



Overview of Absorbents used in Gas Liquid Membrane Contactor for CO₂ absorption

Nihmiya Abdul Rahim

Faculty of Technology, University of Sri Jayewardenepura
nihmiya@sjp.ac.lk

Received: 01 May 2021; Revised: 15 May 2021; Accepted: 25 May 2021; Available online: 10 July 2021

Abstract: Removal of CO₂ from gas streams is one of the essential gas separation processes in many industrial areas such as natural gas processing, flue gas treatment, biogas purification, etc. The separation of CO₂ by gas-liquid membrane contactor modules are promising alternative to conventional techniques such as column absorption. In membrane contactor absorption processes the porous hydrophobic membrane acts as a fixed interface between the gas and the liquid phase without dispersing one phase into another. Proper choice of absorption liquids plays a vital role in determining the performance of gas-liquid membrane contactors for CO₂ separation. Alkanolamines are the widely used chemical absorbents for CO₂ capture. Although CO₂ absorption by alkanolamines is a very matured technology and has been commercialized for many decades it has many draw backs such as low CO₂ loading capacity, high equipment corrosion rate, amine degradation, high energy consumption during high temperature absorbent regeneration and large equipment size. Amino acid salts are attractive solvents due to their unique properties over other solvents such as low environmental impact, high biodegradability, negligible volatility, high resistance to oxidative degradation, viscosities, and surface tensions similar to water. Recently ammonia is identified as an emerging chemical absorbent due to its lower energy demand for regeneration. The CO₂ absorption capacity of Ammonia is comparable to amine CO₂ absorption capacity even though ammonia is cheaper than alkanolamines. In addition ammonia is not corrosive and does not suffer from thermal or oxidative degradation like amines. On the contrary, reusable products can be formed. However, the main operation problem, ammonia slip from the aqueous ammonia solution, limit the widespread use of this hopeful absorption liquid.

Keywords: absorption liquid, carbon dioxide, gas liquid membrane contactor

1 INTRODUCTION

Carbon dioxide is believed to be the main gaseous contaminant in the atmosphere. The emission of greenhouse gases such as CO₂ to the environment causes climatic changes. The greenhouse gas is believed to increase the temperature of the earth; accompanying this temperature increase is extreme weather and a projected sea level rise, which will in turn, be problematic for coastal cities. Therefore, emission of this gas to the atmosphere should be low, necessitating its removal. The traditional method for CO₂ separation is amine scrubbing. Although high product yields and purities can be obtained, the disadvantage of this method is its high energy consumption in combination with high liquid losses due to evaporation of the solvent in the stripper [1], [2]. In addition, as liquid and gas streams cannot be controlled independently, the occurrence of flooding, foaming, channeling, and entrainment of the absorption liquid also limits the process [3].

Membrane technology is a promising method to replace conventional absorption technology. It has high energy efficiency, easy to scale up because of its modular design, and has a high area-to-volume ratio [4]. A limitation can be found in the permeability-selectivity tradeoff relation.

A Gas-Liquid Membrane Contactor (GLMC) combines the advantages of membrane technology with those of absorption liquid [4-12]. As a hybrid approach of conventional chemical absorption/stripping technology and membrane gas separation, GLMC has been considered as one of the possible alternatives to conventional techniques for CO₂ capture. In a GLMC, the microporous membrane acts as an interface between the feed gas and the absorption liquid without dispersing one phase into another. Hence the operational limitations that take place in conventional absorption technology such as flooding, foaming, channeling, and entrainment of the liquid can be resolved. Further, the employment of microporous membrane elucidates the permeability-selectivity tradeoff relation drawback challenged in membrane technology.

In the GLMC, gas and liquid flow on the different sides of the microporous membrane and membrane acts only as a barrier between two phases without dispersing one phase to another. In general, when hydrophobic microporous membranes are used in membrane contactors, the gas-liquid interface is immobilized at the opening of the pores of the microporous membrane by careful control of the pressure difference between the two phases [13]. For applications in gas-liquid absorption/desorption, the driving force is based on the concentration gradient. The gas molecules to be separated diffuse from the concentrated phase to the gas-liquid interface via the membranes' pores, then contacts the diluted phase on the other side. For instance, in the case of CO₂/CH₄ separation, as shown in Fig.1, CO₂ molecules diffuse from the feed gas side through the membrane and are then absorbed in the selective absorption liquid.

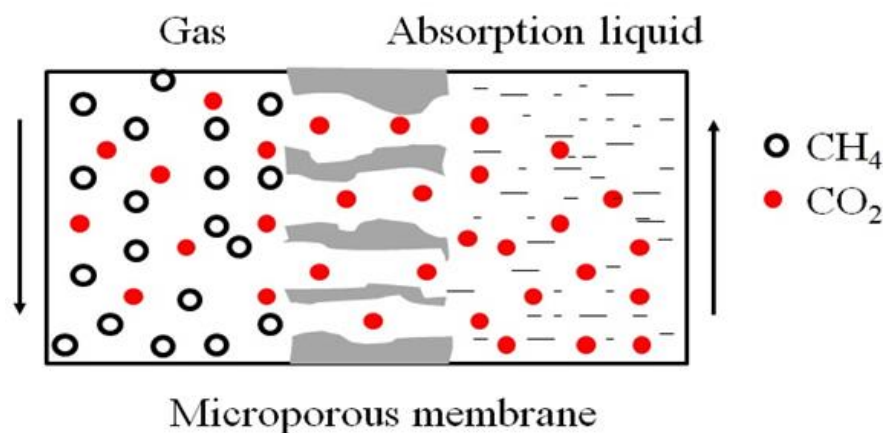


Fig. 1. CO₂ molecule transport through microporous membrane

In GLMC, the mass transfer process consists three steps in series: the transfer from one phase to the membrane surface, transfer within membrane pores and transfer from on other phase interface to the bulk. Fig.2 (a) shows the concentration profiles that are formed when species “i” is transferred from the gas phase to the liquid and if hydrophobic membranes are used. If it is transferred from the liquid to the gas the concentration profile is that shown in Fig.2 (b). In order to describe this mass transfer process between two phases through porous membrane a resistance in series model based on film theory can be used[14]. The resistances to the mass transfer encountered in both cases are those offered by the boundary layers and the membrane and can be drawn, as in Fig.3, by considering an electrical analogy [15], [16].

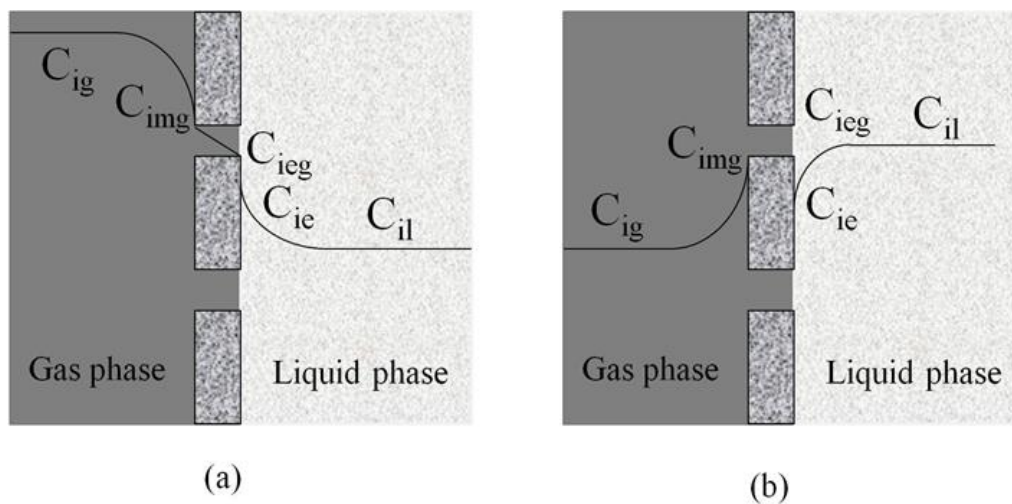


Fig. 2. Concentration profiles formed when species “i” is transferred from gas phase to liquid phase through hydrophobic membrane

As shown in the Fig.3 three resistances exist in the resistance in series model:

- Gas film resistance
- Liquid film resistance
- Membrane resistance

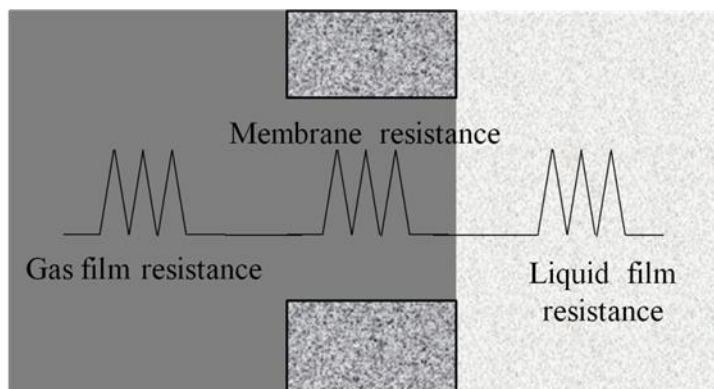


Fig. 3. Resistance in series model

A general expression used to calculate the flux of the species through the membrane is:

$$J = K_{ov}(C_1 - C_2) \quad (1)$$

with

$$\frac{1}{K_{ov}} = \frac{1}{k_G} \frac{d_o}{d_i} + \frac{1}{k_m} + \frac{1}{mk_L} \quad (2)$$

hence

$$K = f(k_G, k_m, k_L, m, E) \quad (3)$$

where J is flux. C_1 and C_2 are concentration of CO_2 in the two phases. K_{ov} is overall mass transfer coefficient. k_G , k_m and k_L are individual mass transfer coefficient of gas phase, membrane and liquid phase respectively. m is physical solubility and E is enhancement factor if any chemical reaction present. The correlations used to calculate these individual mass transfer coefficients are summarized by Zhang et al[17].

Hence overall mass transfer coefficient in GLMC, be determined by three individual mass transfer coefficients, which in turn be influenced by many factors[14]. Firstly, membrane mass transfer coefficient is influenced by many membrane inherent properties such as membrane pore size, porosity and tortuosity, which on the other hand are controlled by adopted fabrication technology. Further membrane mass transfer coefficient also subject to whether the membrane's pores are gas-filled (ideal non-wetted mode) or liquid-filled (non-preferred wetted mode). Next, the gas and liquid mass transfer coefficients as well depend on GLMC module configurations and adopted process parameters during the separation process, such as gas and liquid flow rates, temperature, etc. So detailed understanding of these properties is vitally important for a complete understanding of GLMC.

The GLMC for CO_2 capture has attracted great research interest over the past decade of many researchers. Although the GLMC for CO_2 separation has been extensively studied and proven to be a promising alternative for CO_2 capture, there is still a long way ahead before this technique to completely replace the existing CO_2 separation technology. Because yet there are some inherent problems in GLMC technology, and these problems have to be resolved successfully to completely commercialize the technology.

Firstly, as the membrane itself represents the core of the GLMC process, polymer material, method of fabrication, and fabricating conditions have to be optimized to improve the ultimate membrane morphology and performance. In spite of vital developments still, researchers are making efforts to prepare membranes that provide outstanding performance in GLMC applications. Particularly several researches are going on to fabricate membranes with better hydrophobicity. Further absorption liquid also plays an important role in GLMC separation performance. Generally used absorption liquids such as alkanolamines are inherently problematic due to their volatility, degradability, and high energy consumption for regeneration. Specifically, amine solutions, due to their low surface tension can easily penetrate inside the membrane pores and cause the membrane wetting slowly with time[18], [19]. So absorption liquids with more favorable characteristics for CO_2 capture are thus being requested.

2 ABSORPTION LIQUIDS FOR CO_2 ABSORPTION IN GLMC

In GLMC for CO_2 separation the selectivity is provided by the absorbent liquid rather than the porous membrane. Therefore proper choice of absorption liquids also plays a vital role in determining the performance of GLMC for CO_2 separation. The selection of absorption liquid should be based on the following criteria:

- a) High absorption ability of CO_2 : When in contact with the liquid at the gas liquid interface in the membrane pores, CO_2 absorb into the absorption liquid either physically or chemically. In the case

of physical absorption the absorption liquid should have high CO₂ solubility, whereas in the case of chemical absorption the absorption liquid should have high reactivity with CO₂. In both cases higher the CO₂ absorption rate, higher the CO₂ mass flux. So the resistance of the liquid phase can be suppressed[17], [20], [21].

- b) High surface tension: Ideally the absorbent liquid should be unable to wet the membrane. For that absorbent liquid should have high surface tension. Although the membranes used for CO₂ separation in membrane contactors are usually hydrophobic, liquids with low surface tension have a greater tendency to seep into the membrane pores and wet the membrane. In a wetted membrane the resistance from the stagnant liquid layer in the pores is much and it determines the overall mass transfer resistance[22].
- c) High chemical compatibility: The absorbent liquid should not react with membrane, which leads to changes in membrane morphology and reduction of break through pressure. Chemical compatibility is an important factor that decides the long term stability of the membrane module[17], [20].
- d) High thermal stability: For certain absorbent liquids the chemical reaction with CO₂ can be enhanced by increasing the liquid temperature. Also heating the liquid to higher temperatures is the commonly adopted regeneration method. So the absorbent liquids should possess good thermal stability and be chemically stable within a large range of temperature, so that its thermal degradation can be avoided.
- e) Low vapor pressure: In order to minimize the solvent losses in high temperature applications specifically during regeneration process the solvent should be less volatile. Further if the solvent is volatile, its vapor can fill the membrane pores easily and even penetrate through the membrane into the gas phase. Therefore, solvent with low vapor pressure are preferred.
- f) Low viscosity: Viscosity of the solution increases the liquid side mass transfer coefficient in GLMC applications. Further pumping energy is high to pump the viscous liquid. So ideally the absorbent liquid should be less viscous.
- g) Easiness of regeneration: For the absorbent liquid to be recycled it can be easily regenerated after the CO₂ absorption without deteriorating its fresh liquid features.
- h) Environmental safety: The purpose of removing CO₂ from process gas streams by absorbing in to the absorption liquids is mitigating the harsh environment effect caused by CO₂. This ultimate goal should not be suppressed by using adverse chemical solvents that cause harm to the environment. Hence, the selected absorption liquid should be environmental friendly. The absorption liquid itself should not have any environmental or toxicity issue. Also it should not form any toxic degradation products after CO₂ absorption.

Conventionally used absorbent liquid for CO₂ absorption can be either physical absorbent or chemical absorbent.

2.1 Physical absorbent

The operation of physical absorption is based on Henry's law. Typically in the physical absorption process, CO₂ is absorbed under high pressure and low temperature and desorbed at reduced pressure and

increased temperature. Water has been used as a physical solvent in many CO₂ absorption studies. There are many existing commercial processes such as Selexol Process, Rectisol Process, Purisol process, Morphysorb Process and Fluor process are using chemicals as physical absorbents to absorb CO₂ from process gas streams[23], [24]. The absorbents are dimethyl ether or propylene glycol for Selexol Process, methanol for Rectisol Process, N-methylpyrrolidone for Purisol Process, morpholine for Morphysorb Process and propylene carbonate for Fluor Process. The major advantage of using the physical absorbent is that it can be regenerated easily. However, the physical absorbent in GLMC have been studied by only a few researchers[25], [26]. Because of its low CO₂ absorption flux and removal efficiency, the physical absorbent is not an ideal choice.

2.2 Chemical absorbent

The operation of chemical absorption is based on the chemical reaction between the absorbent liquid and CO₂. CO₂ is absorbed into the liquid by reacting with the chemical species in the liquid and is commonly desorbed by increasing the liquid temperature to a higher value. Alkanolamines are the widely used chemical absorbents for CO₂ capture[17], [20], [24], [27], [28]. Although CO₂ absorption by alkanolamines is a very matured technology and has been commercialized for many decades, it has many drawbacks such as low CO₂ loading capacity, high equipment corrosion rate, amine degradation, high energy consumption during high temperature absorbent regeneration and large equipment size[20], [24]. Therefore, several researches are going on with the objective of finding effective and efficient absorbent liquid for CO₂ capture.

Various types of physical solvents have been studied as absorption in liquid in GLMC application[29]. Due to the enhanced flux and high removal efficiency chemical absorbents rather than physical solvents are preferred in GLMCs. Conventionally used alkanolamines have been widely studied as an absorbent liquid in GLMC[17], [20], [28]. Other solvents like NaOH, K₂CO₃, amino acids, ammonia and ionic liquids also attract special interest, and currently, these liquids are widely studied by researchers as a promising alternative to conventional absorption liquids[24]. Subsequent paragraphs describe the chemistry of mostly used absorption liquids and compare the pros and cons of these absorption liquids in GLMC applications.

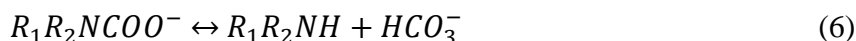
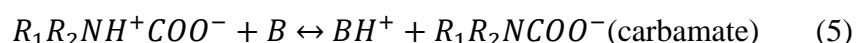
2.2.1 Alkanolamines

Alkanolamines are chemical compounds that contain both hydroxyl (-OH) and amino (-NH₂, -NHR, and -NR₂) functional groups on an alkane backbone. CO₂ absorption into alkanolamine solutions occurs mainly as a result of the amine group of the alkanolamine molecule. The chemical structure of the specific amine determines how it's react with CO₂ and its CO₂ absorption capability. Absorption using alkanolamines is a common industrial method to remove CO₂ from process gases. Molecular structures of commonly used alkanolamines are given in Fig4. Different types of amine have different reaction mechanism and kinetics. Tertiary amines differ from primary, secondary amines and sterically hindered amines differ from non-sterically hindered amines.

Chemical reactions of CO₂ with aqueous alkanolamine solutions

The reaction between CO₂ and amines are highly exothermic acid base reaction. The amino group in the alkanolamines provides the basicity (while the -OH group results in increased solubility of alkanolamine in

water) to its aqueous solutions. So these alkanolamines due to its basicity readily react with acidic CO₂. The reaction of CO₂ with primary, secondary and sterically hindered amines is mostly described by zwitterion mechanism, whereas the reaction of CO₂ with tertiary amines is described by the base-catalyzed hydration mechanism[30]. The chemical reaction involved in CO₂ absorption by primary, secondary and hindered alkanolamine are [31]:



where B is any base, which can be amine, water or OH⁻¹ in an aqueous solution.

Primary amines



Secondary Amines



Tertiary Amines



Hindered Amines



Fig. 4. Molecular structures of commonly used alkanolamines

Commonly it is believed the reaction between CO₂ and primary, secondary or hindered amine is first order in amine and first order in CO₂. According to the steady-state principle to the intermediate zwitterion, the rate of reaction of CO₂ in the aqueous solutions can be expressed as[31], [32]:

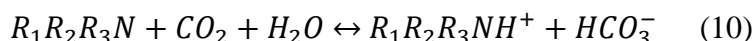
$$r = \frac{k_1(CO_2)(R_1NH_2)}{1 + \frac{k_{-1}}{k_B(B)}} \quad (8)$$

where k_1 and k_{-1} are respectively the forward and backward reaction rate constants for reaction (4). k_B is the backward reaction rate constants for reaction (5). After some modifications and assumptions such as the amine concentration remain constant for a particular case, the reaction equation (8) has been simplified further to have single constant k_{app} and the following pseudo-first order rate expression results[32].

$$r_{CO_2} = k_{app}([CO_2] - [CO_2]_e) \quad (9)$$

where $[CO_2]_e$ is the concentration of molecular CO_2 that is in equilibrium with the other ionic and non-ionic species present in the solution. The significant of reaction equation 9 is, it can be applied to both absorption and desorption.

The chemical reaction involved in tertiary alkanolamine is:



The rate expression for reaction (10) can be written as:

$$r_{CO_2} = -k_3[R_1R_2R_3N][CO_2] + \frac{k_3}{K_3}[R_1R_2R_3NH^+][HCO_3^-] \quad (11)$$

where k_3 is the reaction rate constant of reaction (10). K_3 is equilibrium reaction rate constant of reaction (10).

After some modifications and assumptions such as the forward reaction is the dominant one and that the amine concentration does not change appreciably during one particular process reaction equation (10) can be simplified as Equation (8)[32].

It should be noted the reaction of primary secondary and hindered amine with CO_2 form carbamate whereas the reaction of a ternary amine with CO_2 form bicarbonate. Comparing to carbamate the bicarbonate dissociates easily[24]. Subsequently the CO_2 absortion with ternary amines are more energy intensive than the CO_2 absortion with primary amines in terms of solvent regeneration. Further from reaction equation (6), it can be seen that carbamate can be transformed into free amine molecules for further reaction with CO_2 . The stability of the carbamate determines the enthalpy of dissociation for free amine release in reaction equation (5)[24], [32]. Steric character of amines reduces the stability of the formed carbamate. Therefore strictly hindered amines such as AMP can be regenerated easily for further CO_2 absortion.

Commonly used alkanolamines for CO_2 absorption

The alkanolamine most studied for CO_2 absorption is MEA. The advantage of MEA is its fast reaction with CO_2 and favored complete removal of CO_2 from process gas streams. The reactivity of amines to CO_2 follows the order primary, secondary and ternary amines, for example, the reaction constants with CO_2 are 7,000, 1,200 and $3.5 \text{ m}^3\text{s}^{-1}\text{kmol}^{-1}$ for MEA, DEA and MDEA at 25°C , respectively[24]. The presence of

hydroxyl group enables MEA to readily dissolve into polar solvents such as water and commonly 20 to 30 %w/w MEA solutions are used in industrial applications. Generally, the concentration of MEA in the solution is limited to 30 wt% due to problems with degradation products causing corrosion of the equipment[33]. The reaction of CO₂ with MEA leads to the formation of stable carbamate; thus to regenerate the MEA solution it has to be heated up to 120 °C and needs a heat load of 165 kJ per mole of CO₂. Up to 80% of the total cost of absorption/desorption can be attributed to the regeneration process even with the effective integration of waste heat[34].

Hence tertiary amines such as MDEA, which absorb CO₂ by bicarbonate formation have been considered by several researchers[24], [35]. Although they have lower heat of absorption, the rate of absorption is slow compared to primary and secondary amines. Consequently, to overcome this problematic trade- off between capture rate and energy consumption during regeneration hindered amines and uses of blends of different classes of amines are being explored. Sterically hindered amines such as AMP are chemical compounds containing an amine functional group surrounded by a crowded steric environment. Due to this molecular structure of sterical hindering the carbamate formed by CO₂ absorption is less stable. Generally, the introduction of this type of steric hindrance to the amine group has been found to increase the CO₂ solubility and lower the heat of absorption[24]. So sterically hindered amines have been considered as a promising option for CO₂ capture by several researchers.

The idea of blended amines are to combine an amine presenting a low heat of absorption with a fast-reacting solvent[24]. Most formulations of the blended amines are tertiary amine-based. MDEA is gaining recognition as the key component of the blended amines because of its low energy requirements for regeneration and comparable CO₂ solubility[35]. An addition of a relatively small amount of a primary amine such as MEA or secondary amine such as DEA into the MDEA solution enhances the rate of capturing while maintaining the advantages of MDEA[35], [36]. The fast reacting amine in this process is often called a promoter. Piperazine (PZ), a cyclic diamine which has been also widely used as the promoter for CO₂ capture because of its rapid formation of carbamate with CO₂[24]. As being a great CO₂ capture promoter, PZ have been studied by several researchers[37]–[39].

Numerous alkanolamine based solvents are presently being studied as absorbent liquid in GLMC applications. However, alkanolamines are inherently problematic, due to their volatility, degradability, and high energy consumption for regeneration[40]. Specifically amine solutions due its low surface tension, can easily penetrate inside the membrane pores and cause the membrane wetting slowly with time[18], [19]. So absorption liquids with more favorable characteristics for CO₂ capture are thus being requested.

2.2.2 Amino Acid Salts

Aqueous alkaline salts of amino acids are promising alternatives among various novel solvents that have been investigated with the objective of achieving reduced energy consumption for solvent regeneration and eliminating the operational difficulties encountered in alkanolamines based CO₂ removal systems[33], [41]–[45]. CO₂ absorption using amino acids is a biomimetic approach to CO₂ captures, due to its similarity to CO₂ binding by proteins such as hemoglobin[46]. Amino acid salts (AAS) are attractive solvents due to their unique properties over other solvents such as low environmental impact, high biodegradability, negligible volatility, high resistance to oxidative degradation, viscosities and surface tensions similar to water[18], [19], [41]–[43], [47]. Further AAS shows better stripping performance compared to

conventional amines[48], [49]. These are the ideal properties needed by membrane contactor absorption liquid. Therefore, interest has grown in the performance of different AAS such as sodium, potassium and lithium salt of sarcosine, glycine, alanine, taurine and proline and the CO₂ absorption characteristics for common amino acids salts are under extensive investigation. Until today AAS commercially used for post combustion CO₂ capture and patented processes using amino acids and their alkaline salts in post-combustion capture are summarized elsewhere[50]. Because of its promising characteristics AAS have drawn attention in recent years at both the academic and commercial level for natural gas sweetening in GLMC.

Amino acids are amphiprotic species that contain at least one acidic carboxyl or sulphonyl group and one basic amino group attached to the α- carbon (HOOC-CHR-NH₂)[50]. The chemical variations of the amino acids come from the differences in side chain R, which is an organic substituent also attached to the α carbon. Depend on structure of side chain R it can be primary, secondary or hindered amino acid.

Amino acids present as zwitterions (form II in Reaction (12)) in an aqueous solution. To react with CO₂ it should have the form III in Reaction (12). This deprotonation is favored by adding strong base which fully shifts the equilibrium toward form III in Reaction (12). The reaction scheme between AAS and CO₂ is given in Fig. 5. Since amino acids have the same amine functionality as alkanolamines, AAS solutions have something like same reaction kinetics and mechanism for CO₂ absorption as described for alkanolamines.

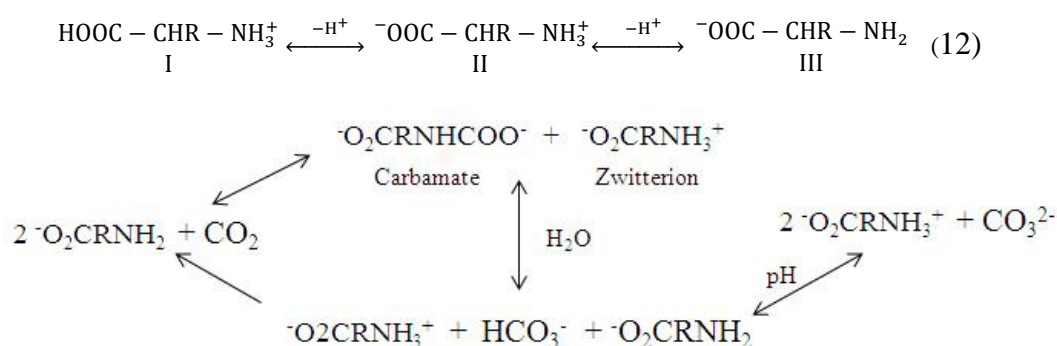


Fig. 5. Reaction scheme for CO₂ absorption in aqueous amino acid salt solution

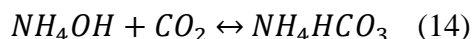
The new proposed method to increase energy efficiency of CO₂ separation process by absorption liquid is enhanced CO₂ desorption (based on pH-shift). Which contribute significantly to reduction of regeneration energy[38], [43]. The pH change decreases the CO₂ solubility of the solvent and emits CO₂ into the gas phase from the absorbent liquid. Also lower pH stimulates the carbamate hydrolysis to zwitterion species. Altogether lower pH shifts the CO₂ reaction equilibrium towards the release of CO₂ (Fig.5). Several methods used by researchers in order to alter the absorbent liquid pH. It is simple to change the amino acid salt solution pH by using asymmetric solutions of amino acid and alkali salt (i.e. solutions containing different molar amounts of amino acid and base).

The main negative aspects of these AAS are the formation of a solid product when absorbing CO₂, which happens especially for solutions at high amino acid salt concentration and at high liquid CO₂ loading. The formation of solids poses challenges such possible plugging and fouling of the gas-liquid membrane contactors and increase mass transfer resistance in long term operation. So these AAS solutions have to be used with care below precipitation regime. Although being more expensive than alkanolamines,

a number of advantages make amino acid salt solutions attractive solvents.

2.2.3 Ammonia

Aqueous ammonia is a weak alkali solution, and CO₂ reacts with ammonia based on acid-base chemical reaction. The reaction between ammonia and carbon dioxide is, similarly to the reaction between CO₂ and primary and secondary alkanolamines, expected to proceed via the well-known zwitterion mechanism[51]. Although the chemical reaction between ammonia and CO₂ happening through a series of chemical reaction, the overall chemical reaction between aqueous ammonia and CO₂ is:



The product from the aqueous ammonia process is ammonium bicarbonate, which can be easily regenerated by heating into NH₃, CO₂ and H₂O compared to carbamate formed by amines and amino acids.

Ammonia is now documented as an emerging chemical absorbent in CCS specifically due to its lower energy demand for regeneration[52]–[55]. Ammonia could significantly reduce the energy regeneration demands and save up to 75% energy compared to MEA. Moreover CO₂ absorption capacity of ammonia is comparable to amine CO₂ absorption capacity even though ammonia is cheaper than alkanolamines[55]. In addition ammonia is not corrosive and does not suffer from thermal or oxidative degradation like amines. On the contrary, reusable products can be formed. For instance when NH₄HCO₃ recovered in crystalline form, it can be used as an ammonia rich fertilizer as well as a feed stock in commercial manufacture[56]. However the main operation problem i.e. the ammonia slip from the aqueous ammonia solution limits the widespread use of this hopeful absorption liquid. Two techniques are investigated by researchers to overcome this ammonia escape problem. One is using chilled ammonia other one is mixing additives inhibiting ammonia escape from the aqueous solution[53], [57].

The use of aqueous ammonia for capturing CO₂ through GLMC has been studied by few researchers[52], [54], [58], [59]. The added advantage is by using GLMC the escape of ammonia from the solution can be controlled. The main problem of adopting aqueous ammonia to absorb CO₂ in GLMC is the extensive membrane wetting caused by aqueous ammonia solution and the resulted mass transfer deterioration during long term operation[22], [58]. Attempts were made by researchers in order to overcome this problem by adding alkaline salts to aqueous ammonia solution[54], [56]. This is because the addition of electrolytes increases the surface tension of the aqueous ammonia solutions as aqueous electrolytes possess surface tensions higher than pure water. Further some researchers tried to use composite membranes to avoid membrane wetting[54], [58]. In composite HFMs a thin dense layer added to a microporous support acts as a physical barrier facing the liquid phase[13], [22]. In that case, wetting is suppressed while mass transport performances can be found comparable to those observed in microporous membrane. Indeed, a chemically resistant composite fiber made of a thin dense layer ideally highly permeable to CO₂ but less permeable to NH₃ could be ideal candidate in GLMC applications as this can potentially lead to a high CO₂ mass transfer intensification while drastically lowering ammonia slip.

3 CONCLUSION

In many industrial processes such as natural gas processing, flue gas treatment, biogas purification, etc. removing CO₂ from gas streams is one of the essential gas separation processes. The traditional method for CO₂ separation is amine scrubbing. Although high product yields and purities can be obtained, the disadvantage of this method is its high energy consumption in combination with high liquid losses due to evaporation of the solvent in the stripper. In addition, as liquid and gas streams cannot be controlled independently the occurrence of flooding, foaming, channeling and entrainment of the absorption liquid also limits the process. Membrane technology is a promising method to replace the conventional absorption technology. It has a high energy efficiency, easy to scale-up because of its modular design and it has high area-to-volume ratio. A limitation can be found in the permeability-selectivity tradeoff relation. A Gas-Liquid Membrane Contactor (GLMC) combines the advantages of membrane technology with those of absorption liquid. As a hybrid approach of conventional chemical absorption/stripping technology and membrane gas separation, GLMC has been considered as one of the possible alternative to conventional techniques for CO₂ capture.

In GLMC for CO₂ separation the selectivity is provided by the absorbent liquid rather than the porous membrane. Therefore proper choice of absorption liquids also plays a vital role in determining the performance of GLMC for CO₂ separation. The selection of absorption liquid should be based on factors such as high absorption ability of CO₂, high surface tension, high chemical compatibility, high thermal stability, low vapor pressure, low viscosity, easiness of regeneration and environmental safety.

Numerous alkanolamine based solvents such as MEA, DEA and MDEA are presently being studied as absorbent liquid in GLMC applications. However, alkanolamines are inherently problematic, due to their volatility, degradability, and high energy consumption for regeneration. Specifically amine solutions due to their low surface tension, can easily penetrate inside the membrane pores and cause the membrane wetting slowly with time.

AAS such as sodium, potassium and lithium salt of sarcosine, glycine, alanine, taurine and proline are attractive solvents due to their unique properties over other solvents such as low environmental impact, high biodegradability, negligible volatility, high resistance to oxidative degradation, viscosities and surface tensions similar to water. Further AAS shows better stripping performance compared to conventional amines. The main negative aspects of these AAS are the formation of a solid product when absorbing CO₂, which causes plugging and fouling of the gas-liquid membrane contactors and increase mass transfer resistance in long term operation.

Ammonia is now documented as an emerging chemical absorbent due to its lower energy demand for regeneration. In addition ammonia is not corrosive and does not suffer from thermal or oxidative degradation like amines. On the contrary, reusable products can be formed. However the main operation problem i.e. the ammonia slip from the aqueous ammonia solution limits the widespread use of this hopeful absorption liquid.

Hence, finally all absorption liquids investigated to be used as absorption liquid in GLMC applications for CO₂ separation have their own pros and cons. So absorption liquids with more favorable characteristics for CO₂ capture are thus being requested.

REFERENCES

- [1] S. Michael, Membrane stripping: Stripper of carbon dioxide from alkali solvents (Doctoral dissertation, University of Melbourne, 2010).
Retrieved from <http://repository.unimelb.edu.au/10187/9150>
- [2] S. Khaisri, D. deMontigny, P. Tontiwachwuthikul, and R. Jiraratananon, CO₂ stripping from monoethanolamine using a membrane contactor, *J. Memb. Sci.*, 376 (1-2), 110–118, 2011.
- [3] T.V. Alonso, High efficiency on CO₂ removal in natural gas with ucarsol™ solvents, Rio Oil & Gas Expo and Conference 2010 Proceedings.
Retrieved from http://oilandgas.dow.com/pdf/rio/gas_natural.pdf
- [4] S. Katja, Membrane technologies For CO₂ capture, Doctoral dissertation, University of Twente, 2010
Retrieved from http://www.utwente.nl/tnw/mtg/publications/mstpublications/pdf/2010_simons.pdf
- [5] M. Simioni, S. E. Kentish, and G. W. Stevens, Membrane stripping: Desorption of carbon dioxide from alkali solvents, *J. Memb. Sci.*, 378 (1-2), 18–27, 2011.
- [6] N. Ghasem, M. Al-Marzouqi, and N. Abdul Rahim, Effect of polymer extrusion temperature on polyvinylidene fluoride hollow fiber membranes: Properties and performance used as gas-liquid membrane contactor for CO₂absorption, *Sep. Purif. Technol.*, 99, 2012.
- [7] N. Ghasem, M. Al-Marzouqi, and N. Abdul Rahim, Modeling of CO₂absorption in a membrane contactor considering solvent evaporation, *Sep. Purif. Technol.*, 110, 1–10, 2013.
- [8] N. A. Rahim, N. Ghasem, and M. Al-Marzouqi, Stripping of CO₂ from different aqueous solvents using PVDF hollow fiber membrane contacting process, *J. Nat. Gas Sci. Eng.*, 21, 2014.
- [9] N. Ghasem, M. Al-Marsouqi, and N. A. Rahim, Modeling and Simulation of Membrane Contactor employed to strip CO₂ from Rich Solvents via COMSOL Multiphysics®, in Proceedings of the COMSOL Conference. Zurich: COMSL, 2014, 1–5.
- [10] N. Ghasem, M. Al-Marsouqi, and N. A. Rahim, Simulation of Gas/Liquid Membrane Contactor via COMSOL Multiphysics®.
- [11] N. A. Rahim, “Modeling and Experimental Study of Carbon Dioxide Absorption/Stripping In Gas Liquid Membrane Contactor”, PhD dissertation, Dept. of Chemical & Petroleum Eng., UAE Univ., Al Ain, UAE, 2015
- [12] N. M. Ghasem, N. A. Rahim, and M. Al-Marzouqi, Carbon Capture From Natural Gas via Polymeric Membranes, in Encyclopedia of Information Science and Technology, Fourth Edition, IGI Global, 3043–3055, 2018.
- [13] J.-G. Lu, Y.-F. Zheng, and M.-D. Cheng, Wetting mechanism in mass transfer process of hydrophobic membrane gas absorption, *J. Memb. Sci.*, 308 (1), 180–190, 2008.
- [14] E. Drioli, A. Criscuoli, and E. Curcio, Membrane Contactors: Fundamentals, Applications and Potentialities: Fundamentals, Applications and Potentialities, 11. Elsevier, 2011.
- [15] H. Kreulen, C. A. Smolders, G. F. Versteeg, and W. P. M. Van Swaaij, Microporous hollow fibre membrane modules as gas-liquid contactors. Part 1. Physical mass transfer processes: A specific application: Mass transfer in highly viscous liquids, *J. Memb. Sci.*, 78 (3), 197–216, 1993.
- [16] H. Kreulen, C. A. Smolders, G. F. Versteeg, and W. P. M. Van Swaaij, Microporous hollow fibre membrane modules as gas-liquid contactors Part 2. Mass transfer with chemical reaction, *J. Memb. Sci.*, vol. 78, no. 3, pp. 217–238, 1993.
- [17] Z. Ze and J. Sx, Hollow fiber membrane contactor absorption of CO₂ from the flue gas: review and perspective, *Glob. Nest J.*, 16, 355–374, 2014.
- [18] P. S. Kumar, J. A. Hogendoorn, P. H. M. Feron, and G. F. Versteeg, New absorption liquids for the removal of CO₂ from dilute gas streams using membrane contactors, *Chem. Eng. Sci.*, 57 (9), 1639–1651, 2002.
- [19] S. Yan *et al.*, Experimental study on the separation of CO₂ from flue gas using hollow fiber membrane contactors without wetting, *Fuel Process. Technol.*, 88 (5), 501–511, 2007.
- [20] J.-L. Li and B.-H. Chen, Review of CO₂ absorption using chemical solvents in hollow fiber membrane contactors, *Sep. Purif. Technol.*, 41 (2), 109–122, 2005.
- [21] S. Bonyadi, T. S. Chung, and R. Rajagopalan, A novel approach to fabricate macrovoid free and highly permeable PVDF hollow fiber membranes for membrane distillation, *AIChE J.*, 55 (3), 828–833, 2009.
- [22] S. Mosadegh-Sedghi, D. Rodrigue, J. Brisson, and M. C. Iliuta, Wetting phenomenon in membrane contactors – Causes and

- prevention, *J. Memb. Sci.*, 452 (0), 332–353, 2014.
- [23] B. Shimekit and H. Mukhtar, *Natural gas purification technologies-major advances for CO₂ separation and future directions*. INTECH Open Access Publisher, 2012.
- [24] C.-H. Yu, C.-H. Huang, and C.-S. Tan, A review of CO₂ capture by absorption and adsorption, *Aerosol Air Qual. Res.*, 12 (5), 745–769, 2012.
- [25] M. H. Al-Marzouqi, M. H. El-Naas, S. A. M. Marzouk, M. A. Al-Zarooni, N. Abdullatif, and R. Faiz, Modeling of CO₂ absorption in membrane contactors, *Sep. Purif. Technol.*, 59 (3), 286–293, 2008.
- [26] M. H. Al-Marzouqi, S. A. M. Marzouk, M. H. El-Naas, and N. Abdullatif, CO₂ Removal from CO₂- CH₄ Gas Mixture Using Different Solvents and Hollow Fiber Membranes, *Ind. Eng. Chem. Res.*, 48 (7), 3600–3605, 2009.
- [27] H. Yang et al., Progress in carbon dioxide separation and capture: A review, *J. Environ. Sci.*, 20 (1), 14–27, 2008.
- [28] A. Mansourizadeh and A. F. Ismail, Hollow fiber gas-liquid membrane contactors for acid gas capture: A review, *J. Hazard. Mater.*, 171 (1-3), 38–53, 2009.
- [29] Y.-S. Kim and S.-M. Yang, Absorption of carbon dioxide through hollow fiber membranes using various aqueous absorbents, *Sep. Purif. Technol.*, 21 (1-2), 101–109, 2000.
- [30] M. Awais, Determination of the mechanism of the reaction between CO₂ and alkanolamines (Master thesis, Norwegian University of Science and Technology, 2013).
- [31] X. Liu, Rate based modelling of CO₂ removal using alkanolamines. (Master thesis, Norwegian University of Science and Technology, 2014).
- [32] A. Jamal, Absorption and desorption of CO₂ and CO in alkanolamine systems. (doctoral dissertation, University of British Columbia, 2002)..
- [33] M.L. Benedict, CO₂ Capture from Flue gas using Amino acid salt solutions (doctoral dissertation, technical University of Denmark, 2012)..
- [34] J. T. Yeh, H. W. Pennline, and K. P. Resnik, Study of CO₂ absorption and desorption in a packed column, *Energy & fuels*, 15 (2), 274–278, 2001.
- [35] B. P. Mandal, M. Guha, A. K. Biswas, and S. S. Bandyopadhyay, Removal of carbon dioxide by absorption in mixed amines: modelling of absorption in aqueous MDEA/MEA and AMP/MEA solutions, *Chem. Eng. Sci.*, 56 (21), 6217–6224, 2001.
- [36] R. Idem *et al.*, Pilot plant studies of the CO₂ capture performance of aqueous MEA and mixed MEA/MDEA solvents at the University of Regina CO₂ capture technology development plant and the Boundary Dam CO₂ capture demonstration plant, *Ind. Eng. Chem. Res.*, 45 (8), 2414–2420, 2006.
- [37] S. A. Freeman, R. Dugas, D. H. Van Wagener, T. Nguyen, and G. T. Rochelle, Carbon dioxide capture with concentrated, aqueous piperazine, *Int. J. Greenh. Gas Control*, 4 (2), 119–124, 2010.
- [38] D. Fu, Z. Li, and F. Liu, Experiments and model for the viscosity of carbonated 2-amino-2-methyl-1-propanol and piperazine aqueous solution, *J. Chem. Thermodyn.*, 68 (0), 20–24, 2014.
- [39] S.-H. Lin, P.-C. Chiang, C.-F. Hsieh, M.-H. Li, and K.-L. Tung, Absorption of carbon dioxide by the absorbent composed of piperazine and 2-amino-2-methyl-1-propanol in PVDF membrane contactor, *J. Chinese Inst. Chem. Eng.*, 39 (1), 13–21, 2008.
- [40] R. Naim and A. F. Ismail, Effect of fiber packing density on physical CO₂ absorption performance in gas-liquid membrane contactor, *Sep. Purif. Technol.*, 115, 152–157, 2013.
- [41] J. P. Brouwer, P. H. M. Feron, and N. A. M. Ten Asbroek, Amino-acid salts for CO₂ capture from flue gases, 5.
- [42] P. H. M. Feron and N. ten Asbroek, New solvents based on amino-acid salts for CO₂ capture from flue gases, *Proceeding GHGT*, 7, 5–9, 2004.
- [43] E. Sanchez-Fernandez, F. de M. Mercader, K. Misiak, L. van der Ham, M. Linders, and E. Goetheer, New Process Concepts for CO₂ Capture based on Precipitating Amino Acids, *Energy Procedia*, 37, 1160–1171, 2013.
- [44] N. A. Rahim, N. Ghasem, and M. Al-Marzouqi, Absorption of CO₂ from natural gas using different amino acid salt solutions and regeneration using hollow fiber membrane contactors, *J. Nat. Gas Sci. Eng.*, 26, 108–117, 2015.
- [45] N. Ghasem, M. Al-Marzouqi, and N. A. Rahim, Absorption of CO₂ from natural gas via gas-liquid PVDF hollow fiber membrane contactor and potassium glycinate as solvent, *J. Teknol. (Sciences Eng.)*, 69 (9), 2014.
- [46] A. Mansourizadeh and A. F. Ismail, A developed asymmetric PVDF hollow fiber membrane structure for CO₂ absorption, *Int. J. Greenh. Gas Control*, 5 (2), 374–380, 2011.

- [47] J. Van Holst, P. P. Politiek, J. P. M. Niederer, and G. F. Versteeg, CO₂ capture from flue gas using amino acid salt solutions.
- [48] S. Yan, Q. He, S. Zhao, H. Zhai, M. Cao, and P. Ai, CO₂ removal from biogas by using green amino acid salts: Performance evaluation, *Fuel Process. Technol.*, 129 (0), 203–212, 2015.
- [49] S. Yan, Q. He, S. Zhao, Y. Wang, and P. Ai, Biogas upgrading by CO₂ removal with a highly selective natural amino acid salt in gas–liquid membrane contactor, *Chem. Eng. Process. Process Intensif.*, 85 (0), 125–135, 2014.
- [50] M. E. Majchrowicz, Amino acid salt solutions for carbon dioxide capture. Gildeprint, 2014.
- [51] H. Chen *et al.*, Studies on absorption and regeneration for CO₂ capture by aqueous ammonia, *Int. J. Greenh. Gas Control*, 6, 171–178, 2012.
- [52] A. McLeod, P. Buzatu, O. Autin, B. Jefferson, and E. McAdam, Controlling shell-side crystal nucleation in a gas–liquid membrane contactor for simultaneous ammonium bicarbonate recovery and biogas upgrading, *J. Memb. Sci.*, 473, 146–156, 2015.
- [53] M. Shuangchen, S. Huihui, Z. Bin, and C. Gongda, Experimental study on additives inhibiting ammonia escape in carbon capture process using ammonia method, *Chem. Eng. Res. Des.*, 91 (12), 2775–2781, 2013.
- [54] C. Makhoulfi, E. Lasseguette, J. C. Remigy, B. Belaissaoui, D. Roizard, and E. Favre, Ammonia based CO₂ capture process using hollow fiber membrane contactors, *J. Memb. Sci.*, 455, 236–246, 2014.
- [55] Q. Zhuang, R. Pomalis, L. Zheng, and B. Clements, Ammonia-based carbon dioxide capture technology: issues and solutions, *Energy Procedia*, 4, 1459–1470, 2011.
- [56] B. Zhao, Y. Su, W. Tao, L. Li, and Y. Peng, Post-combustion CO₂ capture by aqueous ammonia: A state-of-the-art review, *Int. J. Greenh. Gas Control*, 9, 355–371, 2012.
- [57] A. Kothandaraman, Carbon dioxide capture by chemical absorption: a solvent comparison study, 2010.
- [58] C. T. Molina and C. Bouallou, Assessment of different methods of CO₂ capture in post-combustion using ammonia as solvent, *J. Clean. Prod.*, 2014.
- [59] C. Toro-Molina and C. Bouallou, Comparison of Post-combustion CO₂ Capture by Solutions of Ammonia and Organic Amines: Assessment Using Direct and Indirect Contactors, *Energy Procedia*, 63, 550–558, 2014.