



The use of catalysis for faster CO₂ absorption and energy-efficient solvent regeneration: An industry-focused critical review

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ABSTRACT

Absorption in an aqueous amine solution is currently the most mature industrial process to capture anthropogenic and native CO₂. The high cost of the technology prevents its massive deployment. There is a growing number of experimental reports on the benefits of using a catalyst to speed up the absorption of CO₂ or to lower the energetic cost of the solvent regeneration. In this review the basics of industrial absorption and regeneration are first reviewed, as well as the mechanisms to catalyze the absorption and the desorption of CO₂. Subsequently, the results in the literature on heterogeneous and homogeneous catalytic CO₂ capture are critically assessed with a focus on the industrial reality of the process. It is shown that a catalyst for the regeneration has only little room for maneuver because the desorption is fundamentally controlled by thermodynamics. The overall benefit of catalyzing the absorption still needs to be proven. The review aims to realign the research with the industrial reality and indicates several key points of attention to perform more industry-focused experiments and to analyze the overall benefit of using a catalyst.

1. Introduction

Global warming due to the greenhouse effect has become a major issue for our society. One of the main greenhouse gases is CO₂ and its concentration in the atmosphere is constantly increasing. To fight against global warming and to reduce the CO₂ emissions scientists are developing technologies to capture the CO₂. The most mature and widespread technology today is absorption by aqueous amine solutions [1,2]. This technology can capture the CO₂, whether it is present at low pressure in industrial flue gases or at high pressure in natural gas. The major obstacle to the implementation of this technology on industrial sites remains its high cost [3], which is today significantly higher than the carbon taxes. The CAPEX (Capital Expenditure) are elevated due to the significant size of the installations, which is primarily determined by the volume of (flue) gas that needs to be treated. The OPEX (Operational Expenditure) are high due to the large amount of energy required for the regeneration of the CO₂-loaded amine solution. The minimum energy

depends strongly on the CO₂ concentration in the gas and on the CO₂ recovery. For an aqueous MEA (MethylEthanolAmine) solution, the average value of 4.2 GJ/tCO₂ is often cited [4], to illustrate the high energy of regeneration. Capturing and compressing CO₂ currently requires ~30% of the energy of a coal power station and would require even more if biomass rather than coal was burned [5–7].

An increasing number of researchers have studied the possibility to catalyze the absorption or the desorption of CO₂ [8–48]. The reasoning is the following: the absorption of CO₂ is limited by the reaction with the amine. Moreover, amines which absorb CO₂ relatively slow typically show a lower regeneration energy. The use of a catalyst would accelerate the CO₂ absorption and thus reduce the solvent flow rate and the size of the column, while maintaining the regeneration energy-efficient. The industrial desorption of CO₂ takes place at elevated temperatures, typically 120–140 °C. Adding a catalyst during the solvent regeneration step would reduce this temperature and result in considerable energy gains.

Abbreviations: AGRU, Acid Gas Removal Unit; BAS, number of Brönsted Acid Sites; B/L, number of Brönsted Acid Sites/number of Lewis Acid Sites; BEA, ButylEthanolAmine; CAPEX, Capital Expenditure; CCUS, Carbon Capture Utilization and Storage; DEA, DiEthanolAmine; DEAPA, 3-(DiethylAmino)PropylAmine; LAS, number of Lewis Acid Sites; LVC, Lean Vapor Compression; LVE, Liquid-Vapor Equilibrium; MAS, Mesoporous Acid Surface; MEA, MethylEthanolAmine; MDEA, MethylDiEthanolAmine; OPEX, Operational Expenditure; PZ, Piperazine; RPB, Rotating Packed Bed; 1DMA2P, 1-DiMethylAmine-2-Propanol.

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The catalysts studied can be divided into two categories: heterogeneous catalysts such as metal oxides or zeolites [9–40] and homogeneous catalysts including carbonic anhydrase and its derivatives [8,41–48]. Both show promising results.

Recent work even focused on improving the performance of the solid catalysts. This has recently been summarized in an elaborate review [49]. Different structural properties of the solid catalysts have been analyzed, with the purpose to find a correlation between the catalyst structure and its efficiency to increase the reaction rate between the amine and CO₂. The surface area of the mesopores and micropores of the zeolites, the mesoporous acid surface (MAS), the number of Brønsted and/or Lewis acid sites as well as their strengths were measured and correlated with the efficiency of the catalysts. An increasing number of authors propose reaction mechanisms to explain the impact of the catalyst on the reaction between the amine and CO₂.

Carbonic anhydrase is a naturally occurring enzyme that catalyzes the hydration reaction of CO₂ into a bicarbonate ion and a proton. A Zinc atom coordinated with three histidine amino acids and whose fourth coordination site is occupied by a water molecule forms the active site of the enzyme responsible for the conversion of CO₂. Some authors [8] have worked to improve the properties of the enzyme to enhance its catalytic activity under industrial conditions. Other groups have sought to synthesize metal complexes with the same reactivity as the enzyme through biomimicry [41–48]. The CO₂ capture with in-situ catalytic conversion of CO₂ has been reviewed recently [50], but this is not in the scope of this work.

Despite the many promising publications, the approach followed in the literature is currently too detached of the industrial process and therefore needs to be more critically assessed. For example, the industrial regeneration, which is primarily a thermodynamic process, takes place at atmospheric pressure and at a high temperature because the CO₂ desorption is thermodynamically favorable at these conditions and because one needs a vapor phase, e.g. steam, to strip the CO₂. Lowering the regeneration temperature at constant pressure, with or without a catalyst, will thus result in a much less efficient solvent regeneration, with significant negative repercussions on the absorption process itself.

The purpose of this review is therefore not to summarize the literature on catalytic CO₂ capture, but rather to confront the approach followed in the literature as well as the observations and conclusions with

the reality of the overall industrial process. This is done with the aim to realign the research with the industrial operation.

The review is organized as follows: first the operation of the industrial process of capturing CO₂ by an aqueous amine solution without a catalyst is covered, with the various phenomena and reactions involved during the absorption and desorption stages. Subsequently, the addition of a catalyst to one of these two steps is studied. In the next part, a critical review is performed of the experiments and the results available in the literature. To conclude, the industrial relevance of the use of catalysis is discussed and several suggestions are made to improve their evaluation in an industrial application.

2. CO₂ capture with an aqueous amine solution: absorption and desorption

2.1. Reactivity of the amines towards CO₂

CO₂ capture is divided into two main stages. The absorption of CO₂ into an aqueous amine solution, to extract the CO₂ from the other gases, takes place in the absorption column. This is followed by the regeneration in a second column where the CO₂-rich solution, also called the loaded amine, is heated to desorb the CO₂ and to regenerate the lean amine solution to recycle it to the absorption column (see Fig. 1).

The absorption and desorption can be further subdivided into different stages. First, mass transfer phenomena result in the encounter of a CO₂ molecule and an amine molecule. Then, chemical reactions transform the CO₂ into non-volatile ions (mainly carbamate or bicarbonate), hence, the CO₂ is captured.

The mass transfer phenomena are illustrated in Fig. 1. The first phenomenon of absorption is the diffusion of CO₂ in the vapor phase to the gas–liquid interface. The second is the transfer of CO₂ from the vapor phase to the liquid phase across the gas–liquid interface. The third step is the diffusion of the CO₂ in the liquid phase until it encounters a reactive species. Mass transfer performance can be characterized in terms of three fundamental parameters [51,52]: k_G , the gas side mass transfer coefficient, k_L , the liquid side mass transfer coefficient, and a_e , the gas–liquid mass transfer area, also referred to as the effective area. The overall mass transfer is a function of several properties of the gas and liquid phase and of the column internals. The density, the viscosity, the

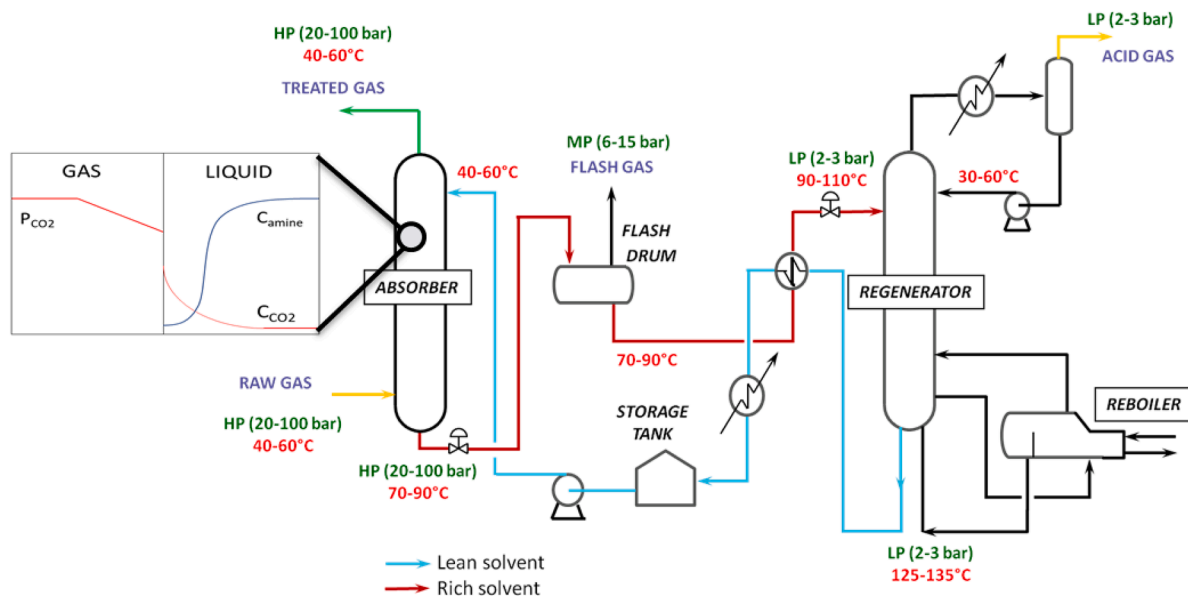


Fig. 1. Simplified process flow diagram of an acid gas removal unit (AGRU), with operating conditions typical for the treatment of natural gas (high pressure absorption column). The scheme is the same for the removal of CO₂ from flue gas, with the main difference that the absorption column is operated at low pressure. Zoom on the gas–liquid mass transfer in the absorption column (two-film model [54]): CO₂ partial pressure profile in the gas phase and CO₂ and amine concentration profile in the liquid phase as obtained from a typical mass transfer model of CO₂ absorption by aqueous amines [55,56].

flow rate (velocity), the composition and the diffusion coefficients of both the gas and the liquid phase, the physical gas–liquid repartition (e.g. Henry coefficients), the gas–liquid surface tension and interfacial area, the liquid phase reactions via a so-called enhancement factor (reactions enhance the mass transfer) and the properties related to the column internals (e.g. geometric area, geometric parameters, etc.) all determine the overall mass transfer of CO₂. The mass transfer is also impacted by the operating conditions (pressure drop, liquid holdup, gas velocities, etc.). A precise knowledge of k_G , k_L and a_e is important for an optimal column design. There exist many experimental correlations often relating dimensionless numbers (e.g. Reynolds, Sherwood, Schmidt, etc) to estimate k_G , k_L and a_e from the gas and liquid properties and from the operating conditions [52,53]. The selection of a correlation which is the most appropriate for a particular system is not straightforward and the choice has a large impact on the design and modelling of the absorption column. In general, for CO₂ absorption, the overall mass transfer of CO₂ is limited by the mass transfer in the liquid phase. In principle, the mass transfer parameters should be experimentally determined for new solvents and for new column internals.

The addition of a homogeneous or heterogeneous catalyst should considerably impact the mass transfer parameters. For example, a homogeneous liquid-phase catalyst in the absorption column might increase the viscosity of the liquid phase and thus considerably impact the operation and slow down the diffusion of CO₂.

After the three stages of mass transfer, a set of chemical reactions involving CO₂, amines and water lead to the chemical absorption of CO₂.

The reaction mechanism to chemically absorb CO₂ varies depending on the class of amine. There are two or even three main categories of amines to capture CO₂. This is shown in Fig. 2A. Primary and secondary amines react directly with CO₂ in two elementary steps to form a carbamate via a zwitterion, as illustrated in Fig. 2B.

The first step is an electrophilic addition, with the amine acting as the nucleophile and the CO₂ as the electrophile [57,58]. The product of

this reaction is a zwitterion. The second step is the deprotonation of the zwitterion, to stabilize it and to form a carbamate. For this a base reacts with the zwitterion, it is mainly the amine that fulfills this role. Having no proton, tertiary amines cannot form carbamates and therefore react only as Brønsted bases to aid in the formation of bicarbonate [59]. Water therefore replaces the amine in the role of nucleophile. The chemical absorption therefore takes place in a single concerted step between water (nucleophile), CO₂ (electrophile) and the amine (Brønsted base). Finally, there are the primary or secondary sterically hindered amines which make up a hybrid category. Due to steric hindrance they form unstable carbamates which will decompose to form bicarbonates [60].

Primary or secondary amines have a high absorption energy which give them the advantage of having a fast absorption rate but also the disadvantage of having a slow desorption rate. The opposite is true for tertiary amines, they show a slow CO₂ absorption rate, but a rapid desorption rate compared to primary or secondary amines [61–63]. Sterically hindered amines are in between the first two categories, their absorption and desorption rates are quite fast [60].

For example, for MEA (a primary amine) the absorption enthalpy is estimated to be $H_{\text{abs}} = -84 \text{ kJ/mol}$ [64,65], for DEA (a secondary amine) $H_{\text{abs}} = -67 \text{ kJ/mol}$ [65,66] and for MDEA (a tertiary amine) $H_{\text{abs}} = -55 \text{ kJ/mol}$ [65,67].

When CO₂ is absorbed as a carbamate, due to the reaction stoichiometry, the absorption capacity is limited to one molecule of CO₂ for two amine molecules, while when it is absorbed as a bicarbonate, the absorption capacity increases to one molecule of CO₂ per amine functional group. Thus, tertiary amines show the largest CO₂ absorption capacity.

The desorption process is identical to the absorption process but in reverse order. First one needs to shift the equilibrium between the carbamate or the bicarbonate and the free CO₂ in the solution. Subsequently the free CO₂ in the liquid phase must migrate from the liquid phase to the gas phase.

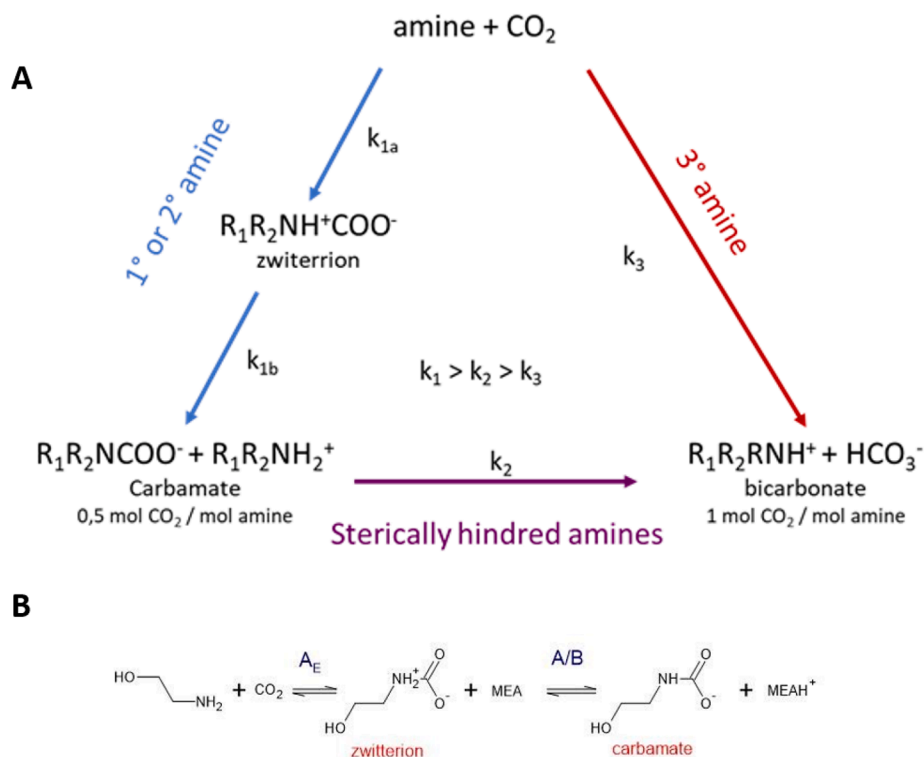


Fig. 2. Reaction mechanisms of CO₂ absorption in aqueous amines. (A) Scheme of the different absorption mechanisms of CO₂ as a function of the type of amine. (B) Chemical absorption of CO₂ with MEA (MonoEthanolAmine). Reaction mechanism of carbamate formation via a zwitterion. MEA is the Brønsted base, A_E is an electrophilic addition. A/B the Acid/Base reaction.

At a given temperature and at thermodynamic equilibrium, Liquid-Vapor Equilibrium (LVE) curves show the partial pressure of CO₂ in the gas phase as a function of the CO₂ loading in the liquid phase (see Fig. 3). The lower the partial pressure of CO₂ in the gas phase for a given loading, the higher the solubility of CO₂. Fig. 3 shows the LVE isotherms at 50 °C, a typical operating temperature in the absorption column, at 120 °C, a typical operating temperature in the regeneration column and at 85 °C, a typical regeneration temperature cited in the literature when the process would be catalytic. These isotherms indicate the thermodynamic limits of both absorption and desorption. For example, during the industrial regeneration, by increasing the temperature from 50 °C to 120 °C at a given CO₂ partial pressure, the CO₂ loading in the liquid phase is significantly lowered (the amine solution becomes lean). Independent of the kinetics, this thermodynamic behavior is the driving force of the desorption process. Lowering the desorption temperature from 120 °C to 85 °C increases the CO₂ loading for a given CO₂ partial pressure in the gas phase and thus results in a lean amine which is regenerated less well and thus closer to the thermodynamic limit of absorption in the absorption column. This will seriously impact the operation of the absorption.

The heat transfer is modelled based on the analogy with the mass transfer. The heat transfer coefficients of the gas and the liquid phase are calculated from the mass transfer correlations using the heat and mass transfer analogy [71]. The thermal conductivity is typically also calculated from empirical correlations. Absorption of CO₂ is an exothermic process, the temperature of the solvent heats up during the process, from 40–60 °C at inlet conditions up to 70–90 °C at the bottom of the column. The raw gas enters at the bottom of the column at 40–60 °C (see Fig. 1) providing some cooling. The result of both opposite effects is a temperature bulge in the column. Heating up the solvent increases the absorption (and desorption) rate of CO₂, but, from a thermodynamic point of view the absorption becomes less favorable at higher temperatures. To avoid desorption, a maximum temperature can thus not be exceeded. Any process increasing the CO₂ absorption rate (e.g. catalysis) will be limited by thermodynamics: a faster absorption rate results in a faster and larger local temperature increase favoring desorption. Intermediate cooling might be a solution.

Now that the reactivity of the amines with respect to CO₂ as well as the mass transfer phenomena and the thermodynamics which are involved in the absorption and the desorption of CO₂ have been briefly

covered, the implementation of this process on the industrial scale will be presented for a better understanding of the industrial challenges and to investigate how the addition of a catalyst might improve the capture of CO₂.

2.2. Industrial implementation of the process

Today, the captured CO₂ originates mainly from two sources: on the one hand the anthropogenic CO₂ present in flue gases produced by human activity and on the other hand the native CO₂ trapped in natural gas. CO₂ capture by an aqueous amine solution occurs in two stages within a unit called Acid Gas Removal Unit (AGRU). This is shown in Fig. 1.

First, the acid gas, CO₂, is absorbed by the aqueous amine solution in the absorption column. The solvent enters from the top of the absorption column and the raw gas to be treated enters from the bottom. The operation of the column is thus in counter-current mode. This column has trays, or, more frequently, a packing to increase the interfacial area between the gas and the liquid phase. The CO₂-enriched amine solution comes out from the bottom of the column and the treated gas, depleted in CO₂, from the top. The CO₂ content in the treated natural gas depends on the application: < 2 m% for pipeline gas, < 50 ppm for liquefied natural gas. For anthropogenic CO₂ capture typically > 90% of the CO₂ of the inlet gas is removed. This absorption step is spontaneous and thus exothermic. The absorption of CO₂ at the industrial scale is governed by the chemical reaction between the solvent and CO₂.

Subsequently, the amine is regenerated in the desorption column, also called stripper, and the desorbed CO₂ is separated from the amine solvent. As with the absorption column, the loaded amine enters from the upper part of the column and the lean amine comes out from the bottom. The CO₂ exits at the top. Contrary to the absorption column, the stripper has a reboiler and a partial condenser with total reflux (see Fig. 1). Therefore, when the hot loaded amine enters the stripper it is in contact with the much colder reflux which is mainly water. The result is a water wash (rectification) which limits the entrainment of amines to the overhead of the column. In the partial condenser the acid gas is cooled to separate it from the steam which is condensed back to water and recycled to the stripper as reflux. The regeneration is endothermic which means that external energy must be provided. The amine solution is heated with a reboiler at the bottom of the column. The temperature of the amine solution is typically increased to around 130 °C, which thermodynamically favors the desorption of CO₂. The desorption of CO₂ in the column is limited by a cascade of thermodynamic equilibria between CO₂ in the gas phase and CO₂ in the liquid phase. In addition, at this temperature, water vapor is generated, which strips the CO₂, and thus also aids the CO₂ to move from the gas phase to the liquid phase. Only a part of the water is vaporized, a typical industrial steam ratio is around 0.12 kg of steam per liter of solvent [72]. It has been observed that the loading of the lean amine, which is the most important parameter when operating the stripper because it impacts the absorption column, is directly related to the temperature of the top of the regenerator. Therefore, in the industrial operation, this temperature is the main process control parameter of the stripper (typically 110–120 °C). It is this temperature that determines the reboiler duty.

The temperature also directly impacts the size and the operation of the column. The McCabe Thiele method is a simplified but standard method which uses the equilibrium curves to obtain a first estimate of the number of theoretical stages required to achieve a desired degree of separation [73]. As an example, the theoretical McCabe Thiele diagrams shown in Fig. 4 illustrate that it takes twelve theoretical stages to deplete the liquid phase of CO₂, from a CO₂ fraction of $x_{\text{CO}_2} = 0.007$ to $x_{\text{CO}_2} = 0.001$ if the temperature is 80 °C and the boil-up ratio of the reboiler 0.025, while if the temperature is 120 °C and the boil-up ratio only 0.05, solely two theoretical stages are needed to reach this specification. It should be noted that at 80 °C this is a purely theoretical exercise as it is not clear if there is enough vapor.

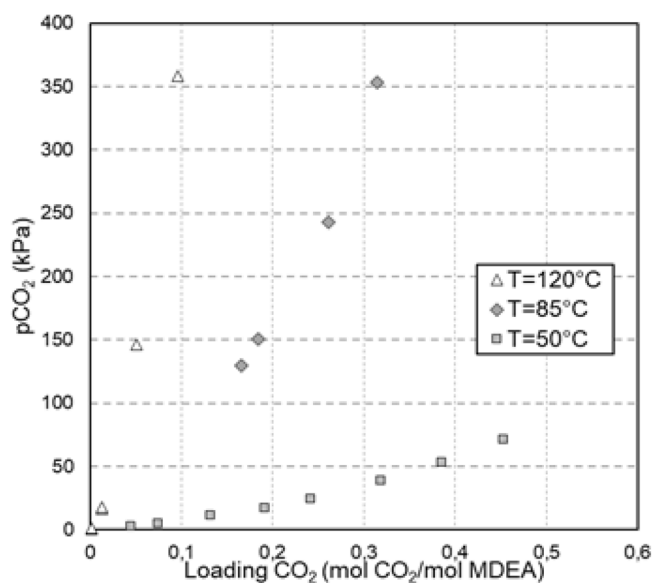


Fig. 3. Thermodynamics of CO₂ absorption. Liquid-Vapor Equilibrium curves for CO₂ and an aqueous MDEA solvent (50 wt% MDEA). The isotherms are shown at 50, 85 and 120 °C [68–70].

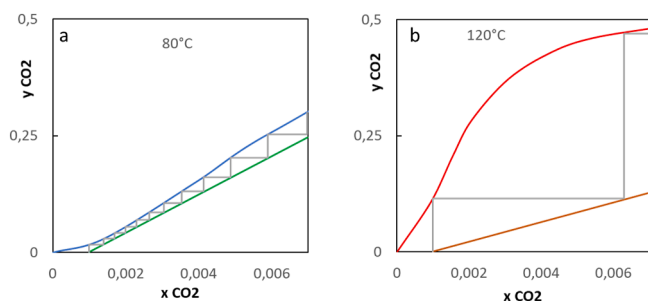


Fig. 4. McCabe Thiele diagrams representing the desorption of CO₂ from an aqueous MDEA solution at two different reboiler temperatures a) $T = 80\text{ }^{\circ}\text{C}$ and boil-up ratio of 0.025 and b) $T = 120\text{ }^{\circ}\text{C}$ and boil-up ratio of 0.05.

2.3. Industry cases

2.3.1. Native CO₂ in natural gas: high pressure CO₂ capture

Two reference systems are provided with two distinct gas flow rates and CO₂ contents: the first case is a natural gas relatively rich in CO₂ since it has a molar fraction of CO₂ between 5 and 15 mol% while the second case, conversely, contains very little CO₂, with a CO₂ fraction between 0.1 and 1 mol%.

For the first case relatively rich in CO₂, the natural gas has a flow rate between 30 and 40 m³/s and a pressure of 60 bar. The gas is divided into two CO₂ capture trains. The absorption columns have a diameter of ~5 m and a height of ~30 m. The CO₂ is captured with an activated MDEA-based aqueous solvent with a flow rate of ~500 kg/s. The solvent has a rich CO₂ loading at the bottom of each column of ~100 g/L. The CO₂-rich solvent is sent to a stripper having similar dimensions as the absorption column. The desorption of CO₂ is carried out at atmospheric pressure, the reboiler duty is between ~100 and 150 MW and the solvent at the bottom of the stripper is heated up to ~120 °C. The concentration of CO₂ in the lean amine at the stripper outlet is <5 g/L. This is equivalent to a regeneration energy of ~2.5 to 3 GJ/tCO₂.

For the second case with a low CO₂ content, the natural gas has a flow rate between 3 and 4 m³/s and a pressure of 80 bar. The absorption column has a diameter of ~5 m and a height of ~20 m. The CO₂ is captured with an activated MDEA-based aqueous solvent with a flow rate of ~50 kg/s. The solvent has a rich CO₂ loading at the bottom of each column of ~70 g/L. The CO₂-rich solvent is sent to a stripper operating at atmospheric pressure and at ~120 °C at the bottom. The heat duty of the reboiler is ~10 MW and the concentration of CO₂ in the lean amine at the stripper outlet is <5 g/L. This is equivalent to a regeneration energy of ~3.0 to 3.5 GJ/tCO₂.

2.3.2. Anthropogenic CO₂ in flue gas: low pressure CO₂ capture

Another source of CO₂ is the flue gas due to industrial activity. The following is a case study of a small to medium-size plant. The gas has a flow rate of ~15 Sm³/s, a CO₂ concentration of ~5 mol% CO₂ and a pressure of 1 bar. The solvent to capture CO₂ is aqueous MEA with an MEA weight fraction of 30%. The solvent flow rate is ~15 kg/s. The absorption column has the following dimensions: a diameter of ~3 m and a height of ~60 m. The rich MEA has a maximum loading of 0.5 mol of CO₂ per mol of MEA and is sent to the stripper (diameter ~2 m, height ~30 m). The reboiler heats the solvent to ~120 °C and the loading of the lean amine is typically 0.2 mol of CO₂ per mol of amine. The regeneration energy is ~4.0 GJ/tCO₂.

2.3.3. Industrial solvents and energy efficiency

The CO₂ levels in the lean amine are very low and less than ~0.03 mol CO₂ per mol MDEA while the levels of CO₂ in the lean amine are much higher for MEA (~0.2 mol of CO₂ per mol of amine). The reason is the following: with MEA CO₂ forms a very stable carbamate. To fully regenerate the aqueous MEA solvent, one needs temperatures well

above 120 °C, but this would result in unacceptable high regeneration energies and accelerate the thermal degradation of the amine leading to more emissions of potentially hazardous degradation products in the atmosphere. On the other hand, the regeneration temperature should not be much lower, otherwise the CO₂ level in the lean amine would be too close to the CO₂ levels in the loaded amine, thus seriously impacting the CO₂ absorption capacity of the absorption column. The smaller the difference in loading between loaded and lean amine, the higher the required solvent flow rate for a given CO₂ recovery, which will in turn enhance the required regeneration energy. The CO₂ level in the lean MEA solvent is thus a compromise between regeneration energy, acceptable thermal degradation and a decent CO₂ absorption capacity of the AGRU. Moreover, whatever the source of the CO₂, the regeneration temperature needs to be above 100 °C to generate water vapor to entrain the CO₂ in the gas phase.

Comparing the volumetric solvent flow rates with the dimensions of the column one can see that the residence times in the columns are relatively short (order of magnitude 100 s). Operating the absorption column at high pressure (natural gas case) allows to improve the absorption of CO₂ compared to the atmospheric pressure anthropogenic CO₂ capture. The regeneration column is typically operated around atmospheric pressure. The regeneration energy is very sensitive to the operating pressure. Operating the stripper at lower (vacuum) pressure (and thus at lower temperature) results in extra investment and energy to recompress the CO₂ and increases the risk of air (and thus oxygen) ingress. In the presence of oxygen, the amine degrades.

Energy efficiency can refer to the solvent itself or to the overall process. There is a thermodynamic minimum work required to separate CO₂ from a gas. This minimum work exponentially depends on the CO₂ concentration in the inlet gas (the lower the CO₂ concentration in the inlet gas, the higher the energy per ton of CO₂ recovered), but also depends on the CO₂ recovery (typically > 90%), the absorption enthalpy (the composition of the solvent), the regenerator pressure, etc. The interplay of those parameters is highly non-trivial and non-intuitive [74,75]. One can estimate that the minimum thermodynamic regeneration energy for post-combustion CO₂ capture with aqueous amines is ~2 GJ/tCO₂ [74]. It will thus be unlikely to achieve lower numbers in the industry with aqueous amines, with or without catalyst.

The variations in regeneration energy are also affected by the fact that for industrial installations the regeneration energies also strongly depend on the design and the thermal integration of the units. Hence, the regeneration energies mentioned in the examples above do not solely contain the energy required to desorb CO₂. It is important to keep this in mind when comparing solvents.

Aqueous MEA and MDEA are considered reference solvents. There is a new generation of industrial solvents showing improved performances. Many use Piperazine [76], often blended with a second, slower yet more energy-efficient, amine, because of its fast absorption rate. Examples are MHI KS-1 (the main commercial solvent), CESAR-1 (EU project), etc. As mentioned above, one needs to be careful when comparing, but these solvents perform much better than MEA, with typical values ranging between 2.5 and 3.5 GJ/t CO₂. The lower range often includes the impact of specific technology like Lean Vapor Compression (LVC), alternate stripper configurations [77–79], an advanced stripper [80], etc. It is a topic of debate in the scientific community whether MEA should even be kept as the reference solvent for anthropogenic CO₂ capture.

2.4. Distribution of the energy consumption of the regeneration stage

The energy consumed during the amine regeneration can be broken down in three terms. The sensible heat corresponds to the rise in temperature of the amine solution, required for the desorption (desorption is endothermic and thus more favored at high temperature). The heat of desorption is the energy to be supplied to compensate for the energy consumed during the desorption reaction. The heat of vaporization

corresponds to the energy required to vaporize the water which will carry the CO₂ from the liquid phase to the vapor phase.

$$H_{\text{regeneration}} = H_{\text{sensible}} + H_{\text{desorption}} + H_{\text{vaporization}}$$

$$H_{\text{sensible}} = \sum_i \nu_i C_{p_i} (T_{\text{des}} - T_{\text{abs}})$$

$$H_{\text{desorption}} = \Delta H_{\text{des}}(\text{CO}_2)$$

$$H_{\text{vaporisation}} = \Delta H_{\text{vap}}(\text{H}_2\text{O})$$

In the next paragraph an attempt is made to estimate the three terms contributing to the regeneration energy. The 30 wt% MEA-water system is considered and it is assumed that all MEA molecules have reacted with CO₂ according to the carbamate-forming mechanism. To extract one molecule of gaseous CO₂ one might assume that one needs to vaporize one water molecule. The enthalpy required to vaporize water is $\Delta H_{\text{vap}}(\text{H}_2\text{O}) = 40.7 \text{ kJ/mol}$, thus, $H_{\text{vaporisation}} = 40.7 \text{ kJ/mol}$. For MEA, the electrophilic addition has an enthalpy of reaction of $\Delta H_1 = 15.5 \text{ kJ/mol}$ [9] and for the deprotonation $\Delta H_2 = 74.3 \text{ kJ/mol}$ [9]. The free enthalpy of desorption of CO₂ with MEA is equal to the sum of the free enthalpies of both reactions. For MEA, the heat of desorption of one mole of CO₂ can thus be estimated: $\Delta H_{\text{des}}(\text{CO}_2) = \Delta H_1 + \Delta H_2 \approx 90 \text{ kJ/mole}$. 30 wt% MEA in the aqueous amine solution corresponds to 11 mol% of MEA. This is equivalent to one mole of MEA for 7.9 mol of H₂O. Thus, to warm up one molecule of CO₂, 2 molecules of MEA and 16 molecules of water will also be heated.

$$\begin{aligned} H_{\text{sensible}} &= \sum_i \nu_i C_{p_i} (T_{\text{des}} - T_{\text{abs}}) \\ &= (2 \times C_{p_{\text{MEA}}} + 16 \times C_{p_{\text{H}_2\text{O}}} + 1 \times C_{p_{\text{CO}_2}}) (T_{\text{des}} - T_{\text{abs}}) (2 \\ &\quad \times C_{p_{\text{MEA}}} + 16 \times C_{p_{\text{H}_2\text{O}}} + 1 \times C_{p_{\text{CO}_2}}) \\ &= 1,5 \text{ kJ/mole.K} \end{aligned}$$

If one considers a $\Delta T = 60^\circ$, $H_{\text{sensible}} = 90 \text{ kJ/mole de CO}_2$. In other words, for each degree saved in reboiler temperature one gains 1.5 kJ/mole of CO₂ desorbed on the regeneration energy of the solvent.

Each of the three energy terms to be supplied to desorb the CO₂ accounts for roughly a third of the global energy (industry rule of thumb). The vaporization enthalpy is lower, but the calculation has been done with MEA, which is a primary amine with a very high desorption energy (worst case amine), and with the assumption that only one water molecule vaporizes per molecule of CO₂. Thus, in other conditions the vaporization energy can quickly become the most important one.

3. Mechanism to catalyze the CO₂ capture

A catalyst speeds up a reaction by lowering the activation energy by changing the reaction path, and without changing the enthalpy of the reaction. In the literature many mechanisms have been proposed to catalyze the CO₂ capture. However, none of the mechanisms with a catalyst described in the literature and reviewed below has yet been proven experimentally or using molecular simulations.

3.1. Mechanism to catalyze the absorption

The kinetically determining step in the absorption of CO₂ by a primary or secondary amine is the formation of the zwitterion [57]. This step is an electrophilic addition, it is thus an electron transfer. One needs to stabilize the transition state to reduce the activation energy. The presence of electrons will speed up the reaction. The free O₂²⁻ ions of the metal oxide attack the CO₂ and bind it to the surface of the catalyst which, according to Afari et al. [10], facilitates the reaction with the amine. Metal atoms at the surface of the material can be unsaturated and therefore they can play the role of Lewis acid site. The transition metal interacts with the oxygens of CO₂. As a result, the partial charge of the

carbon atom of CO₂ will increase. This will enhance the electrophilicity of the carbon, which will accelerate the electrophilic addition.

Xiao et al. [11] explain the effectiveness of the catalyst by arguing that MCM41 reduces the protonation of the amine, Amino-MethylPropanol (AMP), and that the adsorption of the reactants on their surface activates them. Shi et al. [12] shares the opinion that the catalyst gain for absorption lies in the large surface area of the catalyst, which increases the mass transfer.

Another option would be to improve the nucleophilicity of the amine, by increasing the partial charge on the nitrogen atom and/or by deprotonating the amine, or to improve the electrophilicity of CO₂, or to stabilize the transition state (to reduce the barrier energy of the electrophilic addition).

The absorption of CO₂ by a tertiary amine involves only one step, which starts with an electrophilic addition followed by an acid-base reaction. To improve the electrophilic addition, one could target the same parameters as for the primary or secondary amines; namely to enhance the nucleophilicity of water and the electrophilicity of CO₂ and to stabilize the transition state by deprotonating H₂CO₃ rapidly.

3.2. Mechanism to catalyze the desorption

Desorption is an endothermic reaction. The kinetical rate determining step of the desorption reaction mechanism is the deprotonation of the amine, for the amines forming a carbamate as well as for those forming bicarbonate (see Fig. 5). It is important to point out that this deprotonation must be understood as the release of protons in the solution, to accelerate the breakdown of the carbamate or the dissociation of HCO₃⁻ into CO₂ and H₂O. It should not be understood as the regeneration of the neutral form of the amine. Thus, the catalyst should not be a strong base which will strongly retain the protons. The catalyst must make the protons accessible in order to protonate the carbamate and therefore form the zwitterion. If the catalyst has Brönsted acid sites, it will be able to accelerate the formation of the zwitterion. Moreover, if it has Lewis acid sites it will be able to stabilize this zwitterion as well as the transition state of the deprotonation step.

Zhang et al. [13] and Shi et al. [14] propose a mechanism to explain the breakdown of the carbamate formed with MEA. First the the Brönsted basic sites will deprotonate the protonated amine, turning into Brönsted acid sites. Then, the carbamate adsorbs on a Brönsted acid site through hydrogen bonds between the lone pair electrons of the oxygen of the carbamate and the hydrogen of the Brönsted acid site of the catalyst. Subsequently, the proton is transferred from the catalyst to the

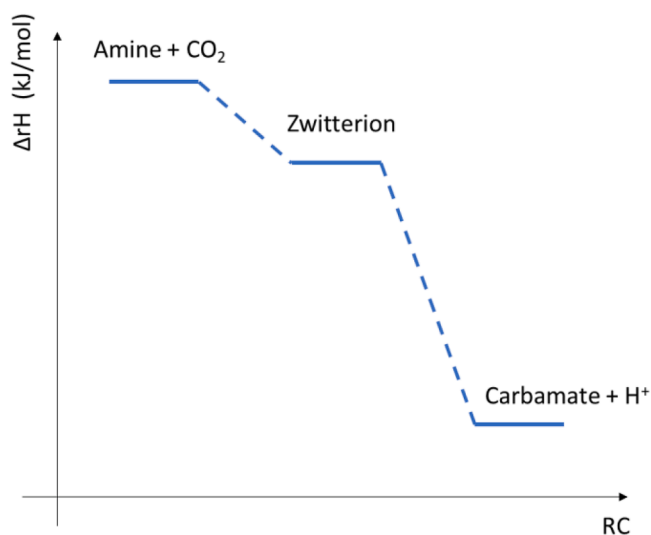


Fig. 5. Energy profile of the reaction to form or to break down the carbamate. RC is the Reaction Coordinate and ΔrH the reaction enthalpy.

carbamate, to protonate the carbamate, and the carbamate adsorbs on a Lewis acid site via its oxygen. Prototropy takes place between the oxygen and the nitrogen to protonate the amine. Finally, the carbon–nitrogen bond breaks and the CO₂ desorbs from the catalyst surface and migrates to the gas phase. This is illustrated in Fig. 6.

Because desorption is primarily governed by thermodynamics, the number of trays is governed by the equilibrium between the CO₂ mole fraction in the liquid and gas phases. The addition of a catalyst will not have an impact on thermodynamics so it will not reduce the number of trays in the stripper. Operating with a catalyst at high temperature will only reduce the size of each tray because the chemical desorption occurs faster with a catalyst. Operating with a catalyst at lower temperature will significantly increase the number of trays required (see Fig. 4). Moreover, as water vapor is required to entrain the CO₂ into the gas phase, one cannot reduce the reboiler temperature significantly.

4. A critical review of the literature

The data from the literature dealing with the catalysis of CO₂ capture is summarized in Table 1 and critically reviewed in the paragraphs below.

4.1. Heterogeneous catalysis

In the literature various categories of nanoparticle materials are presented for enhanced solvent-regeneration by heterogeneous catalysis. By their size, these particles might improve the physical part of the mechanism of desorption. They can break down gas bubbles which will increase the mass transfer surface area between gas and liquid, and they will decrease the mass transfer resistance. Heterogeneous catalysts can be divided into five groups. First, there are transition metal oxides like K/MgO, TiO(OH)₂, γ -Al₂O₃, TiO₂, Ag₂O and sulfated metal oxides like SO₄²⁻/ZrO₂. Metal oxides have both Lewis (unsaturated metal atoms at the surface of the material) and Brönsted (from hydroxyl groups at the surface) acid sites, but they have a low surface area compared to other categories. By deprotonating the surface of these catalysts, the amine will generate basic sites which in turn can (re)act as a base to deprotonate the zwitterion, H₂CO₃ or water. Sulfated metal oxides are like metal oxides but with stronger acidic sites due to the presence of sulfur atoms in the structure. Second, there are zeolites. They have a high surface area and a large number of Brönsted acid sites available because of their mesoporosity. Then, there are mesoporous silica like MCM-41 or SBA-15. They have a regular mesoporous structure but a small number of Brönsted acid sites. Finally, there are hybrid materials which can be formed from a mixture of two different materials.

Afari et al. [10] worked on the catalysis of the desorption with H-

ZSM-5. However, they also looked at 7 catalysts for the absorption: hydrotalcite, BaCO₃, CaCO₃, Cs₂O/ α -Al₂O₃, Cs₂O/Al₂O₃, Ca(OH)₂, et K/MgO. The solvent was a mixture of 2 M ButylEtanolAmine (BEA) and 2 M AminoMethylPropanol (AMP). They concluded that K/MgO is the best catalyst among the seven.

Shi et al. [15] studied CaCO₃, MgCO₃ et BaCO₃. Their analysis to provide figures on the effectiveness of the catalysts is questionable. Indeed, they compared the duration of the absorption at equal CO₂ liquid loading rather than comparing CO₂ liquid loading at the same time of absorption. They observed the time needed to achieve a CO₂ liquid loading of 0.5 with and without catalyst. Thus, the time of the experiment varied with each catalyst.

Different solid catalysts, zeolites and metal oxides, have been studied for the desorption of CO₂: H-ZMS-5, CMK-3-SiO₂, CMK-3-MCM-41 and CMK-3-SBA-15, SO₄²⁻/ZrO₂/SBA-15 (SZ), SAPO-34, MCM-41, SO₄²⁻/TiO₂, V₂O₅, MoO₃, WO₃, TiO₂, Cr₂O₃, Ag₂O, Ag₂CO₃, ZrO₂, ZnO. The use of these catalysts resulted in attractive cuts in energy consumption. Liang et al. [16] announced a reduction of 48% for the heat of regeneration and Shi et al. [17,18] announced 37%, both for H-ZMS-5.

Furthermore, correlations are made between the structural properties of the catalyst and its effectiveness. The mesoporous acid surface (MAS), the number of Brönsted or Lewis acid sites (BAS or LAS) as well as their strength or the ratio between Brönsted and Lewis acid sites (B/L) are factors determining the effectiveness of the catalyst. Another factor is the mesopore volume because it quantifies the accessibility of the acid sites inside of the materials for the reactant. Gao et al. [19] showed that the larger the number of acid sites (protons available to accelerate the stripping of CO₂) and the number of basic sites (to deprotonate the amine) of the catalyst and the larger the MAS*BAS product, the stronger the increase of the CO₂ desorption rate. Liang et al. [16] and Liu et al. [20] showed that the product MAS*B/L is a relevant factor in evaluating the effectiveness of a catalyst. Prasongthum et al. [21] revealed correlations between the number of Brönsted acid sites, the size of the pores and the rate of desorption. Both factors improve the desorption rate, but the first factor has more impact than the second. Zhang et al. [13] showed correlations between BAS or MAS*BAS and the desorption rate.

However, for various reasons it is not obvious to compare the different articles. As can be seen in the previous example of Liang et al. [16] and Shi et al. [17,18], there is an absolute difference of 11% for the reduction of the regeneration heat, which is not negligible. Despite an apparent uniformity of the experimental conditions, many parameters are different: the temperature, the reaction time, the energy supplied, the amine, etc. As another example, a significant difference in heat duty for the non-catalyzed MEA system, which is used as the reference, can be observed between the following two articles: Bhatti et al. [22] obtained a regeneration energy of almost 4000 kJ/mol CO₂, while Liang et al.

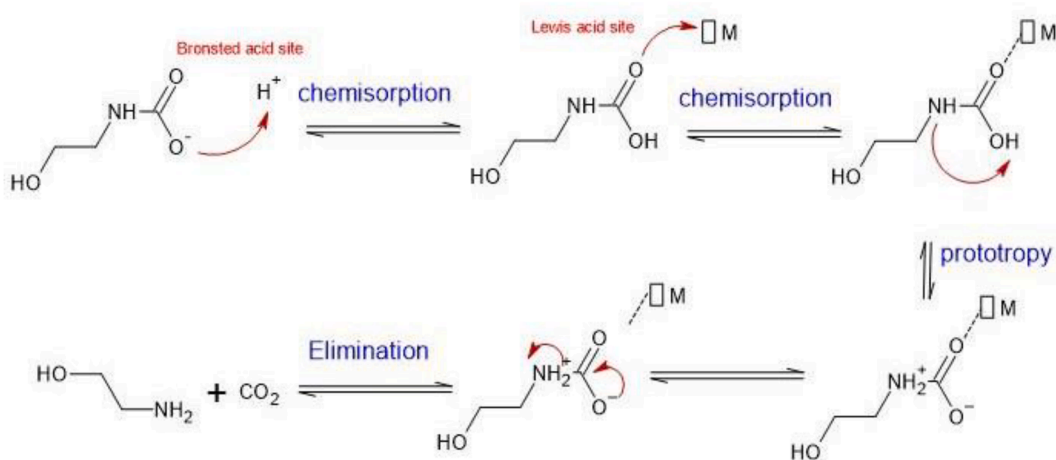


Fig 6. Mechanism of the catalytic breakdown of the carbamate formed with MEA, as proposed by Zhang et al. [13] and Shi et al. [14].

Table 1

Summary of the data in the literature treating the catalysis of CO₂ capture. *t (time) column: when two times are given, the first time corresponds to the time of the measurement and the second time to the entire experiment. **Results column: an rd means the value is for the rate of desorption, ^{ra} the rate of absorption, ^{cc} the cyclic capacity (amount of CO₂ desorbed), ^H the heat duty. *** Comments column: $\Delta\alpha$ compares the cycling capacity of the experiment with a typical cycling capacity obtained under industrial conditions ($\Delta\alpha_{\text{MEA}}^{\text{industrial}} = 0.3\text{molCO}_2/\text{molamine}$; $\Delta\alpha_{\text{MDEA}}^{\text{industrial}} = 0.6\text{molCO}_2/\text{molamine}$).

Ref	Solvent	T(°C)		Catalysts		t (min)	Results	Comments
		abs	des	abs	des			
Afari et al. [10]	MEA (5M) BEA (2M) AMP(2M)	45	85	K/MgO	H-ZMS-5 H-ZMS-5		+38% rd +15% ^{ra}	bench-scale pilot plant experimental setup $\Delta\alpha$ industrial - 71%
Shi et al. [15]	DEA	20		CaCO ₃ MgCO ₃			+14% ^{ra} +11% ^{ra}	Duration of CO ₂ absorption
Shi et al. [12]	MEA(1M) + DEA(4M)	20		CaCO ₃ MgCO ₃			+116% ^{ra} +69% ^{ra}	
Shi et al. [25]	MEA	20						
Xiao et al. [11]	AMP	40		MCM41			+53% ^{ra}	$\Delta t=40$ min
Bairq et al. [26]	MEA (5M)		97		CMK-3-SiO ₂ , CMK-3-MCM-41 CMK-3SBA-15		+97% rd +57% rd +54% rd	Not the same final equilibria. $\Delta\alpha$ industrial - 60%
Bairq et al. [27]	MEA (5M)		97		SZ SZS 15%	180	+10% ^h 36% ^h	Not the same final equilibria $\Delta\alpha$ industrial - 60%
Bhatti et al. [28]	MEA (5M)		35-86		V ₂ O ₅ MoO ₃ WO ₃ TiO ₂ Cr ₂ O ₃		+ 43% rd +105% rd	CO ₂ loading in lean amine, reaction time are not specified
Bhatti et al. [29]	MEA (5M)		40-80		Ag ₂ O Ag ₂ CO ₃		+52% ^{cc} +74% ^{cc}	After an absorption time of 80 min the equilibrium is still not reached
Bhatti et al. [30]	MEA (5M)		40-86		ZrO ₂ ZnO	140	+31% ^{cc} +32% ^{cc}	$\Delta\alpha$ -17%
Bhatti et al. [22]	MEA (5M)		40-82		HZMS-5 HZ-0,2 HZ-0,5 HZ-0,7	100	+31% ^{cc} +24% ^{cc}	$\Delta\alpha$ -33%
Bhatti et al. [23]	MEA (5M)		40-85		Ag ₂ O Nb ₂ O ₅ NiO CuO MnO ₂ H-ZMS-5	140	+152% rd +119% rd +57% rd +48% rd +26% rd +38% rd	$\Delta\alpha$ -17%
Gao et al. [19]	MEA (5M)		60-98		SZS SBA-15 H-ZMS-5	150	+26% ^{cc} +15% ^{cc} +15% ^{cc}	Not the same final equilibria $\Delta\alpha$ -57%
Hu et al. [31]	DEAPA (2,5M)		90		SAPO-34 MCM-41 SO ₄ ²⁻ / TiO ₂	120	+24% rd +15% rd +9% rd	
Lai et al. [32]	MEA (20wt%) MDEA (20wt%)		88		TiO(OH) ₂	25	+75% ^{ra} +86% rd	$\Delta\alpha$ -67%
Liang et al. [16]	MEA (5M)		50-105		H-ZMS-5 γ -Al ₂ O ₃ H-Y	30-120	+48% ^h +36% ^h 13% ^h	$\Delta\alpha$ -33%
Liu et al. [20]	5M MEA		98		H-ZSM-5 MCM-41 SO ₄ ²⁻ /ZrO ₂	90-540	+29% rd +21% rd +11% rd	$\Delta\alpha$ -60%
	5M MEA +1M MDEA				H-ZSM-5 MCM-41 SO ₄ ²⁻ /ZrO ₂	90-540	+21% rd +17% rd +13% rd	
	5M MEA +1M 1DMA2P				H-ZSM-5 MCM-41 SO ₄ ²⁻ /ZrO ₂	90-540	+29% rd +17% rd +13% rd	
	5M MEA +1M DEEA				H-ZSM-5 MCM-41 SO ₄ ²⁻ /ZrO ₂	90-540	+23% rd +13% rd +9% rd	
	2M BEA + 2M AMP		85			30		

(continued on next page)

Table 1 (continued)

Ref	Solvent	T(°C)		Catalysts		t (min)	Results	Comments
		abs	des	abs	des			
Prasongthum et al. [21]				Ce(SO ₄) ₂ /ZrO ₂			+77% rd +31% rd	Δα –50% Not the same final equilibria
Srisang et al. [33,34]	MEA (5M)		75-85-95	H-ZMS-5 Si/Al=10			+17% ^{ra} +16% rd +25% ^{ra} +31% rd	(Liquid flow rate 60 mL/min) Δα –63%
	MEA + MDEA			γ-Al ₂ O ₃ H-ZMS-5			+9% ^{ra} +13% rd 12% ^{ra} +21% rd	
	MEA+DEAB			γ-Al ₂ O ₃ H-ZMS-5			+8% ^{ra} +14% rd 15% ^{ra} +19% rd	
Zhang et al. [35]	MEA (5M)		96	SO ₄ ²⁻ /TiO ₂ SAPO-34		120-540	+17% rd 24% rd	Δα –63%
Zhang et al. [36]	5M MEA, 3M MEA-2,5M MDEA-0,5M PZ		96	SO ₄ ²⁻ /TiO ₂ SAPO-34		120-540	+4% rd +10% rd +19% rd +23% rd	Δα –60%
				γ-Al ₂ O ₃ H-ZMS-5				
Zhang et al. [24]	5M MEA MEA-AMP-PZ		60-98	H-modernite H-ZMS-5 γ-Al ₂ O ₃ Hβ		90-480	+16% rd +21% rd +19% rd +29% rd	Δα –53%
Zhang et al. [37]	MEA (5M)		96	HZSM-5 γ-Al ₂ O ₃ Al-ZMS2/1		120-540	+19% rd +21% rd 34% rd	Δα –53%
Zhang et al. [38]	MEA (5M)		98	SZ MCM-41 SZM1/1		90-480	+13% rd +17% rd +25% rd	Δα –53%
Zhang et al. [39]	MEA (5M)		96	γ-Al ₂ O ₃ H-ZSM-5 Al-ZSM2/1		120-540	+26% rd +25% rd +52% rd	Δα –53%
Zhang et al. [40]	MEA (5M)		98	γ-Al ₂ O ₃ SZ SZA1/1		120-540	+11% rd +17% rd +34% rd	Δα –53%
Zhang et al. [13]	MEA (5M)		98	MCM-41		90	+16% rd	Δα –53%
				MCM-41/10%		-480	+49% rd	
				Fe			+33% rd	
				MCM-41/50%			+44% rd	
				Mo MCM-41/50% Al				

[16] mentioned approximately 250 kJ/mol CO₂. This difference illustrates the difficulty to compare the articles.

Finally, the experimental conditions remain far from the industrial conditions: the temperature is often low (T < 100 °C), there is no stripping with water vapor and, the CO₂ loading of the lean amine is very high (sometimes hardly lower than the loaded amine), which means the solvent is barely regenerated, which is expected at lower temperature given the thermodynamic nature of the process. If the CO₂ loading in the lean amine is elevated, the cyclic capacity of solvent is drastically reduced. To absorb the same quantities of CO₂ with a barely regenerated solvent, one needs to increase the flow rate of solvent. With the rise in solvent flow rate the heat of vaporization and the sensible heat also increase, and thus the benefit of using a catalyst vanishes.

The experiments at low temperature, often with one of the worst amines for desorption (amines with a very high desorption energy, like MEA), and the absence of stripping all seriously (artificially) enhance the effectiveness of the catalyst. It would not be surprising if these yields were significantly lower at real industrial conditions. Increasing the temperature (to have steam) and using a catalyst with a more recent generation of amines which have larger desorption rates will decrease

the effectiveness of a catalyst. This is highlighted in the works of Bhatti et al. [23], Zhang et al. [24] and Shi et al. [18].

4.2. Homogeneous catalysis

Homogenous catalysis can be divided into two categories: enzymes and biomimetic complexes.

4.2.1. Carbonic anhydrase

Carbonic anhydrase enzymes catalyze the hydration of CO₂: CO₂ + H₂O = HCO₃⁻ + H⁺ [45–48]. There are many carbonic anhydrase families in nature. The catalytic site of the enzyme is a Zinc atom. It is linked to three histidine amino acids in its natural configuration and the fourth coordination site is occupied by a water molecule. However, for some other configurations of carbonic anhydrase, the Zinc atom is not linked in the same way. Alvizo et al. [8] described the catalytic site as a Zinc atom linked to Cys55, Asp57, Arg59, His108, Cys111. For homogenous catalysts, two parameters are decisive for the efficiency of the catalyst. First, an optimum affinity between metal and ligand must be found. It means that a strong interaction is needed between metal and

ligand to form the complex, but at the same time a good lability of HCO_3^- is required to have a good regeneration of the catalyst. Secondly, the second coordination sphere of the complex needs to be able to transfer the proton outside of the active site.

One of the main challenges when using a carbonic anhydrase enzyme as a catalyst for absorption or desorption is the stability of the enzyme: during the CO_2 capture cycle, the enzyme is subjected to the high temperatures of the desorption ($T > 100^\circ\text{C}$) and to elevated pH values which can reach up to $\text{pH} = 12$ due to the high amine concentration. These two factors can lead to the degradation of the enzyme which results in a loss of catalytic activity. Through mutations Codexis has succeeded to increase the half-life of the enzymes from 15 min to 14 weeks, in a 4.2 M MDEA solution at 50°C [8]. Although this is an impressive improvement in stability, it is still small compared to the typical operational durations in the industry (several years). Atmospheric pilot plant tests with carbonic anhydrase in a 2.1 M solution of MDEA have shown a significant increase in (liquid phase) mass transfer for the absorption of CO_2 . Whether this increase in liquid phase mass transfer will result in significant savings remains to be studied. Indeed, the size of the absorption column is mainly determined by the volumetric flow rate of the gas, for anthropogenic CO_2 capture at atmospheric pressure no special material is required for the absorption column and thus reducing its size will not necessarily have a noticeable impact on the CAPEX, etc. Moreover, the use of a catalyst is not the only way to significantly increase the mass transfer. For example, using a rotating packed bed (RPB) reactor might increase both the gas and liquid mass transfer (but requires energy for the rotation).

4.2.2. Derivatives of carbonic anhydrase

Several groups [41–44] have worked on catalysts that are bio-inspired by the carbonic anhydrase catalyst. Zinc complexes have been synthesized to achieve the same catalytic behavior as carbonic anhydrase. Carbonic anhydrase-like complexes tend to dimerize or to bind strongly with anions, preventing them from having a catalytic activity. This can be explained by the second coordination sphere being different from the first one. The environment of the enzyme participates in the deprotonation step of the coordinated water molecule. To successfully copy the behavior of the enzyme there are still challenges to overcome. One needs to successfully modify the Lewis acidity of the Zn^{2+} cation to reduce its acidity so that the HO^- and HCO_3^- ions are labile while maintaining a sufficiently strong coordination bond to stabilize these species. Furthermore, one needs to be able to imitate the role of the second coordination sphere of the enzyme, and of the amino acids Thr 199 and Glu 106 in particular as they lower the pK_a of the deprotonation of the water molecule complexed with the Zinc by forming a hydrogen bond network. In addition to these two constraints, the Zinc complex needs to be soluble in water. The mechanism is illustrated in Fig. 7.

Not only Zn, but also other elements like CO, Ni, Cu, and borate species have been studied. Those materials have recently been reviewed [80].

5. Conclusions and perspectives

Because the desorption is fundamentally controlled by thermodynamics, and because one also needs to heat the solvent to generate water vapor to strip the CO_2 from the liquid phase, a catalyst has only little room for maneuver. Moreover, the figures on the reduction in regeneration heat reported in the literature are not obtained at relevant industrial conditions. First there is the frequent choice to use MEA to test the catalyst. MEA is an amine with one of the worst desorption rates and for which the impact of the catalysts will be highest. Although MEA is still often used as an R&D reference solvent, it is not a reference commercial solvent anymore and there exist now many (commercial and R&D) solvents with much better energy performances. Second, the tests are often performed at low temperature to enhance the impact of the catalyst, but this results in high lean amine loadings. At constant solvent

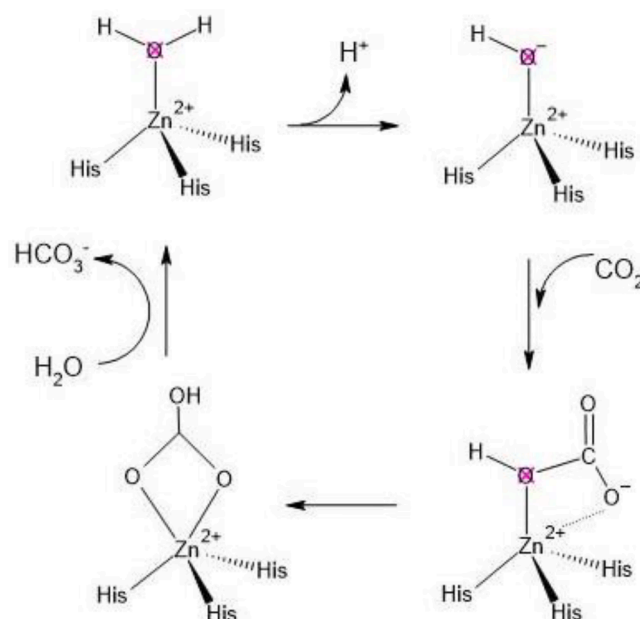


Fig. 7. Homogeneous catalysis of CO_2 absorption: deprotonation step of the coordinated water molecule, addition of CO_2 and the formation of bicarbonate.

flow rate this significantly impacts the CO_2 absorption capacity. At iso- CO_2 recovery this will result in much higher solvent flowrates, and thus the benefits of the catalyst will vanish. With a more recent commercial amine and under realistic industrial stripping conditions, the impact of the catalyst is significantly lower.

Adding a catalyst in an absorption column should accelerate the reaction. This should result in a reduction of the absorption column size and maybe of the solvent flow rate. However, the size of the column is primarily determined by the gas volume. For anthropogenic, low pressure CO_2 capture normal steel is used and a reduction in size (with the extra complexity due to the addition of a catalyst) doesn't necessarily translate into a significant reduction in CAPEX. Thus, the overall attractiveness of using a catalyst for absorption still needs to be proven. Moreover, the use of contactors other than a packed column, like e.g. a rotating packed bed, might also enhance the mass transfer, with the advantage that they increase both the gas and liquid phase mass transfer.

Carbonic anhydrase or its bio-inspired derivatives can be interesting alternatives to the solid catalyst. On the one hand, because the catalytic activity of the enzyme shows an attractive effectiveness and on the other hand because they can catalyze both absorption and desorption. However, the enzymes do not yet have sufficiently long lifetimes for industrial applications. Molecular catalysts do not yet have satisfactory catalytic properties.

Catalysis of one or both stages of CO_2 capture is a technology that still needs to mature. In addition, catalysis is a very empirical science with many parameters to consider. It is thus difficult to theoretically predict the gain of a catalyst without verifying it experimentally. For the moment the studied catalysts do not have satisfactory yields and have not yet been studied under industrially relevant conditions. The impact of the catalyst is expected to be much lower under industrial conditions. It might, however, be too early to conclude that catalyzing CO_2 capture might not be beneficial at all, and this review points out how to perform more industry-focused experiments and analyses.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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