

## Advances in Liquid Absorbents for CO<sub>2</sub> Capture: A Review

Aishah Rosli, Abdul Latif Ahmad,\* Jit Kang Lim and Siew Chun Low

School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus,  
14300 Nibong Tebal, Pulau Pinang, Malaysia

\*Corresponding author: [chlatif@usm.my](mailto:chlatif@usm.my)

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**ABSTRACT:** *The emission of greenhouse gases, especially carbon dioxide (CO<sub>2</sub>) has been a major concern worldwide for several years now, as it causes global warming. Even though various CO<sub>2</sub> capture technologies have been researched, liquid absorption is widely considered a popular and effective method for the removal of CO<sub>2</sub>. For this reason, the choice of absorbent used to absorb the greenhouse gas is of vital importance. This article provides a brief overview of various liquid absorbents that have been investigated for this purpose, both in absorption columns and membrane contactor settings. Research journals currently available show that the usage of common amines and their combinations have been investigated, as well as several alternatives, additions and enhancements to existing liquid absorbents to improve the capture of CO<sub>2</sub> and these are discussed in this article.*

**Keywords:** CO<sub>2</sub> capture, absorption, liquid absorbents, greenhouse emission, removal of CO<sub>2</sub>

### 1. INTRODUCTION

The removal of carbon dioxide (CO<sub>2</sub>) using absorption is widely necessary in many industries such as natural gas processing, hydrogen and ammonia manufacture, and coal gasification. CO<sub>2</sub> is also used in other industries such as food, beverage and petroleum. In addition, CO<sub>2</sub> absorption is a promising process to reduce the greenhouse effect stemming from the emission of greenhouse gases, of which CO<sub>2</sub> is a main contributor. In an attempt to reduce the emission of CO<sub>2</sub> into the atmosphere, many agreements and protocols have been signed, including the Kyoto

Protocol and the Copenhagen Accord. There are various technologies that can be utilised for capturing CO<sub>2</sub>, namely physical absorption,<sup>1,2</sup> chemical absorption,<sup>3-5</sup> adsorption<sup>6,7</sup> and membrane.<sup>8</sup>

In physical absorption process, CO<sub>2</sub> is absorbed under high pressure and low temperature conditions and desorbed at lower pressure and higher temperature. Several existing commercial processes that use physical absorption are Selexol, Rectisol, Purisol, Morphysorb and Fluor process.<sup>9</sup> In chemical absorption process, the gas enters the absorber from the bottom and contacts counter-currently with the absorbent. After the process, the CO<sub>2</sub>-rich absorbent is then regenerated by a stripper and recycled back into the absorber.

Among the available technologies, chemical absorption into a liquid solvent is considered to be the most suitable process for capturing CO<sub>2</sub>. This process has the advantage of being the most matured technology and has been commercialised for decades, as well as suitable to retrofit already existing plants. However, this technology has several drawbacks such as low CO<sub>2</sub> loading capacity, equipment corrosion, and amine degradation. It is possible to improve on these disadvantages by refining the solvents used. Commonly used solvents for this purpose are aqueous solutions of alkanolamines, such as monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA) and methyldiethanolamine (MDEA). Other than alkanolamines, sterically hindered amines such as 2-amino-2-methyl-1-propanol (AMP) are also used as solvents to absorb CO<sub>2</sub>.

Due to its fast rate of reaction with CO<sub>2</sub>, MEA is the most widely used solvent. However, the cost of the MEA absorption system is high as it has a high regeneration energy requirement as well as being corrosive and easily degradable. DEA, DIPA and AMP are less reactive with CO<sub>2</sub> but present fewer problems with corrosion and degradation while MDEA is the least reactive with CO<sub>2</sub> but does not pose operational problems.<sup>4</sup>

Other than coming up with alternatives for the commonly used solvents, there is increasing interest in absorption solvents blends, as these blends are supposed to combine the strengths of the individual solvents while suppressing their weaknesses.

## 2. CHEMICAL ABSORPTION CONFIGURATIONS

### 2.1 Absorption Column

CO<sub>2</sub> separation using absorption columns have been extensively used in the industry for many decades now. However, this process has a significant cost and energy consumption, and there is still room for improvement. It is possible to modify the process design to reduce the capital and energy costs, as well as to enhance the absorbents used to augment system performance. A number of improvements on the system is being done by several developers such as Fluor, Mitsubishi Heavy Industries (MHI) and Cansolv Technologies.<sup>10</sup> MHI has developed a new process where the usage of a new amine solvent is the key component.<sup>11</sup>

Research and development efforts in the future can be directed towards modifying the column packing to reduce pressure drop and increase contact between the gas and solvent, enhancing heat integration so that energy consumption can be reduced, and improving absorbent regeneration.

### 2.2 Membrane Contactor

In membrane contactors, the membrane is a barrier between the gas and the absorbent. The membrane poses limited mass transfer resistance as long as the membrane is not wetted by the absorbent and the mass transfer resistance is on the liquid side of the system. Various configurations of membrane contactors can be utilised to separate CO<sub>2</sub> from the gas stream, but arguably the most popular is the hollow fibre membrane, which costs less than the spiral-wound module, the other popular configuration. In this configuration, gas would flow through the hollow fibre membranes, while the absorbent flows through the shell side of the membranes. CO<sub>2</sub> would then pass through the membrane into the absorbent and impurities would be blocked by the membranes, which would decrease the loss of absorbent. As with the absorption column, CO<sub>2</sub>-rich absorbent that leaves the membranes would then be regenerated and recycled.

The advantages of using the membrane contactor are the absence of flooding, entrainment, channelling and foaming, not motion-sensitive, easy to scale up and has higher specific area for the same equipment size as the absorption column. deMontigny et al. found that membrane contactors performed better than absorption columns in similar operating conditions, but the degree of improvement depended on the membrane configuration and the type of membrane used. They also observed that gas flow rate, absorbent flow rate and the absorbent concentration affects membrane contactors in a similar manner that they affect absorption columns.<sup>12</sup>

However, membrane contactors have limitations that include pressure drop that increases with surface area and significant reduction of performance due to the membrane mass transfer resistance once the membrane is wetted by the absorbent. In addition, depending on the membrane manufacturing process, the hollow fibre cannot exceed a few meters in length.<sup>13</sup>

In the future, advances in membrane application may involve membrane contactors being more widely used for natural gas treatment, refineries and petrochemical plants, where the gas streams are condensable and plasticising, which would negatively affect the performance of the membrane. Therefore, research on more robust membranes will be of paramount importance. Increasing the membrane selectivity and permeability as well as reducing the cost are also the research pathways for the improvement of this system, while membrane wetting can be solved by improving the membrane or the absorbent used. Other than the selectivity and permeability, membranes are also required to be thin and low-cost, so these are also viable areas to work on.<sup>14</sup>

### **3. LIQUID ABSORBENTS**

#### **3.1 Common Alkanolamines**

Of the common alkanolamines used for the purpose of CO<sub>2</sub> absorption, MEA seems to be the most efficient. Figure 1 shows the CO<sub>2</sub> removal efficiency for several common single alkanolamine solutions while Table 1 gives some properties of common alkanolamine solutions used to absorb CO<sub>2</sub>.<sup>4</sup> From Figure 1, it is clear that MEA, DEA and AMP achieved complete removal of CO<sub>2</sub> while MDEA gives the lowest performance in terms of removal efficiency. According to Aroonwilas and Veawab, under typical service conditions, the reaction rate constant depends on the absorbent's rate of CO<sub>2</sub> absorbance.<sup>4</sup> For the absorbents they investigated, they found the order to be MEA > DEA > AMP > DIPA > MDEA. Kim and Yang compared the performances of different amines as absorbents for CO<sub>2</sub> absorption using polytetrafluoroethylene (PTFE) hollow fiber membrane modules at several temperatures.<sup>15</sup> In their research, MDEA failed to reach the desired removal, AMP managed to achieve the required removal rate and MEA succeeded in getting a high rate of CO<sub>2</sub> removal even at very low liquid flow rates.

Lv et al. also came to the same conclusion regarding MEA in their investigation of CO<sub>2</sub> absorption using deionised water, MDEA and MEA at low concentrations in polypropylene (PP) hollow fibre membrane with several different operating parameters.<sup>16</sup> Their results show that MEA is most efficient in removing CO<sub>2</sub>,

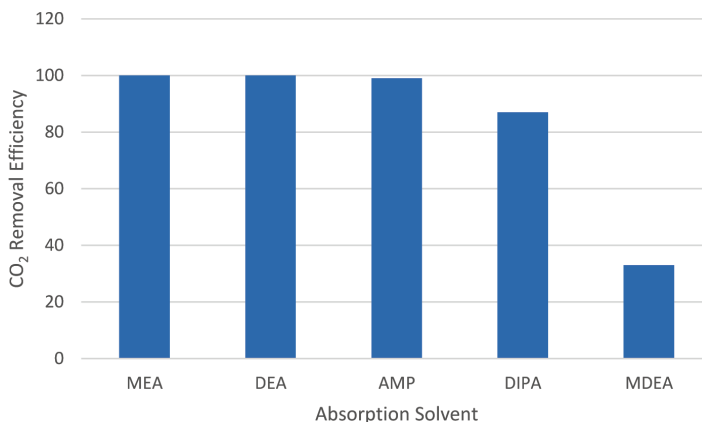
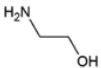

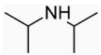
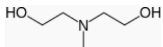

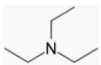


Figure 1: CO<sub>2</sub> Removal efficiency of single alkanolamine solutions under 0.00 mol/mol CO<sub>2</sub> loading and 10 m<sup>3</sup>/m<sup>2</sup>.h liquid load (Aroonwilas and Veawab).<sup>4</sup>

followed by MDEA and deionised water. Another study that directly compares various alkanolamine solutions with different structural characteristics was done by Kim et al.,<sup>17</sup> in which the solubility of CO<sub>2</sub> in MEA, DEA, triethanolamine (TEA) and AMP, and the heat of absorption between the absorbent and CO<sub>2</sub> were investigated. All investigated solutions showed higher CO<sub>2</sub> loadings with lower temperature, and AMP which is a sterically hindered amine, has the highest CO<sub>2</sub> loading while TEA, the tertiary amine has the lowest CO<sub>2</sub> loading.

Table 1: Properties of several common alkanolamines used for CO<sub>2</sub> absorption.

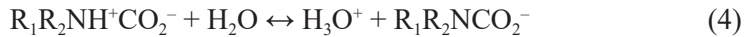
Absorbent	Molecular structure	Molecular weight (g/mol)	Density (293K) (g/cm <sup>3</sup> )	Boiling point (K)	Vapour pressure (293K)(kPa)	CO <sub>2</sub> Absorption capacity (mol CO <sub>2</sub> /mol absorbent)
MEA		61.08	1.012	443	0.064	0.5
DEA		105.14	1.097	544.2	<0.001	0.5
DIPA		101.19	0.722	356–358	0.0067	–
MDEA		119.16	1.038	520.2	0.001	1.0
AMP		89.14	0.934	438	0.1333	1.0
TEA		101.19	0.7255	361.7–362.9	6.899–8.506	–

Typical alkanolamine solutions used for the purpose of CO<sub>2</sub> absorption: AMP, DEA and MDEA were used by Wang et al. in a theoretical simulation to observe their performances in a hollow fibre membrane.<sup>18</sup> The results indicate that AMP and DEA both have much higher CO<sub>2</sub> absorption fluxes compared to MDEA. However, the concentrations of the two former solutions drop dramatically as they were depleted. It was concluded that the liquid flow velocity, initial solvent concentration and the dimensions of the hollow fibre play important roles on the absorption by AMP and DEA as their reactions with CO<sub>2</sub> are instantaneous. McCann et al. developed a model to simulate the absorption and desorption of CO<sub>2</sub> by MEA with focus on predicting the enthalpy associated with the processes.<sup>19</sup>

CO<sub>2</sub> reacts with primary amine solutions like ammonia to form ammonium bicarbonate:



This reaction allows for a maximum loading of 0.5 mol of CO<sub>2</sub>/mol of ammonia. On the other hand, sterically unhindered primary and secondary alkanolamines react instantaneously with CO<sub>2</sub> by forming intermediate zwitterions that is deprotonated by amine producing carbamate:



Reaction (3) is the determining step; when the concentration of the alkanolamine is high, the deprotonation of zwitterions is a second-order reaction while at a low concentration the reaction is a first-order reaction. The stable carbamate production is limited to a maximum loading of 0.5 mol CO<sub>2</sub>/mol amine.

The ease of absorbent regeneration is important, as for most processes in consideration the absorbent is recycled. Even though the CO<sub>2</sub> absorption performance of MEA surpasses the performance of AMP, MEA requires more energy for regeneration so AMP is ultimately a better choice as absorbent.<sup>15</sup> According to Zhang et al. even though AMP may be a sterically hindered amine, it is easier to regenerate with little loss of absorption capacity compared to other amines such as MEA, DEA, diethylenetriamine (DETA) and MDEA.<sup>20</sup> Kim et al. concluded that the reaction temperature increases with the reaction rate, and that the regeneration energy of absorbents is directly related to the heat of reaction and is therefore higher when the binding force between the absorbents and CO<sub>2</sub> molecules are stronger.<sup>17</sup>

In membrane gas absorption, membrane wetting is undesirable as it leads to an increase in mass transfer resistance and deterioration of performance. Lv et al. found that CO<sub>2</sub> removal efficiency increases with increase of the liquid flow rate and solvent concentration, while the CO<sub>2</sub> mass transfer rate increases with increase in liquid flow rate, CO<sub>2</sub> volume fraction in the feed gas, solvent concentration and gas flow rate.<sup>16</sup> The increase of solvent concentration is usually in favour of CO<sub>2</sub> absorption performance, however, increased solvent concentration accelerates membrane wetting, so the solvent concentration needs to be compromised between efficiency and membrane wetting to obtain efficient removal with long membrane life.

Lv et al. investigated the wetting mechanism by immersing PP hollow fibres in MEA, MDEA and deionised water.<sup>21</sup> Characterisations of the immersed membranes show that the absorbent molecules diffuse into the polymers and cause them to swell. Contact angle for fibres immersed in water is the highest, followed by MEA then MDEA. This is the same order as the absorbents' surface tension, implying that the decrease in contact angle is dependent on the absorbent's surface tension, as the absorbent with lower surface tension can diffuse more easily into the pores of the membrane. The membrane pore deformation is also dependent on the surface tension of the absorbent, with pore average diameter being larger when the absorbent has a lower surface tension. In terms of surface roughness, the immersed fibres have significantly higher surface roughness compared to the non-immersed fibres, with an increase in the surface roughness when the immersion absorbent has a lower surface tension. High surface roughness generally leads to high hydrophobicity, which is desired in membrane gas absorption processes. The breakthrough pressure order is as follows: MDEA < MEA < deionised water < non-immersed, which is also the same order of the absorbents' surface tension.

The effect of DEA absorbent on PP membranes was investigated by Wang et al.<sup>22</sup> Two types of PP hollow fibre membranes were used, and at the end of the experiment both membranes went through changes in pore structure and surface roughness. It was suspected that the chemical reaction between the membrane and absorbent may have reduced the hydrophobicity of the membranes, causing partial wetting. In terms of corrosion, Veawab et al. found that MEA is the most corrosive, followed by AMP and DEA, with MDEA being the least corrosive.<sup>23</sup>

These alkanolamines have been used for both research and industrial use, and it is apparent that each absorbent has its own advantages and drawbacks. For a better performance at a lower cost, research and development efforts have been put into improving these absorbents, by combining them or by adding additives.

### 3.1.1 Hybrid absorbents

After observing the performance of common alkanolamines in absorbing CO<sub>2</sub>, these common alkanolamines are blended in an attempt to combine the advantages of each type of amine. Generally, primary and secondary alkanolamines provide fast kinetics and high absorption capacity, while tertiary and sterically hindered amines can be regenerated at low cost. Table 2 lists down some of the hybrid absorbents made from mixing alkanolamine absorbents to improve their characteristics.

Table 2: Several mixtures of alkanolamine researched for CO<sub>2</sub> absorption.

Mixture	Process	Reference
MEA-MDEA	Absorption column	Aroonwilas and Veawab <sup>4</sup> Veawab et al. <sup>23</sup> Thitakamol and Veawab <sup>24</sup> Liao and Li <sup>25</sup> Dubois and Thomas <sup>26</sup>
DEA-MDEA	Absorption column	Aroonwilas and Veawab <sup>4</sup> Veawab et al. <sup>23</sup> Thitakamol and Veawab <sup>24</sup>
MEA-AMP	Absorption column	Aroonwilas and Veawab <sup>4</sup> Veawab et al. <sup>23</sup> Choi et al. <sup>27</sup> Thitakamol and Veawab <sup>24</sup>
DEA-AMP	Absorption column	Aroonwilas and Veawab <sup>4</sup> Barzagli et al. <sup>28</sup>
AMP-MDEA	Absorption column Membrane contactor	Barzagli et al. <sup>28</sup> Lu et al. <sup>29</sup>
AEE-MDEA	Absorption column	Bonenfant et al. <sup>30</sup>
AEE-TEA	Absorption column	Bonenfant et al. <sup>30</sup>

Hybrid absorbents have the potential to exceed the performance of single absorbent as proven by Yeon et al.<sup>31</sup> They used MEA and TEA as absorbents to remove CO<sub>2</sub> from flue gas in a hollow fiber module membrane contactor. For the hybrid absorbent containing 5wt% TEA and 5wt% MEA, the process operated for 80 h with a CO<sub>2</sub> removal efficiency of 90%–95%. However, for MEA absorbent,



the CO<sub>2</sub> removal efficiency went down to 75% after 8 h and remained constant at 75%. This is due to the chemical and mechanical deterioration as the MEA solution penetrated into the pores of the membrane. In addition, when the MEA – TEA hybrid absorbent was used, there is a decrease in the stripping temperature, providing a more economical process.

Two alkanolamines' mass transfer parameters were investigated by Rodriguez et al. by using the individual solvents as well as mixtures of the two.<sup>32</sup> From the results, the average overall volumetric coefficients of mass transfer of MEA and the mixture based on it are higher compared to AMP. In addition, the MEA:AMP mixture gave a better performance in removing CO<sub>2</sub> compared to AMP alone, which may be due to a synergistic effect between the two solutions. Blends of MEA and AMP were also investigated by Choi et al.,<sup>27</sup> proving that the blends have a higher CO<sub>2</sub> loading than MEA and a higher reaction rate than AMP, thus indicating that the blends managed to combine the desirable characteristics of both individual solutions.

The tendency of several absorbents to produce foam was investigated by Thitakamol and Veawab.<sup>24</sup> Foaming poses a severe operational problem in plants that remove CO<sub>2</sub> and hydrogen sulfide (H<sub>2</sub>S) using gas absorption into alkanolamines. Negative impacts brought by foaming include excessive loss of absorption solvents, products off-specification and premature flooding, all of which raise the expenditures of the plant. A blend of MEA and AMP of 2:1 ratio tended to foam, as well as MEA and MDEA. However, blends of MEA and MDEA at 1:1 ratio and MEA and AMP at 1:2 ratio did not exhibit foaming. In terms of corrosion, Veawab et al. found that MEA is the most corrosive, followed by AMP and DEA, with MDEA being the least corrosive.<sup>23</sup> The blends of these amines have corrosion rates that lie between the individual amines. Figure 2 demonstrates the corrosion rates of the hybrid absorbents.

Other than MEA, many have used AMP as a component in hybrid absorbents. In an experiment to compare the performances of DEA, MDEA and AMP for CO<sub>2</sub> absorption by Barzagli et al., it was discovered that AMP is the most efficient absorbent while MDEA regenerates the easiest at any concentration and temperature.<sup>28</sup> AMP was blended with MDEA and DEA with 1:2 and 2:1 molar ratios respectively, and these blended solutions showed better absorption efficiency within the range of 7%–14% compared to single amines. Of the two blends, AMP-MDEA showed better performance than AMP-DEA due to lower efficiency of DEA carbamate. However, Thitakamol and Veawab found that the blend DEA and AMP did not exhibit foaming.<sup>24</sup>

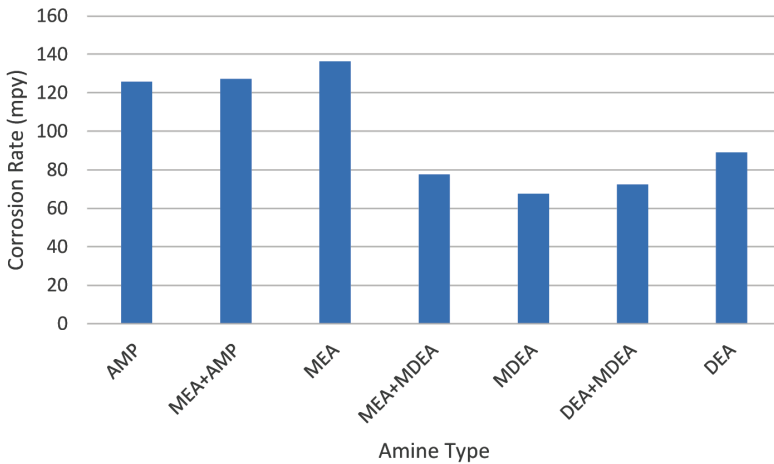


Figure 2: Corrosion rates of mixed amine systems and their precursors under  $3 \text{ kmol/m}^3$  with a mixing ratio of 1:1,  $80^\circ\text{C}$  and  $\text{CO}_2$  saturation (Veawab et al.<sup>23</sup>).

Aronwilas and Veawab found that under typical service conditions, the absorbents' rate of  $\text{CO}_2$  absorbance follows the order of the reaction rate constant. For the absorbents they investigated, they found the order to be:  $\text{MEA} > \text{MDEA} > \text{AMP} > \text{DIPA} > \text{MDEA}$ .<sup>4</sup> It was also discovered that the performance of the blends of alkanolamines are between the individual alkanolamines but not necessarily linear to them. AMP-based blends also perform better compared to those of MDEA-based. For blends with MDEA as base, at low  $\text{CO}_2$  loading it was observed that the  $\text{CO}_2$  concentration profiles are similar to the profiles of the promoters (MEA and DEA). This behaviour is due to the combined kinetic/thermodynamic competition between the base and the promoter species. At low  $\text{CO}_2$  loading, the rate promoters (MEA and DEA) are dominant in reaction with  $\text{CO}_2$  as they react with it at a much higher rate than MDEA. However, when  $\text{CO}_2$  loading increases the ratio of unreacted promoter to unreacted MDEA decreases, and MDEA starts to determine the  $\text{CO}_2$  absorption rate. On the other hand, the MEA-AMP blend approaches that of MEA regardless of  $\text{CO}_2$  loading, indicating that MEA improves this blend more effectively compared to the MEA-MDEA blend. The DEA-AMP blend did not affect the performance as much, simply because the individual solutions are already comparable in the first place. Liao and Li also found that small additions of MEA to aqueous MDEA enhance  $\text{CO}_2$  absorption significantly.<sup>25</sup>

2-(2-aminoethylamino)ethanol (AEE) solution and its blends with MDEA and TEA were used by Bonenfant et al. to absorb  $\text{CO}_2$  in the presence of sulfur dioxide ( $\text{SO}_2$ ) to evaluate their influence on AEE's performance.<sup>30</sup> It was found that the presence of  $\text{SO}_2$  lowers the  $\text{CO}_2$  absorption rate and loading, while additions of

5 and 10 wt% of MDEA and TEA do not visibly influence the absorption rate. In addition, MDEA slightly increases the CO<sub>2</sub> absorption capacity of AEE while TEA decreases the absorption capacity.

### 3.2 Other Absorbents

So far, MEA is one of the most common absorbents used for the purpose of CO<sub>2</sub> absorption. However, researchers deem that different absorbents for the absorption of CO<sub>2</sub> are worth looking into. Some research done on the capability of less common absorbents to absorb CO<sub>2</sub> are listed in Table 3. In a research by Kothandaraman, MEA was used as a base case system.<sup>33</sup> The overall energy consumption for the CO<sub>2</sub> capture systems with MEA, potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) and chilled ammonia as absorbents were calculated. From the simulations it was discovered that CO<sub>2</sub> generation takes up 60% of the energy consumption while the compression work accounted for about 30% of the energy consumption. Potassium carbonate is more flexible and less energy consuming compared to MEA as it lacks degradation and it has the ability to tolerate high temperatures. However, the operation would only be feasible at high pressures. The chilled ammonia system, on the other hand, requires a larger operating unit and more energy consumption would be incurred for refrigeration of ammonia and flue gas.

Several studies on the use of ammonia (NH<sub>3</sub>) as a solvent for CO<sub>2</sub> absorption have been done, such as the one by Gonzalez-Garza et al.<sup>36</sup> They studied NH<sub>3</sub> as a solvent and compared its performance with traditional alkanolamine solvents. The comparative study revealed that carbon dioxide absorption is most effectively carried out by ammonia compared to MEA, DEA and MDEA, with the absorption capacity of ammonia being three times more than MEA. The appropriate temperature and concentration of aqueous ammonia for CO<sub>2</sub> absorption according to a study done by Kim et al. are 26°C and 13 wt%, respectively.<sup>37</sup>

Aqueous potassium hydroxide (KOH) solution, a highly reactive absorbent was used by Korikov and Sirkar, who found that the experimental film estimates of the liquid film resistance is significantly higher than that estimated from the theory, perhaps due to the fast chemical reaction.<sup>38</sup>

For processes involving membrane usage, there has to be good compatibility between the membrane and the liquid absorbent, as this would play an important part in the long-term stability of the membrane. Barbe et al. explored this using water and calcium chloride (CaCl<sub>2</sub>), finding that after 72 h of contact with water, the surface of two different PP membranes both increased in several morphology parameters such as the porosity and the pore area.<sup>39</sup> The membranes left in

Table 3: Other absorbents investigated for CO<sub>2</sub> absorption.

Absorbent	Process	Reference
K <sub>2</sub> CO <sub>3</sub>	Absorption column	Kothandaraman <sup>33</sup>
	Membrane contactor	Ghosh et al. <sup>34</sup> Chun and Lee <sup>35</sup>
NH <sub>3</sub>	Absorption column	Kothandaraman <sup>33</sup>
		Gonzalez-Garza et al. <sup>36</sup>
		Kim et al. <sup>37</sup>
KOH	Membrane contactor	Korikov and Sirkar <sup>38</sup>
CaCl <sub>2</sub>	Membrane contactor	Barbe et al. <sup>39</sup>
PG	Membrane contactor	Yan et al. <sup>40</sup>
PAMAM	Membrane contactor	Kosaraju et al. <sup>41</sup>
Amino Acid Salts	Membrane contactor	Kumar et al. <sup>42</sup>
Li <sub>4</sub> SiO <sub>4</sub>	Absorption column	Essaki et al. <sup>43</sup>
CORAL	Membrane contactor	Feron and Jansen <sup>44</sup>
Amine-A	Absorption column	Murai et al. <sup>45</sup>
AHPD	Absorption column	Tourneux <sup>46</sup>
SG	Absorption column	Zhao et al. <sup>47</sup>
TEPA-based Polyamine	Absorption column	Filippis et al. <sup>48</sup>
AEEA	Absorption column	Kim and Svendsen <sup>49</sup>
Triethylamine	Absorption column	Bonenfant et al. <sup>50</sup>
Pyridine	Absorption column	Bonenfant et al. <sup>50</sup>
Pyrrolidine	Absorption column	Bonenfant et al. <sup>50</sup>
AEE	Absorption column	Bonenfant et al. <sup>50</sup>
AEPDNH <sub>2</sub>	Absorption column	Bonenfant et al. <sup>50</sup>
Sarcosine	Absorption column	Simons et al. <sup>51</sup>
NaOH	Membrane contactor	Mansourizadeh et al. <sup>52</sup>
		Xu et al. <sup>53</sup>
DEAB	Absorption column	Maneeintr et al. <sup>54</sup>
Piperazine	Absorption column	Dubois and Thomas <sup>26</sup>
		Aroua and Salleh <sup>55</sup>

contact with  $\text{CaCl}_2$ , on the other hand, did not experience significant change in morphology. This was attributed to the higher surface tension of  $\text{CaCl}_2$  compared to water, lowering the degree of intrusion into the membrane pores.

Yan et al. also investigated an uncommon absorbent, potassium glycinate (PG), as well as MEA and MDEA using PP hollow fibre membrane to remove  $\text{CO}_2$ .<sup>40</sup> They found that PG has a lower potential of membrane wetting in a continuous operation with removal efficiency of approximately 90%, but unlike conventional absorbents, its mass transfer decreases with increasing liquid temperature. Another novel absorbent, polyamidoamine (PAMAM) dendrimer of generation 0 was used continuously in a  $\text{CO}_2$  absorption operation for 55 days in a study done by Kosaraju et al.<sup>41</sup> PP hollow fiber membranes were used, and PAMAM, a nonvolatile amine managed to provide a stable performance with no membrane wetting.

Research has also been done on alternative, novel absorbents to replace the traditional alkanolamine solutions, such as one done by Kumar et al. in which they used a new absorption liquid based on amino acid salts in membrane contactors.<sup>42</sup> The wetting characteristic for the new solution was studied by measuring the surface tension of the liquid and the breakthrough pressure of the liquid into the membrane pores, and it was found that the new liquid does not wet the polypropylene membrane, while having good reactivity towards  $\text{CO}_2$ .

Lithium Silicate ( $\text{Li}_4\text{SiO}_4$ ), a novel  $\text{CO}_2$  absorbent developed by Toshiba was reported by Essaki et al.<sup>43</sup> In the experiment, 20 vol %  $\text{CO}_2$  gas was used, and the reactor achieved 100%  $\text{CO}_2$  removal at  $500^\circ\text{C}$ . The reaction between  $\text{Li}_4\text{SiO}_4$  and  $\text{CO}_2$  is exothermic, significantly heating the reactor and gas stream, which could be used to improve the energy consumption for this process. Feron and Jansen used novel absorption liquids (CORAL) to absorb  $\text{CO}_2$  through PP hollow fibre membranes, changing several parameters and comparing the performance with other systems.<sup>44</sup> It was apparent that these new liquids are superior in terms of stability and mass transfer.

A novel hindered amine absorbent-A which contains the amine A was evaluated based on the  $\text{CO}_2$  absorption rate, absorption capacity and heat of reaction by Murai et al.<sup>45</sup> This novel absorbent has a higher absorption capacity, higher absorption rate and a relatively lower heat of reaction compared to 30 wt% MEA solution, which can reduce the regeneration energy. Another sterically hindered amine, 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD) was used to absorb  $\text{CO}_2$  in a enzymatic process relying on type II human carbonic anhydrase in Tourneux's research.<sup>46</sup> It was proven that the solubility of  $\text{CO}_2$  increases with higher AHPD concentration

and lower temperature, and that the enzyme does not seem to have an impact on the solubility of  $\text{CO}_2$ .

Sodium glycinate (SG) solution was used to absorb  $\text{CO}_2$  in a study done by Zhao et al.<sup>47</sup> It was observed that in terms of  $\text{CO}_2$  absorption rate, SG is superior to commonly used alkanolamine solutions, and that temperature increase positively affects regeneration efficiency of the SG solution. Compared to amines such as MEA, MDEA and DEA, aliphatic polyamines are less often considered for  $\text{CO}_2$  absorption because even though they easily absorb acidic gases, they are difficult to regenerate. Tetraethylenepentamine (TEPA) was reacted with formaldehyde and phenol to produce modified polyamines by Filippis et al.<sup>48</sup> The synthesised product had higher absorption rate and lower degradation compared to DEA, as well as having a lower heat of regeneration.

Kim and Svendsen found that 2-(Aminoethyl)ethanolamine (AEEA), a diamine, has a higher  $\text{CO}_2$  absorption capacity than MEA, even though the heats of absorption for the two solutions are similar.<sup>49</sup> Bonenfant et al. compared various amine solutions' performances for  $\text{CO}_2$  absorption and regeneration.<sup>50</sup> Figure 3 shows the detailed result of the experiment. The solutions used are ammonia, MEA, TEA, triethylamine, pyridine, pyrrolidine, AEE and *N*-(2-aminoethyl)-1,3-propanediamine (AEPD $\text{NH}_2$ ). Out of the solutions tested, it was concluded that TEA, AEE and AEPD $\text{NH}_2$  are superior in terms of  $\text{CO}_2$  loading and regeneration capacity.

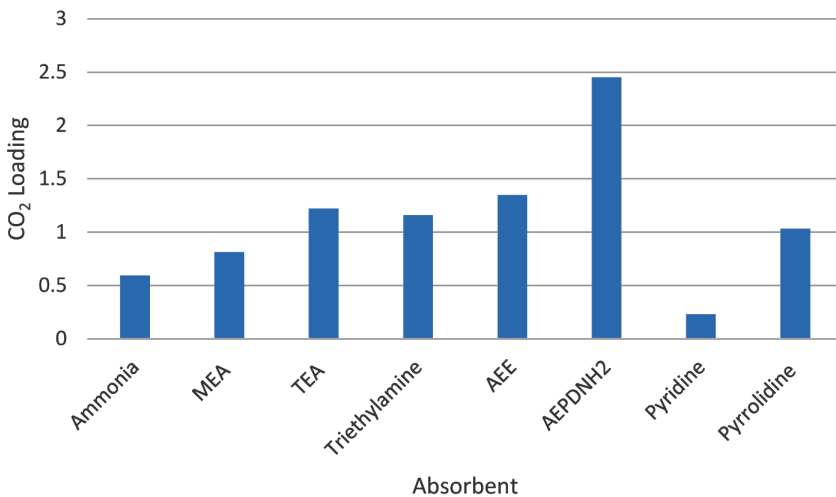


Figure 3:  $\text{CO}_2$  Loading of various absorbents (Bonenfant et al.<sup>50</sup>).

Considering that amino acid salt solutions for CO<sub>2</sub> removal has the potential to be better than alkanolamines due to their ionic nature and low evaporation, Simons et al. investigated sarcosine.<sup>51</sup> The reaction rate for CO<sub>2</sub> absorption into potassium sarcosinate was significantly higher compared to MEA. Mansourizadeh et al. and Xu et al. investigated sodium hydroxide (NaOH) in addition to the more common MEA and DEA absorbents.<sup>52,53</sup> Mansourizadeh et al. found that for distilled water as absorbent, physical absorption occurs and the CO<sub>2</sub> solubility is paramount to the performance while for NaOH, chemical absorption takes place, and as such, the absorbent temperature controls the process, as it affects the reaction rate.<sup>52</sup> The latter found that of the three absorbents, MEA has the best CO<sub>2</sub> removal efficiency.<sup>53</sup> CO<sub>2</sub> can be fixed into sodium carbonate and sodium bicarbonate with NaOH as the absorbent, while pure CO<sub>2</sub> can be produced using MEA or DEA.

4-diethylamino-2-butanol (DEAB), a new amino alcohol developed by Manecintr et al. was compared with MEA in terms of CO<sub>2</sub> absorption performance.<sup>54</sup> Even though the CO<sub>2</sub> mass transfer was higher in the MEA system compared to the DEAB system, the very high solubility and easy regeneration of DEAB should be utilised by formulating a solvent that comprises of both MEA and DEAB.

### 3.3 Addition of Additives

Other methods to enhance absorbents have also been explored, like in the research done by Dang and Rochelle, in which the amine concentration was varied by blending in piperazine (PZ).<sup>56</sup> They found that PZ at 24 mol% of the total amine enhances CO<sub>2</sub> absorption rate by 50%–100%, and that the rate in MEA with 0.6 to 1.2 M PZ is 1.5–2.5 times higher than pure MEA. Lu et al. also used the activator PZ and compared the CO<sub>2</sub> capture performance for MDEA and activated MDEA as absorbents.<sup>57</sup> From the experiment, it was found that the performance of activated MDEA is far superior to that of MDEA, with the removal efficiency of over 99% achieved with the activated MDEA. A list of additives used to augment the performance of the absorbent is given in Table 4.

In terms of absorption performance, normally primary and secondary amines are superior, but for regeneration efficiency, tertiary amines are preferred. In an attempt to combine the advantages of these alkanolamines, Dubois and Thomas mixed both types of solvents using MEA, MDEA and PZ.<sup>26</sup> For individual amine systems, MEA and PZ gave the best CO<sub>2</sub> absorption rates, with PZ showing a better performance at a lower concentration. For blended solutions, the activator effect shows a positive impact on the absorption performance, especially when the activator contained PZ. In general, PZ on its own behaves in a similar fashion to other amines.<sup>55</sup>

Table 4: Additives used to enhance absorbents for CO<sub>2</sub> absorption.

Additive	Absorbent	Process	Reference
Piperazine	MEA	Absorption column	Dang and Rochelle <sup>56</sup>
	MDEA	Membrane contactor	Lu et al. <sup>57</sup>
	MEA + MDEA	Absorption column	Dubois and Thomas <sup>26</sup>
	AMP	Absorption column	Sun et al. <sup>58</sup>
		Membrane contactor	Lin et al. <sup>59</sup>
	Potassium carbonate	Absorption column	Cullinane and Rochelle <sup>60</sup>
DEEA	Absorption column	Vaidya and Kenig <sup>61</sup>	
PZEA	MEA	Absorption column	Dubois et al. <sup>62</sup>
	MDEA	Absorption column	Dubois et al. <sup>62</sup>
	AMP	Absorption column	Dubois et al. <sup>62</sup>
Ferrofluid	MDEA	Absorption column	Komati and Suresh <sup>63</sup>
Nanoparticles	Water	Absorption column	Kim et al. <sup>64</sup>
Boric Acid	Potassium carbonate	Absorption column	Ghosh et al. <sup>34</sup>
			Smith et al. <sup>65</sup>
NaCl	MEA	Membrane contactor	Rongwong et al. <sup>66</sup>
	DEA	Membrane contactor	Rongwong et al. <sup>66</sup>
	AMP	Membrane contactor	Rongwong et al. <sup>66</sup>
Sodium Glycinate	MEA	Membrane contactor	Rongwong et al. <sup>66</sup>
	DEA	Membrane contactor	Rongwong et al. <sup>66</sup>
	AMP	Membrane contactor	Rongwong et al. <sup>66</sup>
EEA	DEEA	Absorption column	Vaidya and Kenig <sup>67</sup>

Lu et al. also used PZ as well as AMP as activators in MDEA solution.<sup>29</sup> Simulations and experiments were done in a hollow fibre module and the results show that the activated MDEA solutions are more efficient in capturing CO<sub>2</sub> compared to the non-activated MDEA solution, with activator PZ having an advantage over AMP in terms of mass transfer enhancement. Sun et al. and Lin et al. also found that the addition of small amounts of PZ into aqueous AMP solution gives a significant impact on the absorption rate of CO<sub>2</sub>.<sup>58,59</sup>



PZ has been proven as an activator that can successfully increase the CO<sub>2</sub> absorption rate, not only in amine absorbents. Cullinane and Rochelle added PZ into aqueous K<sub>2</sub>CO<sub>3</sub> and found that the addition increases the heat of absorption as well as the CO<sub>2</sub> absorption rate, making it comparably favourable with other commonly used amines.<sup>60</sup> The potential of PZ as an activator in other CO<sub>2</sub> absorption solvents was also explored by Vaidya and Kenig using the additive in N,N-Diethylethanolamine (DEEA).<sup>61</sup> Typically, DEEA absorbs CO<sub>2</sub> relatively slowly, being a tertiary amine, but even with a small addition of PZ into DEEA, the CO<sub>2</sub> absorption rate significantly increased.

Another activator, (piperaziny-1)-2-ethylamine (PZEA) was investigated by Dubois et al.<sup>62</sup> Pure PZEA and AMP as well as a mixture of the two with other amines are investigated to compare the performances for CO<sub>2</sub> absorption. The positive effect of the addition of PZEA in MEA, MDEA and AMP were clearly shown through the experiments, while the addition of AMP into MEA also showed interesting activation results.

Komati and Suresh, on the other hand, used a ferrofluid as an additive in MDEA.<sup>63</sup> The addition of the surfactant-coated aqueous magnetic fluid proved to have the ability to increase the CO<sub>2</sub> mass transfer. Another study on CO<sub>2</sub> absorption using nanofluids was done by Kim et al. by comparing the performance of nanoparticles in water and water without nanoparticles.<sup>64</sup> It was found that the capacity coefficient of CO<sub>2</sub> absorption in the former is 4 times higher than the latter, attributed to the fact that the small bubble sizes in the nanofluid having big mass transfer areas and high solubility.

As alkanolamine solutions tend to undergo oxidative degradation at high temperatures, potassium carbonate became an interesting alternative due to the high CO<sub>2</sub> chemical solubility, low solvent costs and low energy requirement for regeneration. However, the rate of absorption of CO<sub>2</sub> into potassium carbonate is relatively slow, making the addition of activators necessary to increase the absorption rate. Instead of the more commonly used PZ, Ghosh et al. opted for boric acid as a promoter and observed that while small additions of boric acid in potassium carbonate gave a significant enhancement to CO<sub>2</sub> absorption rates, the rate is still lower than that of amine based solvents.<sup>34</sup> Smith et al. also agree that further optimisation on the potassium carbonate system is needed in order to compete with amine based systems, but that such a research is worthwhile considering the numerous advantages potassium carbonate system has over the amine based systems.<sup>65</sup>

In addition to MEA, DEA and AMP, Rongwong et al. added SG, which is an organic salt to MEA in order to see the performance of these solvents to absorb CO<sub>2</sub>.<sup>66</sup> In this study, it was found that the mixture of MEA and SG has the highest CO<sub>2</sub> flux, followed by MEA, AMP and lastly DEA. Another study done by Vaidya and Kenig revealed that N-ethylethanolamine (EEA) is also an effective activator for DEEA.<sup>67</sup> It is expected that more research will be done on developing the best absorbent for CO<sub>2</sub> absorption process as the absorbent plays a very significant role in the performance of the process and the energy consumption of the plant.

#### 4. CONCLUSION

Liquid absorbents are deemed to be the best approach for CO<sub>2</sub> absorption. In this review, various liquids that have been used to absorb CO<sub>2</sub> are considered. Several researches on liquid absorbents were explored and their main discoveries are highlighted. Focus was given to common alkanolamines and other less common absorbents, hybrid as well as enhanced absorbents. Most researchers found that MEA is the most effective common alkanolamine, but this absorbent requires a lot of energy for regeneration, which may make it unfeasible for the purpose. Even though AMP is not as effective in absorbing CO<sub>2</sub>, its ease of regeneration may make it a better alternative. As hybrid absorbents have the capacity to surpass individual absorbents, several researchers have combined primary or secondary amines with tertiary or sterically hindered amines, mostly with favourable results. In the future, it is expected that the use of membrane contactors for gas separation in plants will become widespread as more selective, robust membranes that are resistant to fouling are developed. Considerable research has been done to investigate and compare alternative and new absorbents to common ones. A few alternative absorbents prove to give better performance than traditional ones, but often with drawbacks in different aspects. Additives have also been used to enhance the performance of the absorbents, mostly yielding good results. The most popular additive used by researchers is piperazine, but a few others have been investigated. Further research should also be done on additives that can reduce absorbent corrosion on the equipment and allow higher amine concentrations. Given the importance of this process in the oil and gas industry, further investigations on novel and improved absorbents are justified.

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