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Review of carbon capture absorbents for CO$_2$ utilization

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Abstract: Carbon capture technologies have been recognized as a potential alternative to alleviate global warming. Carbon capture and storage (CCS) is preferred over carbon conversion and utilization (CCU) due to its lower operating costs and higher CO$_2$ reduction capability. Nevertheless, CO$_2$ utilization has the potential to be more economical if value-added products are produced. This highlights the importance of assessing CO$_2$ utilization routes and alternatives in carbon management. This review paper aims to evaluate the carbon utilization potential of major CO$_2$-capturing absorbents including amine, hydroxide, ionic liquid, amino acids and carbonate absorbents. All absorbents show potential application for CO$_2$ utilization except for ionic liquids (ILs) due to their unclear CO$_2$ capture mechanisms. Absorbents that require a desorption process for CO$_2$ utilization include MEA, MDEA, K$_2$CO$_3$ and Na$_2$CO$_3$ due to their high absorption capacity. Industries have utilized the desorbed CO$_2$ as chemical feedstocks, enhanced oil recovery (EOR) and mineral carbonation. For hydroxide absorbents and CaCO$_3$, desorption of CO$_2$ is unnecessary as the absorbed CO$_2$ can be directly utilized to produce construction materials. Apart from that, the incorporation of advanced technologies and business models introduced by the fourth industrial revolution are plausible considerations to accelerate the development of carbon capture technologies. © 2022 Society of Chemical Industry and John Wiley & Sons, Ltd.

Keywords: carbon capture; CO$_2$ utilization; post-combustion; chemical absorption; global warming

Introduction

Excessive CO$_2$ emission is regarded as the primary contributor to global warming, which is an inevitable concern that has received worldwide attention.[1,2] The average CO$_2$ concentration rose to approximately 414 ppm CO$_2$ (as of October 2021) which is an increment of approximately 47.86 % as compared to the pre-industrial revolution era (280 ppm).[3,4] The drastic increase in CO$_2$ concentration further contributed to global climate change. Based on

NASA's Goddard Institute for Space Studies,[5] it has been found that the land-ocean temperature index (°C) has increased from −0.16 C° in the year 1880 to 1.02 C° in 2020. In an effort to halt the progression of global warming, developed countries have initiated various environmental agreements such as the Kyoto Protocol in 1997 and the Paris Agreement in 2015.[6,7]

CO$_2$ capture and storage (CCS) is recognized by the United Nations Framework Convention on Climate Change (UNFCCC), Intergovernmental Panel on Climate Change (IPCC), Kyoto Protocol and Paris

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Agreement as one of the potential technologies to combat global warming.[8–10] CCS is the preferred mode of CO_2 capture compared to CO_2 conversion and utilization (CCU), and CO_2 capture, utilization and storage (CCUS).[11–13] This is due to the limited CO_2 reduction capability and high operating costs of CO_2 utilization as compared to CO_2 storage.[14–18] Nevertheless, CCU and CCUS cannot be neglected since both alternatives possess a high potential to convert captured CO_2 to a value-added product while exploiting possible utilization routes for captured CO_2.[12,16,18]

The capture of CO_2 is mainly performed at post-combustion, pre-combustion and oxyfuel combustion. Post-combustion involves installing unit operation after combustion as it aims to separate CO_2 from flue gas after converting a carbon source.[13,19] It has received the most interest due to its ability to easily retrofit existing plants.[20–22] In pre-combustion, CO_2 is removed prior to completing a combustion process via decarbonization.[20,23] This process requires additional equipment such as a catalytic reactor, absorber or separator before the combustion unit, imposing a sizable change to an existing plant's configuration, making it less preferable.[19,20,24] For oxy-fuel combustion, high purity oxygen (O_2) is utilized to combust carbon sources resulting in flue gas production that is free from unwanted gases (i.e., NOx) which ease the CO_2 storage.[25–27] Similar to pre-combustion, its ability to be retrofitted into existing plants is not promising due to the requirement of additional equipment (i.e., air separation unit and oxidizer) before a combustion unit.[20,28]

There are four main CO_2 capture technologies, that is, chemical absorption, adsorption, membrane separation and cryogenic distillation. Chemical absorption is the most researched, implemented and commercialized option among the named separation technologies, especially in post-combustion capture due to its distinct advantages.[11,14,29–35] These advantages include excellent CO_2 absorption efficiency of 80–100%, adaptability to low-pressure conditions and capability to produce high purity CO_2 (up to 99%).[2,12–14,31,32,34,36–41] Adsorption is also a highly regarded CO_2 separation technology due to its excellent CO_2 capture efficiency of up to 90% and flexibility to be implemented in post- and pre-combustion CO_2 capture.[14,31,42–46] Apart from that, most adsorbents are widely available, inexpensive and thermally stable.[2] However, adsorbents are also commonly associated with low adsorption capacity (i.e., 1.8–4.18 mmol of CO_2/g of absorbent) and low CO_2 selectivity.[1,47,48]

For cryogenic distillation, its application in post-combustion CO_2 capture is relatively new as it is typically applied in oxy-fuel combustion operations. Although cryogenic distillation offers excellent CO_2 capture efficiency of up to 95% and is able to capture CO_2 without the need for chemical reagents, its intensive energy requirement for refrigeration still withheld its favourability to be commercialized.[1,31,43] Membrane separation is also an alternative that offers excellent CO_2 capture efficiency (up to 88%), eco-friendly and has a much simpler carbon capture configuration as compared to other carbon capture technologies.[31,43,49] However, its requirement of specific conditions to perform effectively remains a hurdle for its commercialization. For example, flue gas applied to membrane separation system need to be free of impurities (i.e., SOx and NOx), high CO_2 partial pressure to ensure high separation efficiency and low temperature (25°C) for a non-metallic or ceramic membrane to avoid membrane degradation.[14,41,50]

This review looks into chemical absorbents' performance and their utilization pathway as it is the most preferred alternative and most researched among the available separation technologies. Under chemical absorption, there are five major absorbent groups: amine-based absorbent, carbonate absorbent, hydroxide absorbent, ionic liquid (ILs) and amino acid salts. Amine-based absorbents have the most publications from 2001 to 2021 with 4960 publications followed by carbonate absorbents with 704 publications, ILs with 213 publications, hydroxide absorbents with 55 publications and amino acids acid salts with 62 publications from the Scopus database. Amine-based absorbents are dominantly studied due to the early commercialization of monoethanolamine (MEA) for CO_2 capture in the 1970s, popularizing it as a potential absorbent for research. The remaining four absorbent groups have also gained increasing interest as potential CO_2 absorbents with an increment of 150% publications compared to the past 10 years.

Past reviews (from 2001–2021) conducted on chemical absorbents are insightful but do not critically review and benchmark the CO_2 capture performance of all major absorbent groups comprehensively in a single paper. Amine-based absorbents are discussed in Refs. 1, 2, 31, 32, 41, and 51–56 while carbonate absorbents in Refs. 14, 31, 32, 51, and 56 ILs are

presented in Refs. 2, 51, 54, and 57–59 and amino acid salts are reviewed in Ref. 51. In this review, all the aforementioned chemical absorbents are deliberately discussed. Upon the deliberate discussion of major chemical absorbent groups, this review aims to investigate the suitability of absorbents for CO_2 utilization with or without desorption which has never been comprehensively studied. Apart from that, this review also looks at some of the recently developed hybrid or novel absorbents (i.e., amine/ILs, amine/amino acid salts and amine/promoter hybrids) as they possess substantial potential in CO_2 absorption. Therefore, this paper aims not only to perform a deliberate review of all major absorbent groups and evaluate their suitability for CO_2 utilization based on their need for a desorption process but also examine the state-of-the-art synthesized chemical absorbents.

The performance of the CO_2 absorbents is evaluated based on the essential qualities as listed by Davidson.[53] To note, the considered qualities include high CO_2 reactivity in terms of CO_2 capture efficiency or absorption rate, low regeneration temperature, high absorption capacity and low environmental impact.

Chemical absorption absorbent

The following subsections review the unique qualities of each of the five major absorbent groups. The review begins with organic absorbents (amine-based absorbent, amino acid solution and ionic liquid) followed by inorganic absorbents (hydroxide and carbonate absorbent) and then some of the recently developed hybrid or novel absorbents. The discussion focused on are the CO_2 capture capability (CO_2 capture efficiency, CO_2 capture capacity or CO_2 absorption rate) of absorbents, regeneration energy requirement and environmental hazards. Each absorbent's reaction mechanisms are elaborated to grasp the necessary knowledge to perform an overview on their ideal absorption condition, interaction with flue gas composition and end-product of each absorbent.
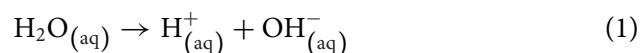
Amine-based absorbent
Primary amines
The primary amine, MEA) is the most well-known and employed absorbent within the CO_2 capture industry.[34,60,61] MEA was popularized due to its exceptional CO_2 removal capability (87.1–100%) while producing a nearly pure CO_2 of > 99%. Other primary

amines include, 2-(2-aminoethoxy) ethanol (DGA), 1-amino-2-propanol (1A2P) and 2-amino-1-butanol (2A1B) but none have reached the commercialization level of MEA. Primary amines are also known for their fast kinetics, high water solubility and low price.[53,62] It should also be noted that amine absorbents are typically applied for CO_2 capture operation in aqueous form instead of their pure state.

The CO_2 capture mechanisms of primary amines consist of four steps. First, is the ionization of water (reaction 1) and then CO_2 hydrolysis and ionization (reaction 2). Next is the protonation of alkanolamine (reaction 3). Lastly, the formation of carbamate (REACTION 4).[60] Each of the reactions is as follows:

$$H_2O_{(aq)} \rightarrow H^+_{(aq)} + OH^-_{(aq)} \qquad (1)$$

$$CO_{2(g)} + H_2O_{(aq)} \rightarrow HCO^-_{3(aq)} + H^+_{(aq)} \qquad (2)$$

$$RNH_{2(aq)} + H^+_{(aq)} \rightarrow RNH^+_{3(aq)} \qquad (3)$$

$$RNH_{2(aq)} + CO_{2(aq)} \rightarrow RNHCOO^-_{(aq)} + H^+_{(aq)} \qquad (4)$$

Although primary amines offer ideal CO_2 capture capability, they have their drawbacks. The most common drawback associated with primary amines is their proneness to degradation. There are two types of degradation for alkanolamines (i.e., thermal degradation and oxidative degradation).[11,63] These degradations can further contribute to more problems such as solvent loss, fouling, increased viscosity and corrosion of downstream equipment.[62] Another unappealing feature of primary amines is their relatively low CO_2 absorption capacity of approximately 0.35 to 0.56 mol CO_2/mol solvent.[64,65] Common pollutants in flue gas such as SOx and NOx would also disrupt the primary amines' CO_2 capture performance.[63] Thus, pre-treatment unit operation needs to be added for flue gas purification. In addition, the regeneration process of primary amines is energy-intensive (3.80–4.20 GJ/ton CO_2) as a high temperature of approximately 70–200°C is required.[13,38,39,66] This has led to a concentrated effort in finding alternatives to minimize solvent regeneration energy consumption.[67–70] Despite all these drawbacks, primary amine or specifically the MEA system is still the most utilized CO_2 capture technology to date.

One of the most recent studies on a pilot-scale CO_2 capture plant with MEA was demonstrated by Akram

et al.[68] in 2021. In this study, a typical 30 wt.% MEA system with a CO$_2$ capture efficiency and capacity of 90% and 1 ton CO$_2$/d, respectively, was used as a benchmark against a 40 wt.% MEA system. The aim of increasing the wt.% of MEA is to improve the CO$_2$ capture performance while reducing the solvent regeneration energy requirement. From their findings, the 40 wt.% MEA system applied to a 6.6 vol.% CO$_2$ gas stream was able to maintain a plausible CO$_2$ capture efficiency of 89.6% while reducing the regeneration energy consumption by 25.1%. It was also presented that if the temperature of the regeneration unit increases from 125.7 to126.8°C, the CO$_2$ capture efficiency and capacity can be increased to 91% and 74.6 g CO$_2$/kg MEA, respectively. However, the main drawbacks of increasing the regeneration temperature are the increase in overall energy consumption by 12.3% and the thermal degradation degree of solvent.

Another recent application of 30 wt.% MEA in a post-combustion capture pilot plant was demonstrated at Niederaussem from August 2017 to February 2019.[71] The capture capacity of this facility is approximately 0.25 tons CO$_2$/d with a capture efficiency of 90%. This study focuses on the degradation of MEA which is defined by the formation of oxidative degradation products (acetate, formate and oxalate) and the accumulation of trace elements (chloride, sulphur, sulphate, nitrate and iron) in the solvent. From the result, it was shown that the degradation of MEA after 100 h was 0.47 wt.%. or in terms of solvent consumption rate is approximately 0.21–0.35 kg MEA per ton of CO$_2$. To reduce the degradation of solvent, Moser et al.[71] proposed a solvent management strategy, namely an ion exchange-based reclaiming process to control the concentration of anionic degradation products and trace elements in MEA. In this process, a proprietary anion exchange resin was used to remove anionic trace elements from the solvent reducing the degradation degree of MEA. However, further analysis is required to optimize this process as this application is still relatively new in CO$_2$ capture operation.

Apart from MEA, Pellegrini et al.[39] also investigated the CO$_2$ absorption capability of DGA. In this comparative study, a 13–27 wt.% MEA and 8–27 wt.% DGA system was used to absorb CO$_2$ from flue gas with 7 wt.% CO$_2$. From the CO$_2$ removal efficiency result, it was shown that a 27 wt.% MEA system was able to achieve high efficiency ($\sim$ 95%) compared to a 27 wt.% DGA system ($\sim$ 88%) if absorber is operated at 20°C. However, from the temperature profile analysis,

it was reported that at a fixed absorber stage, the temperature required for DGA to achieve a 90% CO$_2$ removal efficiency is lower compared to a MEA system. For example, it was shown that in a two-stage absorber, the temperature required for an MEA system to achieve 90% CO$_2$ removal efficiency is approximately 67.5°C whereas DGA only requires a temperature of 63°C to achieve a similar efficiency. It was also shown that the regeneration efficiency of DGA is superior compared to MEA. From the result, it was shown that at a reboiler temperature of 110°C, the regeneration efficiency of DGA is approximately 90 % while MEA is only 66 %. Therefore, depending on the application conditions, both DGA and MEA can offer different advantages to a system. All in all, this shows that primary amines application is still relevant in the current CO$_2$ capture sector and gaps are still available for further research.

Secondary amines

Some examples of secondary amines are 2-(methylamino) ethanol (MMEA), N-ethylmonoethanolamine (EMEA), 2-(tertbutylamino) ethanol (TBMEA) and diethanolamine (DEA) the most applied secondary amine in CO$_2$ capture.[52,64,72,73] The majority of the secondary amines characteristics are similar to primary amines as they also have high reaction rates and high mass transfer toward CO$_2$. Based on Al-Baghli et al.,[52] the difference between the CO$_2$ loading of MEA and DEA (only DEA for comparison as the CO$_2$ loading of most secondary amines is not available) is only 0.0076 mol CO$_2$/mol solvent. Secondary amines also offer an exceptionally high absorption efficiency that ranges from 56.3 to 90%.[52,72,74]

Similar to primary amines, secondary amines also require a tremendous amount of energy for their regeneration process due to carbamate formation. Carbamate possess a relatively high heat of CO$_2$ desorption, thus requiring a high temperature (70 to 200°C) to regenerate the utilized amine.[13,38,66,72] The CO$_2$ capture mechanisms of secondary amines are also similar to primary amines.[38] Thus, Reaction (1) to (4) can be referred to as the CO$_2$ capture mechanisms of secondary amines by changing the RNH$_2$ (primary amines) to R$_2$NH (secondary amines).[38,60] Next, it has a low CO$_2$ absorption capacity of approximately 0.45–0.50 mol CO$_2$/mol solvent.[64] Also, secondary amines can cause adverse environmental and health hazards due to their volatile nature.[11] Thitakamol[75]

reported the loss of a significant amount of amine absorbent due to its volatility, leading to additional operating costs.

One of the most recent studies on unblended secondary amine for CO_2 capture was conducted by Barzagli et al.[74] in 2020. In this lab-scale analysis, primary amine (MEA, DGA, 1A2P, 2A1B), secondary amine (MMEA, EMEA, TBMEA, DEA) and tertiary amine (DMMEA and MDEA) are analyzed for direct air capture (DAC). From the reported result, secondary amine MMEA is shown to possess the highest CO_2 capture efficiency at 88.9 % among all the analyzed amines. Other than MMEA, EMEA, BUMEA and DEA also show plausible CO_2 capture efficiency ranging from 74.5 to 85.9%. However, most of the captured CO_2 by these secondary amines is in the form of carbamate which is typically associated with high solvent regeneration requirements. Among the secondary amines, only TBMEA does not produce carbamate as it is a sterically hindered amine like AMP, DMMEA and MDEA that only tends to produce bicarbonate and carbonate ions. However, within the sterically hindered amines shown here, TBMEA possesses a relatively low CO_2 capture efficiency of 56.3% as compared to AMP having an efficiency of 72.3%. From this study, it is shown that none of the secondary amines possess a good balance between an excellent CO_2 capture efficiency with a low solvent regeneration energy requirement. Thus, secondary amines are typically blended with other solvents for better performance.

In 2021, Wang et al.[76] also conducted another lab-scale experiment on amines CO_2 capture which includes DEA. In this study, an integrated absorption and mineralization process was proposed to absorb CO_2 with amine-based solvents then CO_2-rich solvents are regenerated via a mineralization process with semidry desulfurization slag (DFS). In this process, a gas mixture of 15 vol.% CO_2 and 85 vol.% N_2 was introduced into a 500 ml flask filled with amine solvents to undergo CO_2 absorption. After the absorption process, CO_2-rich solvent is then mixed with DFS (Ca-rich compound) to undergo mineralization to form calcium carbonate while regenerating the utilized solvent using a reflux system. The reported CO_2 loading of rich and lean DEA was approximately 0.73 and 0.18 mol CO_2/mol DEA respectively. For its desorption process, it was shown that the maximum achievable efficiency is 85% which is 13% lower as compared to that of AMP. The reason for this is that carbamate formed post-absorption could

not effectively mineralize the DFS unlike the bicarbonate ions produced by AMP. Nevertheless, this regeneration configuration which no longer requires the operation of a compressor and reboiler was able to reduce the regeneration energy consumption of a conventional amine desorption process by 93.7% from 3.65 to 0.23 GJ/ton CO_2.

Tertiary amines

Tertiary amines (i.e., 2-(dimethylamino)ethanol [DMAE], N-methyldiethanolamine [MDEA] and 2-diethylaminoethanol [DEAE]) have been receiving increasing attention as a CO_2 capture absorbent due to their higher CO_2 absorption capacity of 1 mol CO_2/mol solvent compared to the absorption capacity of primary and secondary amines, which is approximately 0.5 mol CO_2/mol solvent.[60,77] Other than that, due to the absence of $\alpha - H$ atom, tertiary amines are not able to react directly with CO_2 to form carbamates.[60] This would result in the formation of bicarbonate ions which require a much lower regeneration energy of approximately 58.8 kJ/mol CO_2 for tertiary amines to be regenerated compared to primary and secondary amine, which are 86.9 and 68.9 kJ/mol CO_2, respectively.[11,66,72,77]

The common drawback of tertiary amines is their low CO_2 absorption rate (~ 2.13 mol CO_2/h) compared to primary and secondary amines.[77] To make up for this deficiency, promoters such as piperazine (PZ) or carbonic anhydrase (CA) are typically blended with tertiary amines to increase their CO_2 absorption rate.[62,64,65] Based on Lawal et al.,[78] MDEA is prone to oxidative degradation, leading to the diminishing of CO_2 absorption capacity.

The CO_2 capture reaction *via* a tertiary amines-CO_2-H_2O system is as follows[66,77,79]:

$$R_3N_{(aq)} + CO_{2(g)} + H_2O_{(aq)}$$
$$\leftrightarrow R_3NH^+{}_{(aq)} + HCO_3^-{}_{(aq)} \quad (5)$$
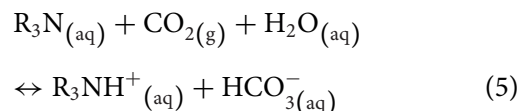
In 2021, Antonini et al.[80] demonstrated the application of an MDEA CO_2 capture facility for the generation of low-carbon hydrogen. In this application, a CO_2 capture configuration (as shown in Figure 1) that utilizes a dual flash, semi-lean recycle and split flow to desorber was implemented to capture CO_2 from syngas that contains 16.27 mol.% CO_2. The optimal CO_2 to MDEA molar ratio and MDEA weight fraction CO_2-free solution obtained via simulation
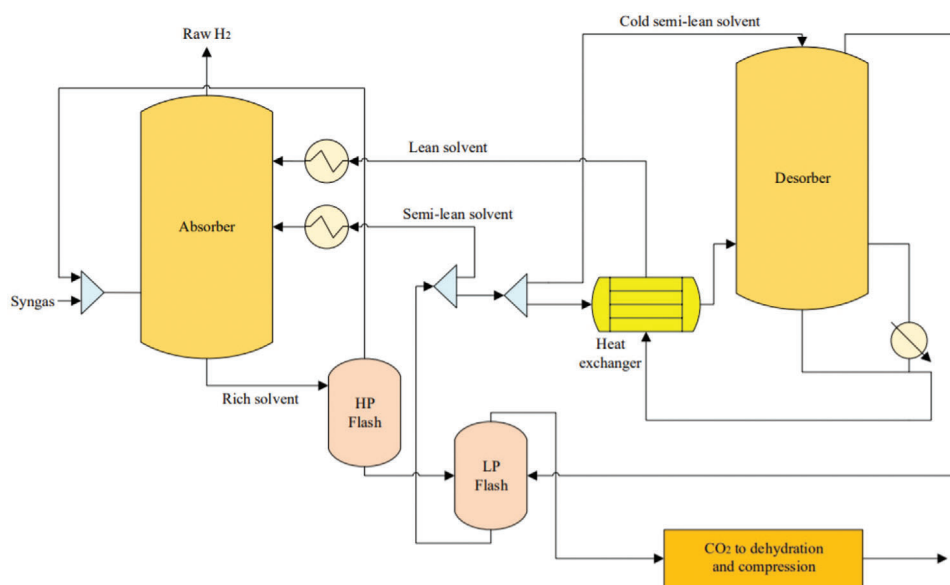
Figure 1. Flowsheet of dual flash, semi-lean recycle and semi-lean splitter CO_2 capture process. Modified with permission from Antonini et al.[80] Copyright 2021 Elsevier B.V.

work are 0.3 and 40 % respectively. Based on the result obtained, it was shown that a regeneration energy requirement of 0.61 MJ/kg CO_2 was obtainable at a CO_2 capture efficiency of 90%. This results in a 54.5% reduction of regeneration energy regeneration. Apart from that, such configuration has the potential to be a sustainable operation due to the production of clean hydrogen and the high CO_2 recovery percentage of > 97% which is suitable for further utilization.

Jaffary et al.[81] have also conducted a study on MDEA CO_2 capture back in 2021. In this study, polyamines (polyethylenimine [PEI-B], tetraethylenepentamine [TEPA] and PZ) are used as activators for MDEA to absorb a 100% CO_2 gas in a 100 ml three-necked round-bottom flask. From the result obtained, it was shown that an unblended 3 M MDEA system possesses the lowest CO_2 loading capacity and specific desorption rate at 0.63 mol CO_2/mol solvent and 0.0313 mol CO_2/mol solvent·min, respectively. Among the three polyamines mentioned, PEI-B was shown to have the best enhancement ability as it was able to increase the CO_2 loading and specific desorption rate of MDEA to 1.08 mol CO_2/mol solvent (i.e., 71.4 %) and 0.0385 mol CO_2/mol amine·min (i.e., 23 %) respectively. However, an increment in viscosity had occurred at the same time (from 2.122 mPa.s (unblended MDEA) to 15.945 mPa.s (0.3 M PEI-B/3 M MDEA)). This is unfavourable as the increase in viscosity can negatively affect the CO_2 absorption rate

of the system.[82] Among the polyamines, only the incorporation of PZ was able to increase the CO_2 and desorption rate performance without having an adverse effect on the viscosity of the solvent. It was observed that the 0.3 M PZ/3 M MDEA blended solvent has a CO_2 loading and specific desorption rate of 0.67 mol CO_2/ solvent and 0.0352 mol CO_2/mol amine.min while only having a slight increase in viscosity (0.2418 mPa.s). The main difference between the enhancement performance of PEI-B and PZ was in the available primary amino groups present in the respective polyamines. In short, PEI-B contains up to six primary amino groups while PZ has none.

Ionic liquid

ILs are salts that exist in a liquid phase at room temperature. ILs can sometimes be referred to as non-volatile liquids and as its name implied, are made up of cations and anions. Factors that have attracted researchers' interest are the remarkable solubility of CO_2 in ILs and the unique characteristics that it possesses, such as negligible vapor pressure, flexible designability, high thermal stability and eco-friendliness.[58,83] As stated by several studies,[57,84,85] ILs can be easily regenerated due to their low or negligible vapor pressure but data on the regeneration of ILs are limited.

Currently, ILs are still not preferred commercially due to their low absorption capacity and high viscosity.[77,86]

Table 1. Different groups of ILs and their respective example.[59]

Ionic liquids (ILs) groups	Examples of ionic liquids (ILs)
Imidazolium-based ionic liquids	• 1-N-Octyl-3-methylimidazolium hexafluorophosphate-C8min • 1-Ethyl-3-methylimidazolium ethyl sulphate-Emim
Ammonium-based ionic liquids	• 2-(2-Hydroxyethoxy)-ammonium lactate • Bis(2-hydroxyethyl)-ammonium acetate
Phosphonium-based ionic liquids	• N-Butyl-4-methylpyridinium tetrafluoroborate-MeBuPy • N-Butyl-4-Methylpyridinium thiocyanate-MeBuPy
Functionalized ionic liquids (TSILs)	• AMPim[NTf2] • AMPim[BF4]

Table 2. Average absorption capacity of different ILs groups.[59]

ILs groups	Average absorption capacity, mol CO_2/mol ILs
Imidazolium-based ionic liquids	0.333
Ammonium-based ionic liquids	0.147
Phosphonium-based ionic liquids	0.507
Functionalized ionic liquids (TSILs)	0.285

However, the CO_2 absorption performance of ILs can be enhanced by incorporating an amine function into the ILs structure.[87] Due to the extremely flexible designability of ILs, ILs need to be reviewed in groups rather than individually. Some well-known ILs groups include imidazolium-based ionic liquids, ammonium-based ionic liquids, phosphonium-based ionic liquids and task-selective ionic liquids (TSILs). Table 1 presents some examples of the respective group.

The absorption condition for different ILs varies considerably. Taking ammonium-based ionic liquids as an example, the ideal absorption condition for 2-(2-hydroxyethoxy)-ammonium lactate is 303 K and 65.7 bar while bis(2-hydroxyethyl)-ammonium acetate is 298.15 K and 15.15 bar.[59] Table 2 shows the average absorption capacity of the fore mentioned ILs groups. Also, the reaction mechanisms vary according to the type of ILs group. Figures 2(A and B) show the CO_2 capture mechanisms in amine-functionalized ILs and the chemical interaction of a phosphonium-based ionic liquid with CO_2, respectively.[58,88]

From a review conducted by Lian et al.[89] on ILs, it was shown that the main advantage that an ILs-based process has over an MEA-based process is in the economical aspect. It was shown that up to 24.8 to 30.01% of energy and 29.99% in primary cost can be saved due to the less energy-intensive absorption and desorption process of an ILs-based process. In the absorption process, the ILs-based process requires the feed gas mixture to be at a lower pressure (30 bar) as compared to an MEA process (> 30 bar) which requires it to have a multistage compressor to achieve this condition. The heat required for an MEA desorption operation is also much higher at 393.75 kW compared to an ILs desorption process which only requires 172.26 kW.[90] Apart from that, it was also presented that there are two proven unblended ILs that can achieve a high CO_2 solubility and low energy consumption compared to MEA. These ILs are 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF$_6$]) and 1-Butyl-3-methylimidazolium bis(trifuloromethanesulfonyl)imide ([Bmin][Tf$_2$N]) which have a CO_2 capture capacity of 0.513 and 0.681 mol CO_2/mol solvent respectively while the solubility of MEA is only 0.5 mol CO2/mol solvent.[83,91] The CO_2 capture energy consumption of [Bmim][PF$_6$] and [Bmim][Tf$_2$N] is also 35.6 (2.70 GJ/ton CO_2) and 71.5 % (1.194 GJ/ton CO_2), respectively lower compared to a typical MEA process (4.195 GJ/ton CO_2).

Amino acid solution

Common natural amino acids are taurine, proline and arginine while some examples of non-natural amino acids include piperazine-2-carboxylic acid, 2-(pyrimidin-2-ylamino) acetic acid and (1-piperazino)-2-propionic acid.[92] Natural amino acids have attracted interest as a CO_2 capture absorbent due to their eco-friendly characteristics. The fact that they exist naturally in the environment helps strengthen this prospect.[93] Also, they are less volatile due to their ionic nature.[37] Amino acid also possess similar functional groups as alkanolamines resulting in their reactivity and CO_2 absorption capacity to be comparable to amine-based absorbents.[2,37,64,92] In addition, amino acid solution have found great success in CO_2 capture implementation in various applications (i.e., biogas upgrading, flue gas decarbonization and natural gas purification).[93]
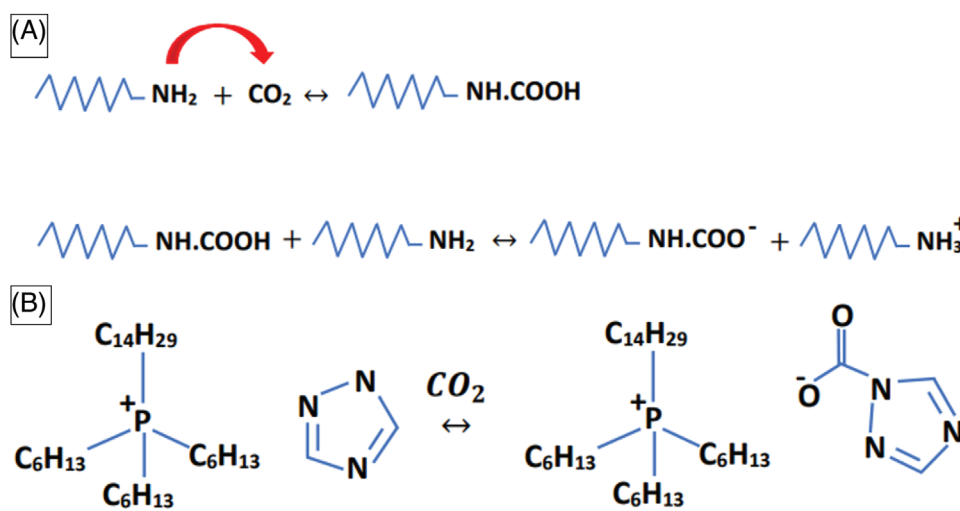
Figure 2. (A) CO$_2$ capture mechanisms in amine-functionalized ILs.[58]; (B) Chemical interaction of a phosphonium-based ionic liquid with CO$_2$.[88]

Although amino acids offer several advantageous features, the intensive regeneration energy requirement has been a concern in its application for CO$_2$ capture. Based on the experimental data presented by Knuutila et al.,[37] the regeneration energy requirement for CO$_2$-rich amino acid solvent ranges from 7.5 to 11.4 MJ/kg CO$_2$. Other than that, the absorption capacity of amino acids after the regeneration process drops drastically. As presented in the work by Munoz et al.,[37] the absorption capacity of most regenerated amino acid solvents dropped by half of their initial capacity. The CO$_2$ capture interaction between amino acid and CO$_2$ produces carbamate, as depicted in Figure 3. Apart from that, Zhang et al.[93] stated that the CO$_2$ capture performance of amino acids solution is greatly dependent on three factors, namely amino acid concentration, pressure and temperature. For example, the CO$_2$ loading of sodium β-alaninate (SA) shows a tremendous variation from 0.353 to 1.864 mol CO$_2$/mol amino acid, with a concentration, pressure and temperature range of 10 to 30 wt.%, 2–25 bar and 303–333 K, respectively.

From the experimental work by Knuutila et al.[37] and Munoz et al.,[92] the absorption capacity and regeneration energy requirement of amino acids vary greatly depending on the amino acid utilized. In general, the absorption capacity of amino acid solution can range from as low as 0.22 to as high as 2.23 mol CO$_2$/mol amino acid.[37,92]

More recently, Kasturi et al.[94] demonstrated the application of aqueous amino acids salt namely glycine to capture CO$_2$ from a simulated flue gas (12.8% CO$_2$) with an approximate capacity of 0.70 mol CO$_2$/mol glycine.[92] This process also incorporated glyoxal-bis(iminoguanidine) (GBIGs) for crystallization of the bicarbonate anions form after CO$_2$ absorption by glycine. This precipitation process generates GBIGH$_2^{2+}$(HCO$_3^-$)$_2$(H$_2$O)$_2$ while regenerating glycine without any high-temperature heating as compared to a typical desorption process. Based on Munoz et al.,[92] the absorption capacity of regenerated glycine may tend to drop from 0.70 to 0.50 mol CO$_2$/mol glycine after one cycle. After the regeneration of glycine, GBIGs can then be regenerated via heating of GBIGH$_2^{2+}$(HCO$_3^-$)$_2$(H$_2$O) and separated CO$_2$ can be stored or utilized. This two-stage regeneration process with an enthalpy of reaction of -28.69 kJ/mol has shown to be favourable compared to a direct regeneration of glycine pathway which requires a reaction enthalpy of 69 kJ/mol.

Hydroxide absorbent
Calcium hydroxide

Ca(OH)$_2$ aqueous solution has the potential to be an effective absorbent for CO$_2$ capture due to the advantageous features it offers. First, Ca(OH)$_2$ is relatively low in cost due to the abundance of both raw materials required for its production which are CaO and H$_2$O.[95] These materials are inexpensive and non-hazardous to the environment. Next, Ca(OH)$_2$ and CO$_2$ reaction mechanism, namely carbonation process, is a typical and well-researched reaction.[96,97]
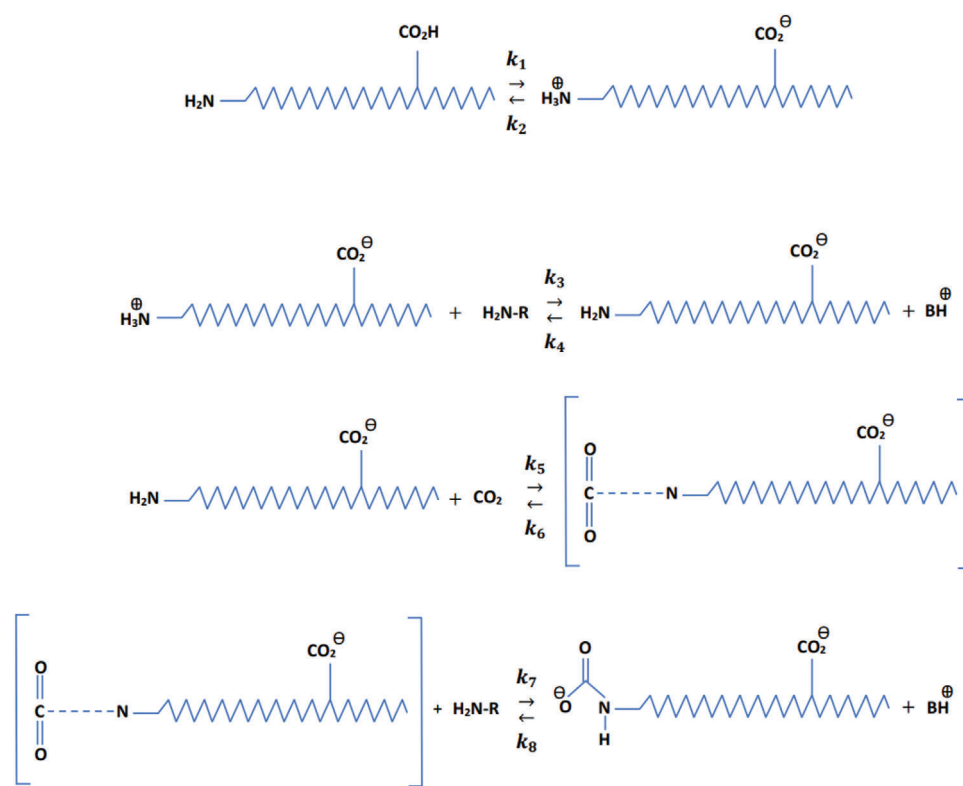
Figure 3. CO_2 capture mechanisms of amino acid salt.[92]

Third, $CaCO_3$ produced via the carbonation process can be easily handled with reclamation and regeneration processes readily available. The reclamation process in CO_2 sequestration offers various advantages such as low environmental risk, long-term storage and inexpensive.[95]

However, the $Ca(OH)_2$ absorbent application has not received much interest due to three main limitations. First is the energy-intensive extraction process required to extract CaO from natural limestone. Apart from that, the extraction process also emits a tremendous amount of CO_2.[95] Second, is the disposal of a large amount of $CaCO_3$ and H_2O produced from the carbonation process. As mentioned, reclamation and regeneration processes are available to handle the disposal of $CaCO_3$. However, handling it in a large amount is problematic as it would impose a high disposal cost.[95] Third, the regeneration process of $Ca(OH)_2$ is energy-intensive.[98] To regenerate $Ca(OH)_2$, $CaCO_3$ needs to undergo a calcination process at a high temperate of approximately 650 to 765°C to obtain CaO, which is a direct source of $Ca(OH)_2$.[98,99]

Based on Moreno et al.,[100] relative humidity (RH) plays a vital role in the CO_2 capture performance of $Ca(OH)_2$. Thus, achieving the required RH would be an additional problem to be taken into consideration. Shih et al.[101] prove that the reaction of $Ca(OH)_2$ and CO_2 to form $CaCO_3$ as shown in Reaction 6, only occur above a critical RH value of 8%.

$$Ca(OH)_{2(s)} + CO_{2(g)} \leftrightarrow CaCO_{3(s)} + H_2O_{(l)} \quad (6)$$
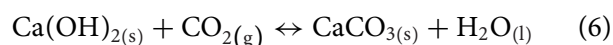
Within the temperature range of 25–750°C, this reaction will be thermodynamically favored.[95] Reaction 6 shown above is a combination of many sub-reactions. Initially, solid $Ca(OH)_2$ will undergo dissolution in water as shown in Reaction 7:

$$Ca(OH)_{2(s)} \leftrightarrow Ca^{2+}_{(aq)} + 2OH^-_{(aq)} \quad (7)$$
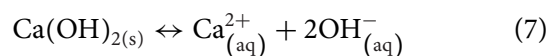
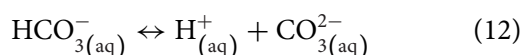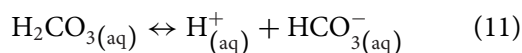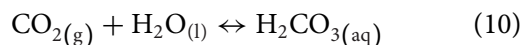The solubility of $Ca(OH)_2$ in water is highly dependent on temperature. Based on Han et al.,[95] the correlation between the $Ca(OH)_2$ solubility in water and temperature can be denoted as:

$$\text{solubility of Ca OH}_2 \, (\text{g/kg of solution})$$
$$= -0.0108T \, (°C) + 1.7465 \quad (8)$$

This reaction is followed by a series of reactions on the hydration of CO_2 to form carbonate ions. These

reactions are presented from Reactions 9–12:

$$CO_{2(g)} \leftrightarrow CO_{2(aq)} \tag{9}$$

$$CO_{2(g)} + H_2O_{(l)} \leftrightarrow H_2CO_{3(aq)} \tag{10}$$

$$H_2CO_{3(aq)} \leftrightarrow H^+_{(aq)} + HCO^-_{3(aq)} \tag{11}$$

$$HCO^-_{3(aq)} \leftrightarrow H^+_{(aq)} + CO^{2-}_{3(aq)} \tag{12}$$

The predominant level of bicarbonate ion and carbonate ion is dependent on the pH of the solution. Formation of CO_3^{2-} and HCO_3^- are favourable at pH > 10.5 and 6.5 < pH < 10.5, respectively.[95] Lastly, Ca ions from the dissolution of $Ca(OH)_2$ will react with CO_3^{2-} to form $CaCO_3$. This reaction is as follows:

$$Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)} \leftrightarrow CaCO_{3(s)} \tag{13}$$
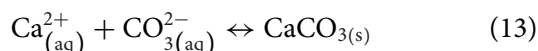
The experiment conducted by Han et al.[95] on CO_2 capture capability of $Ca(OH)_2$ shows the absorption capacity of $Ca(OH)_2$ ranges from 1 to 3.05 g CO_2/g $Ca(OH)_2$.L, the average absorption efficiency ranges from 11.83 to 19% and has an approximate absorption rate of 0.69 to 1.07 g CO_2/min. These data are highly dependent on the pH of the system and the amount of $Ca(OH)_2$ added.
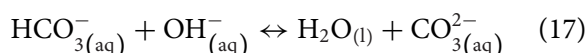
Sodium hydroxide (NaOH)

The usage of NaOH for CO_2 absorption has been studied intensively for the past 80 years. However, the majority of the studies conducted were focused on academic endeavours such as absorption mechanisms and system performance rather than on CO_2 capture.[102,103] NaOH has an excellent CO_2 absorption capacity which is higher than that of MEA absorbent. Yoo et al.[104] stated that the theoretical absorption capacity of NaOH is 1.11 tons CO_2/ton NaOH while MEA is approximately 0.72 tons CO_2/ton MEA. In addition, NaOH is also more abundant and inexpensive as compared to MEA.[104]

However, NaOH cannot be easily regenerated due to the formation of $NaHCO_3$ when reacted with CO_2. Due to its high solubility in an aqueous solution and its decomposed product, Na_2CO_3. Na_2CO_3 is a thermally stable compound that can be decomposed to Na_2O, at a temperature of over 800°C.[105] Na_2O as a direct source of NaOH can be mixed with water to obtain the latter compound.[104]

The overall CO_2 absorption reaction with NaOH is as follows:

$$NaOH_{(aq)} + CO_{2(g)} \rightarrow NaHCO_{3(aq)} \tag{14}$$
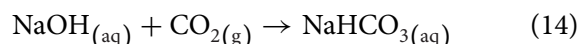
The absorption reaction is initiated by the ionization of Na+ and OH− in pure water. This is followed by the physical absorption of gaseous CO_2 to aqueous CO_2 in the NaOH solution as shown in Reaction 15. Next, aqueous CO_2 reacts with OH− to generate HCO3− and CO_3^{2-} as expressed in Reaction 16 and 17:

$$CO_{2(g)} \leftrightarrow CO_{2(aq)} \tag{15}$$

$$CO_{2(aq)} + OH^-_{(aq)} \leftrightarrow HCO^-_{3(aq)} \tag{16}$$

$$HCO^-_{3(aq)} + OH^-_{(aq)} \leftrightarrow H_2O_{(l)} + CO^{2-}_{3(aq)} \tag{17}$$

Thus, giving the net reaction during the initial stage of overall CO_2 absorption can be expressed as:

$$2NaOH_{(aq)} + CO_{2(g)} \rightarrow Na_2CO_{3(aq)} + H_2O_{(l)} \tag{18}$$
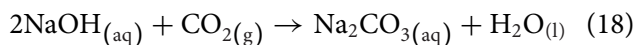
Given that Na_2CO_3 is produced, it exists as Na^+ and CO_3^{2-} ions in the system. As CO_2 is continuously fed into the system, CO_2 is continuously absorbed and reacts with Na_2CO_3 to form $NaHCO_3$ as shown:

$$Na_2CO_{3(aq)} + CO_{2(g)} + H_2O_{(l)} \rightarrow 2NaHCO_{3(aq)} \tag{19}$$
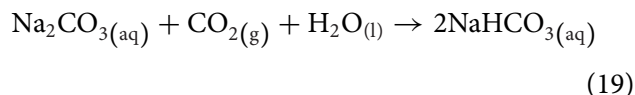
Yoo et al.[104] experimented to investigate the CO_2 capture efficiency of NaOH at varying wt.%. In this study, an NaOH system with a concentration of 1 to 5 wt.% was used to capture a gas mixture with 31.5 vol.% CO_2 in a Pyrex reactor set-up. The obtained results show that as NaOH wt.% increases from 1 to 5%, the CO_2 capture efficiency also increases from 35.73 to 57.99%. It was deduced by the investigator that the CO_2 capture efficiency in a NaOH system is highly dependent on the concentration of the solvent.

In another study conducted by Kordylewski et al.,[106] an NaOH system with a concentration of 0–50% was implemented to capture a gas mixture with a 15 vol.% CO_2 in a Dreschel washer set-up. The results obtained from their experimental work show that the CO_2 removal efficiency increases from approximately 2% in a 0 % NaOH system up to 92% in a 50% NaOH system. The results agree with the deduction and the result obtained by Yoo $et\ al.$[104]. Apart from that, the effect of temperature on the CO_2 capture efficiency of the NaOH system was also investigated. From the result, it was shown that by increasing the absorption

temperature from 25 to 61.5°C, the overall CO_2 capture efficiency can be improved by approximately 5–20%. It was also stated that after the formation of Na_2CO_3 post absorption by NaOH, the carbonate can still capture CO_2 to form $NaHCO_3$ but with relatively low CO_2 capture efficiency of 4–5%.

Additional hydroxide absorbent includes potassium hydroxide (KOH). However, the research on KOH is limited to its CO_2 performance data as a detailed description of its CO_2 capture mechanisms is not available like $Ca(OH)_2$ and NaOH.[107,108]
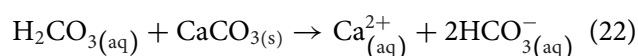
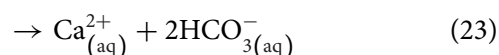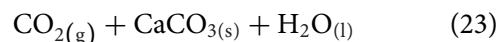## Carbonate absorbent

Calcium carbonate

The utilization of $CaCO_3$ absorbent is typically incorporated in a process called accelerated weathering of limestone (AWL). AWL process is the enhanced version of the naturally occurring carbonate weathering process, which is an extremely slow process. AWL can accelerate the speed of the process due to the higher CO_2 concentration of flue gas compared to atmospheric air.[109] This process is well-known for its economically and environmentally friendly characteristics. Rau et al.[110] stated that the CO_2 mitigation cost offered by AWL could be as low as $3 to $4/ tonne CO_2 as the cost for both its main material, namely limestone and seawater are either extremely low or negligible. For its environmental perk, the discharge of calcium bicarbonate effluent produced via AWL can help combat the ocean's acidification problem.[109,111] However, it was reported by Kircher[109] that about 50% of the captured CO_2 in the effluent disposed into the ocean can re-enter the atmosphere which thus reduces the overall CO_2 capture efficiency of this system. To overcome this, it was recommended that a suitable discharge site and optimal size of waste stream need to be determined prior to disposal of effluent into the ocean.

Apart from that, the large commercialization of AWL system for CO_2 capture is limited by its requirement to be built near coastlines. The purpose of setting AWL system near the coastline is for easier access to seawater and disposal of calcium bicarbonate effluent into the ocean.[12] The CO_2 capture efficiency of this system was reported to be as high as 97% in a lab-scale operation but will be significantly reduced to < 20% for application in small industrial processes.[112,113] The AWL process CO_2 capture mechanisms can be divided into three steps: dissolving of gaseous CO_2 in water to form aqueous CO_2, hydration of CO_2 to form carbonic acid (H_2CO_3) and absorption of H_2CO_3 by limestone to produce calcium bicarbonate. These reactions are as shown:

$$CO_{2(g)} \rightarrow CO_{2(aq)} \tag{20}$$

$$CO_{2(aq)} + H_2O_{(l)} \rightarrow H_2CO_{3(aq)} \tag{21}$$

$$H_2CO_{3(aq)} + CaCO_{3(s)} \rightarrow Ca^{2+}_{(aq)} + 2HCO^-_{3(aq)} \tag{22}$$

The overall net reaction is as presented:

$$CO_{2(g)} + CaCO_{3(s)} + H_2O_{(l)} \tag{23}$$

$$\rightarrow Ca^{2+}_{(aq)} + 2HCO^-_{3(aq)} \tag{23}$$

Currently, the largest operating AWL reactor can be found at a coal-fired power plant in Wilhelmshaven, Germany.[112] In this industrial-scale study led by Kirchner et al.[112], a multi-column absorption set-up was applied for CO_2 capture from flue gas with 10–12 vol.% CO_2. The reported CO_2 capture efficiency of this post-combustion AWL application is 55% and it was reported that the effluent produced has a fivefold increase in alkalinity (10 mM total alkalinity) compared to a precombustion AWL application (2 mM total alkalinity). This indicated that limestone is successfully weathered and long-term storage of capture CO_2 is achievable. Apart from that, no harmful substances (NOx, SOx and heavy metals) were detected in the effluents. Thus, the disposal of effluent into the ocean is considered safe.

Sodium carbonate

Na_2CO_3 is an ideal absorbent for CO_2 capture in terms of environmental consideration as it is non-hazardous, non-volatile and can act as a multi-pollutant capture system. Also, it poses a low equipment corrosion rate and will not cause fouling to the piping system. It was also reported by Barzagli et al.[114] that aqueous Na_2CO_3 possesses a relatively high CO_2 absorption efficiency of 80%.

However, Na_2CO_3 is not feasible due to its economic drawback. Sprigarelli et al.[31] and Valluri et al.[115] state that Na_2CO_3 has a low CO_2 absorption rate due to its low physical mass transfer rate leading to a higher absorption tower requirement. To overcome this problem, several studies focused on improving Na_2CO_3 CO_2 absorption rate by adding additives such as sucrose, PZ, DEA, MEA and hypochloride. These additives were proven to be able to improve the

absorption rate. However, the blended additives will further increase the already high regeneration energy of Na$_2$CO$_3$ which is approximately 3.2 MJ/kg CO$_2$. Thus, increasing the overall operating cost and resulting in a negligible effort on the economic saving.[31]

The CO$_2$ capture mechanisms and precipitation of NaHCO$_3$ via aqueous Na$_2$CO$_3$ is as follows:

$$CO_{3(aq)}^{2-} + H_2O_{(l)} + CO_{2(g)} \rightarrow 2HCO_{3(aq)}^{-} \quad (24)$$

$$Na_{(aq)}^{+} + HCO_{3(aq)}^{-} \leftrightarrow NaHCO_{3(s)} \quad (25)$$
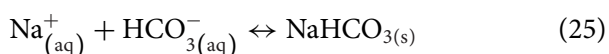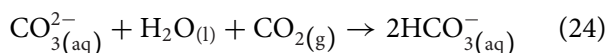
From a reaction simulation conducted by Sprigarelli et al.,[31] the theoretical CO$_2$ absorption capacity of Na$_2$CO$_3$ is approximately 0.73 kg CO$_2$/kg CO$_3{}^{2-}$ which is higher than that of a typical MEA system of 0.40 kg CO$_2$/kg MEA. This CO$_2$ absorption capacity is expected to decrease in the presence of impurities such as SO$_x$ and NO$_x$ but Na$_2$CO$_3$ acts as a multi-pollutant control system.
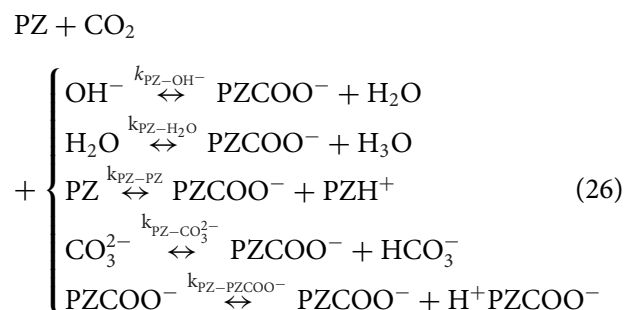
In 2021, Valluri and Kawatra[115] presented a study on post-combustion CO$_2$ capture with dilute sodium carbonate slurry. In this study, the absorption and desorption performance of the Na$_2$CO$_3$ slurry system was investigated. In this mini-pilot scale study, an absorber packed with polypropylene pall rings is used to capture CO$_2$ (16 vol.% CO$_2$) using Na$_2$CO$_3$ slurry at a temperature and pressure of 31 to 38.5°C and 1 bar, respectively. The resulting NaHCO$_3$ solution was sent to a flash drum to undergo regeneration (at 98°C and 2 bar) of Na$_2$CO$_3$ for further CO$_2$ capture and separation of pure CO$_2$ for storage. Based on the results, it was shown that the CO$_2$ capture efficiency of Na$_2$CO$_3$ (40%) is far inferior to the efficiency of an MEA and NaOH system of approximately 95%. It was observed that as the solvent concentration of the respective systems increases from 0.1 to 0.2 M, the CO$_2$ capture efficiency of Na$_2$CO$_3$ increases to 55.6% while the MEA and NaOH only have a 2% increase in their efficiency. However, the CO$_2$ capture efficiency of Na$_2$CO$_3$ is still inferior. Therefore, to overcome this, Valluri and Kawatra[115] added a frother namely DF200 into the Na$_2$CO$_3$ system to enhance its CO$_2$ capture efficiency. With the addition of as little as 10 ppm of DF200, the CO$_2$ capture efficiency of Na$_2$CO$_3$ was enhanced to 99.90% which is approximately 2.9% higher compared to the 0.2 M MEA and NaOH systems. The added frothers helps to modify the bubble surface of the absorbent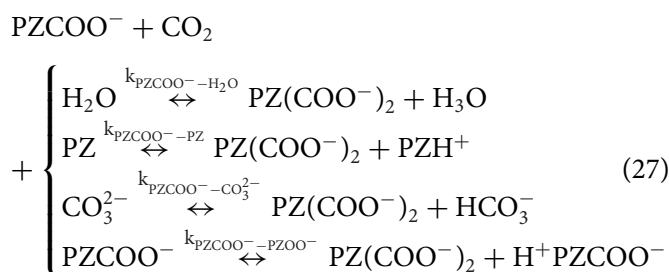 which allows smaller and more uniform bubbles to be produced. This, can in turn, help to increase the contact area of the gas and liquid leading to a better mass transfer. For the regeneration performance of the Na$_2$CO$_3$-DF200 system, it was determined that heat of 3.18 MJ/kg CO$_2$ is required to regenerate the absorbent. It was deduced that the addition of frothers has a negligible impact on the regeneration energy requirement due to its extremely low concentration. All in all, the regeneration energy required for this system is approximately 24.2% lower compared to a typical MEA system.

Potassium carbonate

Aqueous K$_2$CO$_3$ has gained interest as an absorbent due to its various advantageous features such as low cost, low toxicity, high degradation resistance and low enthalpy requirements. However, two disadvantages that limit its applications for CO$_2$ capture are its intensive regeneration energy and low mass transfer rate. It was reported that the energy required for K$_2$CO$_3$ regeneration ranges from 87.1 to 143 kJ/mol.[116,117] Apart from that, the application of K$_2$CO$_3$ in CO$_2$ capture is typically coupled with a promoter to make up for its low mass transfer rate.[32]

Based on the experiment conducted by Sreedhar et al.[32] and Plaza et al.,[118] up to 9 promoters comprised of MDEA, MEA, DEA, glycine, carbonic anhydrase CA, PZ, arginine, sarcosine and proline were tested with K$_2$CO$_3$. With these promoters, the absorption rate of K$_2$CO$_3$ can be enhanced 45-fold as compared to unpromoted K$_2$CO$_3$ while exhibiting excellent absorption efficiency of 80 to 99.4%. However, the addition of these promoters has its drawbacks such as possible losses through evaporation, which can cause degradation and corrosion to downstream equipment.[32] The CO$_2$ capture mechanisms in a PZ-promoted K$_2$CO$_3$ system focus on the reaction interaction of PZ rather than K$_2$CO$_3$.[118] The CO$_2$ capture mechanisms are as follows:

$$PZ + CO_2$$

$$+ \begin{cases} OH^- \overset{k_{PZ-OH^-}}{\leftrightarrow} PZCOO^- + H_2O \\ H_2O \overset{k_{PZ-H_2O}}{\leftrightarrow} PZCOO^- + H_3O \\ PZ \overset{k_{PZ-PZ}}{\leftrightarrow} PZCOO^- + PZH^+ \\ CO_3^{2-} \overset{k_{PZ-CO_3^{2-}}}{\leftrightarrow} PZCOO^- + HCO_3^- \\ PZCOO^- \overset{k_{PZ-PZCOO^-}}{\leftrightarrow} PZCOO^- + H^+PZCOO^- \end{cases} \quad (26)$$

$$PZCOO^- + CO_2$$

$$+ \begin{cases} H_2O \overset{k_{PZCOO^--H_2O}}{\leftrightarrow} PZ(COO^-)_2 + H_3O \\ PZ \overset{k_{PZCOO^--PZ}}{\leftrightarrow} PZ(COO^-)_2 + PZH^+ \\ CO_3^{2-} \overset{k_{PZCOO^--CO_3^{2-}}}{\leftrightarrow} PZ(COO^-)_2 + HCO_3^- \\ PZCOO^- \overset{k_{PZCOO^--PZOO^-}}{\leftrightarrow} PZ(COO^-)_2 + H^+PZCOO^- \end{cases} \quad (27)$$

Bohloul et al.[119] have also conducted a study that aims to investigate the effect of temperature (313.15 to 333.15 K), pressure (0 to 1.2 MPa) and concentration of K_2CO_3 (15 to 30 wt.%) have on the CO_2 absorbability of K_2CO_3. The CO_2 absorption setup is an absorption cell filled with K_2CO_3 solutions to absorb a gas stream with pure CO_2. It was observed from the experimental result that as temperature increases there is a sharp drop in CO_2 loading of K_2CO_3 as much as 0.46 mol CO_2/mol K_2CO_3 whereas as pressure increases, CO_2 loading can be increased by as much as 0.57 mol CO_2/mol K_2CO_3. Other than that, it was also shown that the 20 wt.% K_2CO_3 system has shown the highest CO_2 loading among the proposed concentration. The optimized conditions deduced from this study were 313.15 K, 1 MPa and 20 wt.% K_2CO_3 gives a peaked CO_2 loading of 1.25 mol CO_2/mol K_2CO_3, which is approximately 2.5 times higher than the CO_2 loading of a conventional MEA system.

Hybrid/novel absorbent

From subsections Amine based absorbent–Carbonate absorbent, several absorbents have been identified for the CO_2 capture and utilization system. Although all the absorbents present plausible CO_2 capture and utilization capabilities, some of their applications are restricted by severe limitations. These include toxicity of amine absorbents group and ILs, low CO_2 capture absorption rate for MDEA, limited application data of carbonate absorbents in CO_2 capture, limited direct utilization option of hydroxide absorbents and $CaCO_3$, and uncertainty on the post-absorption product by amino acid salts.[65,107,120–123] To resolve these limitations, researchers have ventured into synthesizing novel absorbents via hybrid mixing and incorporating promoters or enhancers into CO_2 capture systems.[32,38,65,66,83,118,124–126] The purpose of these initiatives is to combine the advantages of the different absorbents to enhance their CO_2 capture performance and overcome their limitations.[89,127] As numerous hybrid absorbents are being proposed over the years,

this subsection only highlights some of the recent development of different hybrid absorbents.

One popular absorbent system developed is the hybrid of alkanolamines and ILs.[125,126,128–131] In 2021, Damanafshan et al.[129] analyzed the carbon capture performance of an aqueous MDEA and [Omin][BF$_4$] IL blend. It was reported that the blended absorbent can enhance CO_2 absorption capacity of approximately 0.05 to 2 mol CO_2/mol amine compared to a typical MDEA solution. In this system, the sole chemical reaction that occurred is MDEA with CO_2 to form bicarbonate while the IL ([Omin][BF$_4$]) only interacts physically with CO_2. Although no data were presented on the handling of the post-absorption product, bicarbonates can be potentially utilized to produce construction material following the chemical reaction shown by Reaction 28 instead of proceeding with the typical regeneration pathway for an amine absorbent.

$$CaO + Ca(HCO_3)_2 \rightarrow 2CaCO_3 + H_2O \quad (28)$$

Other than that, the development of non-aqueous amine solvents is also a promising alternative to be investigated. The application of non-aqueous amines is incredibly limited in the carbon capture industry. However, their reported properties are promising for CO_2 capture application.[132,133] The non-aqueous amine is used as a replacement of water with organic compounds (i.e., ethylene glycol [MEG] and triethylene glycol [TEG]) during the preparation of amines solvent. This replacement leads to lower water content in a non-aqueous amine system compared to a typical aqueous amine system. The CO_2 capture reaction can be redirected towards a less stable carbonate species with the reduced water content, resulting in a lower regeneration temperature.[133] This would not only reduce the regeneration energy requirement but can also curb the degradation and evaporation of solvent while lowering the corrosion rate imposed on operational infrastructure.[133] From a study conducted by Tan et al.,[134] a non-aqueous amine (MEA + TEG) solvent was employed for CO_2 capture. This study shows that the replacement of water with TEG in the preparation of the amine solvent reduces the regeneration energy consumption of a typical MEA system from 4.20 to 1.99 MJ/kg CO_2. Apart from that, the non-aqueous amine system with 0.5 M MEA retained a similar CO_2 loading of approximately 0.50 mol CO_2/mol MEA compared to an aqueous 0.5 M MEA system.

Table 3. CO₂ capture performance of NaADS/PZ/DETA and typical MEA system.[127]

CO₂ capture performance	NaADS/PZ/DETA	30 wt.% MEA	Surplus
CO₂ loading, mol CO₂/mol sovent	0.48 to 0.74	0.31 to 0.48	0.34 to 0.41
CO₂ capture efficiency, %	57.10	70.20	13.1
CO₂ capture rate, CO₂/min	3.79	4.66	0.87

In another study conducted by Xiao et al.,[130] the performance of hybrid absorbents which incorporate MEA and IL; and MDEA and IL were analyzed. The incorporation of MEA into a [Bmim]BF₄ system enhanced its CO₂ loading from approximately 0.02 to 0.12 g CO₂/g absorbent (about a fivefold increment). For MDEA and [Bmim]BF₄ system, an increment of 2.5 times in CO₂ loading was observed. Apart from that, the regeneration of such hybrid absorbent was more energy-efficient than a conventional MEA system. Generally, the desorption temperature required for the hybrid system is lower at 353 K compared to the 369 K required by a conventional MEA system. Herein, it is shown that the post-absorption product will undergo desorption to regenerate the absorbent and separate the captured CO₂. Therefore, it is deduced that the separated CO₂ can be used as a potential feedstock for industrial applications.

Besides the typical IL and amine hybrid, Chen et al.[127] have also proposed mixing amino acid salt with amines. Sodium aliphatic diamine sulphonate (NaADS) was used as a suitable amino acid salt for hybrid mixing with PZ and diethyenetriamine (DETA). The mixing ratio of PZ/DETA/NaADS of 15/15/10 wt.% was used and the CO₂ capture performance of this hybrid solvent was evaluated using a two rotating packed bed set-up. From the reported results, a 30 wt.% unblended NaADS only shows a CO₂ loading and CO₂ capture efficiency of approximately 0.74 mol CO₂/mol NaADS and 37.5 %, respectively. With the addition of PZ and DETA, these values were enhanced to 0.89 mol CO₂/mol solvent (i.e., 20.3%) and 70.2% (i.e., 87.2 %), respectively. As a comparison, Table 3 shows the CO₂ capture performance of the hybrid solvent as compared to a typical MEA system. Apart from that, the proposed solvent also has an upper hand on the regeneration performance as the reported regeneration energy

consumption is only at 3.83 GJ/ton CO₂ which is approximately 0.37 GJ/ton CO₂ lower than a typical MEA system. This is mainly due to the lower vapor pressure and specific heat capacity of NaADS. All in all, it is proven by these researchers that the synthesis of novel absorbents is an essential initiative to foster a more sustainable absorption process. However, as highlighted by Budzianowski et al.,[135] the utilization potential of these novel absorbents has not been evaluated which can withhold its potential to develop a sustainable carbon capture process.

Comparison of CO₂ chemical absorption absorbents

Based on the chemical absorbents for CO₂ capture presented from subsections Amine based absorbents to Hybrids/novel absorbent a summary and comparison are provided in this subsection. Table 4 indicates that most aqueous amine absorbents possess relatively higher CO₂ removal efficiency (80–90%). In addition, a descending trend in the CO₂ absorption rate and regeneration energy requirement of amines can be observed starting from primary amines followed by secondary and tertiary amines. As shown in Table 4, primary amines are typically associated with the highest CO₂ absorption rate and regeneration energy followed by secondary and tertiary amines. The unfavourable properties of amines are their inferior CO₂ capture capacity as compared to some hydroxide absorbents (i.e., Ca(OH)₂) and amino acid solutions (i.e., Arginine, 4-(2-Aminoethyl)piperazine-1-yl acetic acid and 3-(2,5-Dimethylpiperazine-1-yl) propanoic acid).

For ionic liquid absorbents, their CO₂ capture capabilities are inferior compared to other chemical absorbents. However, the standout point of ionic liquids is their high designability, ease of regeneration and eco-friendliness. The flexible designability of ionic liquids allows them to alter their physical and chemical properties to cater to a specific application. This opens up a wide range of applications of ionic liquids for CO₂ capture purposes. For the regeneration of ionic liquids, it was reported that the energy required is only 172.26 kW which is significantly lower than that of MEA (393.75 kW) regeneration process. They are also inflammable and non-volatile making them environmentally friendly.

On the other hand, amino acid solutions have a high average CO₂ capture capacity (> 1 mol CO₂/mol

Table 4. Summary of CO₂ capture absorbents.

Absorbents (Concentration)	Absorption performance				Regeneration performance			Handling modes	Sources
	Capacity, mol CO_2/mol absorbent	Removal Efficiency %	Rate, mol CO_2/hr	Post-absorption product	Regeneration energy requirement, MJ/kg CO_2	CO_2 purity %	Post-regeneration product		
Amine-based absorbent									
MEA (30–40 wt.%)	0.35–0.56	80 – 100	7.35	• $RNHCOO^-$	3.80–4.20	99	• After regeneration will obtain its respective amine absorbents and CO_2	• Regeneration at 70–200° C to regenerate respective absorbents • Utilization of separated CO_2 in food and beverage industry, and urea production	2, 31, 32, 36, 39, 41, 52, 64–66
DGA (8–27 wt.%)	—	88–90	—	•	—	—	•	•	39
1A2P (0.15 mol)	—	88.4	—	•	—	—	•	•	74
2A1B (0.15 mol)	—	87.1	—	•	—	—	•	•	
DEA (30 wt.%)	0.50	82–90	4.15	1.57	—	•	52, 64, 72		
MMEA (0.15 mol)	—	88.9	—	—	—	•	74		
EMEA (0.15 mol)	—	85.9	—	—	—	•			
TBMEA (0.15 mol)	—	56.3	—	—	—	•			
MDEA (30 wt.%)	1	80 – 99	2.13	• $R_1R_2R_3N^+$-H • HCO_3^-	0.61–1.34	—	•		2, 32, 64, 65, 72, 80
DMMEA (0.15 mol)	—	40.8	—	•	—	—	•	74	
DEAE (30 wt.%)	0.46–0.61	—	—	•	1.42	—	•	66	
Ionic liquid (ILs) absorbent									
[Bmin][BF₄]	0.44	—	—	• CH_3NO_2 • $CH_2NO_2^-$ • HCO_3^- • Carbonate salts	2.63–2.80	—	—	—	2, 57, 59, 83, 91, 153
[Bmim][PF₆]	0.51	—	—	•	2.70	—	—	—	—
[Bmim][Tf₂N]	0.68	—	—	•	1.19	—	—	—	—

(Continued)

Table 4. (Continued).

	Absorption performance					Regeneration performance				
Absorbents (Concentration)	Capacity, mol CO$_2$/mol absorbent	Removal Efficiency %	Rate, mol CO$_2$/hr	Post-absorption product		Regeneration energy requirement, MJ/kg CO$_2$	CO$_2$ purity, %	Post-regeneration product	Handling modes	Sources
Bis(2-hydroxyethyl)-ammonium acetate	0.04–0.11	–	–	•		–	–	–	–	–
N-Butyl-4-methylpyridinium tetrafluoroborate-MeBuPy	0.01–0.11	–	–	•		–	–	–	–	–
N-Butyl-4-Methylpyridinium thiocyanate-MeBuPy	0.06–0.1	–	–	•		–	–	–	–	–
AMPim[NTf2]	0.18–0.27	–	–	•		–	–	–	–	–
APMim[BF4]	0.32–0.36	–	–	•		–	–	–	–	–
Amino acid absorbent										
Natural amino acid										92, 122, 159–161
Taurine (1 M)	0.52–1.1	–	–	• Protonated amino acid • Bicarbonate salt of amino acid • Carbamate		–	–	• If undergo regeneration will obtain the respective absorbent and CO$_2$	• Precipitates depend on the type of amino acid salt utilized, if precipitates are desired product, a desorption process is not required • If precipitates are not desired, can opt for regeneration to regenerate absorbents	
Proline (1 M)	0.45–0.89	–	–	•		–	–	–		
Arginine (1 M)	0.80–1.7	–	–	•		–	–	–		
Glycine (1 M)	0.50–0.70	–	–	•		–	–	–		

(Continued)

Table 4. (Continued).

Absorbents (Concentration)	Absorption performance				Regeneration performance				
	Capacity, mol CO₂/mol absorbent	Removal Efficiency %	Rate, mol CO₂/hr	Post-absorption product	Regeneration energy requirement, MJ/kg CO₂	CO₂ purity, %	Post-regeneration product	Handling modes	Sources
Non-natural amino acid									
Potassium sarcosine (4 M)	0.40–0.55	—	—	• Protonated amino acid • Bicarbonate salt of amino acid	7–12	—	• If undergo regeneration will obtain the respective absorbent and CO₂	• Precipitates depend on the type of amino acid utilized, if precipitates are desired product, a desorption process is not required • If precipitates are not desired, can opt for regeneration to regenerate absorbents	
2-(Pyrimidin-2-ylamino) acetic acid (1 M)	0.26–1.08	—	—	•	—	—			
[4-(2-Aminoethyl) piperazin-1-yl] acetic acid (1 M)	1.11–1.86	—	—	•	—	—			
3-(2,5-Dimethylpiperazin-1-yl) propanoic acid (1 M)	1.13–2.23	—	—	•	—	—			
Sodium β-alaninate (10–30 wt.%)	0.353–1.864	—	—	•	—	—	93		
Trisodium phosphate (1–2.5 M)	0.027–0.05	—	—	•	—	—			
Potassium taurinate (2–6 M)	0.057–1.097	—	—	•	—	—			
Potassium threonate (1 M)	0.092–0.753	—	—	•	—	—			

(Continued)

(Continued)

Table 4. (Continued).

| Absorbents (Concentration) | Absorption performance | | | | Regeneration performance | | | | |
	Capacity, mol CO_2/mol absorbent	Removal Efficiency, %	Rate, mol CO_2/hr	Post-absorption product	Regeneration energy requirement, MJ/kg CO_2	CO_2 purity, %	Post-regeneration product	Handling modes	Sources
Hydroxide absorbent									
$Ca(OH)_2$ (1–5 wt.%)	2.02–5.13	3–32.17	0.94–1.46	• $CaCO_3$	4.07	—	• If opt for regeneration will obtain CaO and CO_2	• Direct utilization to produce construction materials • If opt for regeneration, $CaCO_3$ will be decomposed at approximately 650 to 765°C to obtain CaO, a direct source of $Ca(OH)_2$	95, 98, 99, 180
NaOH (1–5 wt.%)	Experimental: 0.0019–0.0020 Theoretical: 0.5–1	46.57–66	—	• $NaHCO_3$	Decomposition of $NaHCO_3$ to Na_2CO_3: 1.95 Decomposition of Na_2CO_3 to Na_2O: 4.09 – 5.07	—	• If opt for regeneration will obtain Na_2CO_3, Na_2O, CO_2 and H_2O	• Stored as $NaHCO_3$ and not preferable to undergo regeneration process due to formation of Na_2CO_3 • If opt for regeneration, $NaHCO_3$ will be decomposed at 160°C to obtain Na_2CO_3 and a second decomposition at 800°C to edcompose Na_2CO_3 to obtain Na_2O, a direct source of NaOH	2, 104, 181, 182

Table 4. (Continued).

Absorbents (Concentration)	Absorption performance				Regeneration performance				
	Capacity, mol CO_2/mol absorbent	Removal Efficiency, %	Rate, mol CO_2/hr	Post-absorption product	Regeneration energy requirement, MJ/kg CO_2	CO_2 purity, %	Post-regeneration product	Handling modes	Sources
KOH (0.5 M)	—	56	—	• K_2CO_3	6.82	—	• If opt for regeneration will obtain K_2O and CO_2	• Direct utilization to produce construction materials • If opt for regeneration, K_2CO_3 will be decomposed at > 899°C to obtain K_2O, a direct source of KOH	107, 158, 183, 184
Carbonate absorbent									
K_2CO_3 (20–40 wt.%)	0.7–1.05	60–99.4	—	• $KHCO_3$	1.98–3.25	—	• K_2CO_3 • H_2O • CO_2	• Regeneration at 100–200°C to decompose $KHCO_3$ back to K_2CO_3 • Utilization of separated CO_2 for dry ice production	32, 118, 145, 146, 185, 186
$CaCO_3$ (11.5 wt.%)	0.91–1	49.64–97	—	• $Ca(HCO_3)_2$	—	—	• Do not undergo regeneration process	• Disposed to ocean to combat ocean acidification	109, 113, 123
Na_2CO_3 (30 wt.%)	1	90	—	• $NaHCO_3$	3.2	—	• Na_2CO_3 • H_2O • CO_2	• Regeneration at 120–160°C to decompose $NaHCO_3$ back to Na_2CO_3 • Utilization of separated CO_2 for dry ice production	31, 145, 146

(Continued)

Table 4. (Continued).

Absorbents (Concentration)	Absorption performance				Regeneration performance				Sources
	Capacity, mol CO$_2$/mol absorbent	Removal Efficiency, %	Rate, mol CO$_2$/hr	Post-absorption product	Regeneration energy requirement, MJ/kg CO$_2$	CO$_2$ purity, %	Post-regeneration product	Handling modes	
Hybrid/Novel Absorbent									
MDEA/[Omin][BF4] (30–50 wt.%/5–20 wt.%)	0.91–1.32	—	—	• R$_1$R$_2$R$_3$N$^+$-H • HCO$_3^-$	—	—	—	—	129
MEA/TEG (0.1–2 M/-)	0.20–0.80	—	—	• RNHCOO$^-$	Only the regeneration energy requirement for the 0.5 M MEA/TEG system was reported to be 1.99 MJ/kg CO$_2$	—	• After regeneration will obtain its respective amine absorbents and CO$_2$	• Regeneration at 80°C to regenerate respective absorbents	130
MEA/[Bmim]BF4] (30/70 wt.%)	0.12	—	—	• RNHCOO$^-$	—	—	—	—	
MDEA/[Bmim][BF4] (30/70 wt.%)	0.05	—	—	• R$_1$R$_2$R$_3$N$^+$-H • HCO$_3^-$	—	—	—	—	
NaADS/PZ/DETA (15/15/10 wt.%)	0.89	70.2	—	—	3.83	—	—	—	127

amino acid) compared to the other absorbent groups. Nevertheless, the desorption process harms the CO_2 absorption capacity of regenerated amino acids. As discussed under amino acid solution subsection, the absorption capacity of most amino acids is halved after regeneration. In addition, the regeneration energy requirement for amino acid solutions varies greatly depending on the amino acid utilized. For example, for non-natural amino acids such as potassium sarcosine, its regeneration energy requirement can be as high as 12 MJ/kg CO_2 while Zhang et al.[93] reported that sterically hindered amino acids such as N-cyclohexyl 1,3-propanediamine possess a lower regeneration energy consumption.[136]

Based on Table 3, Ca(OH)$_2$ exhibits superior CO_2 capture capacity (up to 5.13 mol CO_2/mol Ca(OH)$_2$) not only among hydroxide absorbents but also including the other major absorbent groups as well. As a whole, hydroxide absorbents possess relatively low CO_2 capture efficiency (32.17–66%) and have a reasonably high regeneration energy requirement of 4.07 to 6.82 MJ/kg CO_2. Similar to hydroxide absorbents, carbonate absorbents also require high energy (approximately 3.2 MJ/kg CO_2) for their regeneration process. However, the CO_2 capture capacity (> 1 mol CO_2/mol carbonate) and efficiency (> 90 %) of these absorbents are comparable to those of typical aqueous amine absorbents.

Although the CO_2 capture capabilities of recently developed novel or hybrid absorbents are not as feasible as the major absorbents, their capacity to enhance the standalone absorbent's weakness is the main highlight of these absorbents. For example, in the hybrid/novel absorbent subsection, the low absorption capacity of an ionic liquid namely [Bmim]BF$_4$ was drastically enhanced with the blending of MEA and MDEA. In this case, the CO_2 loading of the blended absorbent of MEA + [Bmim]BF$_4$ (0.12 g CO_2/g absorbent) is higher than that of a standalone [Bmim]BF4 absorbent (0.02 g CO_2/g absorbent). However, the CO_2 loading of the blended absorbent is lower as compared to a standalone aqueous MEA solution (0.25 to 0.40 kg CO_2/kg MEA). The advantageous trade-off for the amine side is the eco-friendly features of ionic liquid. Therefore, the blending of different chemical absorbents is not only to achieve superior CO_2 capture capabilities (i.e., CO_2 capture efficiency, rate, and capacity) but is to achieve a well-rounded quality of an ideal absorbent as stated in the Intorduction.

Absorbents evaluation

This section evaluates absorbents based on their handling method after CO_2 capture. This evaluation aims to separate chemical absorbents into two groups based on their suitability for CO_2 utilization after a desorption process (conversion of separated CO_2) or straight after CO_2 absorption (direct utilization of CO_2). After the absorption of CO_2, the CO_2-rich absorbents will typically undergo a desorption process to regenerate their absorbent and separate the absorbed CO_2 for further utilization. These include the utilization of CO_2 as chemical feedstocks, enhanced oil recovery (EOR), water treatment, production of fire retardants and mineral carbonation.[137–140] In some studies, CO_2 has been directly utilized to form $CaCO_3$, K_2CO_3 and concrete for value-added re-purposing without desorption.[104,107,138,141] Apart from that, novel CO_2 utilization pathways are also presented in this section. It is worth noting that the utilization of the aforementioned hybrid absorbents is not highlighted in the following sections. This is because the maturity of these absorbents is still in its infancy where their actual suitability and practicability for large-scale CO_2 capture application are yet to be tested.[135] The utilization pathway is highlighted because incorporating CO_2 utilization in a CO_2 capture system should be fundamental for carbon management. This can allow the CO_2 capture industry to overcome cost limitations and develop a sustainable process by producing value-added products *via* the utilization pathway.[139] Apart from that, a CCU system can also promote CO_2 capture for large industrial CO_2 emitters that are not accessible to a proper geological CO_2 storage which is a must for typical CCS systems.[142] As the possible leakage of CO_2 from geological storage is also a concern within the carbon capture industry,[143] the application of CCU can also subside this concern.

Potential CO_2 capture absorbents for CO_2 utilization after desorption

This subsection discusses suitable absorbents for CO_2 utilization after undergoing desorption. Typically, CO_2 absorbed via carbon capture and utilization (CCU) technologies will undergo a desorption process to regenerate the utilized absorbent and separate the CO_2 for utilization as a chemical feedstock to produce value-added products, supercritical extraction solvent for separation purposes, in EOR or replacement of

hazardous substance as an alternative medium.[138,139,144] Thus, making absorbents with high absorption capacity and low regeneration energy requirement plausible candidates for this criterion.[32]

The most practical absorbents for industrial application are amine absorbents. After CO_2 absorption, CO_2-rich amine absorbents will undergo desorption to regenerate back the absorbent while separating CO_2 into a CO_2-rich stream.[2,31] Separated CO_2 from amine-based absorbents has been utilized in the food and beverage industry, urea production and EOR operations.[31,60] MEA is the prime candidate in terms of commercialization potential as it is backed up by proven technologies and has been commercialized, unlike the other amine absorbents. Based on Table 4, MEA is also shown to be able to produce a nearly pure CO_2 (99%) stream after its desorption process which is suitable as a chemical feedstock. However, MDEA also possesses substantial potential as it has a relatively high CO_2 absorption efficiency (99%) and requires the lowest energy (1.34 MJ/kg CO_2) to be regenerated compared to the other amine absorbents.[1] Other potential amines such as DEA and DEAE can also fit into this criterion due to their substantial CO_2 capture capacity (0.46 to 0.61 mol CO_2/mol absorbent) and low regeneration energy requirement (1.42 to 1.57 MJ/kg CO_2). Thus, MEA, MDEA, DEA and DEAE are plausible candidates for CO_2 utilization after desorption.

For the carbonate absorbents, CO_2 absorbed by K_2CO_3 and Na_2CO_3 has been separated for dry ice production in the early 1900s.[145,146] Both K_2CO_3 and Na_2CO_3 are suitable candidates for this mode of CO_2 utilization as they are easily regenerated at 100–200°C and 120–160°C, respectively.[31,147,148] For dry ice production, the separated CO_2 stream will undergo a two-stage cooling. First, the gas stream will be cooled down to remove water via condensation. The dried gas stream will then be further cooled down to −110°C for dry ice generation.[149] The production of dry ice is an attractive CO_2 utilization alternative due to its wide range of usage in the modern era. Aside from its application in dry ice blasting for cleaning purposes, dry ice has also been applied in creating entertainment effects and even as insect anesthetics.[150–152] Apart from that, K_2CO_3 and Na_2CO_3 also possess applaudable CO_2 absorption capacity compared to MEA as shown in Table 4. Similar results can be seen comparing the CO_2 absorption and regeneration energy requirement of both carbonate absorbents to MEA.

Next, is the ILs absorbent group. Based on Table 4, the CO_2 absorption capacity of ILs is highly dependent on their preparation process. The flexible designability of ILs plays an important role in their CO_2 utilization ability. As mentioned under the Comparison of CO_2 chemical absorption absorbents section, ILs can alter their chemical and physical properties to fit a specific application. This is the same for the case of CO_2 utilization, where specific ILs with high CO_2 capture capacity and low regeneration energy can be developed to fit this purpose. However, the development of novel ILs with desired properties can be extremely complex and expensive which thus, hinders large-scale application.[83,89,120] In addition, even though certain ILs can achieve high absorption capacity such as amino acid-based ILs, their preparation process is considered to be unfriendly to the environment.[89] It should also be noted that data on the CO_2 capture efficiency and CO_2 absorption rate of ILs are relatively limited and the mechanisms of ILs with carbon capture are still unclear.[89,153] Nevertheless, ILs still present high potential in the CCU sector but for ILs to fit into this criterion, continuous research is required to develop novel ILs that can overcome the above-mentioned limitations.[58,89,120,154]

Apart from the aforementioned past utilization of desorbed CO_2, there are still numerous uncommercialized pathways that can be potentially incorporated into future chemical absorption CCU plants. Based on Alpher and Orhan,[155] there are two groups of such pathways, namely emerging and applied R&D CO_2 conversion technology. The emerging technology refers to technologies that have been demonstrated at the plant level. Some of the modes of utilization include the production of CO_2-based polymers, formic acid and fuels. For the applied R&D technology, these are CO_2 utilization methods that have been tested at a lab-scale level. The value-added products that can be obtained from the offered technologies are isocyanates, organic carbonates, lactone and carboxylic acid. In addition, the utilization of CO_2 for the cultivation of microalgae has attracted increasing attention due to the economic and environmental advantages it offers.[156] In this cultivation process, separated CO_2 can be directly fed into a biological media containing microalgae as a growth nutrient without chemical additives. The microalgae would consume incoming CO_2 and grow into a matured state. Once matured, the microalgae are converted into valuable products ranging from syngas,
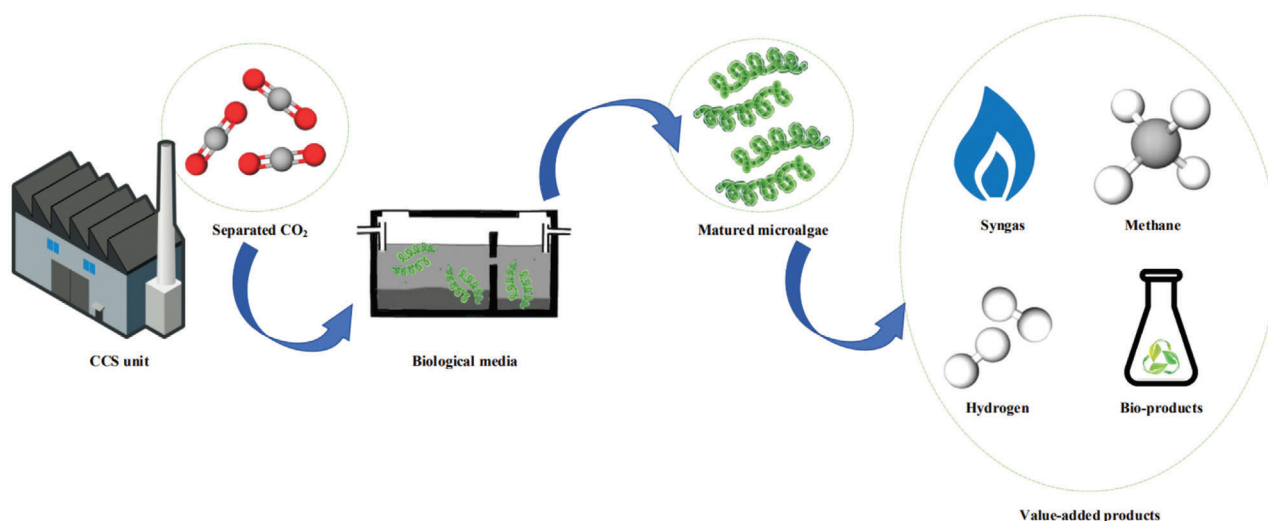
Figure 4. Process flow on CO_2 utilization for microalgae cultivation.[156]

methane, hydrogen to bio-products (bio char, bio-oil, bio-crude, bio ethanol, etc.). The flow diagram for this process is illustrated in Figure 4.

All in all, MEA, MDEA, K_2CO_3 and Na_2CO_3 are some of the potential absorbents for this mode of utilization due to their high absorption capacity. Even though, MEA requires high regeneration energy, its application in the CO_2 capture sector has been proven in numerous industries. For K_2CO_3 and Na_2CO_3, their CO_2 capture capabilities are comparable to MEA. However, MDEA might be the best choice for utilization after desorption as it not only possesses high CO_2 absorption but also requires less energy for its regeneration compared to MEA, K_2CO_3 and Na_2CO_3. For ILs to be a viable option, the stated limitations need to be overcome. Apart from that, there is still tremendous potential for developing the utilization of separated CO_2.

Potential CO_2 capture absorbents for direct CO_2 utilization after absorption

This subsection discusses absorbents that can directly utilize CO_2 after their absorption. Direct utilization of CO_2 after absorption is not a well-known pathway due to its limited application. Nevertheless, it presents a distinctive advantage, where a desorption process is no longer required (lower energy consumption). It is stated by Vega et al.[157] that 50–80% of energy consumption for typical carbon capture operations stems from the regeneration process. Therefore, removing a regeneration process can help converse a large amount of energy thus saving cost.[107]

One of the well-known direct utilizations of waste CO_2 is to produce construction materials. This mode of utilization has been an attention catcher due to its various advantages, including its flexible usability of produced solid carbonates, ability to permanently sequestrate large quantities of CO_2 via its carbonation process, well-known carbonation mechanisms, and it is a thermodynamically favoured reaction.

Table 4 shows that the applicable absorbent for this utilization is the hydroxide absorbent group. The hydroxide absorbents include $Ca(OH)_2$, NaOH and KOH which can react with CO_2 to form $CaCO_3$, $NaHCO_3$ and K_2CO_3, respectively. Although these absorbents can be regenerated, it is still an unpreferred alternative as the thermal decomposition of the produced carbonates requires high temperature, ranging from 650 to > 899°C.[99,104,158] This results in a high requirement of energy for the regeneration process. Thus, highlighting that direct utilization after absorption is the preferred pathway for hydroxide absorbent. $CaCO_3$ has a wide span of utilization, ranging not only in the construction industries but also in the pharmaceutical and cosmetics industries.[141] Whereas the utilization of $NaHCO_3$ is limited to replacing oxalic acid for rare earth precipitation. Based on Ngu et al.,[107] K_2CO_3 was utilized to produce construction material in a mixture of sand and $Ca(OH)_2$. In this process, K_2CO_3 reacts with $Ca(OH)_2$ to precipitate $CaCO_3$ while regenerating KOH without any energy requirement. This utilization process is illustrated in Figure 5. It was suggested that the produced construction material can be applied to road
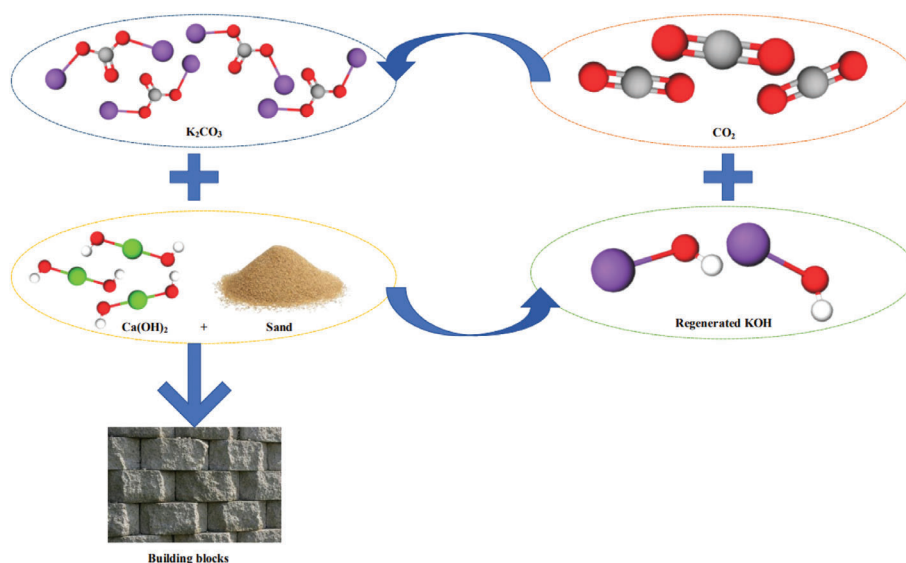
Figure 5. Direct CO_2 utilization process of KOH absorbent.[107]

construction and slab construction. Among the presented hydroxide absorbents, $Ca(OH)_2$ is the most ideal candidate for direct utilization among the hydroxide absorbents due to its various mode of utilization and excellent CO_2 capture capacity of 1.68 to 5.13 mol CO_2/mol absorbent.

For carbonate absorbents, $CaCO_3$ is the only applicable absorbent for direct CO_2 utilization. This unconventional CO_2 direct utilization was proposed by Rau et al.[123] via a process known as AWL that utilizes waste limestone ($CaCO_3$) and seawater to absorb CO_2 to produce calcium bicarbonate solution. As presented in Table 4, the theoretical CO_2 capture efficiency can be up to 97% and can be done at a reasonably low cost. The suggested handling of calcium bicarbonate solution was disposing it into the ocean to combat ocean acidification. However, this is only viable if the forementioned process is carried out near coastal areas. To resolve this location restriction, calcium bicarbonate can be used to precipitate CaO to form $CaCO_3$ to produce construction materials as shown by Reaction 28. The process flow for this process is shown in Figure 6. This boosts the potential of $CaCO_3$ absorbent to be applied for direct CO_2 utilization.

The amino acid solution group has been closely compared to amine absorbents as both absorbent groups possess similar reaction mechanisms with CO_2 due to the identical amino-functional groups' presence in their molecules.[88] Amino acid solutions have the flexibility to opt for both utilization with or without

undergoing a desorption process due to their post-CO_2 absorption products.[159,160] However, opting for a desorption process might not be preferable for amino acid salts as its energy-intensive desorption process is a concern for large-scale applications.[160,161] Therefore, direct utilization of CO_2 is more feasible for amino acid salts. As shown in Table 4, amino acids can form a variety of products ranging from protonated amino acids and bicarbonate salt of amino acids.[160,161] The formation of these products depends on the type of amino acid salts used and tailoring it to an application where the product formed is desired, to promote direct utilization. Hence a preliminary analysis is required to select the exact amino acid salts for desired product production when absorbing CO_2.[122] To summarize, all stated hydroxide absorbents and $CaCO_3$ can be considered as potential absorbents for this mode of utilization. All the mentioned absorbents show comparable results to MEA, proving their substantial CO_2 capture capabilities. Although the direct utilization option mainly focuses on construction materials production, it does not directly result in a limited market for the produced products. This is because of the increasing growth rate of the construction industry globally.[162–165] As the construction industry remains at a high growth rate, the marketability of construction materials will also increase over time. Thus, this utilization option can be a potential pathway to develop a sustainable carbon capture process especially in the construction industry.
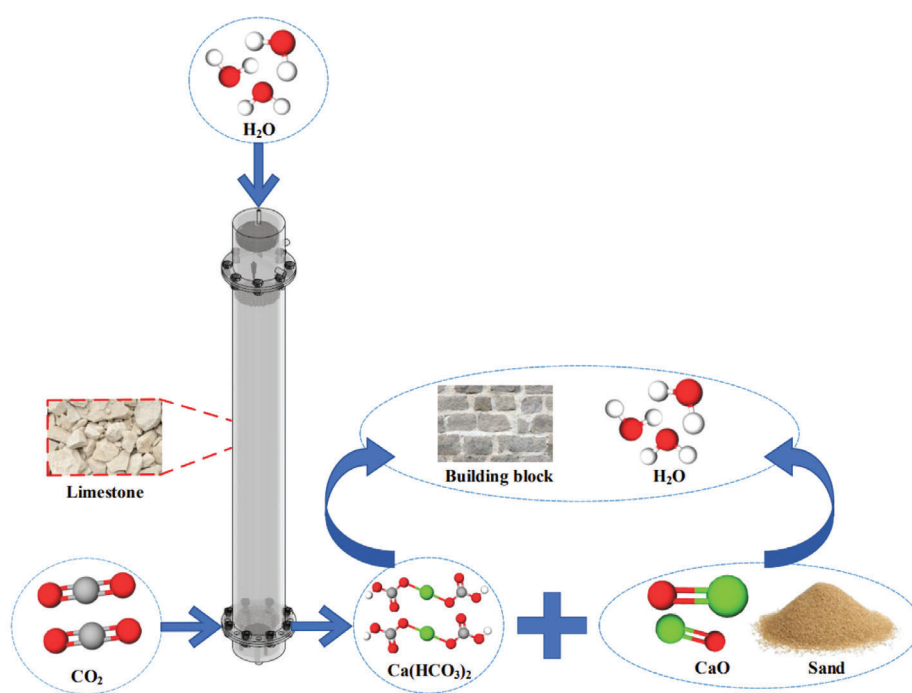
Figure 6. Direct CO_2 utilization process by $CaCO_3$ absorbent to produce building block.

Challenges and future prospect of CO_2 capture technology

As developed nations have widely commercialized renewable energy technologies, the necessity for rapid growth by the CCS sector between 2020 to 2050 is required to advance to the same progress level as in renewable energies.[166,167] Without being at an equivalent level with renewable energy technologies, they may obtain a more vigorous political course of promotion and development over the coming years. Their energy-saving potentials and gradual expansion would contribute to climate protection quicker than carbon capture technologies.[168] Also, renewables might be a preferable option for investors due to the lower levelized electricity generation costs compared to CCS power plant.[167] These facts are especially important as continuous fundings play a crucial role in developing and commercializing carbon capture technologies. However, carbon capture technologies possess the upper hand to reduce existing greenhouse gases (GHG) significantly. As stated by Viebahn et al.,[168] if CCS can be employed successfully, it would significantly reduce CO_2 emission and present an opportunity to reach climate protection. Nevertheless, initiatives or ideas to nudge the development of carbon capture technologies are important directions for future research to ensure that it remains a relevant alternative to achieve climate protection.

Apart from that, the numerous absorbents as discussed under Chemical absorption absorbent section have shown substantial CO_2 capture and utilization capabilities; they are not ready yet for large-scale applications due to the lack of validation data in pilot plants.[122] To note, lab-scale results may vary once applied to a pilot plant or industrial plant. For example, Rau[113] stated that CO_2 capture efficiency via $CaCO_3$ absorbent at lab scale can be as high as 97%. Still, this efficiency was significantly reduced to 21% when applied to pilot plants or industrial plants.[112,169] Thus, before large-scale applications, absorbents must undergo pilot plant validation. Other than that, research on the synthesis of novel absorbents via hybrid mixing has been one of the main focuses for the future development of carbon capture technologies. However, most of the novel absorbents are still in their infancy as most related research has only started in the last 11 years.[32,65,130,170,171] The majority of the current studies only focus on the absorption (i.e., CO_2 loading capacity and reaction rate) and desorption (regeneration energy) capabilities of these novel absorbents and have yet to be coupled with a utilization

potential.[125,126,129,130] Therefore, Damanafshan et al.,[129] in a more recent work, pointed out that ongoing investigations on additional criteria (i.e., degradation rate, vapor pressure, corrosiveness and solvent cost) set by Budzianowski et al.[135] and the respective utilization potential needs to be established to nudge the development of these novel absorbents for industrial scale-up.[139]

On the other hand, CO$_2$ utilization pathway consideration is crucial for developing a sustainable carbon capture process. Nevertheless, there are still some challenges that limit their application. Although CO$_2$ can be utilized to produce various value-added products (as discussed under Absorptions evaluation section), product marketability is an issue for consideration. Huang and Tan[172] mentioned that the market scales for products developed via CO$_2$ utilization are generally small. Thus, it is important to establish a good market to ensure the relevance and profitability of a CO$_2$ utilization application. Apart from that, the necessity to include additional infrastructures or equipment to cater to CO$_2$ utilization processes would impose an increment in the required operation energy. To conduct a comprehensive market and economic analysis, techno-economic analysis (TEA) is a crucial tool for evaluating the technical performance and economic feasibility of a technology.[173] In addition to the increase of the required energy input, the carbon emission level of the system would also be affected negatively. Therefore, to evaluate the carbon emission state for operating a CCU system, life cycle assessment (LCA) needs to analyse its environmental impact. Suppose TEA and LCA of a particular system indicate negative results. In that case, the necessity to explore or develop more energy-efficient and eco-friendly alternatives (i.e., CO$_2$ utilization for microalgae cultivation, energy recovery, heat integration or process integration.) is crucial to overturning the undesirable outcome. It should also be noted that these alternatives can also be employed in accomplished systems to enhance their performance further. The purpose of developing an optimal CO$_2$ utilization (CCU or CCUS) system is as mentioned under the Absorptions evaluation section. Thus, it is believed that efforts in developing an optimal CCU alternative are an important direction for future research.

The arrival of the fourth industrial revolution (IR 4.0) may open opportunities for CO$_2$ capture technologies development. IR 4.0 aims to develop a fully automatized and sustainable industry.[174] This is achievable in the CO$_2$ capture industry via the implementation of applicable business models suggested by experts and the development of production systems by incorporation of new advanced technologies. Four of the five business models, including circular supplies, restoration of resources, extension of product's life cycle, and product as service, are applicable for a CO$_2$ capture system to develop a sustainable process.[174] For developing a fully automated and more efficient process system, the incorporation of advanced digital technologies (artificial intelligence [AI] and big data analysis) and physical technology (3D printing) are crucial.[174,175] By incorporating AI into a CO$_2$ capture system, optimization possibilities are higher, operation risks can be significantly reduced and human errors can be eliminated.[174] This would optimize the process and the managerial processes in a socioeconomic system. The implementation of big data analysis focuses on process optimization, which improves the efficiency of a process.[174–176] Big data analytics can also effectively analyze an extensive set of data and uncover hidden patterns or correlations from a study. This helps enhance the performance of decision making and create products to meet the aim of certain purposes.[177] For example, big data analytics can help screen through different mixing ratios of hybrid absorbents and help researchers determine the optimal ratio for a particular blend. For 3D printing, it would enable old materials to be replaced with renewable resources, provide rapid development for products, allow the production of complex parts to be simplified and ecologically favoured due to the reduction of materials or product transportation.[174,176]

For example, Wu et al.[178] have utilized an artificial neural network (ANN) and particle swarm optimization (PSO) model to develop an intelligent predictive controller (IPC) for large-scale solvent-based post-combustion CO$_2$ capture (PCC) processes. It was shown that in this study, the proposed IPC system was able to determine the best control sequence for a PCC process. For example, in a simulation scenario when flue gas flow rate drops which causes the CO$_2$ capture efficiency of a PCC process to slightly increase, the IPC would detect this anomaly and make the required adjustment (decrease lean solvent flow rate) to allow the system to achieve its intended set-point of 70% CO$_2$ capture efficiency. The rapid adjustment can be crucial as even a slight

increase from the intended CO_2 capture level can increase the operating temperature of a re-boiler to accommodate for the regeneration process of the increased CO_2-rich solvent, resulting in higher energy consumption. Apart from that, this can also reduce the need for manual labour to control operations. This process can help push the commercialization of PCC operations as it can help PCC processes to adapt to unpredictive industrial conditions while significantly reducing any fluctuations in the process. Apart from that, Sarma et al.[179] have also demonstrated the potential of 3D printing in aiding the development of CO_2 capture operations. Their study deduced that the three 3D printed polymers, namely high-density polystyrene (HDPS), acrylonitrile butadiene styrene (ABS) and nylon, were found to be potential candidates to replace conventional steel packing for a CO_2 absorption process. This would reduce the high capital cost associated with a typical amine system. Apart from that, these polymers also show plausible stability even after 5000 h of amine exposure at a temperature of 60°C. Sarma et al.[179] stated that 3D printing has helped to open up opportunities for CO_2 capture development as more studies (i.e., novel packing design) can be conducted on the identified polymers for further CO_2 capture performance improvement. Although all these new technologies offer tremendous potential for the development of carbon capture technologies, they are still not widely incorporated with one another. Thus, incorporating IR 4.0 technologies into CCU development is a considerable direction. Table 5 presents an abridged version of all the present challenges and potential enablers for carbon capture technologies.

Table 5. Challenges of chemical absorbents technologies for CO_2 capture operation and their respective key enablers.

Challenges	Enablers
Majority of existing chemical absorbents possesses poor carbon capture capabilities	• Incorporate IR 4.0' technologies (big data analysis and artificial intelligent (AI)) into studies of hybrid absorbents to enable faster and more efficient screening of potential absorbents.
Lack of data on the economic and environmental performance of CCU operations	• Conduct TEA and LCA for future CCU operation.
Research on newly synthesized chemical absorbents not well rounded as majority of crucial criteria for commercialization have not been investigate	• Prioritize analysis on economic, environmental and utilization prospect of newly synthesized instead of just the typical absorption and desorption analysis.
Majority of carbon capture technologies are unsustainable due to high operational cost and lack of economic revenue	• Venture into the utilization of 3D printing to reduce cost required for material purchases. • Prioritize on the development of CO_2 utilization potential of existing chemical absorbent systems. • Implement IR 4.0' principal (business models and process optimization) into existing CO_2 capture facilities to optimize economic prospect of systems.

Conclusion

Due to the adverse damage that excessive emission of CO_2 has caused to the environment, carbon management alternatives such as CCS and CCU have been actively employed and studied. However, due to the unsustainable nature of typical CCS technologies, the need to develop a sustainable carbon management pathway via CCU is crucial. In the hope of identifying plausible chemical absorbents for CCU processes, this review has deliberately reviewed all major absorbent groups as presented under the Chemical absorption absorbent section. For evaluating the chemical absorbents for CO_2 utilization, the utilization pathways were divided into two groups, that is, (i) CO_2 utilization after desorption and (ii) direct CO_2 utilization after absorption. For the first pathway, chemical absorbents such as MEA, MDEA, K_2CO_3 and Na_2CO_3 are suitable candidates for this utilization pathway. Excluding MEA, the absorbents as mentioned earlier, possess plausible CO_2 capture capacity (0.7 to 1.05 mol CO_2/mol absorbent) and relatively low regeneration energy requirement (0.61 to 3.25 MJ/kg CO_2). Under this utilization pathway, value-added applications include EOR operations, urea, dry ice, food and beverage production. On the other hand, hydroxide absorbents (i.e., $Ca(OH)_2$, NaOH and KOH) and $CaCO_3$ are deduced to be suitable for direct CO_2 utilization based on their past utilization. It was shown that the products produced via the direct CO_2

utilization pathway are limited for construction applications. Although it is limited to the construction industry, the marketability of these products is still extremely high. This is due to the continuous growth rate of the construction industry globally. Thus, the direct CO_2 utilization pathway remains a plausible option for future research. Even though various potential utilization pathways were presented, the large-scale commercialization of these CCU technologies remains very limited. This can be due to the increasing competition from the renewable energy sector, the lack of optimal absorbents for CO_2 utilization and the lack of reliable data (i.e., economic and environmental data) to back-up CO_2 utilization technologies. Therefore, to curb these barriers and promote CCU operations, continuous research and analysis with available tools (i.e., IR 4.0's principle, TEA and LCA) need to be employed for future research.

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