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Use of monoethanolamine (MEA) for CO_2 capture in a global scenario: Consequences and alternatives☆

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ABSTRACT

Recent research on CO_2 capture is focusing on the optimization of CO_2 absorption using amines (mainly monoethanolamine—MEA) in order to minimize the energy consumption of this very energy-intensive process and improve the absorption efficiency. Process optimization is always required and this research is worth and necessary. However, the main concern arises when thinking of the overall process: solvent production, solvent use and regeneration, and environmental effects related to its use/emissions. The production of MEA from ammonia involves important CO_2 emissions during the Haber–Bosch process. The regeneration of the solvent after the absorption is also an indirect source of CO_2 related to the use of fuels (*i.e.*, combustion processes for energy supply). Thus, the evaluation of the overall balance of CO_2 emitted and captured is essential to determine the efficiency of the process. In addition, other environmental impacts associated to the toxicity and environmental fate of the solvent have to be considered. The use of MEA and other amines in CO_2 capture is a point of concern and a global application does not seem to be the best strategy.

This review aims at giving an overview of the main implications of using MEA as absorption solvent for CO_2 capture together with the last advances in research to improve the conventional absorption process. Furthermore, alternatives of using other solvents and/or using other technology and their advantages and weak points will be briefly provided. An approach oriented to produce CO_2-based products with economic value that can be re-integrated in a closed carbon loop, reducing the use of fresh materials and decreasing the production cost, should be the final objective of current research on CO_2 capture.

Contents

1. Introduction

Carbon dioxide (CO_2) is the main greenhouse gas that is leading to dramatic changes in global warming and climate change. The concentration of this gas has increased significantly in the last years, currently reaching values around 400 ppm [52]. The industry accounts for almost 40% of worldwide CO_2 emissions, which is an important point of concern [1]. Several strategies are being considered in order to reduce CO_2 emissions: post-combustion capture, pre-combustion capture, oxyfuel combustion, and electrochemical separation [16,24,39]. A considerable list of large-scale integrated CO_2 capture and storage

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(CCS) projects in the stages of operation or execution can be found on the Global CCS Institute's website (http://decarboni.se), which is included in Table S1 as Supporting Information. Post-combustion plants are found in the execution (in construction) stage.

Post-combustion capture can be considered the most straightforward schema for application in existing processes, although it is also one of the most challenging approaches due to the diluted concentration of CO_2 and its low pressure in the flue gas: 12–15 mol% (in a post-combustion flue gas from a coal-fired power plant) [4] and, the poor value of the recovered compound (carbon in the highest oxidation level: CO_2) [32]. In this case, the CO_2 can be removed in a chemical or physical absorption process. Table 1 shows an overview of the different industrial processes used for CO_2 removal [8]. Two common physical absorption solvents are glycol dimethylethers (Selexol) and propylene carbonate. Regarding the solvents used in chemical absorption processes, they are mainly aqueous amine solutions, such as monoethanolamine (MEA), activated methyl diethanolamine (aMDEA) or hot potassium carbonate solutions. Nevertheless, the MEA process is undoubtedly the most extended for CO_2 capture in post-combustion processes, even though it requires high regeneration energy. Engineering, procurement, construction and service companies, such as KBR (Texas), or leaders in power generation, such as Alstom (France), are betting on this technology, which can be viewed as a retrofit or add-on to the existing power plant. CCS is now a reality in the power industry.

However, if the use of MEA is extended as the main solvent for CO_2 capture in post-combustion processes, an economic and environmental global impact will occur. Recent research is focused on the use of this solvent in a more technically and economically effective way. The objective of this manuscript is to show the global implications of using MEA as the main solvent for CO_2 capture, and review briefly the main research that is focused on the optimization of the MEA process as well as other strategies that try to develop alternatives to the use of MEA. After reading this manuscript, the reader should have developed an initial criterion on the implications of using MEA in a global scale and the degree of current applicability of other alternatives.

2. Implications of a global use of MEA

Using MEA in a global scale would have a large impact on the production and cost of this chemical. Nevertheless, other effects related to the impact of an increased production on the environment due to the emissions of CO_2 during the production process should not be underestimated. In order to detect the main points of concern, the following lines describe briefly the general production process of MEA, based on the reaction between ammonia (NH_3) and ethylene oxide (EO), two of the Top 50 global chemicals produced by mass [4]. The overall process should include the production of NH_3 and EO, in order to be able to see the overall picture of CO_2 emissions. Thus, it can be divided in three parts according to Fig. 1: 1) NH_3 production; 2) EO production; and finally, 3) MEA production.

2.1. Ammonia production

Ammonia is synthesized from nitrogen and hydrogen by the following reaction:

$$N_2 + 3H_2 \rightarrow 2NH_3 \hspace{2cm} \text{Reaction 1}$$

Atmospheric air is the best available source of nitrogen while the hydrogen required can be produced from various feedstocks, although currently it is derived mostly from fossil fuels, including two different production methods depending on the type of fossil fuel: steam reforming or partial oxidation. However, about 80% of the ammonia production capacity worldwide is currently provided by the well-developed steam reforming process [8]. Fig. 2 shows the main steps involved in steam reforming for NH_3 production. A typical size for a single stream ammonia production plant is 1000–1500 tonnes/day (300,000–500,000 tonnes/year) [8].

The first stage, desulphurization, has the objective of elimination of any sulfur compounds since the catalyst used in the steam reforming process is highly sensitive to them. Thus, the feed gas is preheated up to 350–400 °C and the sulfur compounds are hydrogenated to H_2S by typically using a cobalt molybdenum catalyst and adsorbed on pelletized zinc oxide. Next, in the primary reformer, the following reaction takes place, which is highly endothermic and with a conversion rate around 60%:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H_{fo} = 206 \text{ kJ/mol}. \hspace{1cm} \text{Reaction 2}$$
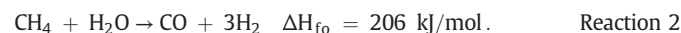
The heat for this reaction is obtained from burning natural gas or other fuels.

In the secondary reformer, nitrogen is supplied for the synthesis and to complete the conversion of the hydrocarbon feed, reducing the content of methane to around 0.2–0.3%. The gas stream from the secondary reformer contains 12–15% CO (dry gas base), which will be converted to CO_2 and H_2 in the shift section, according to:

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H_{fo} = -41 \text{ kJ/mol}. \hspace{1cm} \text{Reaction 3}$$
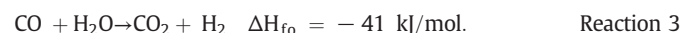
The large concentration of CO_2 that is present in the gas stream has to be removed before the ammonia synthesis. The CO_2 is removed in a

Table 1
Overview of CO_2 removal processes in a post-combustion scenario [8].

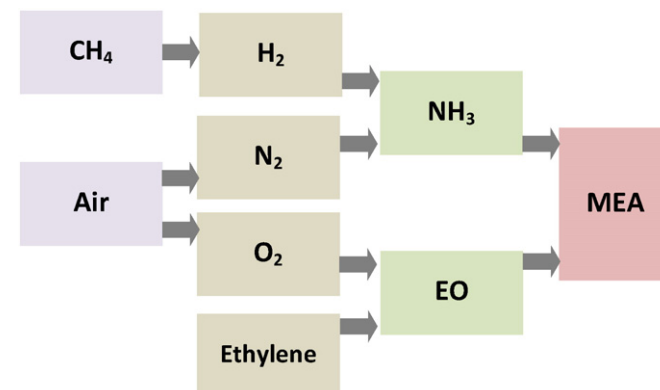| Process name	Solvent/reagent + additives	CO_2 in treated gas (ppm)
Physical absorption systems		
Purisol (NMP)	N-methyl-2-pyrrolidone	Less than 50
Rectisol	Methanol	Less than 10
Fluorsolv	Propylene carbonate	Function of pressure
Selexol	Polyethylene glycol dimethyl ether	Function of pressure
Processes with chemical reagents		
MEA	Water/monoethanolamine (20%)	Less than 50
Promoted MEA	Water/MEA (25–30%) + amine guard	Less than 50
Benfield	Water/K_2CO_3 (25–30%) + DEA, etc	500–1000
Vetrocoke	Water/K_2CO_3 + As_2O_3 + glycine	500–1000
Catacarb	Water/K_2CO_3 (25–30%) + additives	500–1000
Lurgi	Water/K_2CO_3 (25–30%) + additives	500–1000
Carsol	Water/K_2CO_3 + additives	500–1000
Flexsorb HP	Water/K_2CO_3 amine promoted	500–1000
Alkazid	Water/K_2-methylaminopropionate	To suit
DGA	Water/diglycolamine (60%)	Less than 100
MDEA	Water/methyl diethanolamine (40%) + additives	100–500
Hybrid systems		
Sulfinol	Sulphones/DIPA	Less than 100
TEA–MEA	Triethanolamine/monoethanolamine Water/sulpholane/MDEA	Less than 50

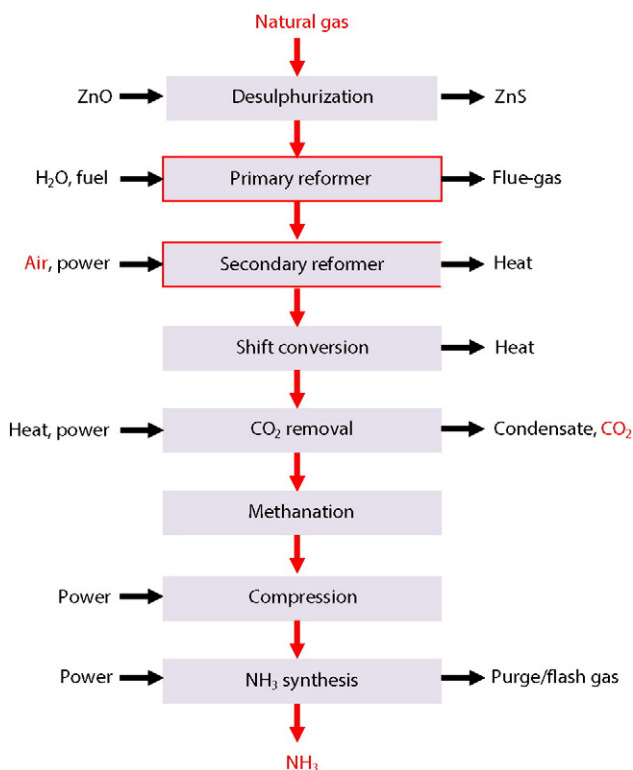**Fig. 1.** Main chemicals involved in MEA production [4].

Fig. 2. NH_3 production by conventional steam reforming [8].

chemical or physical absorption process as indicated in Table 1, typically aqueous amine solutions (*e.g.*, MEA), reducing the CO_2 content to 50–3000 ppmv. The small amounts of CO_2 and CO that are still remaining in the gas stream are a poison for the ammonia synthesis catalyst. Thus, they are removed by hydrogenation to CH_4 during the methanation stage. Finally, after compression of the gas stream to the required level (100–250 bars, 350–550 °C), the synthesis of ammonia takes place on an iron catalyst at pressures usually in the range of 100–250 bars and at temperatures of between 350 and 550 °C:

$$N_2 + 3H_2 \rightarrow 2NH_3 \quad \Delta H_{fo} = -46 \text{ kJ/mol} \qquad \text{Reaction 4}$$
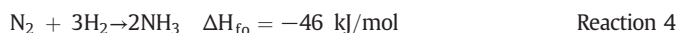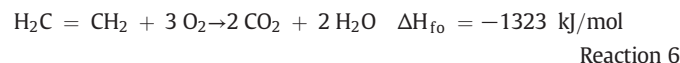
Due to the low conversion efficiency per pass (20–30%) caused by the unfavorable equilibrium conditions, the unreacted gas is recycled after removing the ammonia by liquefaction using a refrigeration compressor.

The production of CO_2 in the steam/air reforming of natural gas is 1.15–1.40 kg/kg NH_3, without including CO_2 in combustion gases. For comparison, in partial oxidation of residual oils, CO_2 production is 2–2.6 kg/kg NH_3 [8]. The produced CO_2 can be recovered for further use as feedstock in a urea plant, for the use in fertilizer production (ODDA process) and/or methanol production or liquefaction, in the beverage industry or as a coolant gas in nuclear reactors. There is, however, an inevitable excess of CO_2 which is released as an emission from the process. This excess is accounted around 500 kg CO_2/t NH_3. In addition, the ammonia production involves the emission of about 0.02–0.04 kg of solvents for CO_2 removal per tonne NH_3, mainly due to leaks, and less than 0.01 kg SO_2/t NH_3 and 0.03 kg CO/t NH_3 [8].

2.2. Ethylene oxide production

Ethylene oxide (EO) is a very versatile chemical intermediate because of its high reactivity caused by its highly strained ring, which can be opened easily [43]. However, this reactivity together with its toxicity makes it a hazardous compound. EO is produced by direct oxidation of ethylene with air or oxygen on the surface of a silver catalyst.

At present, EO is produced mainly by the oxygen-based process. In addition to EO formation (partial oxidation in Reaction 5), complete combustion (total oxidation in Reaction 6) to CO_2 and water also takes place. Both reactions are exothermic, taking place at 250 °C and 1.5 MPa [43].

$$H_2C=CH_2 + \tfrac{1}{2} O_2 \rightarrow \underset{\text{ethylene oxide}}{\triangle} \qquad \Delta H_{fo} = -106.7 \text{ KJ/mol}$$

$$\text{Reaction 5}$$

$$H_2C = CH_2 + 3 O_2 \rightarrow 2 CO_2 + 2 H_2O \quad \Delta H_{fo} = -1323 \text{ kJ/mol}$$

$$\text{Reaction 6}$$

2.3. Monoethanolamine production

Production of monoethanolamine (MEA) takes place by means the reaction between NH_3/water and EO. No catalyst is involved and it is an exothermic reaction. The operating pressure is 50–70 bars to keep the NH_3 in a liquid phase. The NH_3 molecule can react with one, two or three EO molecules, leading to the formation of monoethanolamine (MEA), diethanolamine (DEA) or triethanolamine (TEA), respectively. The composition of the resulted mixture depends on the ratio NH_3/EO and can be oriented to the production of the desired compound: the higher the proportion of NH_3, the more MEA is formed.
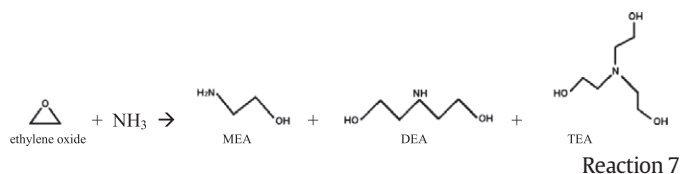
$$\text{Reaction 7}$$

After the reaction, the excess of ammonia is stripped out and the water is removed from the reaction mixture by distillation in order to be returned to the reaction step again [9]. Afterwards, the ethanolamines are separated from each other in a three-step distillation unit. Fig. 3 shows the general flowsheet of MEA production.

As described above, the overall process of MEA production involves energy consumption and direct and indirect CO_2 emissions. These emissions have to be considered in the global account of captured CO_2 in order to develop a realistic approach in which the increase of global MEA production does not cause a negative balance in the general strategy of CO_2 capture. In addition, within the MEA process, published results have pointed out that the reduction of CO_2 emissions into the atmosphere is achieved at the expense of increasing other emissions and corresponding environmental impacts (mainly those related to human toxicity and eutrophication) [47]. For example, emission of MEA and other amines to the environment is not negligible. Post-combustion capture leads to amines losses from the absorber column, involving a potential source of amines and amine degradation products, such as nitrosamines and nitramines [38,41,44]. Amines are not likely to be of toxicological concern to the aquatic environment at current environmental concentrations but degradation reactions may ocurr, leading to the formation of toxic compounds, such as nitrosamines and nitramines, through reactions between precursor amines and oxidants such as nitrite (NO_2^-). This would represent a risk of contamination of drinking water supplies by these often carcinogenic compounds [41]. The formation of nitrosamines and nitramines in the atmospheric oxidation of amines is shown in Fig. 4 [38]. These conversion and degradation reactions will take place in both the gas phase and the atmospheric aqueous phase, which includes water-containing aerosol particles and cloud-, rain- and fog-droplets [38]. Significant evidences for formation of nitrosamines and nitramines through CO_2
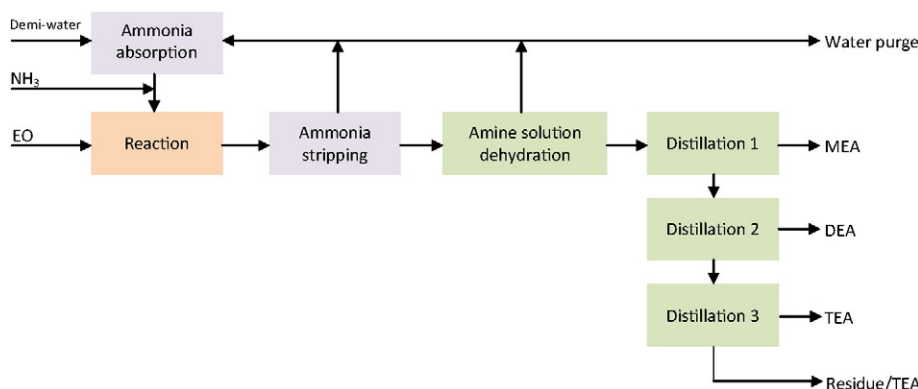
Fig. 3. Production of ethanolamines (MEA, DEA and TEA) from the reaction between ammonia (NH_3) and ethylene oxide (EO).

capture using amine-based solvents have been discovered [35]. Thus, the formation of these toxic compounds has to be considered when defining the viability of post-combustion CO_2 capture using amine-based solvents in a global scenario. In addition, amines also suffer degradation due to the presence of O_2 and SO_2. Results by Supap et al. showed that an increase in temperature and the concentrations of MEA, O_2 and SO_2 resulted in a higher MEA degradation rate [51].

In spite of the major disadvantages of using amine-based post-capture processes, they can be applied to already constructed plants, operated with the plant to capture CO_2, or disconnected to provide maximum power output at times of peak electricity price, and large pilot plants are under operation [18]. Thus, current research considers the use of amines as a realistic approach, aiming at the optimization of the CO_2 capture process using MEA and other amines. Nevertheless, novel solvents and novel technologies are an important alternative under development. The last advances in these areas are shown in the next sections.

3. Current research on CO_2 absorption using MEA

The current research on CO_2 absorption using MEA is mainly focused on the minimization of energy consumption during solvent regeneration [30,34]. Le Moullec et al. [26] elaborated a thorough review based on patents and research articles on the process modifications of CO_2 absorption. Three main categories of research were highlighted with the corresponding sub-categories: 1) absorption enhancement: intercooled absorber, rich solvent recycle, interheated absorber, split flow
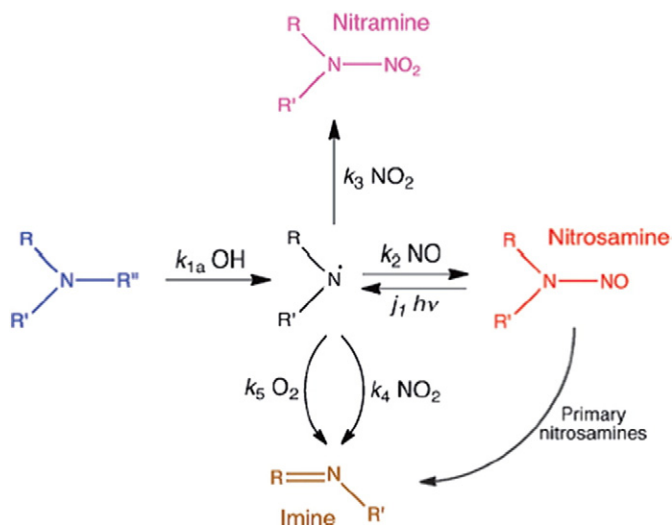

Fig. 4. Routes of atmospheric photo-oxidation of amines. Published with permission from Nielsen et al. [38].

arrangement, double loop absorber, flue gas compression and expansion; 2) heat integration: rich solvent splitting, rich solvent preheating, rich solvent flashing, parallel economizer arrangement, interheated stripper, heat integrated stripper, overhead condenser bypass, vacuum operated stripper, and multieffect stripper; and, 3) heat pump: lean vapor compression, rich vapor compression, integrated heat pump, stripper overhead compression, and multipressure stripper. This study concludes with the existance of a clear lack of pilot plant scale evaluation since most studies have been performed through process modeling. In addition, the energetic performance of the capture process is increased but at the expense of increasing their complexity and cost and reducing their operability.

Indeed, the MEA-based CO_2 capture process has been modeled intensively in the literature [40,60], describing several operation strategies and control configurations that aim at a decrease in energy consumption during solvent regeneration. The liquid residence time in the reboiler was found to be the dominant factor in the response time of the system and there is a linear relationship among the optimal solvent rate, the energy flux to the reboiler and the boiler load [60]. The inlet flue gas flowrate presents also an important role in the number of unconstrained degrees of freedom and several operation regions for the process have been identified [40]. Arce et al. [2] showed that the application of dynamic optimisation approaches, such as model predictive control focused on the reboiler, to exploit the time-varying values of wholesale electricity and CO_2 prices can lead to significant savings in the operating costs associated with post-combustion CO_2 capture processes, reducing the operating cost by an average of approximately 4.66%, and in some cases by as much as 10%. Varying the lean solvent loading, or allowing CO_2 to accumulate in the circulating solvent (in sympathy with prevailing market prices for CO_2 and energy) was found to be a key to enhance the cost-optimality of the process.

Some studies are also developing technological modifications in the conventional process in order to minimize the energy consumption. For example, Jande et al. [22] coupled the CO_2 absorption–desorption system based on MEA with capacitive deionization (CDI) to minimize the hear duty requirement of the stripper. Before the carbon-rich MEA solution is sent to stripper for regeneration, it is concentrated using a CDI cell where ionic species are adsorbed at oppositely charged electrodes during the charging cycle, and an ion free solution is sent back to the absorber. Results indicated that 10–45% of the total energy supplied to the stripper can be conserved because of the high CO_2 loading of the solution. Integration of ultrasounds have also demonstrated an increase in the physical desorption rate and the desorption can be performed at temperatures below 80 °C [14].

García-Abuín et al. [15] developed two alternative processes to the desorption step consisting in removing a reaction product (mainly the bicarbonate ion) and the simultaneous amine deprotonation. Those processes (*i.e.*, treatment of the carbon dioxide-rich amine with calcium hydroxide or with the use of an anionic exchange resin) showed an important

decrease in the energy employed for the regeneration of the investigated tertiary amines (pyrrolidine—PYR, methyldiethanolamine—MDEA, triethanolamine—TEA and triisopropanolamine—TIPA).

Another example is the integration of solar-assisted post-combustion CO_2 capture into a power plant with amine-based chemical absorption for CO_2 capture [27,59]. Solar thermal energy has the potential to support the thermal demand for CO_2 capture and the proposed integration has shown better performance than the conventional process with the limitation of the investment cost. However, due to the global magnitude of CO_2 capture, application of solar thermal energy can be considered a good strategy but its capacity is currently not large enough to cover all the energy requirements.

Thus, the conventional process can still be optimized and improved by modifying the operating conditions or by means of the integration of other emerging technologies.

4. Alternative solvents for CO_2 capture

Another field of recent research is the use of the absorption–desorption process but utilizing a different solvent. The energy penalty that the use of MEA presents is widely known and the search for other solutions conform a large part in the update of the state of the art. One of the possible substituent that has been proposed instead of MEA is the use of aqueous ammonia. Bandyopadhyay presented in 2011 an interesting comparison between the energy consumption and CO_2 emissions caused by the use of MEA *versus* the use of ammonia. The estimated total energy requirement for the NH_3-based process was 1147 kJ/kg-CO_2, which was founded to be around 27% of the energy requirement of the MEA-based process accounted in that work for 4215 kJ/kg-CO_2 using 30% w/w MEA solution [3,11,36]. The reported range of energy requirement when using 30 wt.% MEA varies from 3200 to 5500 kJ/kg-CO_2, and even more recent works using 35 wt.% MEA with advanced stripper configurations could achieve heat duties as low as 2900 kJ/kg [45] but still higher than the NH_3-based process. In addition, using ammonia would lead to the production of ammonium bicarbonate (NH_4HCO_3) among other compounds (ammonium sulfate: $(NH_4)_2SO_4$; ammonium nitrate: NH_4NO_3) by adapting the reaction conditions (temperature, pressure, and concentration of reactants), which is a synthetic N-fertilizer whose use produces about 152 Mt CO_2-equivalent emissions. Then, producing this compound from the CO_2 capture process instead of conventional routes would decrease the overall emissions [3]. Thus, those that defend the use of ammonia as an alternative for CO_2 capture take its lower energy consumption and the possibility of recovering as fertilizer as the main arguments to promote its application in a large scale. In addition, using aqueous ammonia may offer some benefits in comparison with the MEA process: higher loading capacity (mol CO_2 absorbed/mol of absorbent), no corrosion problems, stable in flue gases conditions, lower liquid to gas flow ratio, multi-pollutant capture capability (also used for SO_2 and NO_x removal), less energy consumption during the regeneration of solvent (if the ammonia is recovered instead of used to produce NH_4HCO_3, $(NH_4)_2SO_4$, and/or NH_4NO_3), and it is more economic than MEA. Nevertheless, as commented in the previous sections, not only should the CO_2 emissions related to the absorption process be considered but also the overall emissions caused during the production of ammonia. In this aspect, a large quantity of CO_2 is produced during the Haber–Bosch process. The production of MEA is more energy intensive than the production of ammonia but the much higher necessary ammonia makeup leads to higher energy requirements for solvent production in the ammonia capture processes [50]. Producing fertilizers is not a real solution either. The CO_2 bound up will be probably re-released into the atmosphere. Thus, an approach that does not achieve the recycling of ammonia in a closed loop is not a feasible solution and will lead to a perpetual downward spiral of energy inefficiency and wasted resources. In addition, the necessary reduction of ammonia emissions leads to further energy requirements, and solvent production as well as the remaining ammonia losses to the environment have a more significant

environmental impact than CO_2 removal with MEA [50]. Some technical issues should be also resolved to ensure economic viability, such as: suppression of ammonia vaporization, heat integration, minimization of absorbent flow rate, and bicarbonate-prevalent operation [17]. Thus, ammonia can be a possible alternative as CO_2 absorbent in CO_2 capture but it may not fulfill the expectations of capture of CO_2 in a global scenario due to the intrinsic penalty (energetic and environmental) that takes place during its use and production.

CO_2 capture with aqueous amine solution presents problems related to equipment corrosion, amine degradation [46], and high energy consumption. Thus, mixtures of alkanolamines (monoethanolamine—MEA, diglycolamine—DGA, diethanolamine—DEA and N-methyldiethanolamine—MDEA) with poly(ethylene glycol) (PEG) have been proposed [28]. PEG has a very low vapor pressure and about half of the heat capacity of water, showing less energy consumption during the regeneration step and less corrosion problems. From the work performed by Li et al. [28] on solubility of CO_2 on 30% DGA, DEA or MDEA mixed with 70% PEG200, it was observed that DEA–PEG200 and DGA–PEG200 solutions show relatively high CO_2 capacity at 313.15 K owing to a chemical reaction with CO_2; DEA–PEG200 solutions can achieve full regeneration more easily than aqueous MEA under high temperature; and MDEA–PEG200 solution has much higher loading than pure PEG200 solution under low temperature (*e.g.*, 313 K), presenting the property of physical absorber. Regarding MEA–PEG200 mixtures, they have the lowest temperature at which the weight loss begins (363 K) and thus is not appropriate for CO_2 capture at high temperature.

CO_2 capture with sodium carbonate–bicarbonate slurry has been also proposed as an integrated system with a power plant [23]. The CO_2 absorption produces sodium bicarbonate, which has lower solubility than the carbonate. When the solubility limit is exceeded, solid bicarbonate is precipitated and the capacity of the solvent is increased. The CO_2 rich slurry is then heated in a stripper in order to regenerate the solvent and release the CO_2 captured. The energy requirement of solvent regeneration is estimated around 3.22 MJ/kg-CO_2 captured, which is lower that the energy consumption of the MEA process (3.8 MJ/kg-CO_2 captured). The use of sodium carbonate may be considered as an environmentally friendly option due to the non-hazardous and non-volatile character of this chemical as well as a low corrosion rate is low. However, the absorption rate is very low compared to amines, leading to high absorption towers. As highlighted by Knuutila et al. [23], additives that increase the transfer kinetics may be needed, such as arsenous acid, formaldehyde, hypochloride, phenols, sucrose, dextrose, piperazine, diethanolamine, monoethanolamine, DIPA and piperazine, whose impact in the energy consumption of the entire process is still a pending issue.

Other amines and their blends are currently under research in order to overcome the drawbacks of MEA. Piperazine is an example of an amine solvent that has been investigated due to its high CO_2 capture capacity and absorption rate [28,37]. It has been considered in blends with other compounds or alone [12,13]. However, piperazine presents limited solubility, which motivates its use in blends with other amines or keeping the CO_2 loading in the range of 0.26–0.42 mol-CO_2/mol alkalinity above 20 °C [29]. Nevertheless, the stability of piperazine may condition its use outside a specific range of operating conditions. Mazari et al. [35] presented a review on the recent advances and findings on thermal and oxidative degradation of piperazine. Piperazine may degrade in nitrosamines among which 1-nitrosopiperazine and N,N-dinitrosopiperazine are a main worry due to their high toxicity. From this review, it was concluded that: i) piperazine is thermally stable up to 150 °C; ii) the degradation rate of piperazine increases with increase in temperature, concentration of piperazine, and CO_2 loading; iii) partial pressure of O_2 and temperature has a direct effect on the oxidative degradation of piperazine, and the presence of Cu^{2+} increases its oxidative degradation; and iv) the most abundant thermal and oxidative degradation products of piperazine are N-formylpiperazine,

NH_4^+, N-(2-aminoethyl) piperazine, and ethylenediamine, with 1-nitrosopiperazine in small concentrations. Thus, although piperazine shows interesting properties as substitute of conventional MEA, there are still technical limitations, mainly related to the long-term stability, that slow down the direct use of this solvent in the industry.

Using amino acids as absorption agent is also being considered for CO_2 absorption due to the presence of the same amino functional groups in their molecules as the conventional amines, negligible vapor pressure and resistance to oxidative degradation. L-arginine (ARG) and its salt potassium L-argininate (PA) were compared with MEA, DEA and TEA by Yan et al. [56]. It is shown that PA is a highly CO_2 selective absorbent and has a better affinity towards CO_2 than MEA. Furthermore, using PA allowed a lower solvent concentration, lower liquid velocity and higher reaction temperature in comparison to MEA. Also, PA demonstrated a better flexibility to the change of CO_2 partial pressure than MEA.

Finally, the consideration of ionic liquids as novel absorption liquids is under study. Ionic liquids (ILs) are organic salts with a melting point below 100 °C or even below 25 °C (room temperature ionic liquids). Many ILs have attracted a remarkable interest for CO_2 capture due to their intrinsic properties (e.g., non-volatility, high thermal stability, tuned structure) and, high CO_2 solubility and low energy requirements for regeneration [7,42,57]. The presence of NH_2, F, O, etc., in the IL structure has been shown to play an important role in CO_2 absorption, mainly related to the kind of anion that conform the ionic liquid [19,48,53,58]. SO_2 can also modify the capacity of CO_2 absorption in ionic liquids since recent research has shown that large amounts of SO_2 can be dissolved in ionic liquids reversibly, which is interesting when aiming at eliminating this component from gas streams but it may compete with CO_2 when the latter is the target compound [20,21,61]. Some values of CO_2 absorption capacity can be found in the literature: 0.96 mol-CO_2/mol-IL (at 293 K) was achieved with pure [TETAH][BF_4] and as 2.04 mol-CO_2/mol-IL (at 293 K) with [TETAH][BF_4] containing 40% water [19]; 1-(3-propylamino)-3-butyllimidazolium-tetrafluoroborate ([apbim][BF_4]) absorbed 0.5 mol-CO_2/mol-IL at 1 atm and room temperature [5]; diamino ionic liquid [aemmim][Tau] absorbed 0.9 mol-CO_2/mol-IL at 303 K [55]; 0.32–0.72 mol-CO_2/mol-IL for some amino acid-anion based ILs and 0.1–1.26 mol-CO_2/mol-IL for other aminate ILs [49]. In addition, mixing ionic liquids with amines could result in lower vapor pressure in comparison with the only use of the amine and, a reduction of the heat of vaporization in the regeneration step. However, LaFrate et al. [25] observed that the degradation of carbon capture solvents containing ionic liquids was faster in the presence of CO_2 than other gases (air, N_2 or SO_2) and the presence of the ionic liquid enhanced the degradation. Furthermore, imidazolium and other types of ionic liquids also inherently have ammonia, ethylene and other base feedstocks incorporated into their structures. These aspects put them in economic disadvantage regarding the conventional absorption process based on amines. Thus, the application of the studied ionic liquids for CO_2 capture in large scale does not seem a realistic approach for the moment.

Several solvent alternatives to the use of amines are under research but the perfect solvent that combines high CO_2 absorption, easy regeneration, low energy consumption during production and regeneration, low cost, and low environmental impact has not been identified. The most critical aspect is the development of a closed process that allows the reuse of the solvent at minimum environmental and economic cost. In a perfect scenario, the process would lead to CO_2-based products with economic value that can be re-integrated in a closed carbon loop and avoid the use of raw materials.

5. Concluding remarks and technological alternatives

Current research is focused on the optimization of the CO_2 capture process using MEA and other amines as well as novel solvents. The present review has described briefly the main concerns of using MEA in a global strategy and the last advances in the development of other alternative solvents. One last point that deserves attention is the radical modification of the CO_2 capture process, opting by technologies that intrinsically involve lower energy consumption and even may produce a final product to be reused in the industry.

Adsorption, CO_2 conversion, calcium looping, and membrane technology are the focus of alternatives to the conventional process for CO_2 capture in a post-combustion scenario [32]. Membrane technology is attracting the attention of more and more researchers due to its clear advantages regarding energy consumption, operational flexibility and modularity, based on two main kinds of systems: those in which the membranes act as a selective layer and, those in which the membrane acts as the support and a CO_2-selective liquid has to be used [32]. For the first group, membranes with permeabilities around 10^3 Barrer and CO_2/N_2 selectivity of about 100 are available for CO_2 capture; for the second, overall mass transfer coefficients ranging between 10^{-5} and 10^{-3} m s^{-1} are common in this technology [32]. Several reviews that show the current status of membrane technology for CO_2 capture have been recently published [31–33] and some necessary research paths have been already identified: i) development of new membranes that fit in the framework of low-cost processes to consider an economically affordable replacement of membranes; ii) development of new solvents (when involved) for CO_2 capture with low vapor pressure and low toxicity; and iii) study of process performance under industrial operation conditions (real composition regarding gases such as H_2S, SO_2, NH_3, water, etc.; temperature and pressure) to achieve a system with real implementation in the industry [33]. In addition, multistage or hybrid systems coupled to an economic analysis should be priority research since they may provide the most promising solutions for CO_2 capture [6].

Regardless the chosen technology, it is important to keep in mind that the final objective of the development of any technological option to the conventional process should aim at negative carbon intensity (energy-related CO_2 emissions to the atmosphere in grams of carbon in relation to energy in Joules) [10]. This means that more CO_2 has to be captured than emitted per unit of energy. Budzianowski [10] identified two large groups of potential carbon negative renewable energy technologies: i) carbon negative biofuels (e.g., biogas, liquid biofuels from pyrolysis of biomass, bioethanol from low-input cellulosic biomass, algae energy) and, ii) carbon negative products derived from CO_2 and renewable energy (s renewable solar energy, renewable hydrogen, geothermal energy, conversion of CO_2 to useful carbonate and bicarbonate products). Thus, the development of novel technology must always consider the overall impact of the entire process and the scale in which that technology can be applied to give solutions in a local or a global scale.

More research is still needed but it should be re-oriented towards the development of closed processes that are not only focused on removing CO_2 from a gas stream at any price but thinking of the overall process and integrating the captured CO_2 in the production chain. A process that would lead to CO_2-based products with economic value that can be re-integrated in a closed carbon loop is the best solution. This approach would avoid CO_2 emissions while reducing the use of fresh materials and decreasing the production cost. This target should be always kept in mind in order to produce valuable research that leads to real solutions from a technical, environmental, economic and social point of view. Some of the alternatives shown in this manuscript are a hot topic in the current research but they are quite far from satisfying this objective.

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