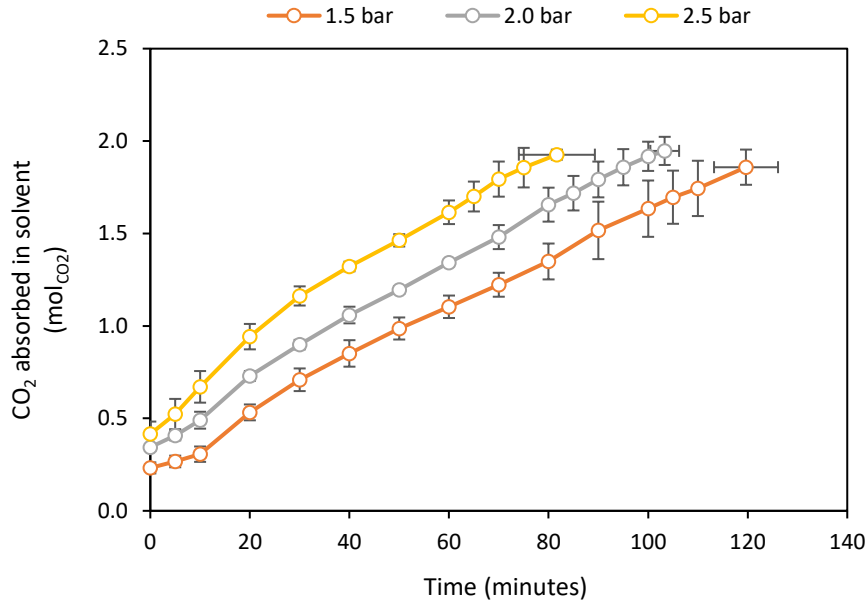


Figure 5.3: Influence of gas pressure on the rate of CO₂ absorption using 3.4 M aqueous ammonia in HFMC over time. Operational conditions: solvent flowrate, 1.5 L min⁻¹; solvent temperature, 7 ± 0.5°C; initial solvent pH, 11; gas flowrate, 1.34 L min⁻¹; CO₂ in feed gas, 90%vol. Gas flowrate, composition and pressure were established gradually over a 30 minute start-up period.

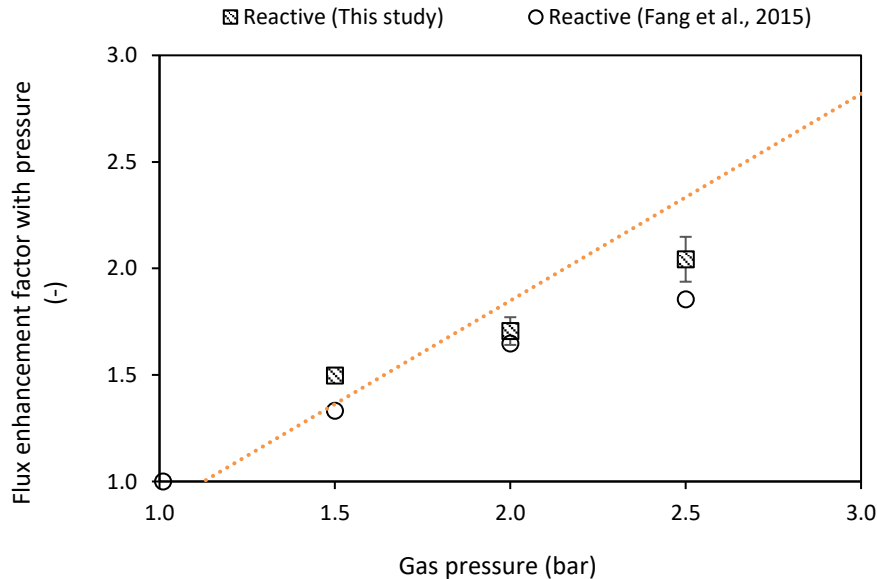
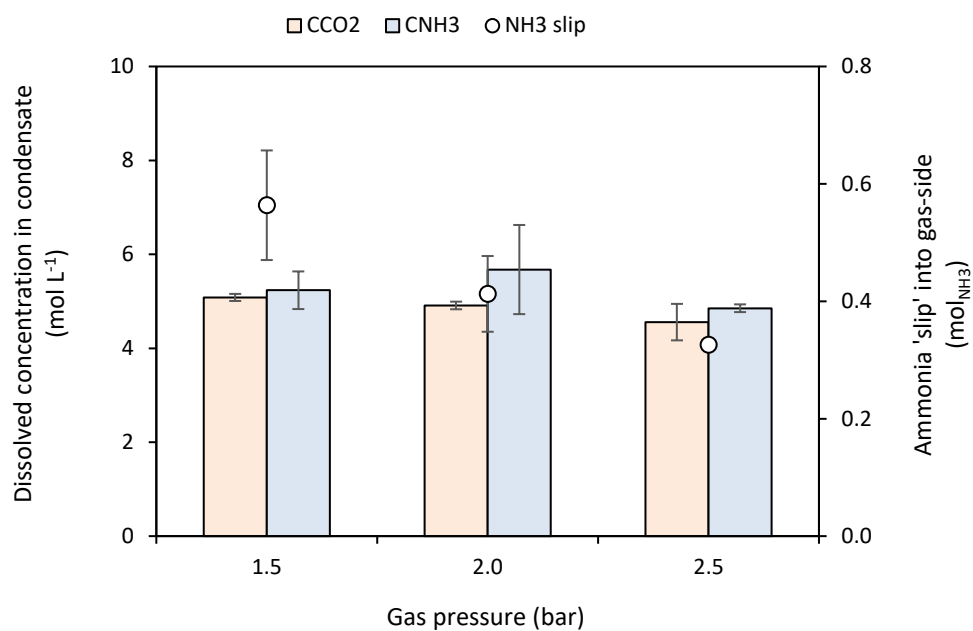


Figure 5.4: CO₂ flux enhancement with pressurisation during reactive absorption in HFMC. Operational conditions: solvent flowrate, 1.5 L min⁻¹; solvent temperature, 7 ± 0.5°C; initial solvent pH, 11; initial solvent concentration, 3.4 mol_{NH₃} L⁻¹; gas flowrate, 1.34 L min⁻¹; CO₂ in feed gas, 90%vol. Dotted line represents best fit for physical flux enhancement (Chapter 3).

5.3.2 High rates of CO₂ loading under pressure will minimise NH₃ 'slip'

Ammonia 'slip' during CO₂ absorption will limit the availability of ammonium in the solvent which is required for nucleation. Ammonia 'slip' has also been associated with gas-phase reactions in HFMC and the formation of liquid and solid products which can disrupt mass transfer (Bavarella et al., 2022; Cui and DeMontigny, 2017; Villeneuve et al., 2018). In this study, gas-phase reactions were evidenced by the collection of a supersaturated condensate ($S = 1.7\text{-}1.9$ at 22°C) in the gas-liquid separator at the lumen outlet. The concentrations of ammonia ($4.9\text{-}5.7\text{ mol L}^{-1}$) and CO₂ ($4.6\text{-}5.0\text{ mol L}^{-1}$) in the condensate were in excess of the solvent (Figure 5.5a). This indicates that liquid was present due to a gas-phase reaction instead of pore wetting through the fibre wall (Bavarella et al., 2022; Cui and DeMontigny, 2017). At 1.5 bar, 0.6 moles of ammonia were transferred from the solvent to the gas-side during CO₂ capture. Increasing the pressure up to 2.5 bar led to a 43% reduction in ammonia losses from the solvent. The mechanism for reduced 'slip' can be related directly to solvent chemistry. The absorption of CO₂ and subsequent formation of HCO₃⁻ will release protons in the solvent (Eq. 5.11). As a consequence, the solvent pH reduced from approximately 10.8 to 8.7 throughout each experiment (Figure 5.5b). Since the ammonia-ammonium equilibrium is a function of pH, this increased the fraction of non-volatile ammonium from 7% to 94% and lowered ammonia vapour pressure from 25 to 2 mbar (Appendix D2) (Bates and Pinching, 1950). Due to enhanced CO₂ absorption at increased pressures, this transition will occur at a greater rate and consequently lower the 'slip' which can occur. This effect was compounded by reduced experimental durations under pressure. By fostering a higher rate of CO₂ loading, pressurisation could therefore offer a critical strategy to reduce ammonia 'slip' and maximise reactant availability to support ammonium bicarbonate crystallisation. Limiting ammonia losses will also favour the process economics, since the purchase of replacement solvent and downstream gas scrubbing to remove ammonia can represent substantial costs for CAP (Pérez-Calvo et al., 2021b; Wang et al., 2018).

(a)



(b)

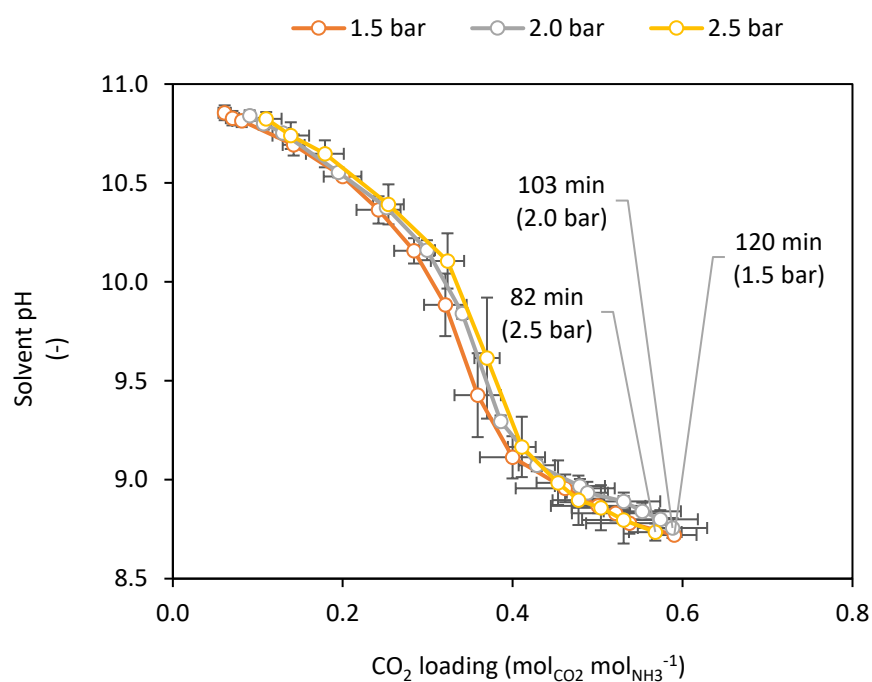


Figure 5.5: Influence of pressure on (a) ammonia 'slip' and gas condensate composition, and (b) rate of pH decline. Operational conditions: solvent flowrate, 1.5 L min^{-1} ; solvent temperature, $7 \pm 0.5^\circ\text{C}$; initial solvent pH, 11; initial solvent concentration, $3.4 \text{ mol}_{\text{NH}_3} \text{ L}^{-1}$; gas flowrate, 1.34 L min^{-1} ; CO_2 in feed gas, 90%vol.

5.3.3 Reactive membrane crystallisation demonstrated under pressure

Two conditions must be satisfied to precipitate ammonium bicarbonate in the $\text{CO}_2\text{-NH}_3\text{-H}_2\text{O}$ system. Firstly, a high CO_2 loading ratio is required to favour the reaction pathway for ammonium bicarbonate (Eq. 5.17) over ammonium carbonate and ammonium carbamate (Eq. 5.15-5.16) (Darde et al., 2010; Thomsen and Rasmussen, 1999). Secondly, both reacting species (NH_4^+ and HCO_3^-) must be present in excess of the solubility limit for ammonium bicarbonate precipitation (Bavarella et al., 2022). Ammonia losses due to 'slip' were accounted for by temporal measurement of the solvent to determine the absolute reactivity. During CO_2 absorption at 1.5 bar (Figure 5.6a), the threshold for CO_2 loading predicted by the extended UNIQUAC model for ammonium bicarbonate formation ($0.53 \text{ mol}_{\text{CO}_2} \text{ mol}_{\text{NH}_3}^{-1}$) was met after approximately 107 minutes (Thomsen & Rasmussen, 1999). Despite ammonia 'slip', the concentration of NH_4^+ increased over time due to the pH shift associated with CO_2 loading and exceeded the solubility limit for ammonium bicarbonate after 63 minutes (Appendix D2). However, there was insufficient HCO_3^- in solution to initiate the crystallisation reaction. As CO_2 absorption progressed and pH declined, a shift in the bicarbonate equilibrium transformed CO_3^{2-} into HCO_3^- and the solubility limit was exceeded after 112 minutes. Nucleation occurred 8 minutes later and could be precisely detected by a sudden increase in turbidity above 50 NTU which indicated the presence of suspended particles (Figure 5.7). This delay is defined as the induction time and indicates the metastability of the system (Kashchiev and Van Rosmalen, 2003). Similar dynamics in solvent chemistry were observed at 2.0 and 2.5 bar, but with compressed time-scales where nucleation occurred after 103 and 82 minutes, respectively, due to greater rates of CO_2 loading (Figure 5.6b,c). In each case, HCO_3^- was the limiting species for crystal formation, and nucleation was detected shortly after the solubility limit had been exceeded. Accurate determination of solvent chemistry in the reactive system then enabled an examination of the influence of pressure on nucleation kinetics.

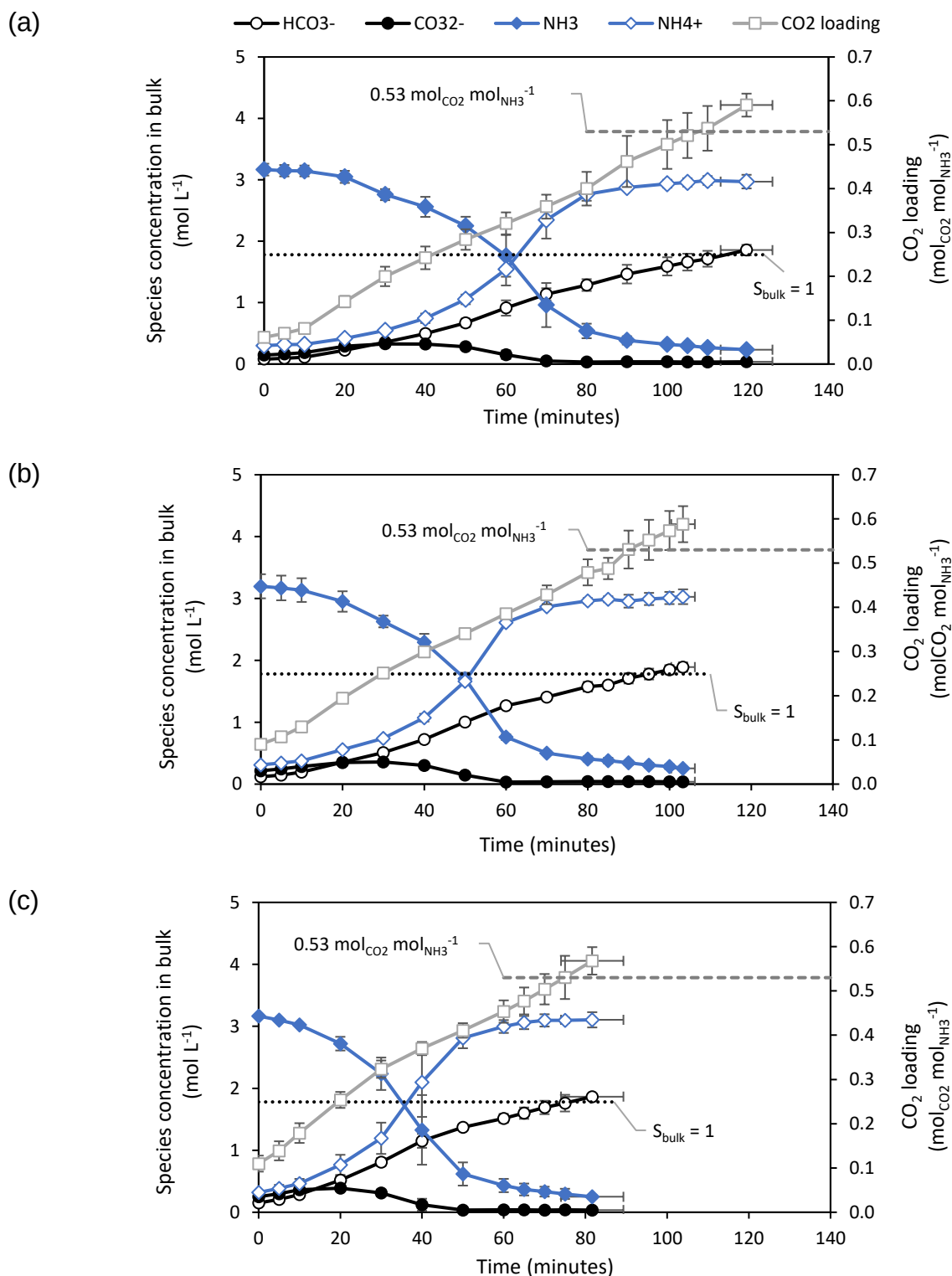


Figure 5.6: Species concentration and CO₂ loading during reactive absorption in HFMC at (a) 1.5 bar, (b) 2.0 bar, and (c) 2.5 bar. Operational conditions: solvent flowrate, 1.5 L min⁻¹; solvent temperature, 7 ± 0.5°C; initial solvent pH, 11; initial solvent concentration, 3.4 mol_{NH₃} L⁻¹; gas flowrate, 1.34 L min⁻¹; CO₂ in feed gas, 90%vol. Dotted line represents the solubility limit for ammonium bicarbonate and dashed line represents CO₂ loading threshold for ammonium bicarbonate formation at solvent temperature.

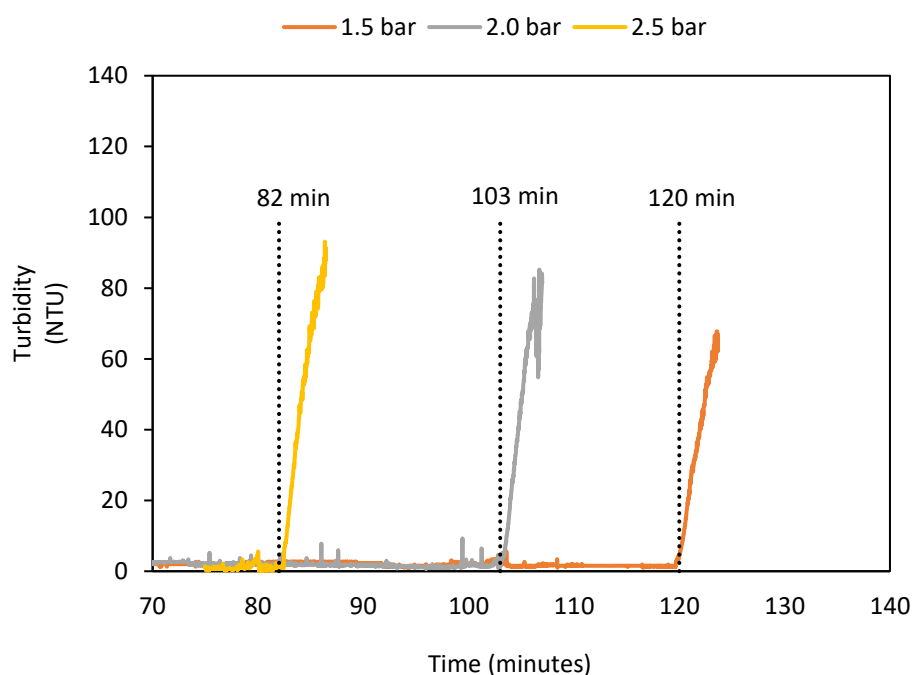


Figure 5.7: Application of online turbidimetry to determine the onset of bulk nucleation during reactive CO₂ absorption by 3.4 M aqueous ammonia in HFMC. Dotted lines represent the bulk nucleation time.

5.3.4 Nucleation kinetics were observed to be independent of pressure

Analysis of the supersaturation level and the induction time at nucleation could elicit the influence of pressurisation on nucleation kinetics. During membrane crystallisation, nucleation is likely to occur first within the interfacial boundary layer. This is because there will be a raised concentration relative to the bulk, and the hydrophobic membrane will lower the energy barrier for heterogenous nucleation (Figure 5.1) (Jiang et al., 2016; Martínez-Díez and Vázquez-González, 1999). During membrane distillation crystallisation, an increase in water vapour transport will result in concentration and temperature polarisation, where the lower temperature at the interface will reduce the solubility limit (Horseman et al., 2021). This collectively increases the metastable zone width, and increases the probability for nucleation in the boundary layer. In contrast, the temperature at the interface will be relatively higher during reactive absorption due to the heat of reaction ($43 \text{ kJ mol}_{\text{CO}_2}^{-1}$) and heat transfer from the gas phase (Appendix D1) (Jilvero et al., 2012). However, this effect was minor due to the limited CO₂ flux range ($<15 \times 10^{-3} \text{ mol m}^{-2} \text{ min}^{-1}$) and so the solubility limit (C_x^*) at the bulk and

interface were closely comparable (Figure 5.8). Across all pressures, the HCO_3^- concentration in the boundary layer was slightly higher than the bulk concentration ($0.03\text{--}0.05 \text{ mol L}^{-1}$) at nucleation (Figure 5.9a). Consequently, a greater supersaturation level (C_x/C_x^*) was observed in the boundary layer which is consistent with nucleation occurring first at the membrane interface (Figure 5.9b) (Horseman et al., 2021). In classical nucleation theory, a greater concentrating rate for the crystallising species should allow the nucleation energy barrier to be exceeded before the system is able to respond, thereby facilitating higher levels of supersaturation (Kashchiev and Van Rosmalen, 2003; Kulkarni et al., 2013). However, despite higher CO_2 flux with increasing pressure, analysis of variance (ANOVA) confirmed that there was not a statistically significant difference in supersaturation levels achieved at 1.5–2.5 bar ($P_{0.95CL} = 0.7$).

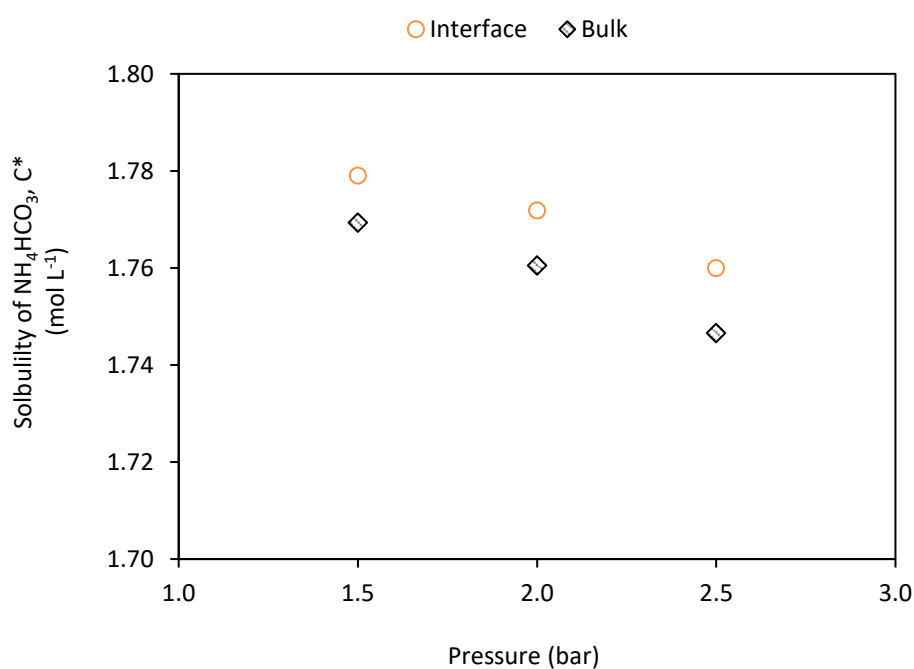


Figure 5.8: Solubility of ammonium bicarbonate in the bulk and interfacial boundary layer. Based upon specific temperatures measured for bulk and estimated for boundary layer by a heat balance (Appendix D1).

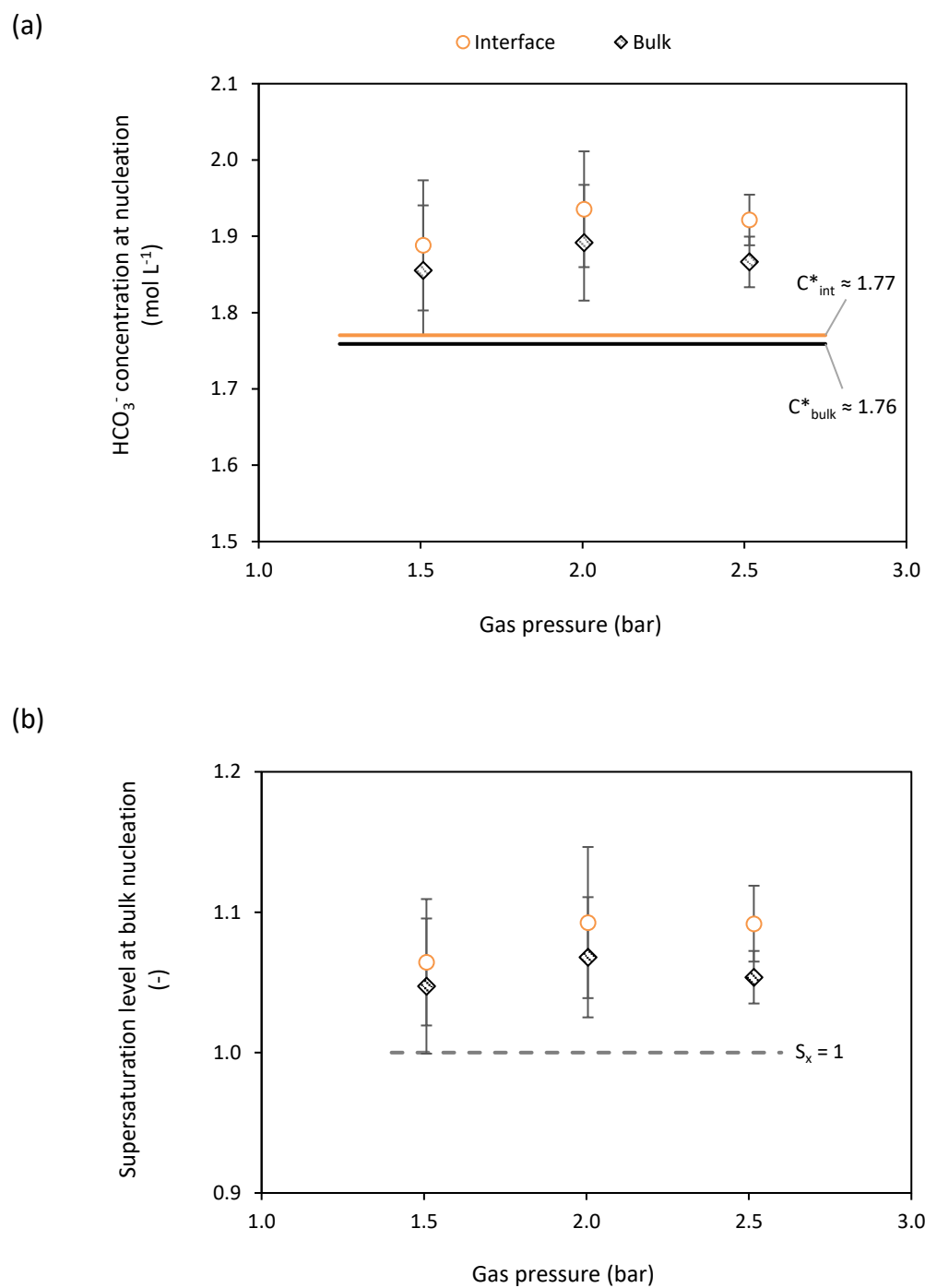


Figure 5.9: Influence of gas pressure on (a) concentration of HCO_3^- in solvent at nucleation, and (b) supersaturation level in solvent at nucleation. Operational conditions: solvent flowrate, 1.5 L min^{-1} ; solvent temperature, $7 \pm 0.5^\circ\text{C}$; initial solvent pH, 11; initial solvent concentration, $3.4 \text{ mol}_{\text{NH}_3} \text{ L}^{-1}$; gas flowrate, 1.34 L min^{-1} ; CO_2 in feed gas, 90%vol.

Unlike physical crystallisation processes, reactive crystallisation is sequential and the rate of crystallisation is dependent on the rate of reaction (Chan et al., 2005; Jiang et al., 2016; McDonald et al., 2021). Whilst ionic crystallisation will occur rapidly (i.e., NH_4HCO_3 formation, Eq. 5.17), a slow reaction rate in the film could enable an excess of CO_2 to accumulate within the solvent prior to nucleation (McDonald et al., 2021). The gradual transition of dissolved CO_2 into HCO_3^- could therefore present a rate limiting step and cause the nucleation energy barrier to be exceeded at the same supersaturation level, despite variation in the rate of CO_2 loading into the film (Schall and Myerson, 2019). This is consistent with induction times across all pressures (8-11 minutes) which were not statistically distinguishable ($P_{0.95CL} = 0.8$), despite variation in the absolute time to nucleation (Figure 5.10). In classical nucleation theory, the nucleation rate (R') can be related to the supersaturation level at induction (i.e. metastable zone width) by a power-law relationship (Eq. 5.23) (Sangwal, 2009). Graphical analysis can inform the influence of pressure on nucleation (Sangwal, 2009). A statistically significant linear response was not exhibited during the power-law analysis (Figure 5.11a), which provides further evidence that nucleation kinetics were not significantly influenced by pressurisation. Similarly, a linear response was not observed between induction time and supersaturation level and so information about the nucleation kinetics could not be inferred from the experimental data (Figure 5.11b) (Kubota, 2008). Crucially, these results were obtained at fixed hydrodynamic conditions. Lowering Gz (by reducing liquid velocity) to maximise reactivity in the film could directly influence the reaction series and thereby influence the relationship between pressure and nucleation kinetics.

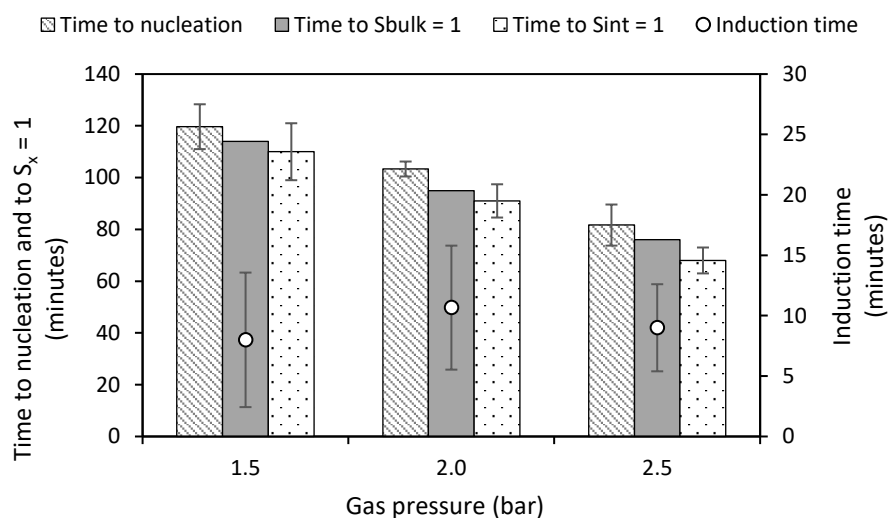
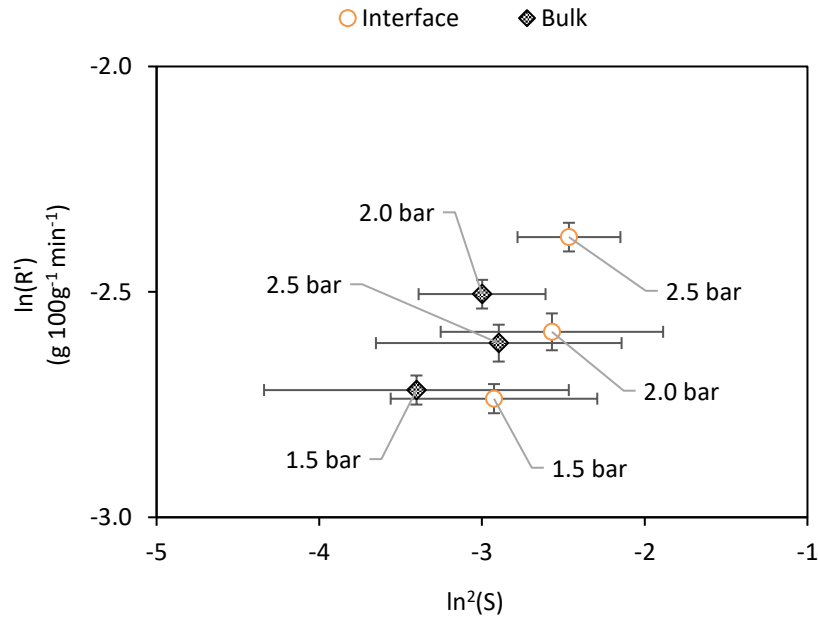


Figure 5.10: Influence of gas pressure on absolute time to nucleation and crystal induction time. Operational conditions: solvent flowrate, 1.5 L min⁻¹; solvent temperature, 7 ± 0.5°C; initial solvent pH, 11; initial solvent concentration, 3.4 mol_{NH3} L⁻¹; gas flowrate, 1.34 L min⁻¹; CO₂ in feed gas, 90%vol.

Recovered crystals were examined using XRD, which generated a sequence of diffraction peaks (2θ) which were closely comparable to a reference sample of pure ammonium bicarbonate (Figure 5.12a) (Bavarella et al., 2020b). For each condition (1.5-2.5 bar) the crystals collected from the solvent were of comparable size (50-100 μm) and exhibited a dendritic morphology (Figure 5.12b). Since size distribution and morphology are influenced by nucleation kinetics (Ulrich and Strege, 2002), this provided further evidence that kinetics were independent of pressure in the reactive system. Dendritic “Christmas tree” structures are indicative of high purity nuclei which have grown at a rapid rate under relatively high levels supersaturation (Ulrich and Stelzer, 2019). This is consistent with their formation via fast ionic crystallisation in a solvent where an excess of reactants was present (Figure 5.9). Bulk crystals can be compared directly against those collected within the condensate produced during gas-phase reactions (Figure 5.12c). These were formed at a substantially higher level of supersaturation ($S = 1.7$ - 1.9), and contained rods up to 1000 μm in length. During crystallisation of ammonium sulphate, Rauls et al. (2000) observed a transition in morphology from compact structures to large rods when supersaturation was increased by a factor of 2-3. In this study, condensate formed spontaneously at the highly

supersaturated condition. Due to the large size of these crystals, they could be readily separated from the condensate and diverted to thermal regeneration whilst the liquid fraction could be recycled to the solvent bulk to lower ammonia losses (Villeneuve et al., 2018). Reactive membrane crystallisation could therefore support inline crystal separation and simplify the solvent regeneration process during CAP.

(a)



(b)

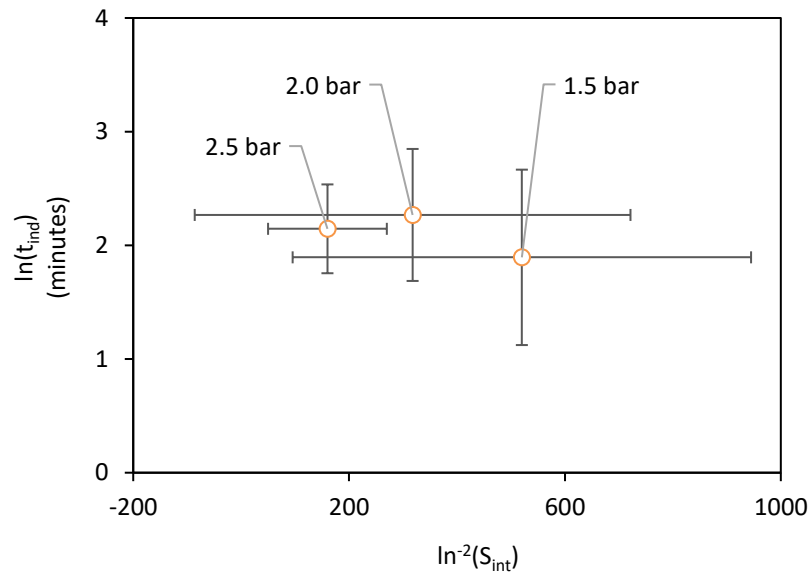


Figure 5.11: Power law relationship between supersaturation level at nucleation and (a) concentrating rate (Eq. 5.23), and (b) induction time to characterise nucleation kinetics and mechanism (Eq. 5.24) (Sangwal, 2009).

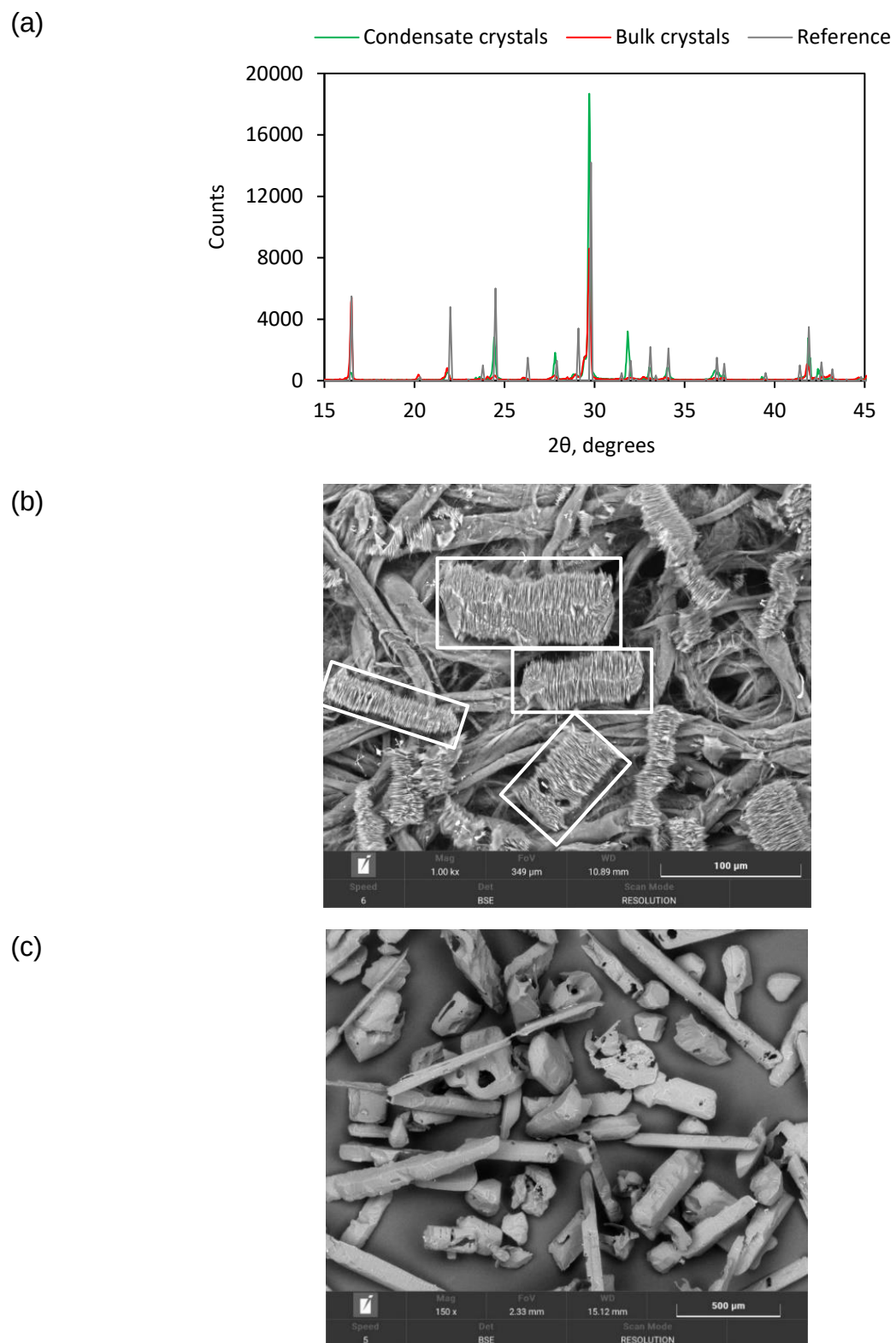


Figure 5.12: Analysis of ammonium bicarbonate crystals: (a) XRD analysis for crystals harvested from solvent and from gas condensate, (b) SEM imaging for crystals harvested from bulk solvent at 1.5 bar ($S_{\text{int}} = 1.06$) at 1000x magnification (example crystals identified by white boxes), and (c) SEM imaging for crystals harvested from gas condensate solvent ($S = 1.7$ -1.9) at 150x magnification. SEM imaging for crystals formed at 2.0 and 2.5 bar available in Appendix D3.

5.4 Conclusion

In this study, reactive absorption and crystallisation in membrane contactors has been conducted under pressurised conditions (up to 2.5 bar) for the first time, representing a critical advancement for process intensification during the chilled ammonia process. Pressurisation enhanced the rate of CO₂ loading in the solvent, and therefore represents an effective strategy to reduce membrane area and capital cost. However, a weaker enhancement in flux with pressure was observed when compared to physical absorption processes. It was determined that CO₂ loading within the film led to a reduction in solvent reactivity which limited further enhancement in mass transfer. Optimisation of the hydrodynamics to lower Gz and extend the reaction zone within the film could support greater mass transfer enhancement with pressurisation. Due to increased CO₂ loading rates, lower ammonia 'slip' was observed at higher pressures. This will maximise the availability of reactants at nucleation and reduce ammonia slip into the gas-phase and the costs associated with solvent replacement and downstream gas scrubbing. Contrary to classical nucleation theory, the enhancement in the CO₂ loading rate did not have a statistically significant impact on the supersaturation level or crystal induction time. This was supported by analysis of the crystals which displayed a consistent size and morphology, indicating formation under similar supersaturation levels. It is proposed that these outcomes were due to the rate limiting reaction within the film, which enabled an excess of CO₂ to accumulate under each condition prior to nucleation. This effectively de-coupled the concentrating rate, and therefore pressure, from nucleation kinetics for the system. By exhibiting consistent crystallisation behaviour across a range of pressures, this study indicates that membrane facilitated CAP could capitalise on the advantages of pressurisation whilst promoting predictable process control during continuous CO₂ absorption and crystallisation.

Acknowledgements

We are grateful for the financial and technical support offered by Anglian Water, Northumbrian Water and Severn Trent Water. We also acknowledge the funding and training resources provided to Benjamin Luqmani from the Engineering and

Physical Sciences Research Council through the STREAM Industrial Doctorate Centre.

Appendix D

D1 Heat balance to determine C^* in solvent boundary layer

Temperature polarisation within the solvent boundary layer during CO₂ absorption was estimated by conducting a heat balance across a single fibre (Figure D2). The total heat flux (W m⁻²) from the gas-side into boundary layer due to the absorption of CO₂ was estimated:

$$\frac{Q_T}{A} = \frac{Q_c}{A} + \frac{Q_a}{A} \quad (\text{Eq. D1})$$

$$\frac{Q_a}{A} = J_{CO_2} (C_p T_{b,g} + \Delta H_r) \quad (\text{Eq. D2})$$

$$\frac{Q_c}{A} = \frac{T_{b,g} - T_{b,l}}{L \left(\frac{1}{h_l d_{out}} + \frac{1}{k_m} \ln \left(\frac{d_{out}}{d_{in}} \right) + \frac{1}{h_g d_{in}} \right)} \quad (\text{Eq. D3})$$

where Q_c/A is the heat flux due to convection and Q_a/A is the heat flux due to CO₂ absorption (W m⁻²); T_b is the bulk temperature (°C/K); C_p is the specific heat capacity for CO₂ at the bulk gas temperature (35 J mol K⁻¹); ΔH_r is the heat of reaction for CO₂ absorption in aqueous ammonia (43120 J mol⁻¹) (Jilvero et al., 2012); L is the fibre length (m); and subscripts g and l indicate the gas and liquid respectively. Liquid and gas film heat transfer coefficients, h_l and h_g (W m⁻² K⁻¹), were estimated using the Nusselt number, Nu (Eq. D4-D5). Nu is analogous to the Sherwood number and so could be determined using Graetz-Leveque solutions developed for mass transfer within the fibre lumen and shellside for HFMC (Baudot et al., 2001; Wang et al., 2017). It was assumed that the velocity within the stagnant liquid film adjacent to the fibre wall was 0.01% of the liquid bulk velocity.

$$h_i = \frac{Nu k_i}{d_{h,i}}, \quad i = l, g \quad (\text{Eq. D4})$$

$$Nu_g = 0.5 Re_g Pr_g \frac{d_{in}}{L}; \quad Nu_l = 0.5 Re_l^{0.62} Pr_l^{0.33} \quad (\text{Eq. D5})$$

where k_i is the thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$); $d_{h,i}$ is hydraulic diameter (m); Re is the Reynolds number (-); and Pr is the Prandlt number (-). The thermal conductivity of the porous membrane, k_m ($\text{W m}^{-1} \text{K}^{-1}$) was calculated as (Martínez-Díez and Vázquez-González, 1999):

$$k_m = \left(\frac{\varepsilon}{k_{gas}} + \frac{1 - \varepsilon}{k_{liquid}} \right)^{-1} \quad (\text{Eq. D6})$$

where ε is membrane porosity (0.4); and k_{gas} and k_{liquid} are the thermal conductivities for the gas ($\text{W m}^{-1} \text{K}^{-1}$) and liquid ($\text{W m}^{-1} \text{K}^{-1}$) respectively and are independent of pressure from 1-10 bar. The temperature required in the stagnant liquid film at the fibre wall, $T_{w,l}$ ($^{\circ}\text{C}$), to provide an equivalent heat flux from the liquid film to the liquid bulk as from the gas into the liquid film and could then be estimated:

$$\frac{Q_T}{A} = h_l (T_{w,l} - T_{b,l}) \quad (\text{Eq. D7})$$

The liquid temperature within the boundary layer, T_{int} ($^{\circ}\text{C}$), was then calculated to be the log-mean of the measured temperature the liquid bulk and the estimated temperature in the stagnant liquid film:

$$T_{int} = \frac{T_w - T_b}{\ln \left(\frac{T_w}{T_b} \right)} \quad (\text{Eq. D8})$$

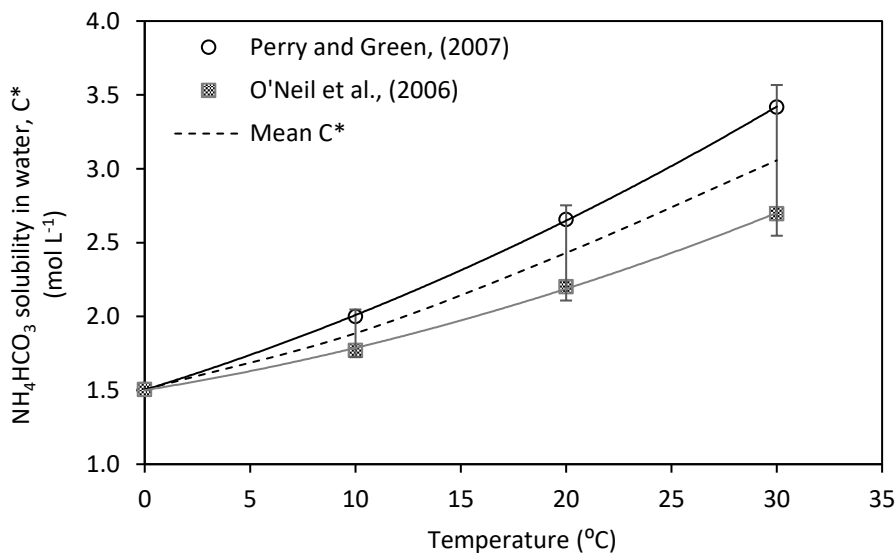


Figure D1: Solubility limit for ammonium bicarbonate in water as a function of temperature. Dotted line represents mean C^* interpolated from literature data (O'Neil, 2006; Perry and Green, 2007).

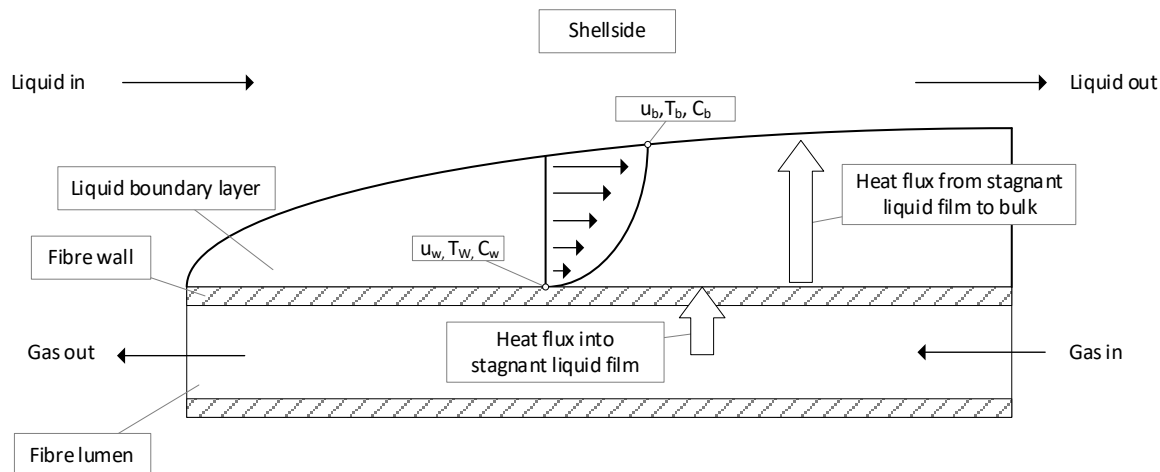


Figure D2: Methodology for estimating fibre wall temperature based on heat fluxes from gas side to liquid bulk.

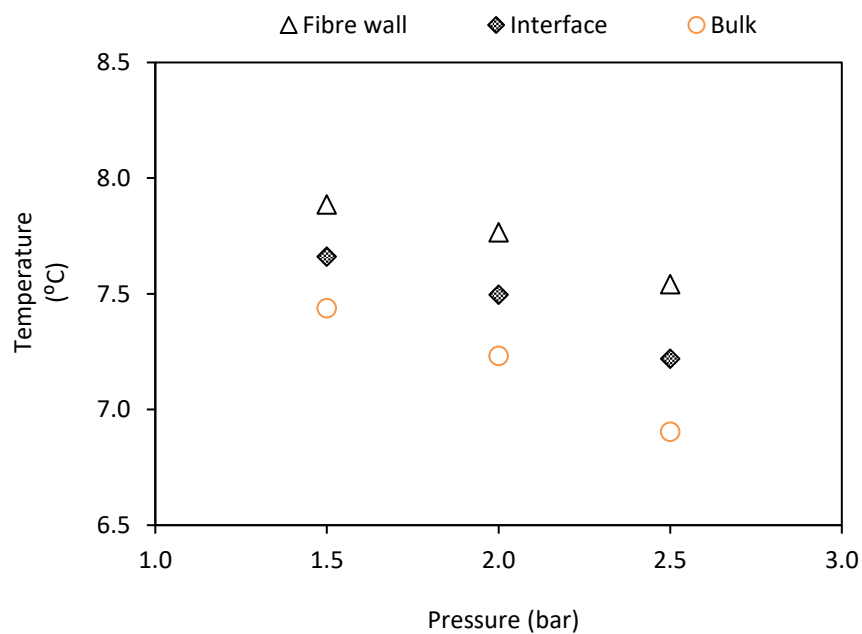
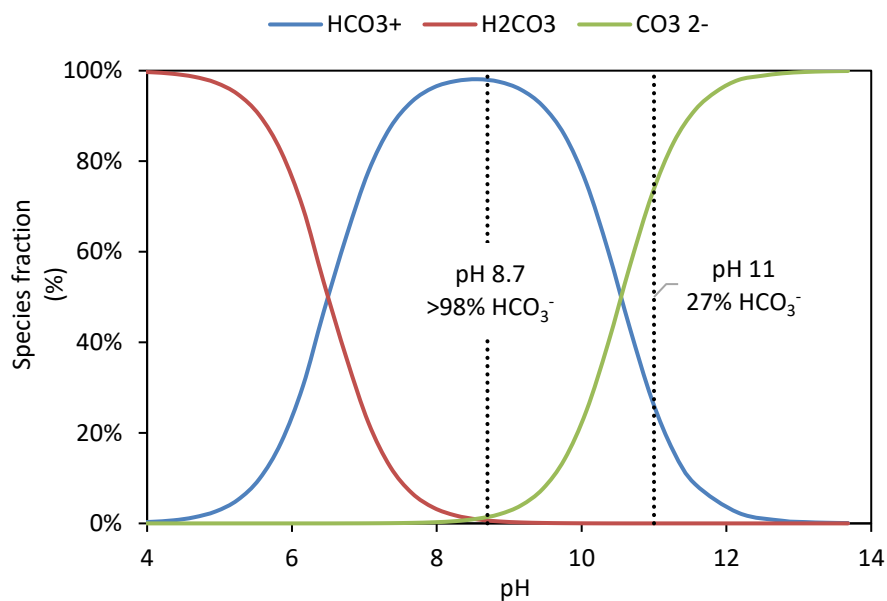


Figure D3: Outcome of temperature polarisation and variations in bulk temperature on (a) the temperature profile in the liquid-side, and (b) C^* in the liquid bulk, boundary layer and at the fibre wall from 1.5 – 2.5 bar.

D2 Chemical speciation with pH and temperature

(a)



(b)

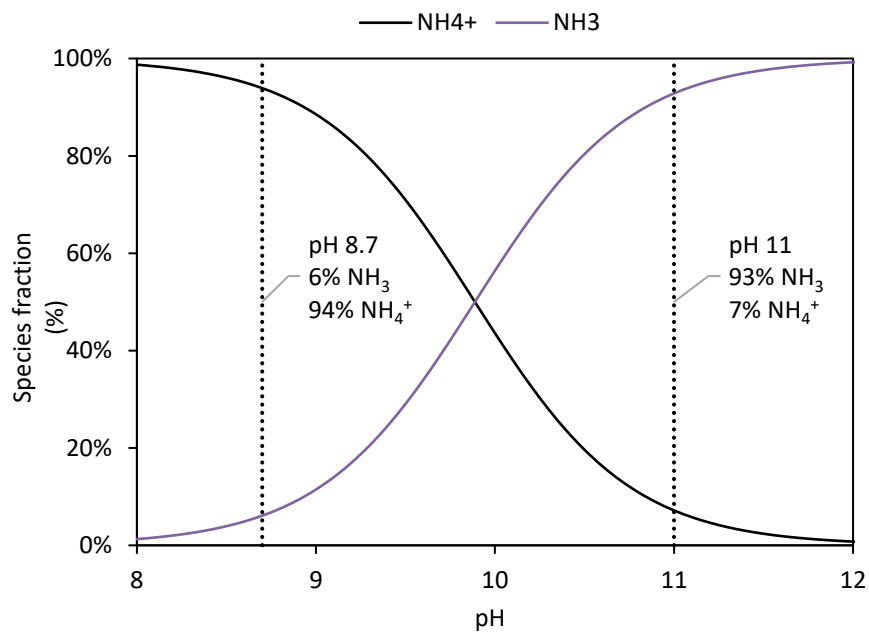
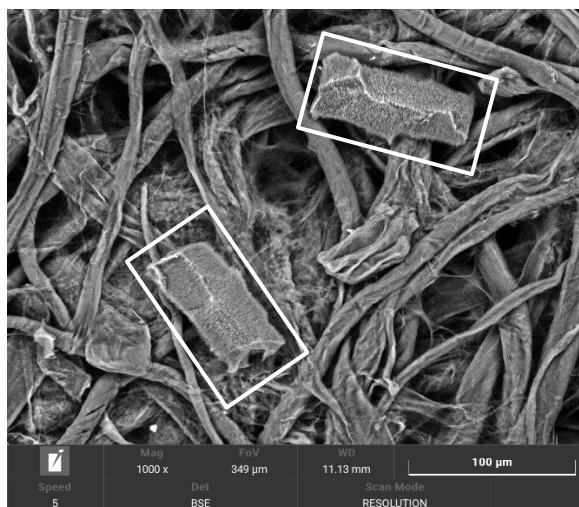


Figure D4: Influence of solvent pH on (a) the bicarbonate equilibrium, and (b) the ammonia-ammonium equilibrium at a solvent temperature of 5-10°C (Bates and Pinching, 1950). Dotted lines indicate the fraction of crystallising species at the initial pH (11) and final pH (~8.7).

D3 – SEM analysis for crystals formed at 2.0 and 2.5 bar

(a)



(b)

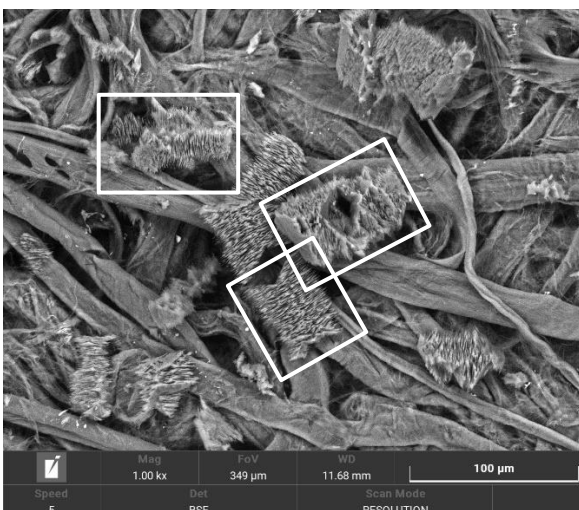


Figure D5: SEM imaging for crystals harvested from bulk solvent ($S = 1.07$ - 1.09) at 1000x magnification at (a) 2.0 bar, and (b) 2.5 bar. Example crystals identified by white boxes.

References

- 3M. (2023). Liqui-Cel EXF Series Membrane Contactors - Cleaning and Storage Guidelines. <https://multimedia.3m.com/mws/media/2282742O/pdf-of-the-cleaning-and-storage-guidelines-for-the-3m-liqui-cel-exf-membrane-contactors.pdf> (accessed 24/04/2023).
- Angelidaki, I., Treu, L., Tsapekos, P., Luo, G., Campanaro, S., Wenzel, H., and Kougias, P. G. (2018). Biogas upgrading and utilization: Current status and perspectives. *Biotechnology Advances*, 36, 452–466.

- Augustsson, O., Baburao, B., Dube, S., Bedell, S., Strunz, P., Balfe, M., and Stallmann, O. (2017). Chilled Ammonia Process Scale-up and Lessons Learned. 13th International Conference on Greenhouse Gas Control Technologies, Lausanne, Switzerland.
- Bates, R. G., and Pinching, G. D. (1950). Dissociation Constant of Aqueous Ammonia at 0 to 50° from E. m. f. Studies of the Ammonium Salt of a Weak Acid. *Journal of the American Chemical Society*, 72, 1393–1396.
- Baudot, A., Floury, J., and Smorenburg, H. E. (2001). Liquid-Liquid Extraction of Aroma Compounds with Hollow Fiber Contactor. *AIChE Journal*, 47, 1780–1793.
- Bavarella, S. (2018). Chemically reactive membrane crystallisation reactor for CO₂ separation and ammonia recovery. PhD thesis. Cranfield University.
- Bavarella, S., Brookes, A., Moore, A., Vale, P., Di Profio, G., Curcio, E., Hart, P., Pidou, M., and McAdam, E. J. (2020a). Chemically reactive membrane crystallisation reactor for CO₂–NH₃ absorption and ammonium bicarbonate crystallisation: Kinetics of heterogeneous crystal growth. *Journal of Membrane Science*, 599, 117682.
- Bavarella, S., Hermassi, M., Brookes, A., Moore, A., Vale, P., Moon, I. S., Pidou, M., and McAdam, E. J. (2020b). Recovery and concentration of ammonia from return liquor to promote enhanced CO₂ absorption and simultaneous ammonium bicarbonate crystallisation during biogas upgrading in a hollow fibre membrane contactor. *Separation and Purification Technology*, 241, 116631.
- Bavarella, S., Luqmani, B., Thomas, N., Brookes, A., Moore, A., Vale, P., Pidou, M., and McAdam, E. J. (2022). CO₂ absorption into aqueous ammonia using membrane contactors: Role of solvent chemistry and pore size on solids formation for low energy solvent regeneration. *Separation and Purification Technology*, 290, 120786.
- Belaissaoui, B., Claveria-Baro, J., Lorenzo-Hernando, A., Albarracin Zaidiza, D., Chabanon, E., Castel, C., Rode, S., Roizard, D., and Favre, E. (2016). Potentialities of a dense skin hollow fiber membrane contactor for biogas

- purification by pressurized water absorption. *Journal of Membrane Science*, 513, 236–249.
- Birkmann, J., Pasel, C., Luckas, M., and Bathen, D. (2018). Uv spectroscopic properties of principal inorganic ionic species in natural waters. *Water Practice and Technology*, 13, 879–892.
- Chan, M. T., Fane, A. G., Matheickal, J. T., and Sheikholeslami, R. (2005). Membrane distillation crystallization of concentrated salts - Flux and crystal formation. *Journal of Membrane Science*, 257, 144–155.
- Chin Yeh, A., and Hsunling, B. (1999). Comparison of ammonia and monoethanolamine solvents to reduce CO greenhouse gas emissions. *The Science of the Total Environment*, 228, 279–284.
- Cui, Z., and DeMontigny, D. (2017). Experimental study of carbon dioxide absorption into aqueous ammonia with a hollow fiber membrane contactor. *Journal of Membrane Science*, 540, 297–306.
- Darde, V., Thomsen, K., van Well, W. J. M., and Stenby, E. H. (2010). Chilled ammonia process for CO₂ capture. *International Journal of Greenhouse Gas Control*, 4, 131–136.
- Dindore, V. Y., Brilman, D. W. F., Feron, P. H. M., and Versteeg, G. F. (2004). CO₂ absorption at elevated pressures using a hollow fiber membrane contactor. *Journal of Membrane Science*, 235, 99–109.
- Dindore, V. Y., Brilman, D. W. F., and Versteeg, G. F. (2005). Hollow fiber membrane contactor as a gas – liquid model contactor. *Chemical Engineering Science*, 60, 467–479.
- Fang, M., Xiang, Q., Yu, C., Xia, Z., Zhou, X., Cai, D., and Wang, Z. (2015). Experimental study on CO₂ absorption by aqueous ammonia solution at elevated pressure to enhance CO₂ absorption and suppress ammonia vaporization. *Greenhouse Gases: Science and Technology*, 5, 210–221.
- Gabelman, A., and Hwang, S. (1999). Hollow fiber membrane contactors. *Journal of Membrane Science*, 159, 61–106.
- Guo, Z., Li, L., Han, W., Li, J., Wang, B., and Xiao, Y. (2017). Interpretation of the microwave effect on induction time during CaSO₄ primary nucleation by a cluster coagulation model. *Journal of Crystal Growth*, 475, 220–231.

- Heile, S., Rosenberger, S., Parker, A., Jefferson, B., and McAdam, E. J. (2014). Establishing the suitability of symmetric ultrathin wall polydimethylsiloxane hollow-fibre membrane contactors for enhanced CO₂ separation during biogas upgrading. *Journal of Membrane Science*, 452, 37–45.
- Hoff, K. A., and Svendsen, H. F. (2013). CO₂ absorption with membrane contactors vs. packed absorbers- Challenges and opportunities in post combustion capture and natural gas sweetening. *Energy Procedia*, 37, 952–960.
- Horseman, T., Yin, Y., Christie, K. S., Wang, Z., Tong, T., and Lin, S. (2021). Wetting, Scaling, and Fouling in Membrane Distillation: State-of-the-Art Insights on Fundamental Mechanisms and Mitigation Strategies. *ACS EST Engineering*, 1, 117–140.
- Houlker, S. (2019). Scale up of hollow fibre membrane contactors for biogas upgrading. EngD thesis. Cranfield University.
- International Energy Agency (IEA). (2022). Global Energy Review: CO₂ Emissions in 2021. <https://iea.blob.core.windows.net/assets/c3086240-732b-4f6a-89d7-db01be018f5e/GlobalEnergyReviewCO2Emissionsin2021.pdf> (accessed 04/05/2023).
- Jiang, X., Lu, D., Xiao, W., Ruan, X., Fang, J., and He, G. (2016). Membrane assisted cooling crystallization: Process model, nucleation, metastable zone, and crystal size distribution. *AIChE Journal*, 62, 829–841.
- Jiang, X., Ruan, X., Xiao, W., Lu, D., and He, G. (2015). A novel membrane distillation response technology for nucleation detection, metastable zone width measurement and analysis. *Chemical Engineering Science*, 134, 671–680.
- Jiang, X., Shao, Y., Sheng, L., Li, P., and He, G. (2021). Membrane Crystallization for Process Intensification and Control: A Review. *Engineering*, 7, 50–62.
- Jilvero, H., Normann, F., Andersson, K., and Johnsson, F. (2012). Heat requirement for regeneration of aqueous ammonia in post-combustion carbon dioxide capture. *International Journal of Greenhouse Gas Control*, 11, 181–187.

- Kashchiev, D., and Van Rosmalen, G. M. (2003). Review: Nucleation in solutions revisited. *Crystal Research and Technology*, 38, 555–574.
- Kim, G. H., Park, S. Y., You, J. K., Hong, W. H., Kim, J. N., and Kim, J. D. (2014). CO₂ absorption kinetics in a CO₂-free and partially loaded aqueous ammonia solution. *Chemical Engineering Journal*, 250, 83–90.
- King, H. H., Lowe Hall, J., and Ware, G. C. (1930). A study of the density, surface tension and adsorption in the water-ammonia system at 20C. *Journal of the American Chemical Society*, 52, 5128–5135.
- Kubota, N. (2008). A new interpretation of metastable zone widths measured for unseeded solutions. *Journal of Crystal Growth*, 310, 629–634.
- Kulkarni, S. A., Kadam, S. S., Meekes, H., Stankiewicz, A. I., and Ter Horst, J. H. (2013). Crystal nucleation kinetics from induction times and metastable zone widths. *Crystal Growth and Design*, 13, 2435–2440.
- Liu, J., Wang, S., Qi, G., Zhao, B., and Chen, C. (2011). Kinetics and mass transfer of carbon dioxide absorption into aqueous ammonia. *Energy Procedia*, 4, 525–532.
- Lv, Y., Yu, X., Tu, S. T., Yan, J., and Dahlquist, E. (2010). Wetting of polypropylene hollow fiber membrane contactors. *Journal of Membrane Science*, 362, 444–452.
- Mani, F., Peruzzini, M., and Stoppioni, P. (2006). CO₂ absorption by aqueous NH₃ solutions: Speciation of ammonium carbamate, bicarbonate and carbonate by a ¹³C NMR study. *Green Chemistry*, 8, 995–1000.
- Martínez-Díez, L., and Vázquez-González, M. I. (1999). Temperature and concentration polarization in membrane distillation of aqueous salt solutions. *Journal of Membrane Science*, 156, 265–273.
- McDonald, M. A., Salami, H., Harris, P. R., Lagerman, C. E., Yang, X., Bommaris, A. S., Grover, M. A., and Rousseau, R. W. (2021). Reactive crystallization: A review. *Reaction Chemistry and Engineering*, 6, 364–400.
- McLeod, A., Buzatu, P., Autin, O., Jefferson, B., and McAdam, E. (2015). Controlling shell-side crystal nucleation in a gas-liquid membrane contactor for simultaneous ammonium bicarbonate recovery and biogas upgrading. *Journal of Membrane Science*, 473, 146–156.

- Milella, F., Gazzani, M., Sutter, D., and Mazzotti, M. (2018). Process synthesis, modeling and optimization of continuous cooling crystallization with heat integration - application to the chilled ammonia CO₂ Capture Process. *Industrial and Engineering Chemistry Research*, 57, 11712–11727.
- O'Neil, M. J. (Ed.). (2006). *The Merck Index - An Encyclopedia of Chemicals, Drugs, and Biologicals*. (1st ed., pp. 88–100). Merck & Co., Inc., Rahway, NJ, USA.
- Pérez-Calvo, J. F., Milella, F., Ammann, K., and Mazzotti, M. (2021a). Density and Viscosity of Aqueous (Ammonia + Carbon Dioxide) Solutions at Atmospheric Pressure and Temperatures between 278.15 and 318.15 K. *Journal of Chemical and Engineering Data*, 66(4), 1787–1801.
- Pérez-Calvo, J. F., Sutter, D., Gazzani, M., and Mazzotti, M. (2021b). Advanced configurations for post-combustion CO₂ capture processes using an aqueous ammonia solution as absorbent. *Separation and Purification Technology*, 274, 118959.
- Perry, R. H., & Green, D. W. (Eds.). (2007). *Perry's Chemical Engineers' Handbook* (8th ed., pp. 2–126). McGraw-Hill, New York, NY, USA.
- Rauls, M., Bartosch, K., Kind, M., Kuch, S., Lacmann, R., and Mersmann, A. (2000). Influence of impurities on crystallization kinetics - a case study on ammonium sulfate. *Journal of Crystal Growth*, 213, 116–128.
- Rongwong, W., Assabumrungrat, S., and Jiraratananon, R. (2013). Rate based modeling for CO₂ absorption using monoethanolamine solution in a hollow fiber membrane contactor. *Journal of Membrane Science*, 429, 396–408.
- Sangwal, K. (2009). A novel self-consistent Nývlt-like equation for metastable zone width determined by the polythermal method. *Crystal Research and Technology*, 44, 231–247.
- Schall, J. M., and Myerson, A. S. (2019). Solutions and Solution Properties. In A. S. Myerson, D. Erdemir, & A. Y. Lee (Eds.), *Handbook of Industrial Crystallization* (3rd ed., pp. 1–31). Cambridge University Press, Cambridge, UK.
- Scholes, C. A., Kentish, S. E., Stevens, G. W., and DeMontigny, D. (2015). Comparison of thin film composite and microporous membrane contactors for

- CO₂ absorption into monoethanolamine. *International Journal of Greenhouse Gas Control*, 42, 66–74.
- Seo, J. B., Jeon, S. Bin, Lee, S. S., Kim, J. Y., and Oh, K. J. (2011). The physical solubilities and diffusivities of N₂O and CO₂ in aqueous ammonia solutions on the additions of AMP, glycerol and ethylene glycol. *Korean Journal of Chemical Engineering*, 28, 1698–1705.
- Shen, S., Kentish, S. E., and Stevens, G. W. (2010). Shell-side mass-transfer performance in hollow-fiber membrane contactors. *Solvent Extraction and Ion Exchange*, 28, 817–844.
- Sutter, D., Gazzani, M., and Mazzotti, M. (2015). Formation of solids in ammonia-based CO₂ capture processes — Identification of criticalities through thermodynamic analysis of the CO₂–NH₃–H₂O system. *Chemical Engineering Science*, 133, 170–180.
- Sutter, D., Gazzani, M., Pérez-Calvo, J. F., Leopold, C., Milella, F., and Mazzotti, M. (2017). Solid Formation in Ammonia-based Processes for CO₂ Capture - Turning a Challenge into an Opportunity. 13th International Conference on Greenhouse Gas Control Technologies, Lausanne, Switzerland.
- Thomsen, K., and Rasmussen, P. (1999). Modeling of vapor-liquid-solid equilibrium in gas-aqueous electrolyte systems. *Chemical Engineering Science*, 54, 1787–1802.
- Ulrich, J., and Stelzer, T. (2019). Melt Crystallization. In A. S. Myerson, D. Erdemir, & A. Y. Lee (Eds.), *Handbook of Industrial Crystallization* (3rd ed., pp. 266–287). Cambridge University Press, Cambridge, UK.
- Ulrich, J., and Strege, C. (2002). Some aspects of the importance of metastable zone width and nucleation in industrial crystallizers. *Journal of Crystal Growth*, 237–239, 2130–2135.
- Villeneuve, K., Roizard, D., Remigy, J. C., Iacono, M., and Rode, S. (2018). CO₂ capture by aqueous ammonia with hollow fiber membrane contactors: Gas phase reactions and performance stability. *Separation and Purification Technology*, 199, 189–197.
- Wang, C. Y., Mercer, E., Kamranvand, F., Williams, L., Kolios, A., Parker, A., Tyrrel, S., Cartmell, E., and McAdam, E. J. (2017). Tube-side mass transfer

- for hollow fibre membrane contactors operated in the low Graetz range. *Journal of Membrane Science*, 523, 235–246.
- Wang, F., Zhao, J., Miao, H., Zhao, J., Zhang, H., Yuan, J., and Yan, J. (2018). Current status and challenges of the ammonia escape inhibition technologies in ammonia-based CO₂ capture process. *Applied Energy*, 230, 734–749.
- Wang, X., Conway, W., Fernandes, D., Lawrance, G., Burns, R., Puxty, G., and Maeder, M. (2011). Kinetics of the reversible reaction of CO₂(aq) with ammonia in aqueous solution. *Journal of Physical Chemistry A*, 115, 6405–6412.

6 The recovery of ammonia and its utilisation within a net zero water sector – a techno-economic analysis

The recovery of ammonia and its utilisation within a net zero water sector – a techno-economic analysis

B. Luqmani^a, M. Powders^a, A. Brookes^b, A. Moore^c, P. Vale^d, M. Pidou^a, E.J.
McAdam^{a,*}

^aCranfield Water Science Institute, Vincent Building, Cranfield University, Bedfordshire, MK43 0AL, UK

^bAnglian Water, Block C-Western House, Peterborough Business Park, Lynch Wood, Peterborough PE2 6FZ, UK

^cNorthumbrian Water, Boldon House, Wheatlands Way, Durham DH1 5FA, UK

^dSevern Trent Water, 2 St. Johns Street, Coventry CV1 2LZ, UK

*Corresponding Author: e.mcadam@cranfield.ac.uk

Abstract

A suite of technologies is emerging which could reposition ammonia as a valuable resource to support the water sector's transition to net zero, but established ammonia recovery systems incur high energy demands and generate low quality products which presents a barrier to implementation. In this study, we explored vacuum thermal stripping for selective ammonia recovery and examined integration strategies for decarbonisation and revenue generation in wastewater treatment. Translation of vacuum thermal stripping from a batch vessel to a gas-liquid contacting column enhanced the volumetric mass transfer coefficient by an order of magnitude, due to greater interfacial surface area ($\text{m}^2 \text{ m}^{-3}$), reduced boundary layer thickness and increased convection. This enabled design projections for a full-scale system, where investment in gas-phase recovery of ammonia (0.25 bar, 50°C) from digester centrate at a centralised treatment works (1.2 million P.E.) represented a cost saving ($-300 \text{ EUR } t_{\text{NH}_3}^{-1}$) over a 20-year economic lifetime relative to nitrogen removal in activated sludge processes. Whilst concentrated gas-phase ammonia (20-25%wt) is a flexible, energy dense product with multiple routes for valorisation, its capture and application as an aqueous solvent (3-5%wt) in biogas upgrading represented the most promising strategic pathway. This could generate revenue from exportation of biomethane (1.2 million EUR y^{-1}) and biogenic CO_2 (0.6 million EUR y^{-1}), whilst recovering purified ammonia for zero carbon energy generation in gas turbines or solid oxide fuel cells (0.08-0.14 million EUR y^{-1}). Selective ammonia recovery and utilisation in biogas upgrading could therefore present a circular economy solution which is aligned with net zero objectives for the water sector and wider society.

Keywords: Ammonia to energy, ammonia recovery, vacuum thermal stripping, circular economy, net zero.

6.1 Introduction

To support global decarbonisation objectives, the European water sector has committed to net zero carbon emissions across all operations by 2030-2050 (Water Europe, 2021; Water UK, 2020). The treatment of ammonia in wastewater presents a significant challenge to delivering these commitments. Dissolved ammonia is produced during the degradation of organic matter in wastewater, food waste and agricultural slurries and its discharge into waterways is harmful to human health and the environment (Kang et al., 2017; Maharaja et al., 2023; Mondor et al., 2008; Ndam, 2017). Conventional wastewater treatment flowsheets employ energy intensive activated sludge processes in which ammoniacal nitrogen is biologically oxidised in an aerobic environment ($5 \text{ kWh}_e \text{ kg}_N^{-1}$) (Garrido et al., 2013). Consequently, this can account for a fifth of power demand during wastewater treatment (Garrido et al., 2013; Wett, 2006). Biological processes are associated with almost half of direct greenhouse gas emissions in wastewater treatment, due to partial oxidation pathways which transform 0.3% of influent nitrogen to nitrous oxide (N_2O) which has a global warming potential 310-times greater than CO_2 (Campos et al., 2016; de Haas and Andrews, 2022; Winter et al., 2012). Furthermore, aeration basins and sludge storage tanks are linked to ammonia gas emissions which are now recognised to form particulate matter in the atmosphere ($\text{PM}_{2.5}$) that can lower air quality (Tian et al., 2022; Upadhyay et al., 2013). Direct emissions are an increasing focus of policymakers which may prompt utilities to deploy capital investment to retrofit covers, gas extraction and scrubbing for biological processes in future (Department for Environment Food and Rural Affairs, 2019; Vrontisi et al., 2016). To improve the quality of waterways, stringent discharge limits for nitrogen in treated wastewater have been introduced within the Urban Wastewater Treatment Directive 91/271/EEC (10 mg L^{-1} for works serving >0.1 million P.E.) (EEC Council, 1991). This is likely to stimulate capital investment in the intensification or expansion of activated sludge basins and their introduction into works where carbonaceous only treatment flowsheets are currently employed, and therefore has the potential to exacerbate existing challenges related to air quality, greenhouse gas emissions and energy demand. Adaptive pathways are

now necessary for the remediation of ammoniacal wastewater which can align with the strategic direction for a sustainable, net zero water sector.

The recovery of ammonia from wastewater presents an opportunity to reduce energy and emissions related to nitrogen removal, whilst generating a sustainable resource. Ammonia recovery has been demonstrated at commercial scales by air and steam stripping in packed columns (Organics Group, 2020; RVT, 2015). These processes often target anaerobic digester centrate, since this stream has a raised ammonia concentration ($1\text{--}2\text{ kg}_{\text{NH}_3}\text{ m}^{-3}$) which will favour the mass transfer driving force for stripping, and can contain 20-40% of the site ammonia load within 1% of the volumetric flow (Figure 6.1) (Mackinnon et al., 2003; Ndam, 2017). Air and steam stripping processes employ high gas-liquid stripping ratios ($>2000\text{ m}^3_{\text{air}}\text{ m}^{-3}_{\text{liquid}}$; $>100\text{ m}^3_{\text{steam}}\text{ m}^{-3}_{\text{liquid}}$) to overcome the high solubility for dissolved ammonia gas (Bonmati and Flotats, 2003; Huang and Shang, 2006; Zeng et al., 2006). This produces dilute gas-phase ammonia (0.01-2%wt) which has limited value. Vacuum thermal stripping has emerged as an alternative process which operates below atmospheric pressure to lower the saturation temperature for the feed (Tian et al., 2019). Due to the higher volatility of ammonia compared to water, heating the feed under this condition will generate an ammonia-rich vapour which can be continuously extracted by the vacuum pump with no requirement for a sweep gas (Tao et al., 2018; Ukwuani and Tao, 2016). Operating below the saturation temperature during vacuum thermal stripping, within the two-phase region for ammonia-water, can limit energy intensive water vapourisation and enhance ammonia selectivity (Chapter 2) (Pátek and Klomfar, 1995). In a batch reactor, selective vacuum stripping enabled the low energy recovery ($<1\text{ kWh}_{\text{th}}\text{ kg}_\text{N}^{-1}$) of a high purity gas-phase product ($>40\%$ wt) in a single stage (Chapter 2). Selectivity was inversely proportional to the mass transfer rate, highlighting a compromise between process size, energy demand and product quality (Chapter 2). Due to the application of batch reactors with limited interfacial surface area ($<40\text{ m}^2\text{ m}^{-3}$), previous researchers have reported volumetric ammonia mass transfer coefficients for vacuum stripping ($0.1\text{--}0.7\text{ h}^{-1}$) which are much lower than commercially established stripping processes ($1.4\text{--}11\text{ h}^{-1}$) (Guida et al., 2022;

Guštin and Marinšek-Logar, 2011; Jiang et al., 2014; Tao et al., 2018; Zeng et al., 2006). To achieve competitive rates of mass transfer, vacuum thermal stripping for ammonia recovery requires translation to a gas-liquid contacting column. However, the impact of process intensification on the regulation of ammonia selectivity during stripping has not yet been explored.

To investigate the trade-off between ammonia selectivity and volumetric mass transfer coefficient during vacuum thermal stripping, a techno-economic evaluation is required for the design and operation of a full-scale system operated across a broad range of conditions. The prevalent technology for ammonia production is the energy intensive Haber-Bosch process ($19 \text{ kWh kg}_\text{N}^{-1}$), which is conventionally reliant on fossil fuels and uses 'grey' hydrogen as a primary reactant (Nayak-Luke et al., 2018). Due to the high agricultural and industrial demands for ammonia, its production is associated with 1.3% of global CO_2 emissions (Nayak-Luke et al., 2018). This has stimulated the development of low or zero carbon ammonia production technologies such as the electrified Haber-Bosch process which can be supplied with renewable electricity and 'green' hydrogen (Cesaro et al., 2021; Morgan, 2013). The levelised cost of ammonia (LCOA) has emerged as a useful tool to evaluate the whole life cost-effectiveness of sustainable ammonia plants, which typically require higher capital investment due to the installation of local wind and solar farms and buffering storage for hydrogen (Cesaro et al., 2021; Morgan, 2013). An evaluation of the LCOA for selective vacuum thermal stripping could therefore contextualise the cost of ammonia production in the water sector within the wider 'green' ammonia economy of the future.

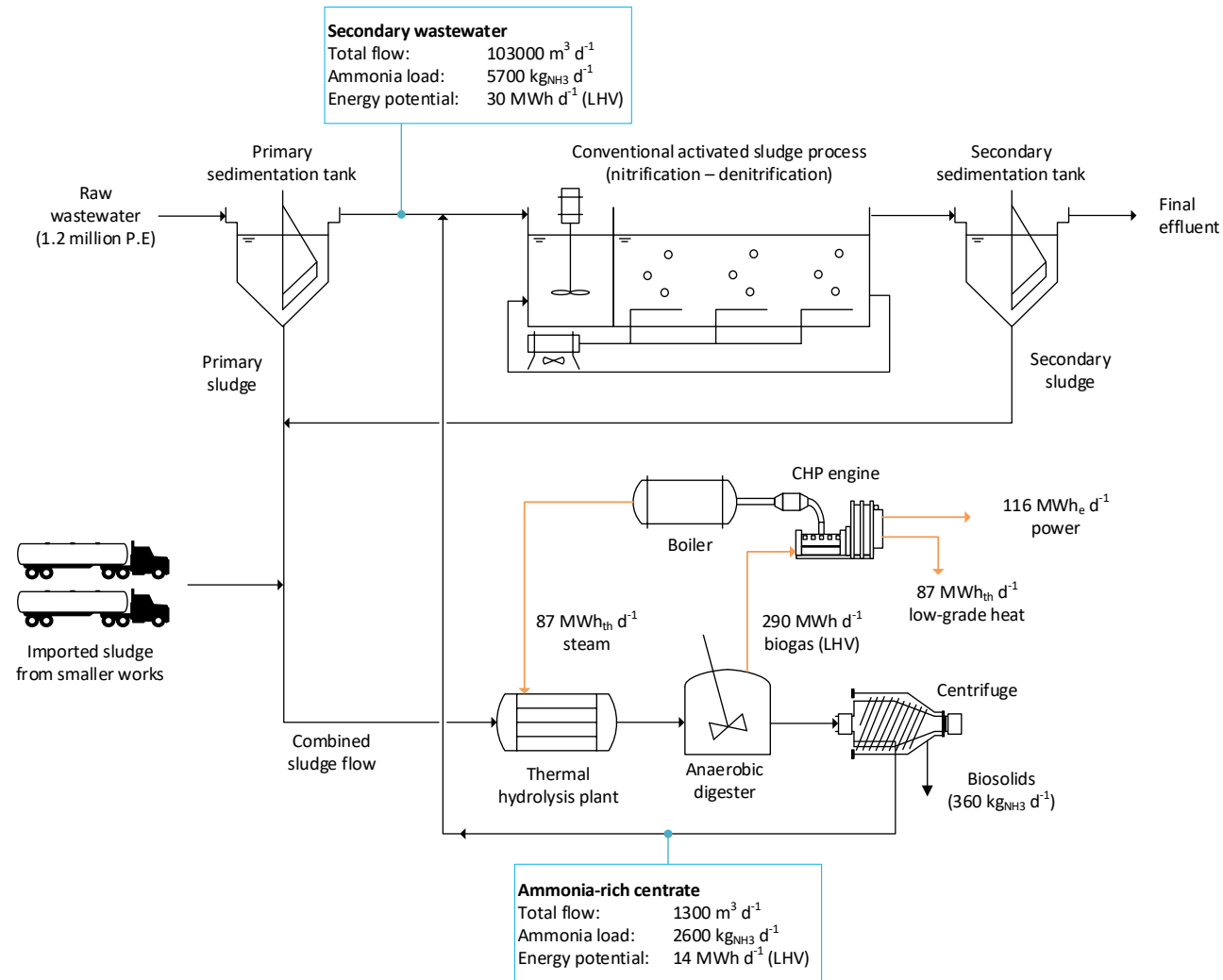


Figure 6.1: Example wastewater treatment works with 1.2 million P.E. design capacity treating domestic and industrial wastewater alongside imported sludge from smaller works in the region (Ndam, 2017).

Once gas-phase ammonia is extracted from wastewater, there are a suite of emerging pathways for its valorisation. Ammonia gas can be captured by acid scrubbing to produce an agricultural nutrient such as ammonium sulphate (Jamaludin et al., 2018; Vaneeckhaute et al., 2017). However, the business case for investment in nutrient recovery is challenged by complex regulatory barriers for the sale of products derived from waste under EU law (EC, 2008). Ammonia is a zero carbon compound with a lower heating value (5.3 kWh kg^{-1}) which is comparable to biogas (6.1 kWh kg^{-1}) (Kobayashi et al., 2019; Moore and Auty, 2013). Hence, its internal utilisation as an energy resource could simplify pathways for adoption within the water sector. Recent advancements have demonstrated the application of ammonia for heat and power generation within gas turbines and high efficiency electrochemical fuel cells (Lan and Tao, 2014; Okafor et al., 2021a). Alternatively, ammonia could undergo thermal cracking or electro-chemical oxidation to generate 'green' hydrogen, which could enable the water sector to access an expanding hydrogen market and attract incentivisation as a developmental transport fuel (Department for Transport, 2021; Jackson et al., 2015; Siddharth et al., 2018). Aqueous ammonia (3-5%wt) is also a next-generation solvent for CO_2 capture and biogas upgrading which could lower capital and operational costs compared to established amines as it has a higher absorption capacity, is less corrosive and requires less energy for regeneration (Darde et al., 2010; Jilvero et al., 2012). An expansion of biogas upgrading across the water sector will enable utilities to access financial incentivisation for the exportation of carbon neutral biomethane as a fossil fuel replacement, and is directly aligned with wider decarbonisation objectives (Angelidaki et al., 2018; Department for Business, Energy and Industrial Strategy, 2021a; Department for Transport, 2021).

The aim of this research is therefore to explore vacuum thermal stripping as an adaptive technology for ammonia recovery from wastewater, and conduct a systems level analysis to identify pathways for its application as a strategic energy resource within a sustainable, net zero water sector. Specific objectives are to:

- i) investigate selective vacuum thermal stripping for ammonia recovery in a gas-liquid contacting column for the first time, to characterise the impact of process intensification on product quality and separation energy and inform a techno-economic evaluation for implementation at commercial scales;
- ii) determine the levelised cost of ammonia production by vacuum thermal stripping, to support its evaluation against both conventional biological nitrogen removal and 'green' ammonia production;
- iii) examine the emerging technological routes for the valorisation of wastewater-derived ammonia as a zero carbon energy resource;
- iv) explore the application of wastewater-derived ammonia as a solvent to support the expansion of biogas upgrading within an innovative, circular economy flowsheet.

6.2 Selective NH₃ stripping translated to a gas-liquid contacting column

Vacuum thermal stripping of synthetic wastewater ($2 \text{ kg}_{\text{NH}_3} \text{ m}^{-3}$) was conducted within a wetted wall column at 40 to 70°C and 0.25 bar (Appendix E1-E2). The volumetric mass transfer coefficient (k_{La}) was an order of magnitude greater than vacuum stripping in batch vessels under equivalent conditions (Figure 6.2) (Guida et al., 2022; Tao et al., 2018, 2019). This was due to the enhancement in interfacial surface area within the wetted wall column (a , $\text{m}^2 \text{ m}^{-3}$), alongside the reduced boundary layer thickness and increased convection which will promote mass transfer at the gas-liquid interface (Elhajj et al., 2014; Liu et al., 2015). Consequently, k_{La} values were comparable with commercially established packed column air strippers (Guštin & Marinšek-Logar, 2011; Jiang, 2009). An inversely proportional relationship was observed between ammonia selectivity and k_{La} . Lowering the stripping temperature below the saturation point at 0.25 bar (65°C) and into the two-phase region promoted selective mass transfer for ammonia (Figure 6.2), consistent with observations at batch scale (Chapter 2) (Pátek and Klomfar, 1995). Ammonia selectivity ($J_{\text{NH}_3}/J_{\text{H}_2\text{O}}$) increased by an order of magnitude when the stripping temperature was lowered to 50°C. Since performance was consistent below 50°C ($0.3\text{-}0.4 \text{ mol}_{\text{NH}_3} \text{ mol}_{\text{H}_2\text{O}}^{-1}$), this may represent the maximum selectivity that can be achieved for the system. Whilst

this represents a substantial enhancement, greater selectivity of up to $1.0 \text{ mol}_{\text{NH}_3} \text{ mol}_{\text{H}_2\text{O}}^{-1}$ was reported during vacuum stripping in a batch vessel (Chapter 2). A higher relative fraction of water vapourisation may have been a result of translation to a continuous batch process. For example, the recirculating feed was maintained in a non-equilibrium state since it was continuously transitioning between atmospheric and vacuum conditions, and the consequent generation of flash vapours at the column entrance contributed to greater rates of water removal.

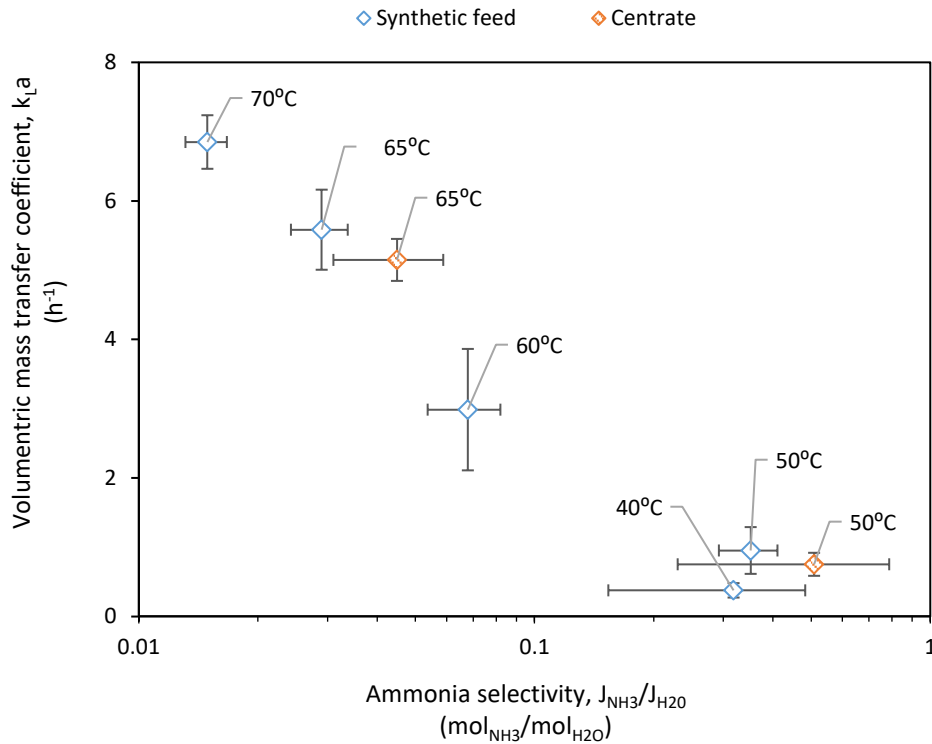


Figure 6.2: Variance of ammonia selectivity and k_{La} under stripping temperatures 40-70°C for synthetic feeds and real centrate. Operational conditions: pressure, 0.25 bar; pH >10; feed rate, 0.5 L min^{-1} .

When anaerobic digester centrate was stripped at 50 and 65°C, selectivity and k_{La} values were comparable to synthetic feeds under the same conditions (Figure 6.2). This indicates that volatile compounds and dissolved gases within centrate (e.g., siloxanes, H_2S , CH_4) did not significantly influence the relative volatilities for ammonia and water, and thus the operating position within the vapour-liquid equilibrium which underpins the separation (Centeno Mora and de Lemos Chernicharo, 2022; Davey et al., 2022). Consequently, this could support simple

translation of the process from synthetic to real wastewater feeds which is a critical requirement for commercialisation. Ammonia selectivity will determine the latent heat demand and the concentration of gas-phase ammonia generated during stripping (Figure 6.3). Since latent heat demand can account for over 90% of energy consumption, enhanced selectivity represents a critical reduction in separation energy (Davey et al., 2022). The downstream applications will determine the quality and type of recovered ammonia product (gas or liquid) that is required (Table 6.1). The design and operation of vacuum thermal stripping under different selectivity's therefore presents an opportunity to directly influence product quality (application), separation energy (operating cost), and mass transfer rate (capital cost).

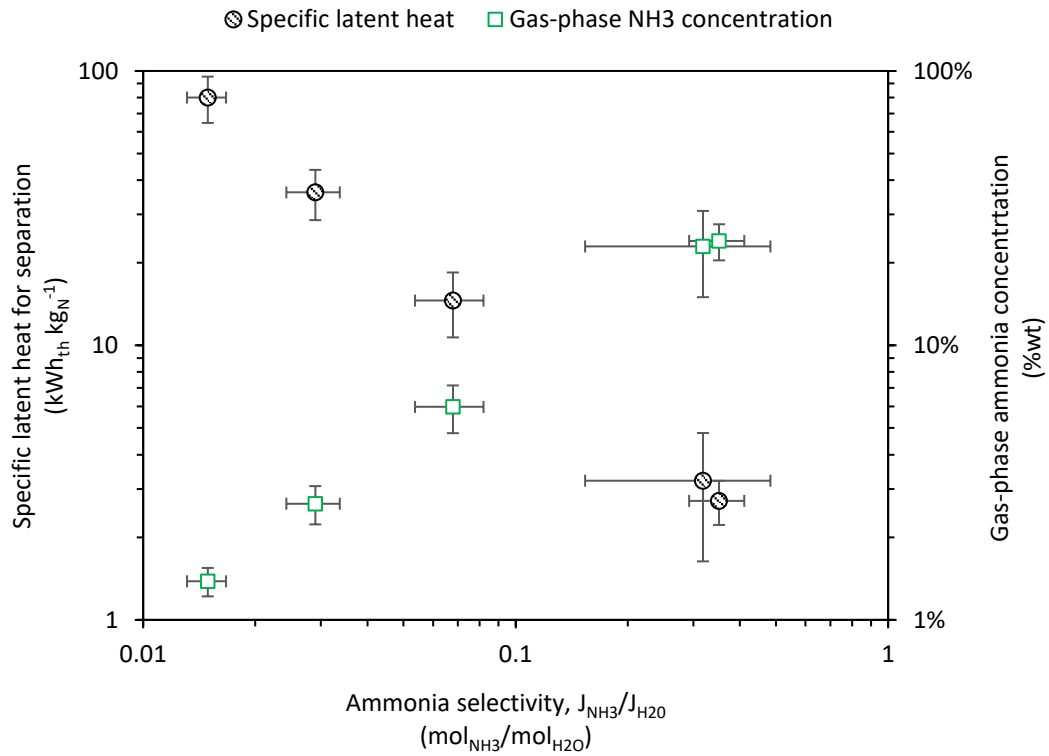


Figure 6.3: Influence of ammonia selectivity on gas-phase ammonia concentration and specific latent heat for separation for synthetic feeds. Operational conditions: pressure, 0.25 bar; pH >10; feed rate, 0.5 L min⁻¹.

Table 6.1: Ammonia to energy technology overview

Technology	Fuel state	Ammonia quality	Electrical efficiency	Heat generation
		%wt NH ₃	%LHV	%LHV
Co-fired NH ₃ -CH ₄ gas turbine	Gaseous ^b	>20% ^{a,b,d}	30-40% ^{c,d}	60-70%
Co-fired NH ₃ -CH ₄ SOFC	Gaseous ^e	>5% ^{e,f}	50-70% ^{c,g}	30-50%
Low temperature AFC	Gaseous/aqueous ^{h,i}	>0.01% ^{h,i}	50-60% ^{c,h}	-
Thermal cracking to H ₂	Gaseous ^{j,k}	5-100% ^{e,j,k}	-	-
Electro-oxidation to H ₂	Aqueous	0.01–35% ^{n,h}	-	-
Biogas upgrading / CCS	Aqueous ^q	3-5% ^{q,r}	-	-

SOFC – solid oxide fuel cell; AFC – low temperature alkaline fuel cell; CCS – carbon capture and storage.

^a (Kurata et al., 2017)

^g (Saadabadi et al., 2020)

^m (Makhloufi and Kezibri, 2021)

^b (Okafor et al., 2021a)

^h (Siddiqui and Dincer, 2019a)

^c (The Royal Society, 2020)

ⁱ (Zhang et al., 2020)

ⁿ (Diaz and Botte, 2015)

^d (Hewlett et al., 2019)

^j (Jackson et al., 2015)

^o (Vitse et al., 2005)

^e (van Linden et al., 2022)

^k (Li et al., 2017)

^p (Cooper and Botte, 2006)

^f (Dekker and Rietveld, 2006)

^l (Nasharuddin et al., 2019)

^q (McLeod et al., 2014)

^r (Darde et al., 2010)

6.3 Techno-economic evaluation for vacuum thermal stripping

Two flowsheets for ammonia stripping from anaerobic digester centrate at 0.25 bar are proposed based upon the experimental data: (i) gas-phase production (40-50°C) (Figure 6.4), and (ii) aqueous production (60-70°C) (Figure 6.5). Each flowsheet can process 1300 m³ d⁻¹ and recover 2340 kg_{NH₃} d⁻¹. This is equivalent to 90% recovery from anaerobic digester centrate for a centralised treatment works with a design capacity of 1.2 million P.E., which treats domestic and industrial wastewaters alongside imported sludge from regional facilities (Figure 6.1). Design and sizing of major equipment enabled capital costs to be estimated using the factorial method developed by Lang (1948) (Appendix E3). Gas-phase flowsheets were associated with the highest capital costs (2.4-4.0 million EUR), due to low *k_{La}* values and the requirement for multiple stripping columns positioned in parallel to deliver the requisite ammonia recovery rate (Figure 6.6a). In contrast, capital costs of 1.1-1.4 million EUR were determined for the production of aqueous ammonia where a single stripping column was required.

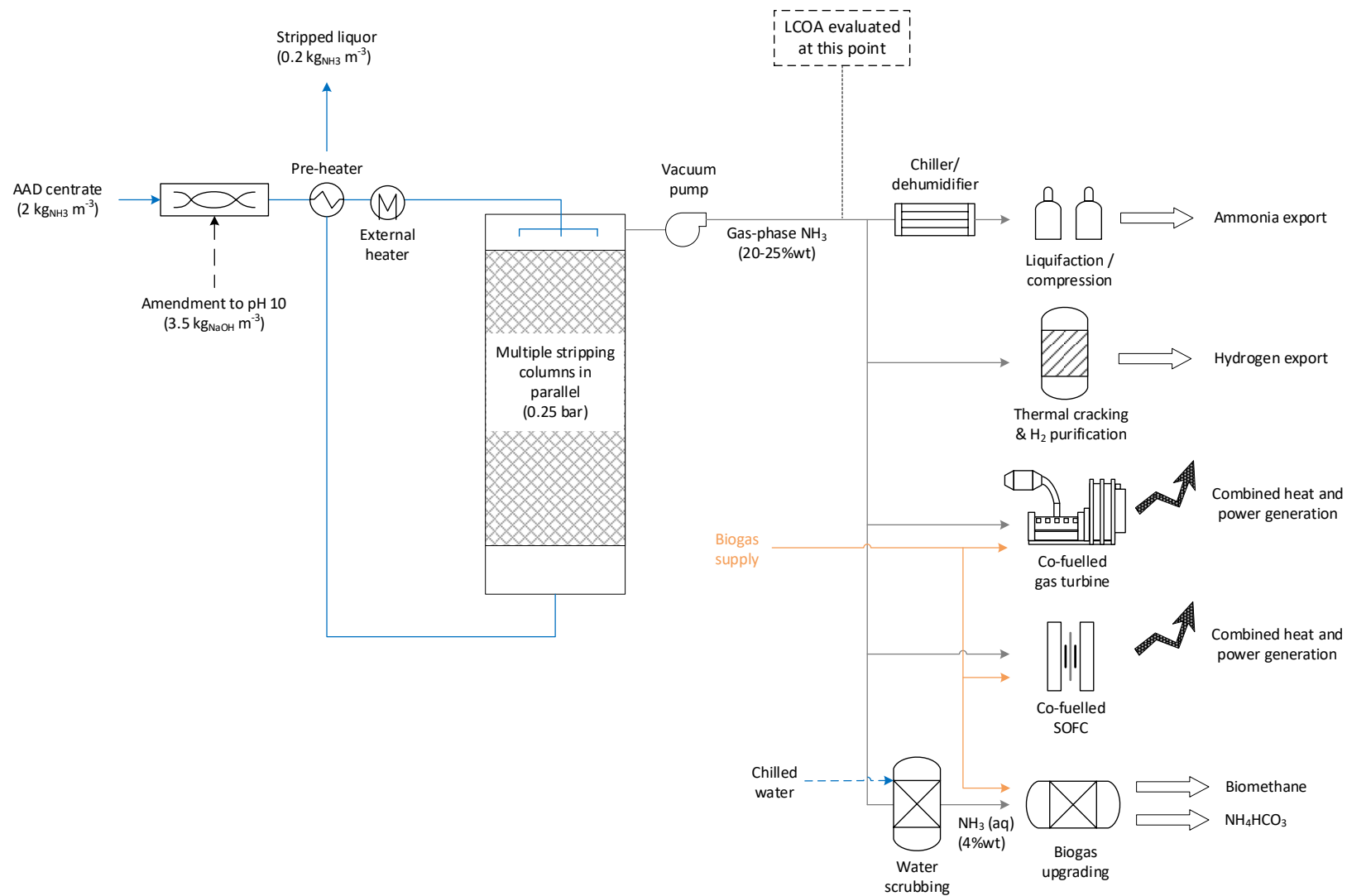


Figure 6.4: Stripping at $40\text{--}50^\circ\text{C}$ and 0.25 bar to recover a gas-phase ammonia product.

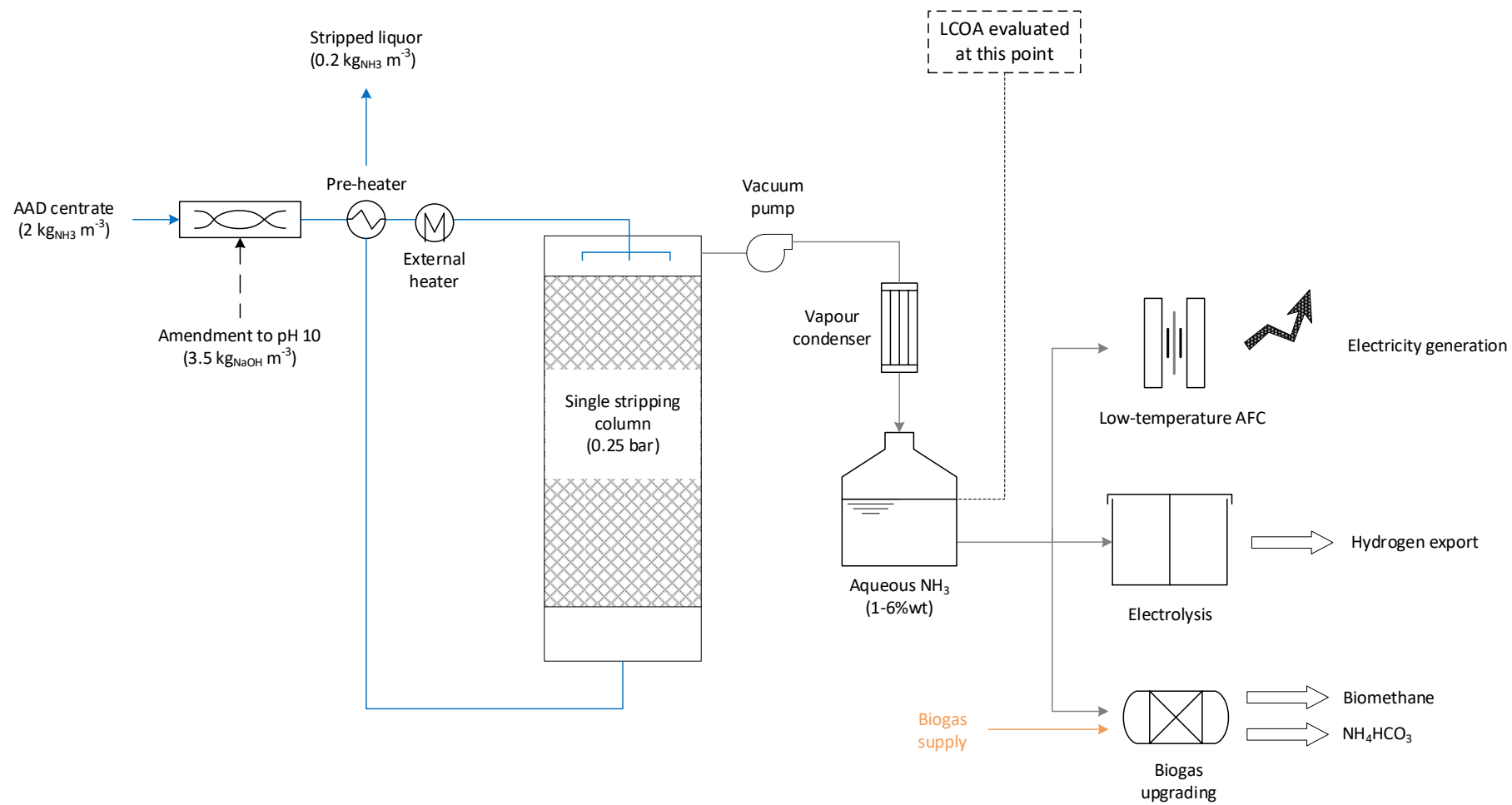


Figure 6.5: Stripping at $60\text{--}70^\circ\text{C}$ and 0.25 bar to recover an aqueous ammonia product.

Operating costs were determined on the basis of energy (thermal and electrical) and alkali consumption (Appendix E4). These could be compared directly to the cost for equivalent ammonia removal ($2340 \text{ kg}_{\text{NH}_3} \text{ d}^{-1}$) in an existing activated sludge process ($0.55 \text{ million EUR y}^{-1}$ for the example works provided). To limit external thermal input, heat recovery was maximised from the stripped liquor whilst low-grade heat (85°C) from onsite biogas engines was incorporated into each flowsheet (Figure 6.1) (Moore and Auty, 2013). Due to minimal latent heat demand for gas-phase production (Figure 6.3), external thermal input was not required. Consequently, gas-phase flowsheets were associated with the lowest energy and chemical costs ($0.54 \text{ million EUR y}^{-1}$) and were competitive with biological nitrogen removal (Figure 6.6a). Declining selectivity and increasing latent heat demand for water vapourisation led to an increase in costs from 0.85 up to $1.47 \text{ million EUR y}^{-1}$ for aqueous ammonia production at 60 and 70°C , respectively. Notably, alkali consumption was a substantial contributor to energy and chemical costs ($>37\%$) across all scenarios. Sodium hydroxide is added to raise centrate pH from 8 to 10 and release over 95% free ammonia, thereby maximising the mass transfer driving force during stripping (Appendix E2) (Bates and Pinching, 1950; Huang and Shang, 2006). Dissolved CO_2 in wastewater will readily desorb during low-volume air or vacuum stripping, and this can raise wastewater up to pH 9 - 10 and increase the free ammonia fraction (Chapter 2) (Kang et al., 2017). This phenomenon could support chemical-free stripping to lower the operating costs and improve sustainability criteria for ammonia recovery. In addition to the direct costs for energy and chemical purchase, effective carbon emissions ($\text{t}_{\text{CO}_2\text{e}}\text{y}^{-1}$) related to their production will incur costs under the market-based Emissions Trading Scheme (ETS) ($60.1 \text{ EUR t}_{\text{CO}_2\text{e}}^{-1}$ in 2023) (Ember, 2023) (Figure 6.6b; Appendix E5). Effective carbon emissions and the associated costs were also determined for an activated sludge plant treating an equivalent ammonia loading, based upon electricity usage and emission of nitrous oxide ($0.49 \text{ million EUR y}^{-1}$) (Winter et al., 2012).

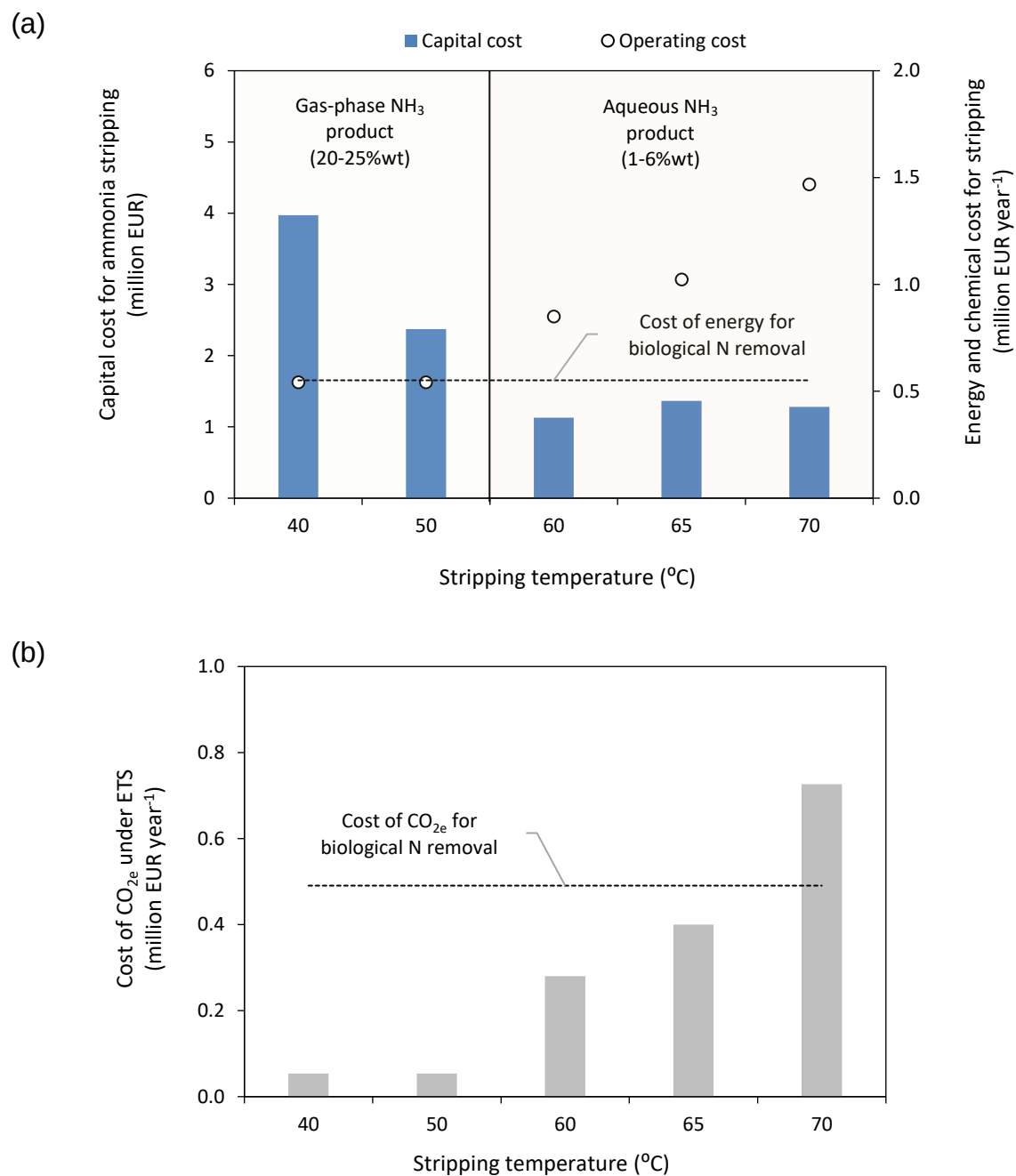


Figure 6.6: Influence of stripping temperature on (a) capital costs and energy and chemical costs, and (b) cost of CO_{2e} emissions under the Emissions Trading Scheme. Equivalent to 90% removal from centrate (2 kg_{NH3} m⁻³) from a centralised works with a design capacity of 1.2 million population equivalent (Ndam, 2017). Dotted lines indicate costs for equivalent ammonia loading in biological nitrogen removal processes. Full methodology for equipment sizing and capital and operating costs determination provided in Appendix E3-E5.

Based upon the capital and operational (energy, chemical and carbon) costs, the levelised cost of ammonia (LCOA) production by vacuum thermal stripping over a 20 year economic lifetime could be determined (Appendix E6). Since ammonia recovery from centrate will reduce loading for an existing activated sludge plant, the costs for equivalent biological nitrogen removal (energy and carbon) were offset against the operational costs for stripping. Despite higher capital costs than aqueous ammonia production, gas-phase flowsheets offer the lowest LCOA (-300 to -150 EUR $t_{NH_3}^{-1}$) due to lower operating costs (Figure 6.7). Negative LCOA values indicate that investment in ammonia recovery represents a cost-saving over the economic lifetime of the process, relative to biological nitrogen removal. Therefore, recovery of the highest quality product (20-25%wt) also presents the most attractive economic solution. A break-even point analysis indicated that investment in the recovery of gas-phase ammonia (50°C) provided a payback period of 5.3 years compared to biological nitrogen removal in an existing process (Figure E4). The LCOA for aqueous ammonia production was evaluated as 210 to 1470 EUR $t_{NH_3}^{-1}$. To provide context, typical LCOA values for ammonia production in conventional gas-fired plants range from 170 to 500 EUR $t_{NH_3}^{-1}$ (Table 6.2) (Morgan, 2013; Nutrien, 2022). Due to their reliance on natural gas and 'grey' hydrogen feedstocks, conventional plants are associated with high greenhouse gas emissions and exposed to energy price volatility (Morgan, 2013). Consequently, 'green' ammonia production is emerging based upon an electrified Haber-Bosch process using renewable energy and hydrogen sources, which is associated with a higher LCOA (420-870 EUR $t_{NH_3}^{-1}$) due to investment in local energy infrastructure (Cesaro et al., 2021; Nayak-Luke et al., 2018). Both gas and aqueous ammonia production could therefore enable the water sector to generate cost-competitive 'green' ammonia. Crucially, ammonia is recovered from wastewater in a non-pure form and so its downstream application is integral to its value. Expansive opportunities are emerging for its utilisation which could include generation of zero carbon energy to directly support the transition to net zero, or integration into a wider circular economy system as a chemical solvent to facilitate biogas upgrading and recovery of solid ammonium bicarbonate.

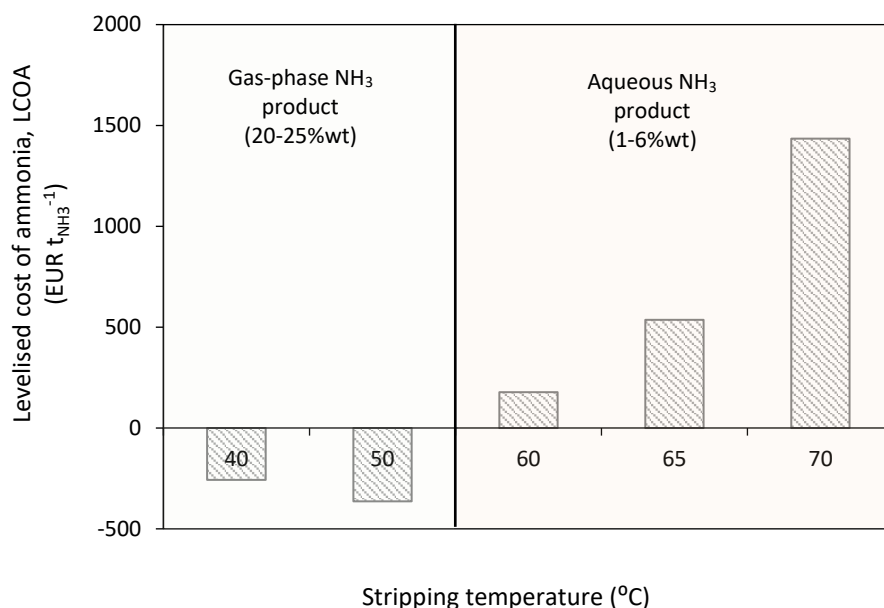


Figure 6.7: Levelised cost of ammonia recovery for a full-scale vacuum thermal stripping system which extracts 2340 kg_{NH3} d⁻¹, relative to a base case where an equivalent ammonia loading is treated in a pre-existing biological nitrogen removal process. Full methodology for LCOA determination provided in Appendix E6.

Table 6.2: Comparison of levelised cost for ammonia (LCOA) for different strategies for wastewater ammonia recovery and ammonia production plants.

Process	LCOA EUR t _{NH3} ⁻¹	Reference
Vacuum strip for gas-phase recovery	-300 to -150 ^a	This study
Vacuum strip for aqueous recovery	210 to 1470	This study
Gas fired ammonia plant	260 ^b	(Morgan, 2013)
Gas fired ammonia plant	170 to 500 ^b	(Nutrien, 2022)
Renewable electrified ammonia plant	870 ^b	(Morgan, 2013)
Renewable electrified ammonia plant	670 ^b	(Nayak-Luke et al., 2018)
Renewable electrified ammonia plant	420 to 630 ^b	(Cesaro et al., 2021)

LCOA – levelised cost of ammonia over 20 year period (Appendix E6).

^a Negative LCOA indicates that investment in ammonia stripping represents a cost saving over the economic lifetime (20 years), relative to biological nitrogen removal.

^b Costs for 2022 based on adjustments for inflation

6.4 Wastewater-derived ammonia as a zero carbon energy resource

A range of technologies are emerging which offer new pathways for the valorisation of ammonia as a zero carbon energy resource. Gas-phase ammonia (20-25%wt) could be refined through a combination of chilling or dehumidification to remove the water fraction to recover anhydrous ammonia (Venegas et al., 2021). This could enable the water sector to access a global ammonia market which is projected to expand by at least 40% by 2050 due to its proposed use as an energy vector within hydrogen economies (International Energy Agency, 2021; Mission Possible Partnership, 2022). In the proposed system where 2340 kg_{NH₃} d⁻¹ is recovered, the sale of anhydrous ammonia represents a potential revenue opportunity of 0.64 million EUR y⁻¹ (Table 6.3). However, the sale of wastewater-derived ammonia is subject to complex regulation under EU law which could deter investment in practice (EC, 2008). Instead, the utilisation of ammonia as an onsite energy resource could directly support decarbonisation objectives (Water Europe, 2021; Water UK, 2020). In the example treatment works, biogas turbines are employed for combined heat and power generation (Figure 6.1). To realise ammonia to energy with minimal investment, biogas turbines could be modified to enable the injection of concentrated gas-phase ammonia (20-25wt%) (Figure 6.4) (Hewlett et al., 2019; Okafor et al., 2021a). Combustion of 2340 kg_{NH₃} d⁻¹ could enhance the electrical output of gas turbines by 1810 MWh_e y⁻¹, consequently lowering costs related to the importation of electricity by 0.08 million EUR y⁻¹. The presence of ammonia can also suppress the formation of soot and contribute to the reduction of NO_x during hydrocarbon combustion, in addition to lowering the specific carbon emissions associated with energy generation (kg_{CO_{2e}} kWh⁻¹) (Montgomery et al., 2021; Okafor et al., 2021b). Co-firing methane and ammonia has been demonstrated in a 2 MW commercial gas turbine and can achieve comparable electrical efficiencies to biogas turbines (30-40% LHV) (Hewlett et al., 2019; Uchida et al., 2019). Whilst 2 MW is 'demonstration-scale' in the context of industrial power plants, it is of comparable size to engines employed widely across wastewater treatment (Moore and Auty, 2013). Therefore, early adoption of co-fired gas turbines could present an

opportunity for the water sector to play a critical role in the translation and scale up of these systems.

Due the maturity of biogas engines, remuneration schemes such as Renewables Obligation Certificates which were central to driving their market expansion are in decline and closed to new applicants (Connor et al., 2015; Houlker, 2019). Solid oxide fuel cells (SOFC), which are not restricted by the Carnot limit and can achieve high electrical efficiencies (60-70% LHV) whilst producing high-grade heat, have been proposed as a successor technology to enable greater economies for onsite biogas utilisation (Saadabadi et al., 2019; Trendewicz and Braun, 2013). As with gas turbines, SOFC can be co-fired with ammonia (<5%wt) (Grasham et al., 2019; van Linden et al., 2022), and so a gas-phase recovery strategy could support a future transition towards SOFC for combined heat and power generation. Recovered ammonia could generate 3170 MWh_e y⁻¹ in SOFC and lower the cost related to energy importation by 0.14 million EUR y⁻¹. The central challenge for the implementation of SOFC is their vulnerability to fatal degradation by trace amounts of hydrogen sulphide (>1 mg m⁻³) and siloxanes (>2 mg m⁻³) (Papadias and Ahmed, 2012; Sasaki et al., 2011). These compounds are present in biogas and may also be present in recovered gas-phase ammonia (Davey et al., 2022; McBean, 2008). Associated infrastructure for trace contaminant removal (e.g., cryogenic, adsorption, gas scrubbing) would therefore be necessary to maximise cell lifetime (Bauer et al., 2013; McBean, 2008). Whilst power generation is also possible using aqueous ammonia in low temperature alkaline fuel cells (AFC) (Figure 6.5), these suffer from critically low power densities relative to SOFC (1-3 orders of magnitude) (Guo et al., 2020; Siddiqui and Dincer, 2019b). This is exacerbated by the presence of dissolved compounds (e.g., VOCs) co-transported during wastewater stripping, which lower the pH and limit free ammonia at the anode (Davey et al., 2022). Consequently, AFC will require larger cell stacks to generate equivalent power output and high capital costs which could present a significant barrier to investment.

The UK and EU have set progressive targets for low-carbon hydrogen production which are expected to deliver 13-35% of their total energy demand by

2050 (Department for Business, Energy and Industrial Strategy, 2021b; European Commission, 2020). Zero carbon hydrogen generation from recovered gas-phase or aqueous ammonia could align with existing investment in hydrogen production by the water sector and invite incentives under the Renewable Transport Fuel Obligation (RTFO) (Figure 6.4-6.5) (Anglian Water, 2021; Jackson et al., 2015; Vitse et al., 2005). Catalytic cracking of gas-phase ammonia is closest to commercialisation, with demonstration projects for the generation of 200 kg d⁻¹ transport-grade hydrogen currently underway to evaluate viability at scale (Siemens Energy, 2022; The Royal Society, 2020; Tyseley Energy Park, 2022). Complete conversion of recovered ammonia could represent an opportunity to generate a 'green' hydrogen resource of up to 4530 MWh y⁻¹. Hydrogen is classified as a developmental transport fuel and invites the highest tier of incentivisation under the RTFO. Hydrogen export therefore represents a revenue opportunity of up to 0.29 million EUR y⁻¹ (Table 6.3) (Department for Transport, 2021). However, cracking can be energy intensive (33-42 kWh kg⁻¹H₂), due to downstream purification for the removal of nitrogen and trace amounts of unreacted ammonia to comply with stringent quality standards for transport-grade hydrogen (<0.1 mg_{NH₃} m⁻³) (EN 17124:2018) (European Standards, 2018; Makhoulfi and Kezibri, 2021; Nasharuddin et al., 2019). Electrolysis of aqueous ammonia could theoretically generate high-purity hydrogen at a substantially lower energy demand (1.55 kWh kg_{H₂}) (Vitse et al., 2005). However, this process is kinetically limited and so additional energy input is necessary in practice to drive ammonia oxidation, whilst poisoning and deactivation of high-activity catalysts presents a major technological hurdle (Cheddie, 2012; Siddharth et al., 2018). Further development and commercialisation is therefore necessary to facilitate energy efficient and economically viable ammonia to hydrogen solutions for the water sector.

Table 6.3: Direct value pathways for wastewater-derived ammonia, based upon the recovery of 2340 kg_{NH3} d⁻¹.

Process	Key product	Quantity	Valourisation route	Unit cost	CO ₂ offset ^a t _{CO2e} y ⁻¹	Total value million EUR y ⁻¹
Purification	Anhydrous NH ₃	855 t y ⁻¹	External sale ^d	750 EUR t ⁻¹	-	0.64
Catalytic cracking	H ₂	4530 MWh y ⁻¹	Export as developmental transport fuel (RTFO) ^e	65 EUR MWh ⁻¹	-	0.29
Solid oxide fuel cell ^b	Electricity	3170 MWh _e y ⁻¹	Onsite utilisation (offset electricity import) ^f	29 EUR MWh _e ⁻¹	740	0.14
Gas turbine ^c	Electricity	1810 MWh _e y ⁻¹			420	0.08

RTFO – Renewable transport fuel obligation.

^a Valued at 60 EUR t_{CO2e}⁻¹ under the Emissions Trading Scheme in 2023 (Ember, 2023)

^b Assumed 70% electrical efficiency (The Royal Society, 2020)

^c Assumed 40% electrical efficiency (Hewlett et al., 2019; Moore and Auty, 2013)

^d For sale into European market (ChemAnalyst, 2023)

^e Hydrogen gas receives 2.29 dRTFC kg⁻¹, with each dRTFC valued at 0.8 GBP (Department for Transport, 2021)

^f Based on UK electricity prices for 2022 (Department for Business, Energy and Industrial Strategy, 2022a)

Table 6.4: Indirect value pathways for wastewater-derived ammonia use as a solvent for biogas upgrading, based upon the recovery of 2340 kg_{NH3} d⁻¹.

Process	Key products	Quantity	Valourisation route	Unit cost	Total value million EUR y ⁻¹
Biogas upgrading with ammonia solvents	Biomethane	18700 MWh y ⁻¹	Export to gas grid (GGSS) ^a	64 EUR MWh ⁻¹	1.20
	NH ₄ HCO ₃	3540 t y ⁻¹	External sale	112 EUR t ⁻¹	0.40
NH ₄ HCO ₃ degradation and purification	Anhydrous NH ₃	855 t y ⁻¹	External sale	750 EUR t ⁻¹	0.64
	Biogenic CO ₂	1970 t y ⁻¹	External sale (RPS 255) ^b	315 EUR t ⁻¹	0.62

^a Biomethane attracts a Tier 1 tariff below 60000 MWh y⁻¹ under GGSS (Department for Energy Security and Net Zero, 2022).

^b (Environment Agency, 2022)

6.5 Wastewater-derived ammonia as a solvent for biogas upgrading

Biomethane is a central component of carbon management plans for the water sector, but established biogas upgrading systems are capital intensive which has limited their adoption to large, centralised treatment works where they can benefit from economies of scale (IEA Bioenergy, 2019). To support wider decarbonisation objectives, recovered ammonia could be applied as a sustainable solvent within an intensified, chilled ammonia process (CAP) for biogas upgrading. When compared to water absorption in packed columns which represent 70% of installed capacity for biogas upgrading across the European water sector (IEA Bioenergy, 2019), ammonia solvents can intensify CO₂ absorption by a factor of 5-15, thereby lowering process size and separation energy (Bauer et al., 2013; Houlker, 2019; McLeod et al., 2014). Reduced solvent flowrates and operating pressures during chemical absorption will directly lower the electrical consumption (0.1 kWh_e Nm⁻³_{biogas}) relative to water absorption (0.3 kWh_e Nm⁻³_{biogas}) (Bauer et al., 2013). Furthermore, chemical absorption processes are associated with low atmospheric methane losses (<0.1%vol) due to limited 'slip' into the solvent compared to water absorption (1-2%vol), maximising product recovery and qualifying for access to biomethane incentivisation under the German tariff system (<0.5%vol) (EEG 2009) (Kvist and Aryal, 2019; Patterson et al., 2011). Although aqueous-phase recovery could generate a suitable solvent (3-5%wt) (Figure 6.5), concentrated gas-phase recovery followed by capture and dilution using water absorption to produce the solvent is more economical due to minimisation of the latent heat penalty during stripping (Figure 6.4). Further process intensification of up to 15-times can be achieved by conducting absorption within a hollow fibre membrane contactor, in which gas and liquid-phases are segregated by a hydrophobic membrane, due to high interfacial surface area and an extended gas loading range (Figure 6.8) (Belaissaoui et al., 2016; Gabelman and Hwang, 1999). Following absorption, CAP processes require a solvent regeneration stage to reverse the chemical reaction and desorb CO₂ gas (Augustsson et al., 2017; Darde et al., 2010). This can represent a substantial energy demand, equivalent to consuming 10% of the raw biogas (based on LHV) and is associated with solvent losses due to the high

volatility of ammonia (Jilvero et al., 2012; Moore and Auty, 2013). However, the costs associated with regeneration (capital, energy and maintenance) and the purchase of chemicals could be avoided when using wastewater ammonia, since a continuous supply of sustainable solvent can be recovered. This could offset the cost of ammonia stripping and improve the investment case for a sidestream recovery process, particularly when compared to a baseline of biological nitrogen removal (Figure 6.6a). As an alternative to regeneration, the solvent could be loaded with CO₂ until the thermodynamic threshold for ammonium bicarbonate formation and precipitation is exceeded (Sutter et al., 2017). Crystallisation would then be promoted by the hydrophobic membrane, which lowers the energy barrier for heterogeneous nucleation, and can facilitate continuous harvesting of solids from the solvent loop (Figure 6.8) (Houlker, 2019; McLeod et al., 2015). This integrated system would therefore produce biomethane, which attracts incentives for injection into the gas network, alongside ammonium bicarbonate (Department for Business, Energy and Industrial Strategy, 2022b; Department for Transport, 2021).

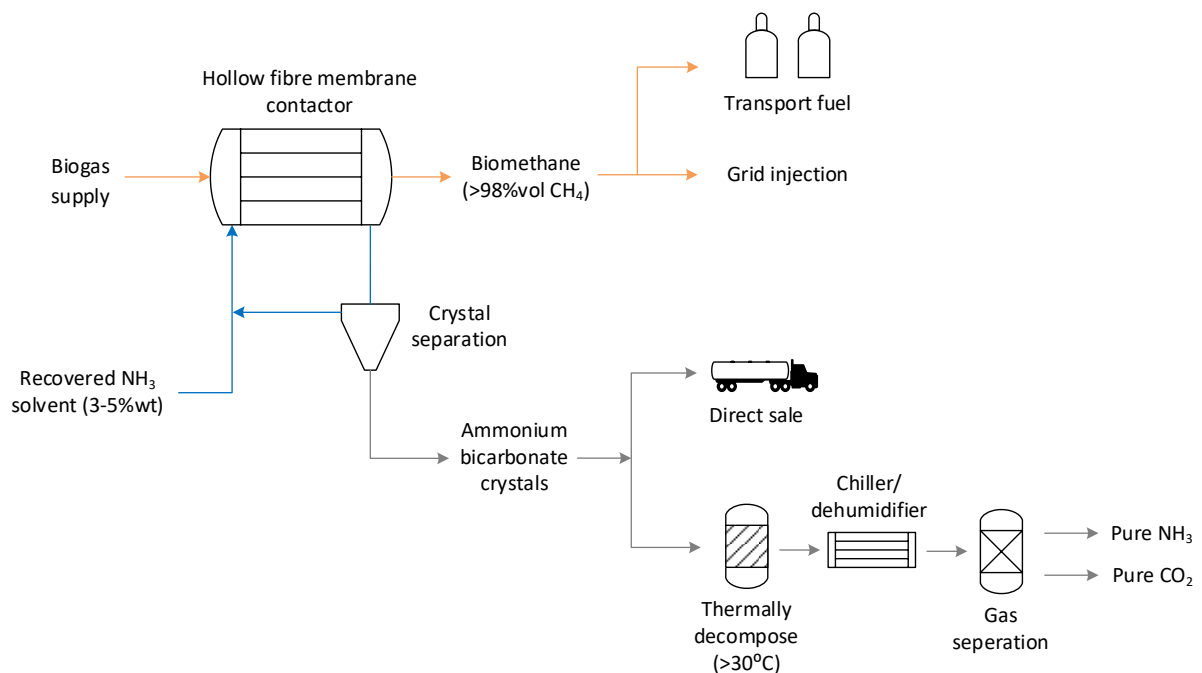


Figure 6.8: Biogas upgrading and ammonium bicarbonate recovery using wastewater-derived ammonia solvents.

In the example treatment works, the recovery of $2340 \text{ kg}_{\text{NH}_3} \text{ d}^{-1}$ could generate enough solvent to upgrade 20% of the biogas resource and produce 18700 MWh y^{-1} biomethane (Table 6.4). Below a threshold of 60000 MWh y^{-1} , biomethane injection into the gas grid qualifies for Tier 1 tariffs (64 EUR MWh^{-1}) under the Green Gas Support Scheme (GGSS), and so this presents a revenue opportunity of 1.2 million EUR y^{-1} (Department for Energy Security and Net Zero, 2022). The application of ammonia for biogas upgrading could therefore unlock greater value than direct utilisation pathways (Table 6.3). Crystallisation of ammonium bicarbonate will omit dissolved contaminants and competing cations within wastewater-derived solvents, thereby generating a high purity product (Bavarella et al., 2020). This could have direct application as a fertiliser (112 EUR t^{-1}) and offer additional revenue of up to 0.40 million EUR y^{-1} , although a market outlet is not guaranteed under existing EU regulations (EC, 2008; McLeod et al., 2014). Ammonium bicarbonate is thermally unstable, and will decompose under mild heat ($>30^\circ\text{C}$) to release CO_2 , ammonia and water vapour (Figure 6.8) (Villeneuve et al., 2018). Chilling or dehumidification to remove the water fraction, followed by gas separation could generate high purity CO_2 and ammonia gas. This could enable the water sector to access an emerging opportunity for the sale of industrial-grade biogenic CO_2 which has been introduced following release of a regulatory positioning statement enabling the possible use of CO_2 from anaerobic digestion (RPS 255), in response to recent disruption in industrial supply chains (Environment Agency, 2022). The sale of CO_2 presents a revenue opportunity of 0.62 million EUR y^{-1} for the example works. Furthermore, the purified ammonia gas provides a flexible and energy dense product for internal use or direct sale. This pathway therefore provides an opportunity for ammonia to be utilised as a sustainable biogas upgrading solvent and then subsequently for zero carbon energy generation, to support an expansion of biomethane production whilst maximising the internal value of this resource.

6.6 Conclusion

This study has explored selective vacuum thermal stripping for ammonia recovery from wastewater and evaluated emerging pathways for the utilisation of

recovered ammonia as a critical resource to support decarbonisation within the water sector. Selective ammonia stripping was demonstrated below the saturation point for digester centrate (40-50°C at 0.25 bar) to facilitate low energy, high quality gas-phase product recovery (20-25%wt). In a critical technological advancement, this process was translated from batch vessels employed in previous work to a gas-liquid contacting column for the first time. Increased interfacial surface area ($\text{m}^2 \text{ m}^{-3}$), reduced boundary layer thickness and greater convection within the column intensified mass transfer by an order of magnitude. Consequently, the system demonstrated comparable volumetric mass transfer coefficients to established air stripping processes ($0.4\text{-}6.8 \text{ h}^{-1}$), indicating potential for scalability and future commercial adoption. Full-scale projections for a centralised wastewater treatment works (1.2 million P.E.) indicated that investment in selective ammonia recovery from digester centrate could offer a cost saving ($\sim 300 \text{ EUR t}_{\text{NH}_3}^{-1}$) over a 20-year economic lifetime, relative to biological nitrogen removal in existing activated sludge processes. High purity ammonia derived from wastewater is a flexible resource which could be exported into an expanding ammonia marketplace or utilised for zero carbon energy and hydrogen generation. However, a systems level evaluation determined that maximum value could be generated from its application as a novel solvent for the intensification of biogas upgrading. This could enable utilities to capitalise on incentives for the exportation of biomethane and emerging opportunities for the sale of biogenic CO_2 , whilst recovering purified ammonia for further application as a zero carbon resource. This circular economy solution presents a holistic strategy which creates innovative value opportunities and is aligned with the transition towards low energy, net zero wastewater treatment.

Acknowledgements

We are grateful for the financial and technical support offered by Anglian Water, Northumbrian Water and Severn Trent Water. We also acknowledge the funding and training resources provided to Benjamin Luqmani from the Engineering and Physical Sciences Research Council through the STREAM Industrial Doctorate Centre.

Appendix E

E1 Vacuum thermal stripping experimental set-up

Vacuum thermal stripping experiments were conducted in a wetted wall column operated in semi-batch mode with a recirculating liquid feed (Figure E1). The column had an internal diameter of 0.05 m and a length of 0.45 m. A spray nozzle distributed the feed over the walls (MPL 0.57N, Bete Ltd., Lewes, England). In each experiment, 4 L of synthetic wastewater or centrate was placed in the feed vessel. The feed was heated up to the target temperature (40-70°C) via a heating coil in the feed vessel and recirculation through a heat exchanger (MPC-K6, Huber, Offenburg, Germany; Quickfit C6/12/SC, Fisher Scientific, Loughborough, UK; AD550, Xylem, New York, USA). The liquid flowrate was set at 0.5 L min⁻¹ using a flow control valve and variable-area flowmeter (Double acting inline control valve, F.lli Tognella Spa, Rome, Italy; MFLX32461-42, Masterflex, Avantor, Radnor, USA). The feed was then recirculated through the stripping column for 10-15 minutes until stable temperatures were achieved at the inlet and outlet. The system pressure was then reduced using two vacuum pumps operating in parallel and controlled at 0.25 bar using a vacuum control valve (ME-1C, Vacuubrand, Wertheim, Germany; SS-4MA-MH, Swagelok, Kings Langley, UK). Stripping temperature and pressure were monitored continuously across the system (Type K, RS Components, Corby, UK; PXM319-010GI, Omega Engineering Ltd, Manchester, UK). Vacuum outlets were located at the top of the column, the base of the column and the outlet vessel to extract ammonia-rich vapours. The vapours were drawn through gas-liquid separators to remove entrained droplets of liquid. The vapours were then passed through a condenser with 250 cm² surface area at 5°C (Quickfit C6/12/SC, Fisher Scientific, Loughborough, UK; LT Ecocool 150, Grant Instruments, Cambridge, UK). Condensate was stored in a chilled, jacketed vessel at 5°C. Finally, the vapour was bubbled through dilute sulphuric acid (0.5 mol L⁻¹) in a gas-tight aspirator bottle to absorb gas-phase ammonia (Schott Duran, VWR, The Netherlands). Each primary data point was collected in triplicate. Standard deviation is represented by error bars.

E2 Experimental analysis

Ammonia mass transfer across the gas-liquid interface is described by the Lewis-Whitman model (Eq. E1) (Heile et al., 2017; Tao and Ukwuani, 2015). Previous research indicates that the equilibrium ammonia concentration (C_{NH3}^*) tends towards zero during thermal stripping (Tao and Ukwuani, 2015; Ukwuani and Tao, 2016). Integration of the Lewis-Whitman model from time = 0 to time = t provides a straight line function in which the gradient represents the volumetric mass transfer coefficient ($k_L a$) (Eq. E2).

$$\frac{dC_{NH3}}{dt} = k_L a (\Phi C_{NH3} - C_{NH3}^*) \quad (\text{Eq. E1})$$

$$-\ln\left(\frac{C_{NH3,t}}{C_{NH3,0}}\right) = k_L a t \quad (\text{Eq. E2})$$

where dC_{NH3}/dt is the rate of ammonia transfer across the gas-liquid interface ($\text{g L}^{-1} \text{h}^{-1}$); $k_L a$ is the volumetric mass transfer coefficient for ammonia (h^{-1}); a is the specific interfacial surface area ($\text{m}^2 \text{m}^{-3}$); Φ is the free ammonia fraction (-); C_{NH3} is the total ammonia concentration (g L^{-1}); t is stripping time (h) and subscripts 0 and t represent time = 0 and time = t respectively. In continuous batch mode, only a fraction of the total feed volume is exposed to vacuum conditions at any time. To determine $k_L a$, time was substituted for hydraulic residence time (HRT) in Eq. E2. The vacuum stripper and outlet vessel were estimated to hold 0.5 L of feed during operation, enabling the HRT to be calculated:

$$HRT = \frac{v}{V_t} * t \quad (\text{Eq. E3})$$

where v is the feed volume exposed to the vacuum condition (0.5 L) and V_t is the total feed volume at time = t (L). Ammonia concentration in the feed, condensate and acid trap, and the condensate mass were recorded over time. The fraction of ammonia and water vapourised from the feed and ammonia fraction in the stripped vapour were then calculated:

$$\eta_{NH3} = \frac{m_{NH3,0} - m_{NH3,t}}{m_{NH3,0}} \quad (\text{Eq. E4})$$

$$\eta_{H2O} = \frac{m_{H2O,0} - m_{H2O,t}}{m_{H2O,0}} \quad (\text{Eq. E5})$$

$$x_{NH3} = \frac{(m_{NH3,0} - m_{NH3,t})}{(m_{H2O,0} - m_{H2O,t}) + (m_{NH3,0} - m_{NH3,t})} \quad (\text{Eq. E6})$$

where η_{NH3} and η_{H2O} represent the fraction of ammonia and water vapourised from the feed respectively (%wt); m_{NH3} and m_{H2O} is the mass of ammonia and water in the feed (g); x_{NH3} is the ammonia fraction within the stripped vapour (%wt). Ammonia will partially dissociate in wastewater to form non-volatile ammonium (Eq. E7). The fraction of free ammonia in the feed was estimated from the pH and temperature (Eq. E8-E9) (Bates and Pinching, 1950).



$$\Phi = \frac{1}{1 + 10^{(pK_{a,T}^s - pH)}} \quad (\text{Eq. E8})$$

$$pK_{a,T}^s = pK_{a,25C}^s + 0.0324(25 - T) \quad (\text{Eq. E9})$$

where Φ is the fraction of free ammonia (-); $pK_{a,T}^s$ and $pK_{a,25C}^s$ are the negative logarithm of the acid dissociation constant at temperatures T and 25°C respectively [-].

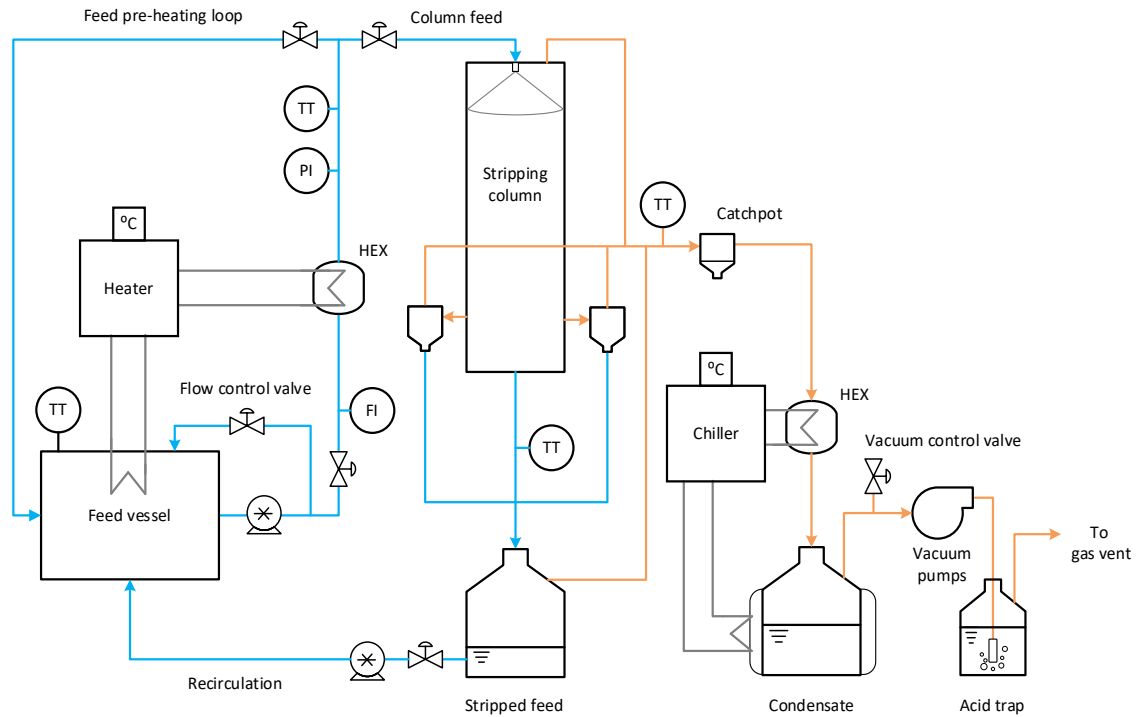


Figure E1: Experimental set-up for semi-batch vacuum thermal ammonia stripping column.

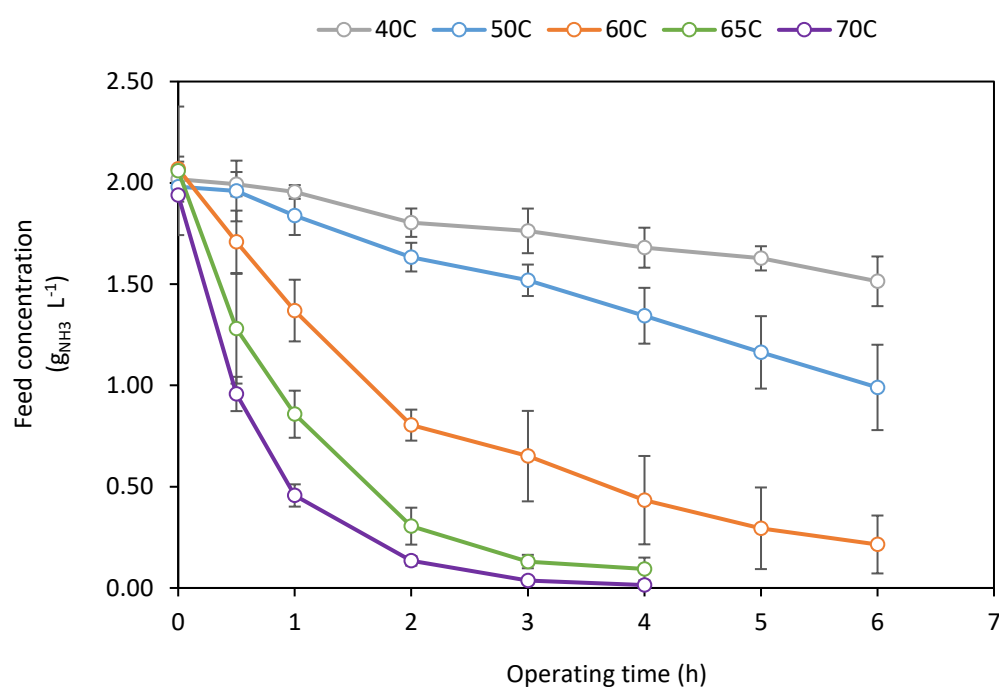


Figure E2: Influence of temperature on ammonia removal over time in vacuum thermal stripping column. Operational conditions: pressure, 0.25 bar; pH >10; feed rate, 0.5 L min⁻¹.

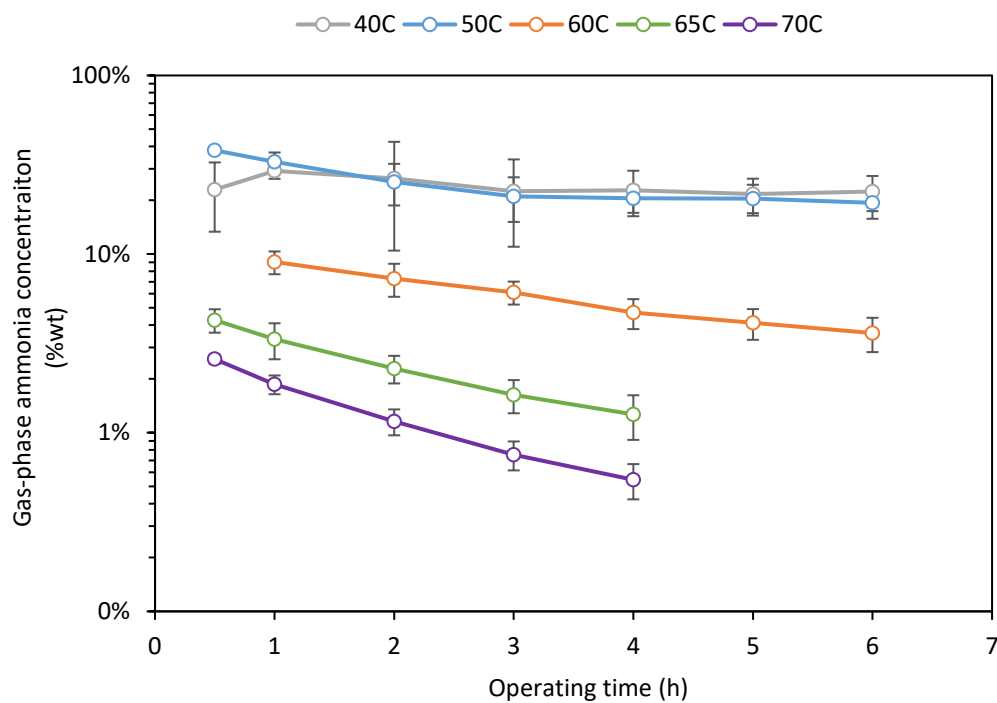


Figure E3: Influence of temperature on gas-phase ammonia concentration in vacuum thermal stripping column. Operational conditions: pressure, 0.25 bar; pH >10; feed rate, 0.5 L min⁻¹.

E3 Capital cost estimation

The costs for mechanical equipment related to vacuum thermal stripping processes for gas-phase or aqueous ammonia recovery (Figure 6.4-6.5) were estimated using the factorial method developed by Lang (1948):

$$C_m = f_L C_e \quad (\text{Eq. E10})$$

where C_e is the estimated mechanical costs for major capital equipment (EUR); f_L is the Lang factor for a fluids processing plant (4.7); and C_m is the total mechanical cost (EUR). Allowances for associated civils (C_c) and instrumentation, control and automation (C_{ICA}) were estimated as 30% and 10% of the total mechanical cost (EUR), respectively. This enabled estimation of the total capital costs (C_t) as:

$$C_t = C_m + C_c + C_{ICA} \quad (\text{Eq. E11})$$

For the feed-side, major capital equipment for both flowsheets consisted of a pre-heater to recover sensible heat from the stripped liquor, and a secondary heater raise the feed to the stripping temperature. Determination of the heating duties enabled calculation of the heat transfer area (Eq. E12-E14). The pre-heater had a 5°C approach temperature ($T_{h,out} - T_{f,in} = 5^\circ\text{C}$). Both pre-heater and secondary heater were countercurrent shell and tube heat exchangers comprised of carbon steel. Based on the design data, heat exchanger costs could be estimated based on aggregated costing data (Table E1) (Sinnot, 2004). All equipment costs were inflation adjusted up to 2022 (Bank of England, 2023).

$$Q = m'_c C_p (\Delta T_f) \quad (\text{Eq. E12})$$

$$\theta_{LM,h} = \frac{(T_{h,in} - T_{f,out}) - (T_{h,out} - T_{f,in})}{\ln \frac{(T_{h,in} - T_{f,out})}{(T_{h,out} - T_{f,in})}} \quad (\text{Eq. E13})$$

$$A = \frac{Q}{U \theta_{LM}} \quad (\text{Eq. E14})$$

where Q is the duty (kJ s^{-1}); m'_c is the centrate mass flow (15 kg s^{-1}); C_p is the specific heat capacity for centrate (assumed to be equivalent to water, $4.2 \text{ kJ mol}^{-1} \text{ }^\circ\text{C}^{-1}$); ΔT_f is the change in centrate temperature across the heater ($^\circ\text{C}$); T_h is the heating water temperature ($T_{h,in}$ = stripper temperature for pre-heater; $T_{h,in} = 85^\circ\text{C}$

for the secondary heater); $\theta_{LM,h}$ is the log mean temperature difference across the heater (°C); and subscripts *in* and *out* refer to the inlet and outlet of the heater, respectively.

Wetted wall stripping columns were designed on the basis of the experimental k_{La} data (Figure 6.2) and sized to provide the requisite flux to achieve an ammonia removal rate of $2340 \text{ kg}_{\text{NH}_3} \text{ d}^{-1}$ (equivalent to 90% recovery from AAD centrate for a centralised works serving 1.2 million population equivalent; Ndam, 2017). The maximum diameter and height for each column was set at 2 m and 15 m, respectively. The target mass transfer rate could be satisfied within individual columns at 60-70°C, whilst multiple columns were required in parallel when stripping at 40 and 50°C, respectively. Columns were costed as vertical pressure vessels, comprised of stainless steel to provide necessary chemical resistance due to direct contact with corrosive ammonia vapours (Table E1) (Sinnot, 2004). Aqueous ammonia recovery flowsheets also required a condenser. The condenser was designed to be countercurrent and isothermal. Heat exchange duty was calculated using the mass flow of water vapour and the latent heat of vapourisation (Eq. E15-E16). It was assumed that the condenser could utilise treated wastewater as the cooling fluid, with mean temperature of 15°C ($T_{c,in}$), enabling calculation of the log-mean temperature across the condenser ($\theta_{LM,c}$). Condenser mass transfer area could then be calculated. This was applied to determine cost, based upon a shell and tube heat exchanger with stainless steel tubes to provide chemical resistance for corrosive ammonia vapours (Table E1) (Sinnot, 2004).

$$Q = m'_v \Delta H_v \quad (\text{Eq. E15})$$

$$\theta_{LM,c} = \frac{(T_{v,in} - T_{c,out}) - (T_{v,out} - T_{c,in})}{\ln \frac{(T_{v,in} - T_{c,out})}{(T_{v,out} - T_{c,in})}} \quad (\text{Eq. E16})$$

where m'_v is the mass flow of water vapour from the stripper (kg s^{-1}); T_v is the vapour temperature (equal to stripping temperature: 60, 65, or 70°C); T_c is the cooling water temperature (°C); and ΔH_v is the latent heat of water vapourisation (assumed to be constant at 2345 kJ kg^{-1}).

Table E1: Capital costing estimation for vacuum stripping systems designed to recover 2340 kg_{NH3} d⁻¹ and operated at 40 to 70°C.

Major equipment	Characteristic size	Qty	Materials	Pressure	Cost ^a (EUR)
Gas-phase recovery (40°C)					
Feed pre-heater	HTA = 110 m ²	1	CS	1-10 bar	37,363
Feed top-up heater	HTA = 6 m ²	1	CS	1-10 bar	5,604
Stripping column	d = 2.0 m; h = 14 m	3	SS	<1 bar	560,439
Estimated mechanical cost (Lang factor = 4.7) ^b					2,836,008
Estimated capital cost (including civils and ICA) ^c					3,970,411
Gas-phase recovery (50°C)					
Feed pre-heater	HTA = 215 m ²	1	CS	1-10 bar	56,044
Feed top-up heater	HTA = 8 m ²	1	CS	1-10 bar	5,604
Stripping column	d = 1.5 m; h = 14 m	2	SS	<1 bar	298,901
Estimated mechanical cost (Lang factor = 4.7) ^b					1,694,581
Estimated capital cost (including civils and ICA) ^c					2,372,413
Aqueous recovery (60°C)					
Feed pre-heater	HTA = 300 m ²	1	CS	1-10 bar	74,725
Feed top-up heater	HTA = 15 m ²	1	CS	1-10 bar	7,473
Stripping column	d = 1.5 m; h = 9 m	1	SS	<1 bar	74,725
Condenser	HTA = 20 m ²	1	CS-SS	1-10 bar	14,719
Estimated mechanical cost (Lang factor = 4.7) ^b					806,715
Estimated capital cost (including civils and ICA) ^c					1,129,401
Aqueous recovery (65°C)					
Feed pre-heater	HTA = 300 m ²	1	CS	1-10 bar	74,725
Feed top-up heater	HTA = 20 m ²	1	CS	1-10 bar	13,077
Stripping column	d = 1.0 m; h = 11 m	1	SS	<1 bar	63,516
Condenser	HTA = 45 m ²	1	CS-SS	1-10 bar	56,044
Estimated mechanical cost (Lang factor = 4.7) ^b					974,603
Estimated capital cost (including civils and ICA) ^c					1,364,445
Aqueous recovery (70°C)					
Feed pre-heater	HTA = 300 m ²	1	CS	1-10 bar	74,725
Feed top-up heater	HTA = 40 m ²	1	CS	1-10 bar	22,418
Stripping column	d = 1.0 m; h = 9 m	1	SS	<1 bar	52,308
Condenser	HTA = 65 m ²	1	CS-SS	1-10 bar	45,288
Estimated mechanical cost (Lang factor = 4.7) ^b					915,270
Estimated capital cost (including civils and ICA) ^c					1,281,379

HTA – heat transfer area; d - diameter; h - height; CS – carbon steel; SS – stainless steel; ICA – instrumentation, control and automation.

^a Design data was applied to determine equipment costs from aggregated costing data (Sinnot, 2004). All costs adjusted for inflation up to 2022 and converted to EUR based on 2022 exchange rate (Bank of England, 2023; European Central Bank, 2023)

^b Major equipment costs multiplied by Lang factor for a fluid handling plant (Lang, 1948)

^c Includes allowance for cost of civils and ICA as an additional 30% and 10% of total mechanical cost, respectively.

E4 Energy and chemical cost estimation

Energy and chemical costs associated with ammonia recovery were compared against a base case where AAD centrate is returned to a pre-existing mainstream activated sludge process for biological nitrogen removal ($5 \text{ kWh}_e \text{ kg}_N^{-1}$) (Garrido et al., 2013) (Table E2). As with capital costing, calculations were based upon treatment of $2340 \text{ kg}_{\text{NH}_3} \text{ d}^{-1}$. The thermal demand is comprised of sensible heating of the centrate feed and latent heat duty for water evaporation in the stripper. Heat was recovered from the stripped feed in the pre-heater to reduce external thermal demand. Due to relatively low stripping temperatures ($<70^\circ\text{C}$), heating duty could be supplemented by the utilisation of low-grade waste heat. An audit for a centralised wastewater treatment works indicated that 50-70 kWh of hot water (85°C) could be recovered per m^3 digested sludge liquor from biogas engines co-located with an anaerobic digestion facility (Moore and Auty, 2013; Ndam, 2017). For the case of gas-phase ammonia recovery, the total thermal demand could be satisfied through heat integration and waste heat application. The electricity demand for stripping was based upon the vacuum pump power rating. Liquid-ring vacuum pumps were selected as they can achieve the pressure and vapour flow required for this application and sizing was based on a methodology outlined by Bannwarth (2005). The power rating is a function of vapour flowrate, which is substantially lower for gas-phase recovery compared to aqueous recovery flowsheets. Prior to stripping, alkali is added to raise the centrate pH up to 10 to release $>95\%$ free ammonia, maximising the driving force for ammonia mass transfer (Bates and Pinching, 1950; Huang and Shang, 2006). This places a substantial economic burden on the process, which is exacerbated by the requirement for sodium hydroxide over lower cost calcium hydroxide since the latter can lead to the precipitation of a fouling sludge in concentrated wastewaters (Limoli et al., 2016).

Table E2: Operational expenses for vacuum stripping systems designed to recover 2340 kg_{NH3} d⁻¹ and operated at 40°C to 70°C.

Scenario		Thermal demand	Power demand	Alkali demand	Annual expense ^a
		MWh _{th} t _{NH3} ⁻¹	MWh _e t _{NH3} ⁻¹	kmol t _{NH3} ⁻¹	EUR y ⁻¹
Base	ASP	0	4.1 ^b	0	551,461
Gas-phase recovery	40°C	0	0.04	49	541,528
	50°C	0	0.04	49	541,528
Aqueous recovery	60°C	12	0.11	49	848,957
	65°C	18	0.25	49	1,022,732
	70°C	35	0.37	49	1,467,948

ASP – Activated sludge process for biological nitrogen removal

^a Unit costs: 29 EUR MWh_{th}⁻¹, 157 EUR MWh_e⁻¹, 13 EUR kmol_{NaOH}⁻¹ (ChemAnalyst, 2022; Department for Business, Energy and Industrial Strategy, 2022a; European Central Bank, 2023).

^b (Garrido et al., 2013)

E5 Cost of carbon under the Emissions Trading Scheme

Effective carbon emissions (t_{CO2e} year⁻¹) were determined for each scenario based upon the carbon intensity of imported heat (0.184 kg_{CO2e} kWh_{th}⁻¹), electricity (0.233 kg_{CO2e} kWh_{th}⁻¹) and sodium hydroxide manufacture (0.02 kg_{CO2e} mol⁻¹) (Bulb, 2023; Kumar et al., 2021). Carbon emissions were also determined for an activated sludge plant treating an equivalent ammonia loading. This was based upon electricity usage and nitrous oxide using an emission factor of 0.035 kg_{N2O} kg_{Nin}⁻¹ (Davey et al., 2022; Winter et al., 2012). Carbon emissions incur costs under the Emissions Trading Scheme (60.1 EUR t_{CO2e}) (Ember, 2023).

E6 Levelised cost of ammonia determination

The LCOA has emerged as a useful tool to evaluate the whole life cost for sustainable ammonia plants, which typically require larger capital investment related to the installation of local wind and solar farms and buffering storage for hydrogen to support continuous operation with an intermittent energy supply (Beerbühl et al., 2014; Nayak-Luke et al., 2018). An established method for LCOA computation has been applied (Eq. E17) (Cesaro et al., 2021; Nayak-Luke et al., 2018). To evaluate this as a replacement technology for an existing activated sludge plant, this expression has been adapted to include the annual cost of

energy, chemical and carbon (under ETS) for each ammonia stripping scenario (ECC_t), offset against the annual cost of energy and carbon for biological nitrogen removal ($EC_{t,ASP}$). The economic lifetime of the plant was assumed to be 20 years and the initial capital investment was divided equally across this period. Operational and maintenance expenses (excluding energy and chemical usage) were assumed to represent 3% of the total capital investment (Morgan, 2013).

$$LCOA = \frac{\sum_{t=0}^n \frac{C_t + OM_t + ECC_t - EC_{t,ASP}}{(1+r)^t}}{\sum_{t=0}^n \frac{A_t}{(1+r)^t}} \quad (\text{Eq. E17})$$

where LCOA is the levelised cost of ammonia (EUR tonne_{NH₃}⁻¹); C_t is the capital investment in year t (EUR) (Table E1); OM_t is the operational and maintenance expenses in year t (EUR); ECC_t is energy, chemical and carbon costs in year t (EUR) (Table E2); $EC_{t,ASP}$ is energy and carbon costs for an activated sludge plant treating equivalent ammonia loading (EUR); A_t is the annual ammonia recovery in year t (855 t_{NH₃}⁻¹); r is the weighted average cost of capital (7%); and n is the economic lifetime of the plant (20 years).

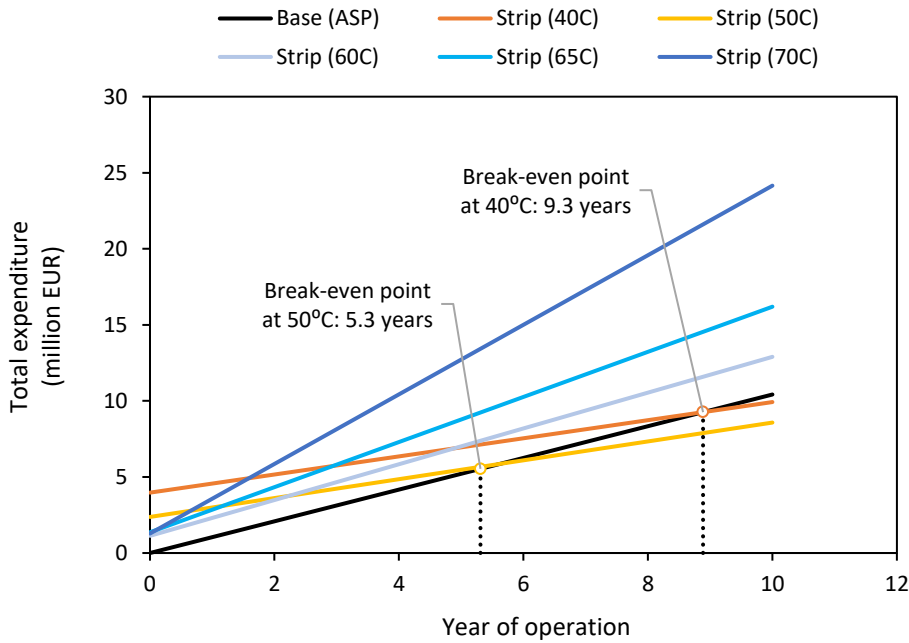


Figure E4: Break-even point analysis based upon the total expenditure (capital, operational, and carbon costs) for the installation of an ammonia stripping system compared against the total expenditure for a pre-existing activated sludge plant (operational and carbon costs) to treat equivalent ammonia loading.

References

- Angelidaki, I., Treu, L., Tsapekos, P., Luo, G., Campanaro, S., Wenzel, H., and Kougias, P. G. (2018). Biogas upgrading and utilization: Current status and perspectives. *Biotechnology Advances*, 36, 452–466.
- Anglian Water. (2021). Ofwat Breakthrough Challenge Success. <https://www.anglianwater.co.uk/news/ofwat-breakthrough-challenge-success/> (accessed 31/03/2023).
- Augustsson, O., Baburao, B., Dube, S., Bedell, S., Strunz, P., Balfe, M., and Stallmann, O. (2017). Chilled Ammonia Process Scale-up and Lessons Learned. 13th International Conference on Greenhouse Gas Control Technologies, Lausanne, Switzerland.
- Bank of England. (2023). Inflation calculator. <https://www.bankofengland.co.uk/monetary-policy/inflation/inflation-calculator> (accessed 31/05/2023).
- Bannwarth, H. (2005). *Liquid Ring Vacuum Pumps, Compressors and Systems: Conventional and Hermetic Design* (1st ed., pp. 157–238). Wiley VCH, Weinheim, Germany.
- Bates, R. G., and Pinching, G. D. (1950). Dissociation Constant of Aqueous Ammonia at 0 to 50° from E. m. f. Studies of the Ammonium Salt of a Weak Acid. *Journal of the American Chemical Society*, 72, 1393–1396.
- Bauer, F., Hulteberg, C., Persson, T., and Tamm, D. (2013). Biogas upgrading – Review of commercial technologies. SGC. http://vav.griffel.net/filer/C_SGC2013-270.pdf (accessed 31/03/2023).
- Bavarella, S., Hermassi, M., Brookes, A., Moore, A., Vale, P., Moon, I. S., Pidou, M., and McAdam, E. J. (2020). Recovery and concentration of ammonia from return liquor to promote enhanced CO₂ absorption and simultaneous ammonium bicarbonate crystallisation during biogas upgrading in a hollow fibre membrane contactor. *Separation and Purification Technology*, 241, 116631.
- Beerbühl, S. S., Kolbe, B., Roosen, C., and Schultmann, F. (2014). Ammoniaksynthese als Beispiel einer stofflichen Nutzung von intermittierend erzeugtem Wasserstoff. *Chemie Ingenieur Technik*, 86, 649–657.

- Belaissaoui, B., Claveria-Baro, J., Lorenzo-Hernando, A., Albarracin Zaidiza, D., Chabanon, E., Castel, C., Rode, S., Roizard, D., and Favre, E. (2016). Potentialities of a dense skin hollow fiber membrane contactor for biogas purification by pressurized water absorption. *Journal of Membrane Science*, 513, 236–249.
- Bonmati, A., and Flotats, X. (2003). Air stripping of ammonia from pig slurry: characterisation and feasibility as a pre- or post-treatment to mesophilic anaerobic digestion. *Waste Management*, 23, 261–272.
- Bulb. (2023). Carbon tracker. <https://bulb.co.uk/carbon-tracker/#:~:text=With Bulb%2C annual CO2 emissions for the energy,0.00 kg of CO2 per kWh of gas.> (accessed 01/04/2023).
- Campos, J. L., Valenzuela-Heredia, D., Pedrouso, A., Val Del Río, A., Belmonte, M., and Mosquera-Corral, A. (2016). Greenhouse Gases Emissions from Wastewater Treatment Plants: Minimization, Treatment, and Prevention. *Journal of Chemistry*, 379635.
- Centeno Mora, E., and de Lemos Chernicharo, C. A. (2022). Simultaneous removal of dissolved sulphide and dissolved methane from anaerobic effluents with hollow fibre membrane contactors. *Environmental Science and Pollution Research*, 90549–90566.
- Cesaro, Z., Ives, M., Nayak-Luke, R., Mason, M., and Bañares-Alcántara, R. (2021). Ammonia to power: Forecasting the levelized cost of electricity from green ammonia in large-scale power plants. *Applied Energy*, 282, 1–19.
- Cheddie, D. (2012). *Hydrogen Energy - Challenges and Perspectives* (1st ed., pp. 333–362). IntechOpen, London, UK.
- ChemAnalyst. (2022). Caustic Soda Price Trend and Forecast - Europe 2022. <https://www.chemanalyst.com/Pricing-data/caustic-soda-3> (accessed 20/03/2023).
- ChemAnalyst. (2023). Ammonia Price Trend and Forecast. <https://www.chemanalyst.com/Pricing-data/ammonia-37> (accessed 11/06/2023)

- Connor, P. M., Xie, L., Lowes, R., Britton, J., and Richardson, T. (2015). The development of renewable heating policy in the United Kingdom. *Renewable Energy*, 75, 733–744.
- Cooper, M., and Botte, G. G. (2006). Hydrogen Production from the Electro-oxidation of Ammonia Catalyzed by Platinum and Rhodium on Raney Nickel Substrate. *Journal of The Electrochemical Society*, 153, A1894.
- Darde, V., Thomsen, K., van Well, W. J. M., and Stenby, E. H. (2010). Chilled ammonia process for CO₂ capture. *International Journal of Greenhouse Gas Control*, 4, 131–136.
- Davey, C. J., Luqmani, B., Thomas, N., and McAdam, E. J. (2022). Transforming wastewater ammonia to carbon free energy: Integrating fuel cell technology with ammonia stripping for direct power production. *Separation and Purification Technology*, 289, 120755.
- de Haas, D., and Andrews, J. (2022). Nitrous oxide emissions from wastewater treatment - Revisiting the IPCC 2019 refinement guidelines. *Environmental Challenges*, 8, 100557.
- Dekker, N. J. J., and Rietveld, G. (2006). Highly efficient conversion of ammonia in electricity by solid oxide fuel cells. *Journal of Fuel Cell Science and Technology*, 3, 499–502.
- Department for Business Energy and Industrial Strategy. (2021a). Future Support for Low Carbon Heat and the Green Gas Levy: government response to consultation.
https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/970565/green-gas-levy-future-support-low-carbon-heat-govt-response.pdf (accessed 01/04/2023).
- Department for Business Energy and Industrial Strategy. (2021b). UK Hydrogen Strategy.
https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/1011283/UK-Hydrogen-Strategy_web.pdf (accessed 31/03/2023).
- Department for Business Energy and Industrial Strategy. (2022a). Gas and electricity prices in the non-domestic sector.

- <https://www.gov.uk/government/statistical-data-sets/gas-and-electricity-prices-in-the-non-domestic-sector> (accessed 31/03/2023).
- Department for Business Energy and Industrial Strategy. (2022b). Green Gas Support Scheme (GGSS): Annual Tariff Review 2022. <https://www.gov.uk/government/publications/green-gas-support-scheme-ggss-annual-tariff-reviews-and-tariff-change-notice/green-gas-support-scheme-ggss-annual-tariff-review-2022> (accessed 10/04/2023).
- Department for Energy Security and Net Zero. (2022). Green Gas Support Scheme: budget management guidance. <https://www.gov.uk/government/publications/green-gas-support-scheme-budget-management/green-gas-support-scheme-budget-management#:~:text=Tariffs for biomethane injection in,40%2C000 MWh – 3.53 p%2F kWh> (accessed 11/06/2023).
- Department for Environment Food and Rural Affairs. (2019). Clean air strategy 2019. https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/770715/clean-air-strategy-2019.pdf (accessed 18/05/2023).
- Department for Transport. (2021). Targeting net zero - Next steps for the Renewable Transport Fuels Obligation. <https://www.gov.uk/government/consultations/amending-the-renewable-transport-fuels-obligation-rfto-to-increase-carbon-savings-on-land-air-and-at-sea> (accessed 01/04/2023).
- Diaz, L. A., and Botte, G. G. (2015). Hydrodynamic analysis and simulation of a flow cell ammonia electrolyzer. *Electrochimica Acta*, 179, 529–537.
- EC (European Community). (2008). 2008/98/EC of 19 November 2008 on waste and repealing certain Directives. *Official Journal of the European Union*, 3–30. <http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32008L0098&from=EN%3E> (accessed 31/03/2023).
- EEC Council. (1991). 91/271/EEC of 21 May 1991 concerning urban waste-water treatment. *Official Journal of the European Communities*, 40–52. <http://eur->

- lex.europa.eu/legal-content/en/ALL/?uri=CELEX:31991L0271 (accessed 31/03/2023).
- Elhajj, J., Al-Hindi, M., and Azizi, F. (2014). A review of the absorption and desorption processes of carbon dioxide in water systems. *Industrial and Engineering Chemistry Research*, 53, 2–22.
- Ember. (2023). Carbon Price Tracker. <https://ember-climate.org/data/data-tools/carbon-price-viewer/> (accessed 11/06/2023).
- Environment Agency. (2022). Treating, storing, and using carbon dioxide from anaerobic digestion: RPS 255. <https://www.gov.uk/government/publications/treating-storing-and-using-carbon-dioxide-from-anaerobic-digestion-rps-255> (accessed 01/04/2023).
- European Central Bank. (2023). Euro foreign exchange reference rates. https://www.ecb.europa.eu/stats/policy_and_exchange_rates/euro_reference_exchange_rates/html/eurofxref-graph-gbp.en.html (accessed 01/05/2023).
- European Commission. (2020). Communication COM/2020/301: A hydrogen strategy for a climate-neutral Europe. <https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:52020DC0301> (accessed 18/05/2023).
- European Standards. (2018). EN 17124:2018. Hydrogen fuel. Product specification and quality assurance for hydrogen refuelling points dispensing gaseous hydrogen - Proton exchange membrane (PEM) fuel cell applications for vehicles.
- Gabelman, A., and Hwang, S. (1999). Hollow fiber membrane contactors. *Journal of Membrane Science*, 159, 61–106.
- Garrido, J. M., Fdz-Polanco, M., and Fdz-Polanco, F. (2013). Working with energy and mass balances: A conceptual framework to understand the limits of municipal wastewater treatment. *Water Science and Technology*, 67, 2294–2301.
- Grasham, O., Dupont, V., Camargo-Valero, M. A., García-Gutiérrez, P., and Cockerill, T. (2019). Combined ammonia recovery and solid oxide fuel cell use at wastewater treatment plants for energy and greenhouse gas emission improvements. *Applied Energy*, 240, 698–708.

- Guida, S., Van Peteghem, L., Luqmani, B., Sakarika, M., McLeod, A., McAdam, E. J., Jefferson, B., Rabaey, K., and Soares, A. (2022). Ammonia recovery from brines originating from a municipal wastewater ion exchange process and valorization of recovered nitrogen into microbial protein. *Chemical Engineering Journal*, 427, 130896.
- Guo, Y., Pan, Z., and An, L. (2020). Carbon-free sustainable energy technology : Direct ammonia fuel cells. *Journal of Power Sources*, 476, 228454.
- Guštin, S., and Marinšek-Logar, R. (2011). Effect of pH, temperature and air flow rate on the continuous ammonia stripping of the anaerobic digestion effluent. *Process Safety and Environmental Protection*, 89, 61–66.
- Heile, S., Chernicharo, C. A. L., Brandt, E. M. F., and McAdam, E. J. (2017). Dissolved gas separation for engineered anaerobic wastewater systems. *Separation and Purification Technology*, 189, 405–418.
- Hewlett, S. G., Valera-Medina, A., Pugh, D. G., and Bowen, P. J. (2019). Gas turbine co-firing of steelworks ammonia with coke oven gas or methane: A fundamental and cycle analysis. *Proceedings of the ASME Turbo Expo 2019: Turbomachinery Technical Conference and Exposition*, Phoenix, AZ, USA.
- Houlker, S. (2019). Scale up of hollow fibre membrane contactors for biogas upgrading. EngD thesis. Cranfield University.
- Huang, J., and Shang, C. (2006). Air Stripping. In L. K. Wang, Y. Hung, & N. K. Shamas (Eds.), *Advanced Physicochemical Treatment Processes* (1st ed., pp. 47–79). The Humana Press Inc., Totowa, NJ, USA.
- IEA Bioenergy. (2019). Task 37: Energy from Biogas Upgrading Plant List 2019. International Energy Agency. <https://task37.ieabioenergy.com/plant-lists/> (accessed 01/04/2023).
- International Energy Agency. (2021). Ammonia Technology Roadmap. <https://iea.blob.core.windows.net/assets/6ee41bb9-8e81-4b64-8701-2acc064ff6e4/AmmoniaTechnologyRoadmap.pdf> (accessed 31/03/2023).
- Jackson, C., Fothergill, K., Gray, P., Haroon, F., Makhoulfi, C., Kezibri, N., Davey, A., Lhote, O., Zarea, M., Davenne, T., Greenwood, S., Huddart, A., Makepeace, J., Wood, T., David, B., and Wilkinson, I. (2015). Ammonia to Green Hydrogen Project.

- https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/880826/HS420_-_Ecuity_-_Ammonia_to_Green_Hydrogen.pdf (accessed 31/03/2023).
- Jamaludin, Z., Rollings-Scattergood, S., Lutes, K., and Vaneeckhaute, C. (2018). Evaluation of sustainable scrubbing agents for ammonia recovery from anaerobic digestate. *Bioresource Technology*, 270, 596–602.
- Jiang, A. (2009). Ammonia recovery from digested dairy manure as nitrogen fertilizer. PhD thesis. Washington State University.
- Jiang, A., Zhang, T., Zhao, Q. B., Li, X., Chen, S., and Frear, C. S. (2014). Evaluation of an integrated ammonia stripping, recovery, and biogas scrubbing system for use with anaerobically digested dairy manure. *Biosystems Engineering*, 119, 117–126.
- Jilvero, H., Normann, F., Andersson, K., and Johnsson, F. (2012). Heat requirement for regeneration of aqueous ammonia in post-combustion carbon dioxide capture. *International Journal of Greenhouse Gas Control*, 11, 181–187.
- Kang, J., Kwon, G., Nam, J. H., Kim, Y. O., and Jahng, D. (2017). Carbon dioxide stripping from anaerobic digestate of food waste using two types of aerators. *International Journal of Environmental Science and Technology*, 14, 1397–1408.
- Kobayashi, H., Hayakawa, A., Somarathne, K. D. K. A., and Okafor, E. C. (2019). Science and technology of ammonia combustion. *Proceedings of the Combustion Institute*, 37, 109–133.
- Kumar, A., Du, F., and Lienhard, J. H. (2021). Caustic Soda Production, Energy Efficiency, and Electrolyzers. *ACS Energy Letters*, 6, 3563–3566.
- Kurata, O., Iki, N., Matsunuma, T., Inoue, T., Tsujimura, T., Furutani, H., Kobayashi, H., and Hayakawa, A. (2017). Performances and emission characteristics of NH₃-air and NH₃-CH₄-air combustion gas-turbine power generations. *Proceedings of the Combustion Institute*, 36, 3351–3359.
- Kvist, T., and Aryal, N. (2019). Methane loss from commercially operating biogas upgrading plants. *Waste Management*, 87, 295–300.

- Lan, R., and Tao, S. (2014). Ammonia as a suitable fuel for fuel cells. *Frontiers in Energy Research*, 2, 1–4.
- Lang, H. J. (1948). Simplified approach to preliminary cost estimates. *Chemical Engineering*, 55, 112–113.
- Li, G., Kanezashi, M., and Tsuru, T. (2017). Catalytic ammonia decomposition over high-performance Ru/graphene nanocomposites for efficient CO_x-free hydrogen production. *Catalysts*, 7, 23.
- Limoli, A., Langone, M., and Andreottola, G. (2016). Ammonia removal from raw manure digestate by means of a turbulent mixing stripping process. *Journal of Environmental Management*, 176, 1–10.
- Liu, B., Giannis, A., Zhang, J., Chang, V. W. C., and Wang, J. Y. (2015). Air stripping process for ammonia recovery from source-separated urine: Modeling and optimization. *Journal of Chemical Technology and Biotechnology*, 90, 2208–2217.
- Mackinnon, I. D. R., Barr, K., Miller, E., Hunter, S., and Pinel, T. (2003). Nutrient removal from wastewaters using high performance materials. *Water Science and Technology*, 47, 101–107.
- Maharaja, P., A, M., K, P. M., Sekar, K., S, S., Srinivasan, S. V., K, S. B., and G, S. (2023). Synchronous COD removal and nitrogen recovery from high concentrated pharmaceutical wastewater by an integrated chemo-biocatalytic reactor systems. *Journal of Environmental Management*, 329, 117048.
- Makhloufi, C., and Kezibri, N. (2021). Large-scale decomposition of green ammonia for pure hydrogen production. *International Journal of Hydrogen Energy*, 46, 34777–34787.
- McBean, E. A. (2008). Siloxanes in biogases from landfills and wastewater digesters. *Canadian Journal of Civil Engineering*, 35, 431–436.
- McLeod, A., Buzatu, P., Autin, O., Jefferson, B., and McAdam, E. (2015). Controlling shell-side crystal nucleation in a gas-liquid membrane contactor for simultaneous ammonium bicarbonate recovery and biogas upgrading. *Journal of Membrane Science*, 473, 146–156.

- McLeod, A., Jefferson, B., and McAdam, E. J. (2014). Biogas upgrading by chemical absorption using ammonia rich absorbents derived from wastewater. *Water Research*, 67, 175–186.
- Mission Possible Partnership. (2022). Making net-zero ammonia possible. <https://missionpossiblepartnership.org/wp-content/uploads/2022/09/Making-1.5-Aligned-Ammonia-possible.pdf> (accessed 31/03/2023).
- Mondor, M., Masse, L., Ippersiel, D., Lamarche, F., and Massé, D. I. (2008). Use of electrodialysis and reverse osmosis for the recovery and concentration of ammonia from swine manure. *Bioresource Technology*, 99, 7363–7368.
- Montgomery, M. J., Kwon, H., Dreyer, J. A. H., Xuan, Y., McEnally, C. S., and Pfefferle, L. D. (2021). Effect of ammonia addition on suppressing soot formation in methane co-flow diffusion flames. *Proceedings of the Combustion Institute*, 38, 2497–2505.
- Moore, A., and Auty, D. (2013). Digestion and Greenhouses – Synergistic Resource Recovery. 18th European Biosolids & Organic Resources Conference & Exhibition, Manchester, UK.
- Morgan, E. R. (2013). Techno-economic feasibility study of ammonia plants powered by offshore wind. PhD thesis. University of Massachusetts Amherst.
- Nasharuddin, R., Zhu, M., Zhang, Z., and Zhang, D. (2019). A technoeconomic analysis of centralised and distributed processes of ammonia dissociation to hydrogen for fuel cell vehicle applications. *International Journal of Hydrogen Energy*, 44, 14445–14455.
- Nayak-Luke, R., Bañares-Alcántara, R., and Wilkinson, I. (2018). “green” Ammonia: Impact of Renewable Energy Intermittency on Plant Sizing and Levelized Cost of Ammonia. *Industrial and Engineering Chemistry Research*, 57, 14607–14616.
- Ndam, N. E. (2017). Treatment technologies for recycle liquors: Nutrient removal, mass balances, and potential recovery at wastewater treatment plants. PhD thesis. Newcastle University.
- Nutrien. (2022). Nutrien Fact Book 2022. https://nutrien-prod-asset.s3.us-east-2.amazonaws.com/s3fs-public/uploads/2022-06/Nutrien_2022_Fact_Book.pdf (accessed 16/06/2023).

- Okafor, E. C., Kurata, O., Yamashita, H., Inoue, T., Tsujimura, T., Iki, N., Hayakawa, A., Ito, S., Uchida, M., and Kobayashi, H. (2021a). Liquid ammonia spray combustion in two-stage micro gas turbine combustors at 0.25 MPa; Relevance of combustion enhancement to flame stability and NO_x control. *Applications in Energy and Combustion Science*, 7, 100038.
- Okafor, E. C., Yamashita, H., Hayakawa, A., Somarathne, K. D. K. A., Kudo, T., Tsujimura, T., Uchida, M., Ito, S., and Kobayashi, H. (2021b). Flame stability and emissions characteristics of liquid ammonia spray co-fired with methane in a single stage swirl combustor. *Fuel*, 287, 119433.
- Organics Group. (2020). Removal, Recovery and Re-use of Ammoniacal Nitrogen from Wastewater for Power Generation. <https://organicsgroup.com/recovery-and-re-use-of-of-ammonia/> (accessed 31/03/2023).
- Papadimas, D., and Ahmed, S. (2012). Biogas Impurities and Cleanup for Fuel Cells. Biogas and Fuel Cells Workshop, Golden, CO, USA.
- Pátek, J., and Klomfar, J. (1995). Simple functions for fast calculations of selected thermodynamic properties of the ammonia-water system. *International Journal of Refrigeration*, 18, 228–234.
- Patterson, T., Esteves, S., Dinsdale, R., and Guwy, A. (2011). An evaluation of the policy and techno-economic factors affecting the potential for biogas upgrading for transport fuel use in the UK. *Energy Policy*, 39, 1806–1816.
- RVT. (2015). Ammonia recovery Removal from liquids and gases. http://www.rvtpe.net/wp-content/uploads/prospekte/RVT_Ammonia_Recovery_120529.pdf (accessed 31/03/2023).
- Saadabadi, S. A., Patel, H., Woudstra, T., and Aravind, P. V. (2020). Thermodynamic Analysis of Solid Oxide Fuel Cell Integrated System Fuelled by Ammonia from Struvite Precipitation Process. *Fuel Cells*, 20, 143–157.
- Saadabadi, S. A., Thallam Thattai, A., Fan, L., Lindeboom, R. E. F., Spanjers, H., and Aravind, P. V. (2019). Solid Oxide Fuel Cells fuelled with biogas: Potential and constraints. *Renewable Energy*, 134, 194–214.

- Sasaki, K., Haga, K., Yoshizumi, T., Minematsu, D., Yuki, E., Liu, R.-R., Uryu, C., Oshima, T., Taniguchi, S., Shiratori, Y., and Ito, K. (2011). Impurity Poisoning of SOFCs. *ECS Transactions*, 35, 2805–2814.
- Siddharth, K., Chan, Y., Wang, L., and Shao, M. (2018). Ammonia electro-oxidation reaction: Recent development in mechanistic understanding and electrocatalyst design. *Current Opinion in Electrochemistry*, 9, 151–157.
- Siddiqui, O., and Dincer, I. (2019a). Development and performance evaluation of a direct ammonia fuel cell stack. *Chemical Engineering Science*, 200, 285–293.
- Siddiqui, O., and Dincer, I. (2019b). Experimental investigation and assessment of direct ammonia fuel cells utilizing alkaline molten and solid electrolytes. *Energy*, 169, 914–923.
- Siemens Energy. (2022). Press release. [https://www.siemens-energy.com/uk/en/energy/game-changing-green-ammonia-prototype.html#:~:text=The ammonia cracker system will provide the potential,using FFI's Metal Membrane Technology %28MMT%29 purification process. \(accessed 02/03/2023\).](https://www.siemens-energy.com/uk/en/energy/game-changing-green-ammonia-prototype.html#:~:text=The ammonia cracker system will provide the potential,using FFI's Metal Membrane Technology %28MMT%29 purification process. (accessed 02/03/2023).)
- Sinnot, R. K. (2004). Costing and Project Evaluation. In J. M. Coulson & J. F. Richardson (Eds.), *Chemical Engineering Design* (2nd ed., pp. 243–283). Butterworth-Heinemann, Oxford, UK.
- Sutter, D., Gazzani, M., Pérez-Calvo, J. F., Leopold, C., Milella, F., and Mazzotti, M. (2017). Solid Formation in Ammonia-based Processes for CO₂ Capture - Turning a Challenge into an Opportunity. 13th International Conference on Greenhouse Gas Control Technologies, Lausanne, Switzerland.
- Tao, W., Bayrakdar, A., Wang, Y., and Agyeman, F. (2019). Three-stage treatment for nitrogen and phosphorus recovery from human urine: Hydrolysis, precipitation and vacuum stripping. *Journal of Environmental Management*, 249, 109435.
- Tao, W., and Ukwuani, A. T. (2015). Coupling thermal stripping and acid absorption for ammonia recovery from dairy manure: Ammonia volatilization kinetics and effects of temperature, pH and dissolved solids content. *Chemical Engineering Journal*, 280, 188–196.

- Tao, W., Ukwuani, A. T., and Agyeman, F. (2018). Recovery of ammonia in anaerobic digestate using vacuum thermal stripping - Acid absorption process: Scale-up considerations. *Water Science and Technology*, 78, 878–885.
- The Royal Society. (2020). Ammonia: zero-carbon fertiliser, fuel and energy store. Policy Briefing. <https://royalsociety.org/topics-policy/projects/low-carbon-energy-programme/green-ammonia/> (accessed 31/03/2023).
- Tian, J., Yan, C., Alcega, S. G., Hassard, F., Tyrrel, S., Coulon, F., and Nasir, Z. A. (2022). Detection and characterization of bioaerosol emissions from wastewater treatment plants: Challenges and opportunities. *Frontiers in Microbiology*, 13, 958514.
- Tian, X., Gao, Z., Feng, H., Zhang, Z., Li, J., and Wang, A. (2019). Efficient nutrient recovery/removal from real source-separated urine by coupling vacuum thermal stripping with activated sludge processes. *Journal of Cleaner Production*, 220, 965–973.
- Trendewicz, A. A., and Braun, R. J. (2013). Techno-economic analysis of solid oxide fuel cell-based combined heat and power systems for biogas utilization at wastewater treatment facilities. *Journal of Power Sources*, 233, 380–393.
- Tyseley Energy Park. (2022). Tyseley Energy Park to host world-leading ammonia to hydrogen project with new Government backing. <https://www.tyseleyenergy.co.uk/ammonia/> (accessed 02/03/2023).
- Uchida, M., Ito, S., Suda, T., and Fujimori, T. (2019). Performance of Ammonia/Natural Gas Co-Fired Gas Turbine with Two-Stage Combustor. 2019 AIChE Annual Meeting., Orlando, FL, USA.
- Ukwuani, A. T., and Tao, W. (2016). Developing a vacuum thermal stripping – acid absorption process for ammonia recovery from anaerobic digester effluent. *Water Research*, 106, 108–115.
- Upadhyay, N., Sun, Q., Allen, J. O., Westerhoff, P., and Herckes, P. (2013). Characterization of aerosol emissions from wastewater aeration basins. *Journal of the Air and Waste Management Association*, 63, 20–26.
- van Linden, N., Spanjers, H., and van Lier, J. B. (2022). Fuelling a solid oxide fuel cell with ammonia recovered from water by vacuum membrane stripping. *Chemical Engineering Journal*, 428, 131081.

- Vaneeckhaute, C., Lebuf, V., Michels, E., Belia, E., Vanrolleghem, P. A., Tack, F. M. G., and Meers, E. (2017). Nutrient Recovery from Digestate: Systematic Technology Review and Product Classification. *Waste and Biomass Valorization*, 8, 21–40.
- Venegas, T., Qu, M., Nawaz, K., and Wang, L. (2021). Critical review and future prospects for desiccant coated heat exchangers: Materials, design, and manufacturing. *Renewable and Sustainable Energy Reviews*, 151, 111531.
- Villeneuve, K., Roizard, D., Remigy, J. C., Iacono, M., and Rode, S. (2018). CO₂ capture by aqueous ammonia with hollow fiber membrane contactors: Gas phase reactions and performance stability. *Separation and Purification Technology*, 199, 189–197.
- Vitse, F., Cooper, M., and Botte, G. G. (2005). On the use of ammonia electrolysis for hydrogen production. *Journal of Power Sources*, 142, 18–26.
- Vrontisi, Z., Abrell, J., Neuwahl, F., Saveyn, B., and Wagner, F. (2016). Economic impacts of EU clean air policies assessed in a CGE framework. *Environmental Science and Policy*, 55, 54–64.
- Water Europe. (2021). Unleash the Potential of the Water-Energy Nexus in the Energy Efficiency Directive Joint Declaration. <https://watereurope.eu/wp-content/uploads/Joint-Declaration-EU-ASE-.-WE-2.pdf> (accessed 31/03/2023).
- Water UK. (2020). Net Zero 2030 Routemap. <https://www.water.org.uk/routemap2030> (accessed 31/03/2023).
- Wett, B. (2006). Solved upscaling problems for implementing deammonification of rejection water. *Water Science and Technology*, 53, 121–128.
- Winter, P., Pearce, P., and Colquhoun, K. (2012). Contribution of nitrous oxide emissions from wastewater treatment to carbon accounting. *Journal of Water and Climate Change*, 3, 95–109.
- Zeng, L., Mangan, C., and Li, X. (2006). Ammonia recovery from anaerobically digested cattle manure by steam stripping. *Water Science and Technology*, 54, 137–145.
- Zhang, M., Zou, P., Jeerh, G., Chen, S., Shields, J., Wang, H., and Tao, S. (2020). Electricity Generation from Ammonia in Landfill Leachate by an Alkaline

Membrane Fuel Cell Based on Precious-Metal-Free Electrodes. ACS Sustainable Chemistry and Engineering, 8, 12817–12824.

7 Discussion

7.1 Discussion

An expansion of biogas upgrading is required to support the delivery of net zero carbon commitments for major European nations by 2050 (Department for Business, Energy and Industrial Strategy, 2021a; European Commission, 2019). Maximising biogas upgrading could deliver up to 1000 TWh of biomethane in 2050 which is equivalent to 30-40% of the projected natural gas demand for Europe (European Biogas Association, 2021; Pavicic et al., 2022). To capitalise on this, the development of next-generation technologies is necessary to lower the whole life cost of biomethane without reliance on governmental incentivisation schemes which have been gradually degressed over the past decade (Department for Business, Energy and Industrial Strategy, 2021b; Houlker, 2019). Contributions to knowledge developed through this thesis underpin the advancement of a novel biomethane technology which could be applied within wastewater treatment to lower barriers to investment through a circular economy approach in which ammonia products are simultaneously recovered (Figure 7.1). To contextualise the potential impact of this research and its relevance to delivering net zero, the outcomes are explored around a set of key questions.

7.1.1 Could HFMC offer a competitive alternative to absorption columns?

Gas-liquid absorption columns are the dominant technology for biogas upgrading and represent 70% of installed capacity across the European water sector (IEA Bioenergy, 2019). Hollow fibre membrane contactors (HFMC) could lower capital costs by almost 40-times due to their high interfacial surface area (Belaissaoui et al., 2016; Houlker, 2019). This thesis has demonstrated further process intensification through a combined strategy of solvent chilling and gas pressurisation which can increase CO₂ flux and selectivity, thereby reducing the membrane area and path length for biogas upgrading (Chapter 3). Consequently, this will lower the solvent requirements and methane 'slip' alongside the number of modules positioned in parallel and in series to produce industrial quality biomethane (Houlker, 2019; Kapoor et al., 2019). Chilled conditions will also promote wetting resilience and favour the application of microporous membranes which are simpler to fabricate and 40% cheaper than nonporous membranes

(Chapter 3). Whilst synthetic biogas was applied in this work, previous trials have indicated that microporous membranes do not suffer performance degradation when exposed to real biogas containing trace contaminants such as siloxanes (Houlker et al., 2021; McBean, 2008). Microporous HFMC are also technologically mature for applications including dissolved gas extraction and are available at commercial scales (single module liquid flows up to $125 \text{ m}^3 \text{ h}^{-1}$), lowering investment risks for industrial adoption (3M, 2023; Cookney et al., 2016). Infrastructure requirements for HFMCs could be minimal relative to existing absorption systems due to their modularity and ease of integration (Belaissaoui et al., 2016; Chabanon et al., 2011). Since chillers are often present in biogas pipelines to remove free-water and prevent condensation during compression, these could readily support adaption to a low temperature upgrading process (Bauer et al., 2013; Houlker et al., 2021). Furthermore, biomethane is injected into a pressurised network (2-7 bar) and so the energy and equipment for gas pressurisation are already a baseline requirement (Northern Gas Networks, 2020). By exploiting positive interactions between membrane material, temperature and gas pressure, this work has therefore advanced the development of HFMC as a successor technology for biogas upgrading.

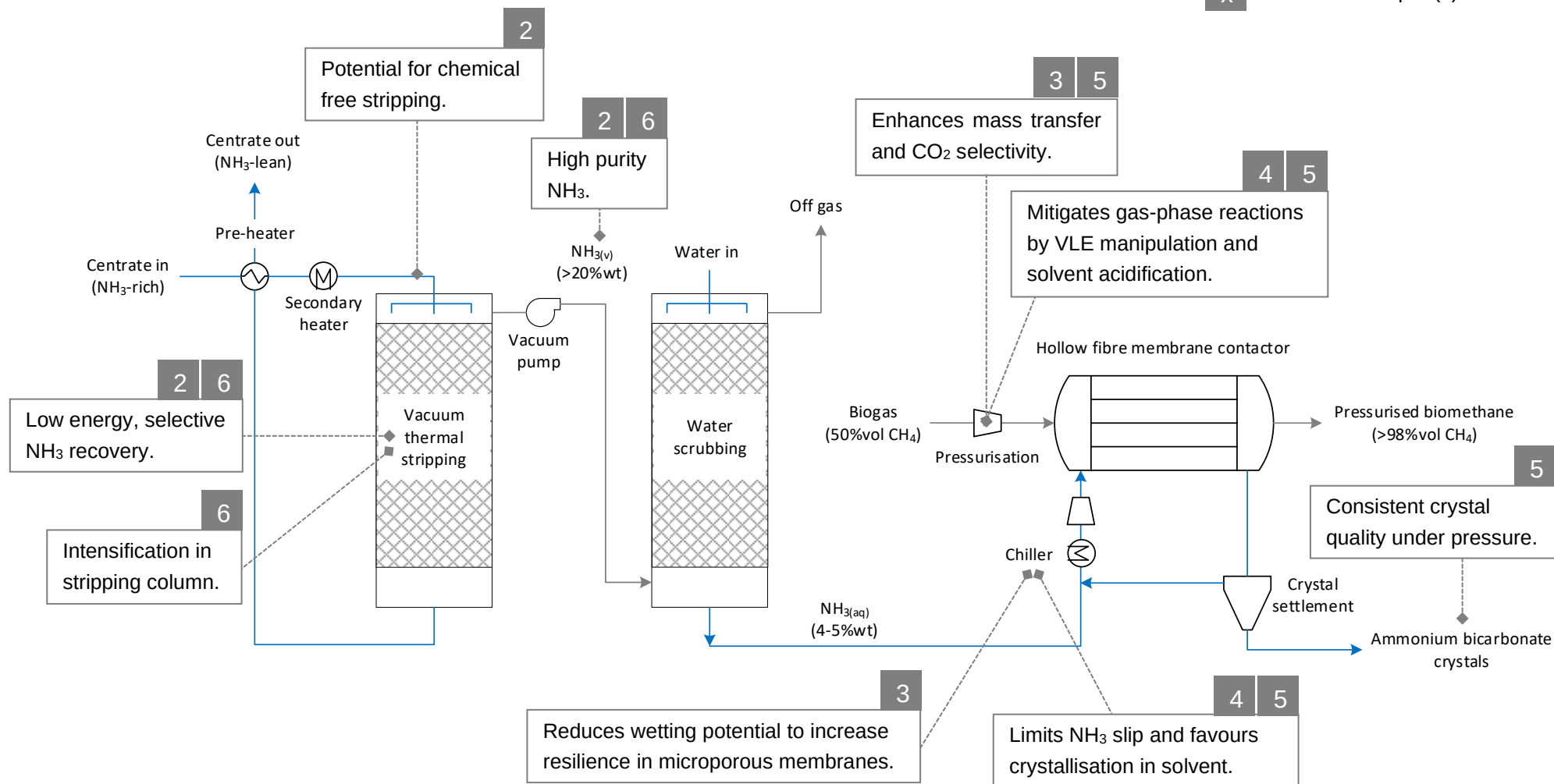


Figure 7.1: Key scientific outputs in this thesis towards the development of reactive biogas upgrading and crystallisation in HFMC using wastewater-derived ammonia solvents.

7.1.2 What are the synergies and opportunities for reactive biogas upgrading?

Hollow fibre membrane contactors are vulnerable to ammonia 'slip' during reactive biogas upgrading which can result in destabilising gas-phase reactions (Bavarella et al., 2022; Villeneuve et al., 2018). For the first time, the mechanism underpinning gas-phase reactions was determined and related to component interactions within the ternary $\text{CO}_2\text{-NH}_3\text{-H}_2\text{O}$ system (Chapter 4). This highlighted preventative strategies to limit gas-phase reactions by minimising ammonia 'slip' through solvent chilling and acidification, and by gas pressurisation to manipulate the relative composition of the ternary system (Chapter 4). Gas pressurisation (up to 2.5 bar) was subsequently employed during reactive absorption in HFMC for the first time and successfully lowered the intensity of gas-phase reactions (Chapter 5). In a positive synergy, the absorption of CO_2 under chilled, pressurised conditions which favour membrane resilience and mass transfer will therefore offer inherent benefits to process stability. These insights can inform the operation and design of reactive biogas upgrading at full-scale and are directly translatable for the use of emerging ternary solvents in HFMC which may be critical to lowering the cost barrier for post-combustion carbon capture and storage (Liu et al., 2019; Zhao et al., 2023). Controlled crystallisation and harvesting of ammonium bicarbonate during reactive biogas upgrading can eliminate the requirement for solvent regeneration and the associated capital cost, energy and chemical demands (Jilvero et al., 2012; McLeod et al., 2015). Biogenic CO_2 captured within the solid product would facilitate carbon negative biomethane production. This could limit exposure to regulatory uncertainty surrounding the incorporation of biogenic CO_2 within the Emission Trading Scheme (ETS), a market-based mechanism for the reduction of greenhouse gases across the EU (2003/87/EC) (EC, 2018). Alternatively, ammonium bicarbonate can be degraded under mild heat ($>30^\circ\text{C}$) and the resultant gas could undergo separation to generate ammonia and CO_2 of high purity, since the crystallisation process will omit dissolved gases and volatile compounds present in the wastewater-derived solvent which may otherwise affect product quality (Bavarella et al., 2020; Villeneuve et al., 2018). Ammonia gas could be pressurised to yield a liquified product and sold into existing supply chains for

fertiliser manufacture or into a growing market as a critical energy vector for the emerging hydrogen economy (Cesaro et al., 2021; Nayak-Luke et al., 2018). This would also enable operators to capitalise on an emerging opportunity for the sale of biogenic CO₂ following new regulation introduced in response to shortfalls in industrial supply (RPS 255) (Environment Agency, 2022). In a critical step for the realisation of this technology, ammonium bicarbonate crystallisation in HFMC was demonstrated under pressurised conditions for the first time (Chapter 5). Unlike conventional crystallisers which rely upon cooling or evaporation, ammonium bicarbonate nucleation was controlled by reactions within the solvent boundary layer (Chapter 5) (McDonald et al., 2021). Crystal formation was therefore observed to occur at a consistent CO₂ loading ratio and supersaturation level, independent of pressure (Chapter 5). This could support the translation of this process across different pressures at scale, by informing simple control philosophies based upon solvent pH and conductivity (indicators of CO₂ loading) using inline probes which are robust and commercially available (Chapter 5). Nucleation under consistent levels of supersaturation will also produce crystals of similar size and shape, thereby simplifying the unit design for their continuous extraction from the solvent by inline filtration or gravity settlement (Ulrich and Strege, 2002). This work therefore represents a critical advancement for the feasibility and operability of a novel, membrane facilitated reactive crystallisation process which could lower the cost barrier for biomethane production whilst generating value through the recovery of sustainable end products.

7.1.3 Does vacuum stripping present a disruptive solution for nitrogen removal?

The low energy and economic recovery of ammonia solvents (4-5%wt) from wastewater is a critical enabler for the proposed biogas upgrading flowsheet. Raised concentrations within centrate from anaerobic digestion (AD) (1-2 kg_{NH₃} m⁻³) will benefit the driving force for commercially established air and steam stripping processes (Organics Group, 2020; RVT, 2015). These rely upon high gas-liquid stripping ratios to overcome the solubility of ammonia in water (air >2000 m³ m⁻³; steam >100 m³ m⁻³) and will generate dilute gas-phase ammonia (0.01-2%wt) (Figure 7.2) (Bonmati and Flotats, 2003; Huang and Shang, 2006;

Zeng et al., 2006). Consequently, further purification stages (i.e., distillation) would be necessary to achieve the required solvent quality, incurring substantial capital cost and energy consumption (Grasham et al., 2019; Teichgraber and Stein, 1994). In this work, the two-phase region for ammonia-water was exploited to facilitate highly selective, low energy recovery of ammonia from wastewater during vacuum thermal stripping (Chapter 2). Notably, this is a contrasting strategy to previous researchers who have operated vacuum stripping close to the dew point curve to maximise mass transfer, resulting in high water evaporation which will dilute the ammonia product and incur high latent heat penalties ($44 \text{ kWh}_{\text{th}} \text{ kg}_{\text{N}}^{-1}$) (Davey et al., 2022; Han et al., 2022; Tian et al., 2019). Selective stripping was translated to a gas-liquid contacting column where ammonia could be extracted from concentrated wastewater with minimal energy demand ($2.9 \text{ kWh}_{\text{th}} \text{ kg}_{\text{N}}^{-1}$) (Chapter 6). Crucially, a techno-economic evaluation indicated that investment in gas-phase ammonia recovery (20-25%wt) for AD centrate could represent a cost saving over a 20-year economic lifetime ($-300 \text{ EUR } t_{\text{NH}_3}^{-1}$), when compared against nitrogen removal in an activated sludge process (Chapter 6). The capture of gas-phase ammonia by water scrubbing to generate ammonia solvents (3-5%wt) could therefore present an efficient and sustainable pathway which is cost competitive with 'green' ammonia production (Figure 7.1) (Morgan, 2013; Nayak-Luke et al., 2018).

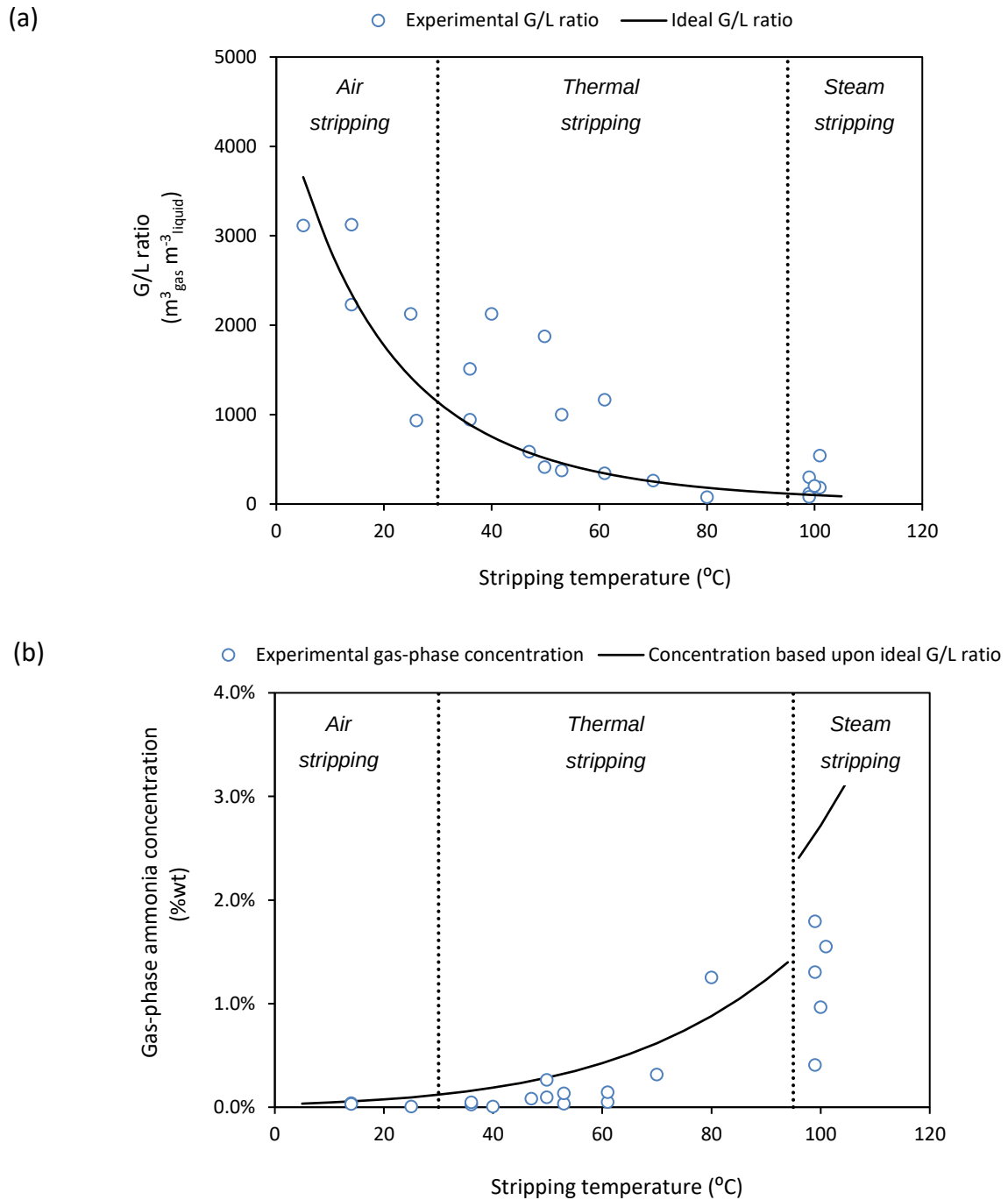


Figure 7.2: Influence of temperature during air and steam stripping on (a) G/L ratio and (b) gas-phase ammonia concentration in stripped vapour (based on mean reported $C_{\text{NH}_3} = 1.6 \text{ kg}_{\text{NH}_3} \text{ m}^{-3}$). Ideal G/L ratio determined for theoretical 100% ammonia removal (Huang and Shang, 2006). Dotted lines represent approximate boundaries for technology classification. Experimental data sampled across 12 studies (Alitalo et al., 2012; Boardman and McVeigh, 1998; Bonmati and Flotats, 2003; Gopalakrishnan et al., 2000; Guštin and Marinšek-Logar, 2011; Jiang, 2009; Katehis et al., 1998; Kim et al., 2021; O'Farrell et al., 1973; Teichgraber and Stein, 1994; Wickramanayake et al., 1992; Zeng et al., 2006).

Vacuum stripping is a thermally driven process where the primary energy input could be satisfied using intrinsic resources within wastewater facilities such as biogas combustion or integration with low-grade heat recovered from biogas engines (Moore and Auty, 2013). Where energy importation is necessary, the cost for a unit of heat (kWh_{th}) is typically 4-5 times lower than for a unit of power (kWh_{e}) (Department of Business, Energy and Industrial Strategy, 2022). Sidestream ammonia recovery could therefore present a low cost, circular economy alternative to electrically driven biological deammonification which consumes $1\text{--}2 \text{ kWh}_{\text{e}} \text{ kg}_{\text{N}}^{-1}$ and has been the focus of substantial investment over the past decade (Ramalingam et al., 2017; The Water Research Foundation, 2019). Deammonification also generates nitrous oxide (a potent greenhouse gas) which leads to effective emissions up to $3.4 \text{ kg}_{\text{CO}_2\text{e}} \text{ kg}_{\text{Ninfluent}}^{-1}$ and has been linked with harmful air pollutants including volatile organic compounds, ammonia and atmospheric formation of particulate matter ($\text{PM}_{2.5}$) (de Haas and Andrews, 2022; The Water Research Foundation, 2019; Zhang et al., 2017). Consequently, the vacuum thermal stripping approach developed in this work offers a standalone value proposition which could be implemented independently of the biogas upgrading system. The recovered gas-phase ammonia could be upgraded by removal of water vapour in advanced dehumidification processes (i.e., desiccant coated heat exchangers) and pressurised to yield a liquified ammonia product (Venegas et al., 2021). Alternatively, ammonia could be repositioned as a zero carbon energy resource to support the decarbonisation of the water sector since it has a heating value of 5.3 kWh kg^{-1} (comparable to biogas, 6.1 kWh kg^{-1}) and could be applied for heat and power generation in gas turbines and electrochemical fuel cells (Table 7.1) (Hewlett et al., 2019; van Linden et al., 2022).

7.1.4 What are the systems level opportunities for wastewater treatment?

This thesis has targeted vacuum thermal stripping of AD centrate which comprises approximately 30% of the site ammonia load, and could generate enough solvent to upgrade 20% of biogas for a centralised works (Mackinnon et al., 2003; Ndam, 2017). Total ammonia recovery could be achieved through integration with ion exchange processes, which have the capability to extract

ammoniacal nitrogen from primary wastewater ($<0.05 \text{ kg}_{\text{NH}_3} \text{ m}^{-3}$) (Thornton et al., 2007). Over multiple regeneration cycles, ammonia can be transferred into a concentrated brine ($>0.5 \text{ kg}_{\text{NH}_3} \text{ m}^{-3}$) suitable for stripping and ammonia recovery (Canellas-Garriga, 2018; Guida et al., 2022). This approach offers strong synergies for existing works with carbonaceous-only activated sludge processes in addition to emerging mainstream anaerobic flowsheets which cannot remove nitrogen, supporting utilities to meet increasingly stringent nitrogen discharge limits for the protection of waterways (EEC Council, 1991; Environmental Audit Committee, 2018; Huang et al., 2020). Recovery of ammonia solvents from the entire wastewater flowsheet would facilitate an expansion up to 70% biogas upgrading (Ndam, 2017). This could enable operators to respond to a shift in incentivisation from mature biogas turbines, which have undergone steep tariff regression within schemes such as the Renewable Heat Incentive, towards biomethane for injection into the gas network (Green Gas Support Scheme) or as a renewable transport fuel (Renewable Transport Fuel Obligation) (Department for Business, Energy and Industrial Strategy, 2021b, 2016; Department for Transport, 2021). Crucially, upstream ammonia recovery would help operators access incentives within the Green Gas Support Scheme which stipulates that ammonia emissions mitigation related to sludge and digestate must be considered during the design of new biomethane installations (Department for Business, Energy and Industrial Strategy, 2021b). Recovered ammonia could also play a key strategic role as a replacement energy source to support the transition from biogas combustion to biomethane production and exportation. For example, harvested ammonium bicarbonate could be thermally degraded to ammonia gas for onsite generation and could satisfy the total heating demand for a conventional AD plant or raise almost 50% of the steam required for thermal hydrolysis in an advanced AD plant. Systems level integration for technologies developed in this thesis alongside emerging ammonia to energy solutions could therefore have a transformative impact within wastewater treatment, enhancing operational revenue and supporting the delivery of decarbonisation commitments.

Table 7.1: Summary of schemes proposed to recover waste ammonia for utilisation as a zero carbon energy resource

Waste source	NH ₃ recovery and/or concentration	NH ₃ utilisation	Performance	Reference
Ammonia vapour from steel works (32-38%wt)	-	Co-fuel gas turbine with methane or coke oven gas	36-39% electrical efficiency ^a	(Hewlett et al., 2019, 2020)
Synthetic wastewater (1-10 kg _{NH3} m ⁻³)	Vacuum membrane stripping, recovery of 1-11%wt NH _{3(v)} .	SOFC	1-2 kW m ⁻² 30-43% electrical efficiency ^b	(van Linden et al., 2022)
Primary sludge liquor ^c	Struvite precipitation and harvesting, thermal degradation of struvite, vapour distillation to recover 30-90%wt NH _{3(v)} .	SOFC	1 kW m ⁻² 53% electrical efficiency ^a	(Saadabadi et al., 2020)
Wastewater ^c	Vacuum membrane stripping, recovery of 3-100% NH _{3(v)} .	SOFC	2-3 kW m ^{-2 a}	(Stoeckl et al., 2020)
Digested sludge liquor (1.8 kg _{NH3} m ⁻³)	Thermal air stripping (75°C), water scrubbing for NH ₃ capture, flash distillation to recover 3.9%wt NH _{3(v)} .	Co-fuel SOFC with biomethane	1 kW m ⁻² 48% electrical efficiency ^a	(Grasham et al., 2019)
Landfill leachate (3 kg _{NH3} m ⁻³)	Electro-deionisation, capture of NH ₃ -H ₂ gas formed at cathode.	Co-fuel SOFC with biogas	10-12 kW m ⁻² 50% electrical efficiency	(Xu et al., 2017)
Pickling wastewater (0.5 kg _{NH3} m ⁻³)	Bipolar membrane electrodialysis, capture of NH ₃ -H ₂ gas formed at cathode.	Co-fuel SOFC with biogas	5 kW m ^{-2 d} 60% electrical efficiency	(Xu et al., 2022)
Digested sludge liquor (2 kg _{NH3} m ⁻³)	Vacuum thermal stripping, condensation to recover 17 kg m ⁻³ NH _{3(aq)} .	Low-temperature AFC	5x10 ⁻⁵ kW m ⁻²	(Davey et al., 2022)
Digested sludge liquor (1.5 kg _{NH3} m ⁻³)	Thermal air stripping (64°C), water scrubbing for NH ₃ capture, distillation to produce NH _{3(v)} ^c .	Steam reformation-WGS to produce H ₂ , PSA for purification.	-	(Grasham et al., 2020)

SOFC – solid oxide fuel cells; AFC – low temperature alkaline fuel cell; WGS – water gas shift; PSA – pressure swing absorption

^a Modelled results

^c Concentration not specified

^b Based on outcomes for 5-10%wt NH_{3(v)}

^d Based on real gas mixtures

References

- 3M. (2023). 3M Liqui-Cel EXF Series Membrane Contactor. https://www.3m.com/3M/en_US/p/d/b5005009009/ (accessed 23/04/2023).
- Alitalo, A., Kyro, A., and Aura, E. (2012). Ammonia Stripping of Biologically Treated Liquid Manure. *Journal of Environmental Quality*, 41, 273–280.
- Bauer, F., Hulteberg, C., Persson, T., and Tamm, D. (2013). Biogas upgrading – Review of commercial technologies. SGC. http://vav.griffel.net/filer/C_SGC2013-270.pdf (accessed 31/03/2023).
- Bavarella, S., Hermassi, M., Brookes, A., Moore, A., Vale, P., Moon, I. S., Pidou, M., and McAdam, E. J. (2020). Recovery and concentration of ammonia from return liquor to promote enhanced CO₂ absorption and simultaneous ammonium bicarbonate crystallisation during biogas upgrading in a hollow fibre membrane contactor. *Separation and Purification Technology*, 241, 116631.
- Bavarella, S., Luqmani, B., Thomas, N., Brookes, A., Moore, A., Vale, P., Pidou, M., and McAdam, E. J. (2022). CO₂ absorption into aqueous ammonia using membrane contactors: Role of solvent chemistry and pore size on solids formation for low energy solvent regeneration. *Separation and Purification Technology*, 290, 120786.
- Belaissaoui, B., Claveria-Baro, J., Lorenzo-Hernando, A., Albarracin Zaidiza, D., Chabanon, E., Castel, C., Rode, S., Roizard, D., and Favre, E. (2016). Potentialities of a dense skin hollow fiber membrane contactor for biogas purification by pressurized water absorption. *Journal of Membrane Science*, 513, 236–249.
- Boardman, G. D., and McVeigh, P. J. (1998). Use of Air Stripping Technology to Remove Ammonia from Biologically Treated Blue Crab Processing Wastewater. *Journal of Aquatic Food Product Technology*, 7, 81–97.
- Bonmati, A., and Flotats, X. (2003). Air stripping of ammonia from pig slurry: characterisation and feasibility as a pre- or post-treatment to mesophilic anaerobic digestion. *Waste Management*, 23, 261–272.
- Canellas-Garriga, J. (2018). Tertiary ammonium removal with zeolites. PhD thesis. Cranfield University.

- Cesaro, Z., Ives, M., Nayak-Luke, R., Mason, M., and Bañares-Alcántara, R. (2021). Ammonia to power: Forecasting the levelized cost of electricity from green ammonia in large-scale power plants. *Applied Energy*, 282, 1–19.
- Chabanon, E., Roizard, D., and Favre, E. (2011). Membrane contactors for post combustion carbon dioxide capture: Wetting resistance on long time scales. *Industrial & Engineering Chemistry Research*, 50, 8237–8244.
- Cookney, J., Mcleod, A., Mathioudakis, V., Ncube, P., Soares, A., Jefferson, B., and McAdam, E. J. (2016). Dissolved methane recovery from anaerobic effluents using hollow fibre membrane contactors. *Journal of Membrane Science*, 502, 141–150.
- Davey, C. J., Luqmani, B., Thomas, N., and McAdam, E. J. (2022). Transforming wastewater ammonia to carbon free energy: Integrating fuel cell technology with ammonia stripping for direct power production. *Separation and Purification Technology*, 289, 120755.
- de Haas, D., and Andrews, J. (2022). Nitrous oxide emissions from wastewater treatment - Revisiting the IPCC 2019 refinement guidelines. *Environmental Challenges*, 8, 100557.
- Department for Business Energy and Industrial Strategy. (2016). The Renewable Heat Incentive, A reformed and refocused scheme. https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/505132/Consultation_Stage_Impact_Assessment_-_The_RHI_-_a_reformed_and_refocussed_scheme.pdf (accessed 01/04/2023).
- Department for Business Energy and Industrial Strategy. (2021a). Build Back Greener: Net Zero Strategy. <https://www.gov.uk/government/publications/net-zero-strategy> (accessed 01/04/2023).
- Department for Business Energy and Industrial Strategy. (2021b). Future Support for Low Carbon Heat and the Green Gas Levy: government response to consultation. https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/970565/green-gas-levy-future-support-low-carbon-heat-govt-response.pdf (accessed 01/04/2023).

- Department for Business Energy and Industrial Strategy. (2022). Gas and electricity prices in the non-domestic sector. <https://www.gov.uk/government/statistical-data-sets/gas-and-electricity-prices-in-the-non-domestic-sector> (accessed 31/03/2023).
- Department for Transport. (2021). Targeting net zero - Next steps for the Renewable Transport Fuels Obligation. <https://www.gov.uk/government/consultations/amending-the-renewable-transport-fuels-obligation-rtfo-to-increase-carbon-savings-on-land-air-and-at-sea> (accessed 01/04/2023).
- EC (European Community). (2018). 2018/410 of 14th March 2018 amending Directive 2003/87/EC to enhance cost-effective emission reductions and low-carbon investments, and Decision (EU) 2015/1814. Official Journal of the European Union. <https://eur-lex.europa.eu/eli/dir/2003/87> (accessed 27/04/2023).
- EEC Council. (1991). 91/271/EEC of 21 May 1991 concerning urban waste-water treatment. Official Journal of the European Communities, 40–52. <http://eur-lex.europa.eu/legal-content/en/ALL/?uri=CELEX:31991L0271> (accessed 31/03/2023).
- Environment Agency. (2022). Treating, storing, and using carbon dioxide from anaerobic digestion: RPS 255. <https://www.gov.uk/government/publications/treating-storing-and-using-carbon-dioxide-from-anaerobic-digestion-rps-255> (accessed 01/04/2023).
- Environmental Audit Committee. (2018). UK Progress on Reducing Nitrate Pollution. House of Commons. <https://publications.parliament.uk/pa/cm201719/cmselect/cmenvaud/656/656.pdf> (accessed 24/04/2023).
- European Biogas Association. (2021). EBA Statistical Report. <https://www.europeanbiogas.eu/wp-content/uploads/2021/11/EBA-STATISTICAL-REPORT-2021-SHORT-VERSION.pdf> (accessed 24/04/2023).

- European Commission. (2019). A European Green Deal. https://commission.europa.eu/strategy-and-policy/priorities-2019-2024/european-green-deal_en (accessed 01/04/2023).
- Gopalakrishnan, K., Anderson, J., Carrio, L., Abraham, K., and Stinson, B. (2000). Design and operational considerations for ammonia removal from centrate by steam stripping. Proceedings of Water Environment Federation 2000, Anaheim, CA, USA.
- Grasham, O., Dupont, V., Camargo-Valero, M. A., García-Gutiérrez, P., and Cockerill, T. (2019). Combined ammonia recovery and solid oxide fuel cell use at wastewater treatment plants for energy and greenhouse gas emission improvements. *Applied Energy*, 240, 698–708.
- Grasham, O., Dupont, V., Cockerill, T., Camargo-Valero, M. A., and Twigg, M. V. (2020). Hydrogen: via reforming aqueous ammonia and biomethane co-products of wastewater treatment: environmental and economic sustainability. *Sustainable Energy and Fuels*, 4, 5835–5850.
- Guida, S., Van Peteghem, L., Luqmani, B., Sakarika, M., McLeod, A., McAdam, E. J., Jefferson, B., Rabaey, K., and Soares, A. (2022). Ammonia recovery from brines originating from a municipal wastewater ion exchange process and valorization of recovered nitrogen into microbial protein. *Chemical Engineering Journal*, 427, 130896.
- Guštin, S., and Marinšek-Logar, R. (2011). Effect of pH, temperature and air flow rate on the continuous ammonia stripping of the anaerobic digestion effluent. *Process Safety and Environmental Protection*, 89, 61–66.
- Han, Y., Agyeman, F., Green, H., and Tao, W. (2022). Stable, high-rate anaerobic digestion through vacuum stripping of digestate. *Bioresource Technology*, 343, 126133.
- Hewlett, S. G., Pugh, D. G., Valera-Medina, A., Giles, A., Runyon, J., Goktepe, B., and Bowen, P. J. (2020). Industrial wastewater as an enabler of green ammonia to power via gas turbine technology. Proceedings of the ASME Turbo Expo 2020: Turbomachinery Technical Conference and Exposition, London, UK.

- Hewlett, S. G., Valera-Medina, A., Pugh, D. G., and Bowen, P. J. (2019). Gas turbine co-firing of steelworks ammonia with coke oven gas or methane: A fundamental and cycle analysis. Proceedings of the ASME Turbo Expo 2019: Turbomachinery Technical Conference and Exposition, Phoenix, AZ, USA.
- Houlker, S. (2019). Scale up of hollow fibre membrane contactors for biogas upgrading. EngD thesis. Cranfield University.
- Houlker, S., Rutherford, T., Herron, D., Brookes, A., Moore, A., Vale, P., Pidou, M., and McAdam, E. (2021). Demonstrating commercial hollow fibre membrane contactor performance at industrial scale for biogas upgrading at a sewage treatment works. *Water (Switzerland)*, 13, 172.
- Huang, J., and Shang, C. (2006). Air Stripping. In L. K. Wang, Y. Hung, & N. K. Shamas (Eds.), *Advanced Physicochemical Treatment Processes* (1st ed., pp. 47–79). The Humana Press Inc., Totowa, NJ, USA.
- Huang, X., Guida, S., Jefferson, B., and Soares, A. (2020). Economic evaluation of ion-exchange processes for nutrient removal and recovery from municipal wastewater. *Npj Clean Water*, 3, 7.
- IEA Bioenergy. (2019). Task 37: Energy from Biogas Upgrading Plant List 2019. International Energy Agency. <https://task37.ieabioenergy.com/plant-lists/> (accessed 01/04/2023).
- Jiang, A. (2009). Ammonia recovery from digested dairy manure as nitrogen fertilizer. PhD thesis. Washington State University.
- Jilvero, H., Normann, F., Andersson, K., and Johnsson, F. (2012). Heat requirement for regeneration of aqueous ammonia in post-combustion carbon dioxide capture. *International Journal of Greenhouse Gas Control*, 11, 181–187.
- Kapoor, R., Subbarao, P. M. V., and Vijay, V. K. (2019). Integration of flash vessel in water scrubbing biogas upgrading system for maximum methane recovery. *Bioresource Technology Reports*, 7, 100251.
- Katehis, D., Diyamandoglu, V., and Fillos, J. (1998). Stripping and recovery of ammonia from centrate of anaerobically digested biosolids at elevated temperatures. *Water Environment Research*, 70, 231–240.

- Kim, E. J., Kim, H., and Lee, E. (2021). Influence of Ammonia Stripping Parameters on the Efficiency and Mass Transfer Rate of Ammonia Removal. *Applied Sciences*, 11, 441.
- Liu, H., Chan, C., Tontiwachwuthikul, P., and Idem, R. (2019). Analysis of CO₂ equilibrium solubility of seven tertiary amine solvents using thermodynamic and ANN models. *Fuel*, 249, 61–72.
- Mackinnon, I. D. R., Barr, K., Miller, E., Hunter, S., and Pinel, T. (2003). Nutrient removal from wastewaters using high performance materials. *Water Science and Technology*, 47, 101–107.
- McBean, E. A. (2008). Siloxanes in biogases from landfills and wastewater digesters. *Canadian Journal of Civil Engineering*, 35, 431–436.
- McDonald, M. A., Salami, H., Harris, P. R., Lagerman, C. E., Yang, X., Bommarius, A. S., Grover, M. A., and Rousseau, R. W. (2021). Reactive crystallization: A review. *Reaction Chemistry and Engineering*, 6, 364–400.
- McLeod, A., Buzatu, P., Autin, O., Jefferson, B., and McAdam, E. (2015). Controlling shell-side crystal nucleation in a gas-liquid membrane contactor for simultaneous ammonium bicarbonate recovery and biogas upgrading. *Journal of Membrane Science*, 473, 146–156.
- Moore, A., and Auty, D. (2013). Digestion and Greenhouses – Synergistic Resource Recovery. 18th European Biosolids & Organic Resources Conference & Exhibition, Manchester, UK.
- Morgan, E. R. (2013). Techno-economic feasibility study of ammonia plants powered by offshore wind. PhD thesis. University of Massachusetts Amherst.
- Nayak-Luke, R., Bañares-Alcántara, R., and Wilkinson, I. (2018). “green” Ammonia: Impact of Renewable Energy Intermittency on Plant Sizing and Levelized Cost of Ammonia. *Industrial and Engineering Chemistry Research*, 57, 14607–14616.
- Ndam, N. E. (2017). Treatment technologies for recycle liquors: Nutrient removal, mass balances, and potential recovery at wastewater treatment plants. PhD thesis. Newcastle University.
- Northern Gas Networks. (2020). Biomethane: a producer’s handbook. <https://biomethane.northerngasnetworks.co.uk/wp->

- content/uploads/2020/07/NGN_BiomethaneHandbook_0420_St04A.pdf
(accessed 31/03/2023).
- O'Farrell, T. P., Bishop, D. F., and Cassel, A. F. (1973). Nitrogen Removal by Ammonia Stripping. US EPA.
- Organics Group. (2020). Removal, Recovery and Re-use of Ammoniacal Nitrogen from Wastewater for Power Generation. <https://organicsgroup.com/recovery-and-re-use-of-of-ammonia/> (accessed 31/03/2023).
- Pavicic, J., Mavar, K. N., Brkic, V., and Simon, K. (2022). Biogas and Biomethane Production and Usage: Technology Development, Advantages and Challenges in Europe. *Energies*, 15, 2940.
- Ramalingam, K., Fillos, J., Mehrdad, M., Halim, D., Deur, A., and Orpianesi, M. (2017). Side stream treatment nitrogen removal: Alternatives for New York city. *Water Practice and Technology*, 12, 179–185.
- RVT. (2015). Ammonia recovery Removal from liquids and gases. http://www.rvtpe.net/wp-content/uploads/prospekte/RVT_Ammonia_Recovery_120529.pdf (accessed 31/03/2023).
- Saadabadi, S. A., Patel, H., Woudstra, T., and Aravind, P. V. (2020). Thermodynamic Analysis of Solid Oxide Fuel Cell Integrated System Fuelled by Ammonia from Struvite Precipitation Process. *Fuel Cells*, 20(2), 143–157.
- Stoeckl, B., Preininger, M., Subotić, V., Megel, S., Folgner, C., and Hochenauer, C. (2020). Towards a wastewater energy recovery system: The utilization of humidified ammonia by a solid oxide fuel cell stack. *Journal of Power Sources*, 450, 227608.
- Teichgraber, B., and Stein, A. (1994). Nitrogen elimination from sludge treatment reject water – comparison of the steam-stripping and denitrification processes. *Water Science and Technology*, 30, 41–51.
- The Water Research Foundation. (2019). Deammonification. <https://www.waterrf.org/sites/default/files/file/2021-07/Deammonification.pdf> (accessed 21/04/2023).

- Thornton, A., Pearce, P., and Parsons, S. A. (2007). Ammonium removal from digested sludge liquors using ion exchange. *Water Research*, 41, 433–439.
- Tian, X., Gao, Z., Feng, H., Zhang, Z., Li, J., and Wang, A. (2019). Efficient nutrient recovery/removal from real source-separated urine by coupling vacuum thermal stripping with activated sludge processes. *Journal of Cleaner Production*, 220, 965–973.
- Ulrich, J., and Strege, C. (2002). Some aspects of the importance of metastable zone width and nucleation in industrial crystallizers. *Journal of Crystal Growth*, 237–239, 2130–2135.
- van Linden, N., Spanjers, H., and van Lier, J. B. (2022). Fuelling a solid oxide fuel cell with ammonia recovered from water by vacuum membrane stripping. *Chemical Engineering Journal*, 428, 131081.
- Venegas, T., Qu, M., Nawaz, K., and Wang, L. (2021). Critical review and future prospects for desiccant coated heat exchangers: Materials, design, and manufacturing. *Renewable and Sustainable Energy Reviews*, 151, 111531.
- Villeneuve, K., Roizard, D., Remigy, J. C., Iacono, M., and Rode, S. (2018). CO₂ capture by aqueous ammonia with hollow fiber membrane contactors: Gas phase reactions and performance stability. *Separation and Purification Technology*, 199, 189–197.
- Wickramanayake, G. B., Evers, D. P., Kittel, J. A., and Gavaskar, A. (1992). Bench-Scale Evaluation of Ammonia Removal from Wastewater by Steam Stripping. US EPA.
- Xu, L., Dong, F., Yang, J., Liu, W., Zhu, L., He, Q., Wang, X., Li, H., and Wang, X. (2022). Electricity generation and acid and alkaline recovery from pickled waters/wastewaters through anaerobic digestion, bipolar membrane electrodialysis and solid oxide fuel cell hybrid system. *Energy Conversion and Management*, 251, 114973.
- Xu, L., Dong, F., Zhuang, H., He, W., Ni, M., Feng, S. P., and Lee, P. H. (2017). Energy upcycle in anaerobic treatment: Ammonium, methane, and carbon dioxide reformation through a hybrid electrodeionization–solid oxide fuel cell system. *Energy Conversion and Management*, 140, 157–166.

- Zeng, L., Mangan, C., and Li, X. (2006). Ammonia recovery from anaerobically digested cattle manure by steam stripping. *Water Science and Technology*, 54, 137–145.
- Zhang, C., Geng, X., Wang, H., Zhou, L., and Wang, B. (2017). Emission factor for atmospheric ammonia from a typical municipal wastewater treatment plant in South China. *Environmental Pollution*, 220, 963–970.
- Zhao, D., Dong, S., Bai, L., Li, D., and Liu, H. (2023). Experimental method and mathematical method for VLE plots in 3DMA1P-CO₂-H₂O system. *Separation and Purification Technology*, 307, 122800.

8 Conclusions and further work

8.1 Conclusions

This thesis has developed reactive biogas upgrading and crystallisation in hollow fibre membrane contactors (HFMC) using wastewater-derived ammonia solvents as a disruptive, circular economy solution to support the delivery of a decarbonised water sector. The following conclusions can be drawn from this thesis:

1. An expanded two-phase region for selective ammonia-water separation was identified during vacuum stripping of ammonia solutions analogous to wastewater ($x_{\text{NH}_3} < 0.002$). Exploitation of this region supports low energy recovery of high purity gas-phase ammonia and presents an energetically favourable solution for sidestream nitrogen removal which could enable utilities to meet stringent discharge limits whilst recovering sustainable ammonia (**Objective 1**).
2. During vacuum thermal stripping, rapid desorption of dissolved CO_2 raised the pH of concentrated wastewater and facilitated continuous ammonia recovery. This could enable chemical-free stripping in a single process unit, lowering the capital and operating costs whilst improving the sustainability criteria for gas-phase ammonia recovery (**Objective 1**).
3. Conducting CO_2 absorption at low temperatures will improve the resilience of microporous membranes by suppressing solvent vapour pressure and limiting pore wetting by condensation. In a positive synergy, solvent chilling will intensify mass transfer due to enhanced CO_2 solubility. Consequently, technologically mature and low-cost microporous membranes could offer superior mass transfer characteristics for biogas upgrading than nonporous membranes, favouring lower membrane area, capital cost and simpler translation to industrial scales (**Objective 2**).
4. Pressurisation during biogas upgrading in HFMC can simultaneously enhance the driving force for CO_2 mass transfer and minimise gas-phase resistance. This will intensify CO_2 flux, raise biomethane quality, and lower atmospheric methane losses. Translation to comparable pressures employed by commercial absorption columns (7-10 bar) could therefore lower membrane

area, path length and favour commercial competitiveness for HFMC systems (**Objective 2**).

5. The mechanism underpinning gas-phase reactions between $\text{CO}_2\text{-NH}_3\text{-H}_2\text{O}$ in HFMC was related to an established model for ternary systems. Consequently, suppression of ammonia volatility and pressurisation of the feed gas could maintain the CO_2 fraction in the gas-phase above the thermodynamic limit for liquid and solid formation. These conditions will promote stable mass transfer during reactive biogas upgrading, and could be directly translated for the application of emerging ternary solvents for CO_2 capture in HFMC (**Objective 3**).
6. Gas pressurisation during reactive CO_2 absorption in HFMC enhanced the driving force for mass transfer and intensified flux whilst simultaneously limiting ammonia 'slip' in to the gas-phase. Pressurisation therefore presents a synergistic strategy to lower membrane area and capital cost, whilst avoiding fugitive ammonia emissions and solvent losses (**Objective 4**).
7. Crystallisation of ammonium bicarbonate in HFMC was demonstrated under pressurised conditions up to 2.5 bar. Absorption was reaction limited within the solvent boundary layer, and nucleation kinetics were consequently independent of pressure. This could support simplified process control for mediating continuous crystallisation and solids recovery, to lower the energy penalty for solvent regeneration which is the critical barrier for industrial adoption of post-combustion CO_2 capture (**Objective 4**).
8. Selective, low energy vacuum thermal stripping for gas-phase ammonia recovery (20-25%wt) was translated to a gas-liquid contacting column and demonstrated comparable mass transfer coefficients to commercially established air stripping processes. High-level costing analyses indicated that investment in selective stripping for anaerobic digester centrate could represent a cost saving (-300 EUR tNH_3^{-1}) over a 20-year economic lifetime relative to biological nitrogen removal in activated sludge processes (**Objective 5**).
9. A techno-economic analysis identified that value from recovered gas-phase ammonia (20-25%wt) could be maximised in a centralised wastewater

treatment works through its capture and application as an aqueous solvent (3-5%wt) in biogas upgrading. This could generate revenue from exportation of biomethane (1.2 million EUR y⁻¹) and biogenic CO₂ (0.6 million EUR y⁻¹), and enable the subsequent recovery of purified ammonia for zero carbon energy generation in gas turbines or solid oxide fuel cells (0.08-0.14 million EUR y⁻¹) to support a decarbonised water sector (**Objective 5**).

8.2 Further work

Based upon the outcomes of this thesis, the following opportunities have been identified for further research:

1. This thesis identified an expanded two-phase region for ammonia-water in dilute solutions ($x_{\text{NH}_3} < 0.002$) at 0.25 bar, which supported low energy, high purity ammonia recovery. Further exploration of the two-phase region across different pressures and ammonia concentrations is recommended to characterise the operating envelope for selective ammonia recovery and identify optimal operational conditions.
2. It was proposed that ammonia recovered from wastewater could be utilised directly for energy generation (i.e., gas turbines and electrochemical fuel cells). Further work could focus on the development and demonstration of an integrated flowsheet for selective ammonia recovery and power generation. A particular focus could be on the co-transportation of dissolved compounds in wastewater during stripping, and their impact on the performance and lifespan of energy generation technologies.
3. In this thesis, a commercial nonporous HFMC exhibited high mass transfer resistance at low temperatures due to limited CO₂ permeability across the 1 micron dense layer. An exploration of emerging nonporous HFMC with ultrathin dense layers (~0.1 micron) is recommended, since these could offer both resilience and improved mass transfer characteristics for biogas upgrading.
4. Countercurrent ammonia 'slip' across microporous HFMC during CO₂ absorption was causally linked to the initiation of gas-phase reactions. Further work could explore the application of nonporous HFMC as a mitigation

strategy, since the selective dense layer could limit ammonia transport and therefore maintain the $\text{CO}_2\text{-NH}_3\text{-H}_2\text{O}$ system below the critical threshold required for reactions to occur.

5. Reactive CO_2 absorption in pressurised HFMC was explored under fixed hydrodynamic conditions in this thesis. Lowering the solvent velocity to reduce the Graetz number will extend the reaction zone in the boundary layer, and could facilitate greater mass transfer enhancement under pressure. Future work could therefore explore manipulation of hydrodynamic conditions alongside pressurisation to maximise process intensification.
6. In this thesis, membrane facilitated crystallisation was conducted using a synthetic biogas feed. Further work is necessary to explore the impact of trace contaminants (e.g., H_2S and siloxanes) within real biogas on the crystallising reaction and the chemical composition of the ammonium bicarbonate product.
7. An innovative, circular economy solution for biogas upgrading has been developed in this thesis. To advance this technology towards commercialisation, the integration of selective ammonia stripping for solvent recovery and biogas upgrading in HFMC is necessary to support pilot trials and process optimisation in a wastewater treatment facility.