Chapter 5

Bio-inspired Systems for Carbon Dioxide Capture, Sequestration and Utilization

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Additional information is available at the end of the chapter

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Abstract

This chapter reviews the study and development of biological, enzymatic and bio-molecular systems for carbon dioxide capture and further sequestration or even utilization. Regardless of the interest on the use of the captured CO_2 as C1 synthon on the manufacture of added-value compounds, there is a tremendous unbalance between the requirements of the contemporary society (leading to a massive production of carbon dioxide) and the framework of commercialization of the products from CO_2 utilization. In this context, viable options are storage as a solid in the form of calcium or magnesium carbonate and conversion into other energetic frameworks. In addition, it is important to highlight that the conventional energy resources are progressively being replaced by renewable resources. While the change in energetic paradigm is not accomplished, systems that capture and convert carbon dioxide are highly sought. To this end, bio-inspired systems will be presented, starting from the use of compounds from the chiral pool, such as amino acids, saccharides and related bio-polymers, involved in the physical and chemical capture, sequestration and/or utilization of CO_2. Additionally, enzymatic systems are presented in the context of sequestration of CO_2 in the form of solid carbonates or even utilization of this C1 synthon in the preparation of fuels and commodity chemicals. Carbonic anhydrase is by far the most studied enzyme, as it catalyses the inter-conversion between CO_2 and hydrogencarbonate in an effective mode. The biological option comprises the utilization of methanogens, acetogens and other organisms leading to the formation of added-value compounds. Most of the described systems are based on microbial electro-synthesis model and microbial carbon-capture cell prototypes.

Keywords: carbon dioxide, amino acids, saccharides, bio-polymers, enzymes, carbonic anhydrase

1. Introduction

In the present context, our civilization's standards of life are grounded on enormous emissions of Green House Gases (GHGs) to the atmosphere, in concrete carbon dioxide. Simultaneously, biological systems available in nature have restricted capacity on the fixation of CO_2, and accumulation of this GHG is creating impact on our environment. It is essential to develop and implement technologies that simultaneously avoid further accumulation and increase the rate of CO_2 incorporation in added value products. The use of renewable energies, such as solar, hydroelectric, wind, geothermic, hydrogen, tides and biofuels are progressively being implemented depending on the specific resources of each country and commercial adjustment of the energetic paradigm that can be valid and affordable for the near 7.5 billion human habitants in our planet (2016) [1]. Regardless of the progresses on the implementation of renewable energy resources, conventional fuels continue to be the main source of energy worldwide, leading to accumulation of CO_2 in the atmosphere.

The most recent data from IPCC is clear [2]. The total cumulative anthropogenic emissions linked to CO_2 (1750–2011) are 2040 ± 310 $GtCO_2$. Nearly 50% of the cumulative emissions took place in the last 40 years (1970–2011), consistent with a steady rise in CO_2 emissions during that period. It is important to highlight that 40% of the anthropogenic emissions (1750–2011) persisted in the atmosphere (880 ± 35 $GtCO_2$). While the anticipated change of the energetic paradigm is not assimilated, systems that capture CO_2 in an effective mode, and incorporate it in safe and useful products, are highly desirable.

An additional point, that should be presented, is illustrated in **Figure 1**, corresponding to the pattern of GHG emissions by economic sector, being useful in the definition of target sectors more able to be optimized in respect to the CO_2 footprint and development of innovative strategies adjusted to a specific challenge. The most representative sector is electricity and heat production applied to the other segments as an indirect source of CO_2 emissions (except other energy). The first sector is followed by agriculture, forestry and other land use (AFOLU). Industry, transport, other energy and buildings are the other sectors, with lower percentage on direct GHG emissions. The data here presented (**Figure 1**) is associated with the year 2010 (the most recent data available from IPCC).

From the more representative GHGs emitted to the atmosphere, CO_2 presents by far, the highest percentage of associated emissions (**Figure 2**, 2010) which demonstrates the importance of the commercially available systems for CO_2 capture and fixation, urgency in the development and implementation of straightforward and sustainable alternative systems complementary to the change in the energetic paradigm already on course.

In order to accomplish an effective CO_2 uptake exist diverse prototypes and mature technology: (A) absorption; (B) adsorption; (C) cryogenic; (D) membrane [3]. All the pointed instances, except (C), incorporate bio-inspired systems, as represented in the literature, and will be described briefly.

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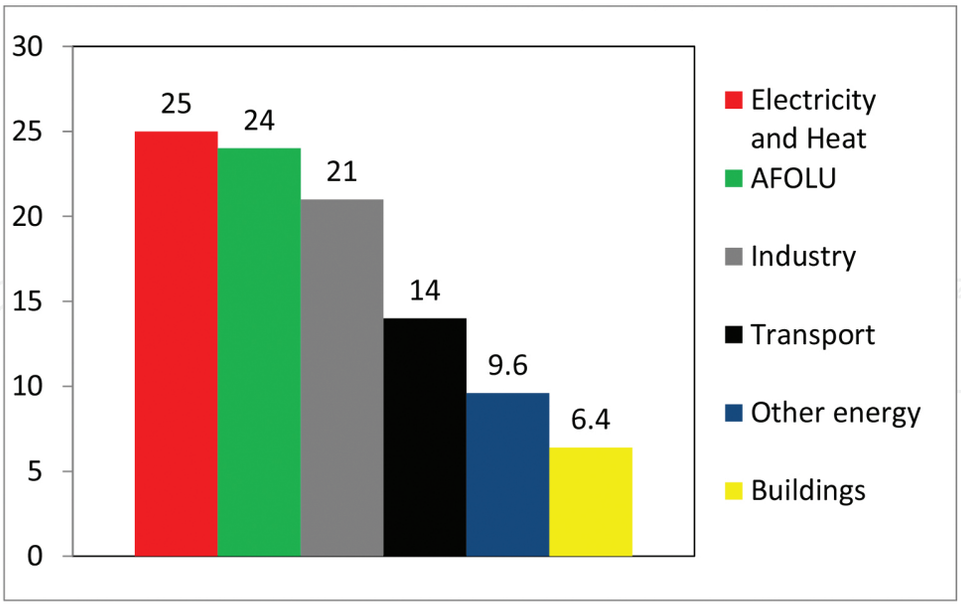

Figure 1. Percentages of direct GHG emissions by economic sector from a total of 49 Gt CO_2-equivalent during 2010. AFOLU: Agriculture, Forestry and Other Land Use [2].

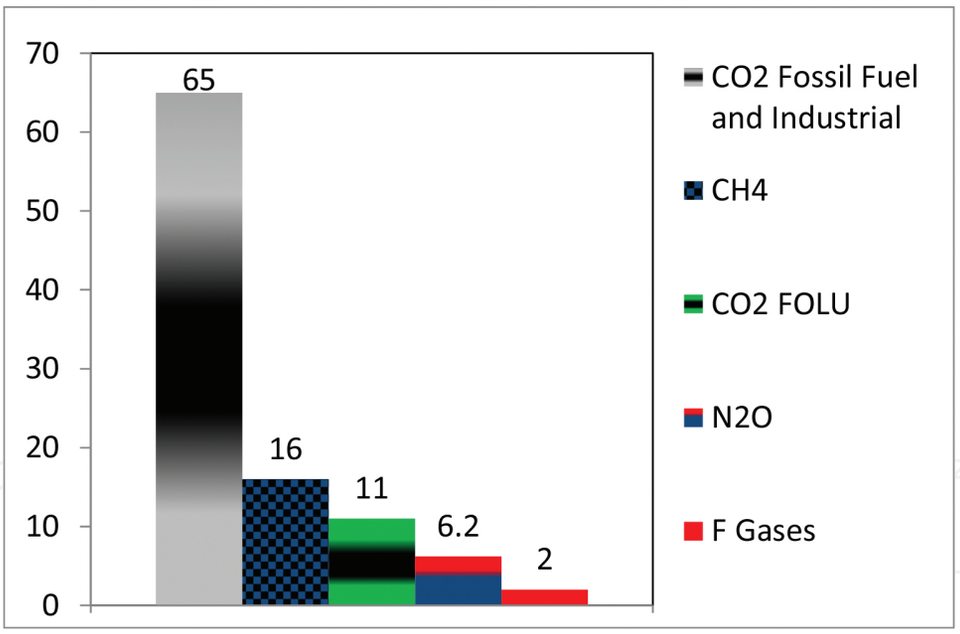

Figure 2. Percentages of GHGs from the 49 Gt CO_2-equivalent emissions during 2010. FOLU: Forestry and Other Land Use, F Gases: fluorinated gases covered under the Kyoto Protocol [2].

(A) Absorption: this topic includes physical and chemical absorption. In both situations, CO_2 is captured in the volume of a solution. The first framework comprises the physical interaction between high-pressure CO_2 and a solution by intermolecular interactions. In this context, molecular solvents and ionic liquids as well carry out this action. Chemical absorption is conventionally performed with solutions of alkanolamines (**Figure 3**):

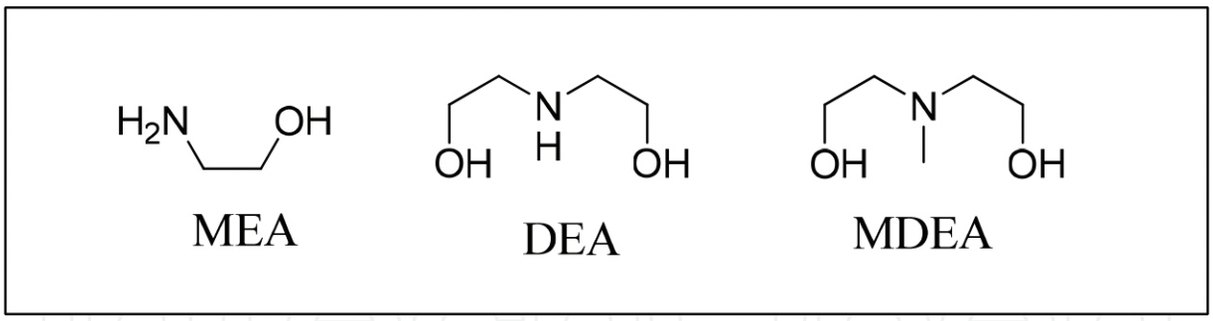

Figure 3. Conventional amines used in chemical absorption of CO_2. MEA: Monoethanolamine; DEA: Diethanolamine; MDEA: Methyldiethanolamine.

This established technology presents various drawbacks, such as the compulsory dilution of the alkanolamine in the aqueous environment to avoid deterioration of materials and excessive release of heat when reaction is performed. The utilization of these systems leads to mitigated CO_2 uptake (7 wt% using a 30 wt% aqueous solution of MEA). Moreover, there is a high-energy penalty incorporated into the system due to a high-heat capacity of the aqueous environment acting as a sink in the process of CO_2 release [4, 5]. Finally, the solvent is volatilized during the operations precluding, an effective regeneration of the CO_2 capture system. These strategies are used when the concentration of CO_2 is low.

The mechanism associated with these systems encompasses the formation of carbamates, in a 0.5:1 stoichiometry (half of the converted alkanolamine is in the form of carbamate and the other is presented as ammonium). Two different paths lead to this same end: The two-step Zwitterion mechanism is started by a nucleophilic attack of the amine group on CO_2 leading to the presence in the same moiety of positive and negative charges. In a further step, a proton is transferred to another alkanolamine, and a salt is formed. In the single-step termolecular mechanism, the nucleophilic attack and proton transfer occurs simultaneously. The other product of reaction is hydrogencarbonate corresponding to the product of reaction between CO_2 and water. This reaction is slower; nevertheless, the stoichiometry of CO_2 incorporation is one, which is a factor of two superior to the formation of carbamate by the same quantity of aminoalcohol. Giving the product, the conventional capture agents can act as generic bases or nucleophiles in the specific instance of CO_2 as well. Another property associated with these systems is that, at given pH, hydrogencarbonate might coexist with carbonic acid and carbonate. The hydroxide anion has a lower expression, though the reaction with CO_2 is faster than with water. Another mechanism associated with these systems is the hydrolysis of carbamate to generate hydrogencarbonate. Given the degree of substitution, the amine functionality can be more CO_2-philic or more alkaline, with a concomitant contribution on the definition of the reaction profile.

(B) Adsorption is obtained by the capture of CO_2 when interacting with a solid surface. Contrarily to chemical absorption, the interaction between CO_2 and the surface is moderated (intermolecular forces). Activated carbons and molecular sieves are conventionally used. Three different modes of action characterize this type of framework, related with the 'switch' used

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between adsorption/desorption: pressure, temperature and electric power control the behaviour of these systems.

(D) Membrane is a partially permeable structure that separates CO_2 from gas mixtures. With this recent technology, CO_2 is separated from diverse sources, such as post-combustion flue gas, syngas and natural gas. Two operational methods are available: (a) Gas separation membrane: based on the preferential permeation of a specific component of a mixture. (b) Gas absorption membrane: centred on the specific affinity of the previously referred chemical absorber solutions towards CO_2.

The bio-inspired systems described in the following topics represent an effective alternative to the available frameworks, with potential to be integrated in the previously mentioned capture systems as well as in sequestration and utilization frameworks.

Aqueous solutions of amino acids are straightforward alternatives to alkanolamine-based systems. The amino acid frameworks are presented as stand-alone salts, as zwitterionic structures activated by bases, or as salts doped with superbases. Different mechanisms of reaction/association are presented according the structure and composition of the system. A different case study is based on the use of highly abundant saccharides and related biopolymers, which may constitute invaluable systems for CO_2 capture, sequestration and/or utilization, presented as liquid solutions, gels, confined hydrated foams or solid adsorbents.

Enzymes, especially carbonic anhydrase (CA), are useful catalysts for CO_2 sequestration and utilization. In the case of CA, the high rates of reaction and the mild reaction conditions constitute clear advantages of these systems in the laboratory environment. But on a pilot or even industrial scale, harsh conditions of temperature and the presence of contaminants in CO_2 streams hinder the utilization of this enzyme. Possible solutions already on praxis are expression of the genetic code associated with this enzyme from thermophiles on readily available organisms, immobilization on diverse supports or generation of catalysts inspired on the mode of action of carbonic anhydrase.

Finally, the use of microbes is addressed in this chapter on the production of added value products from CO_2, with special focus on the use of methanogens and acetogens in microbial electro-synthesis and microbial capture cell frameworks.

2. Bio-inspired systems

The systems proposed here (biological, enzymatic and bio-molecular) constitute solid alternatives to the conventional platforms available in the market. These bio-inspired frameworks present diverse advantages such as low corrosion, easy disposal and biodegradability, naturally produced and possibility to tune capacity of CO_2-incorporation according to the configuration of the system. Nevertheless, there are practical issues that should be addressed in order to make the current technology available thrive in the various challenges assigned.

2.1. Bio-molecular

2.1.1. Amino acids

The amino acid systems highlighted include the use of these frameworks as anions, in the presence of an inorganic cation (sodium or potassium), as aprotic ionic liquids or as protic mixtures, using either organic or inorganic bases. The main advantage of amino acid-based systems over conventional alkanolamines relies on high stability to oxidative degradation, high chemical reactivity with CO_2, low vapour pressures (compatible with temperature of flue gases), and high surface tension (fundamental on the design of membranes). Various studies exist when an inorganic cation is used [6–18]. Here a selection will be emphasized to establish the structure of amino acid/CO_2 absorption-desorption properties relationship (**Figure 4**, **Table 1**). In this comparative study, the conventional MEA aqueous solution is used as a reference. It presents considerably high initial rates of CO_2 absorption and desorption, and high CO_2 uptake is obtained as well (**Table 1**).

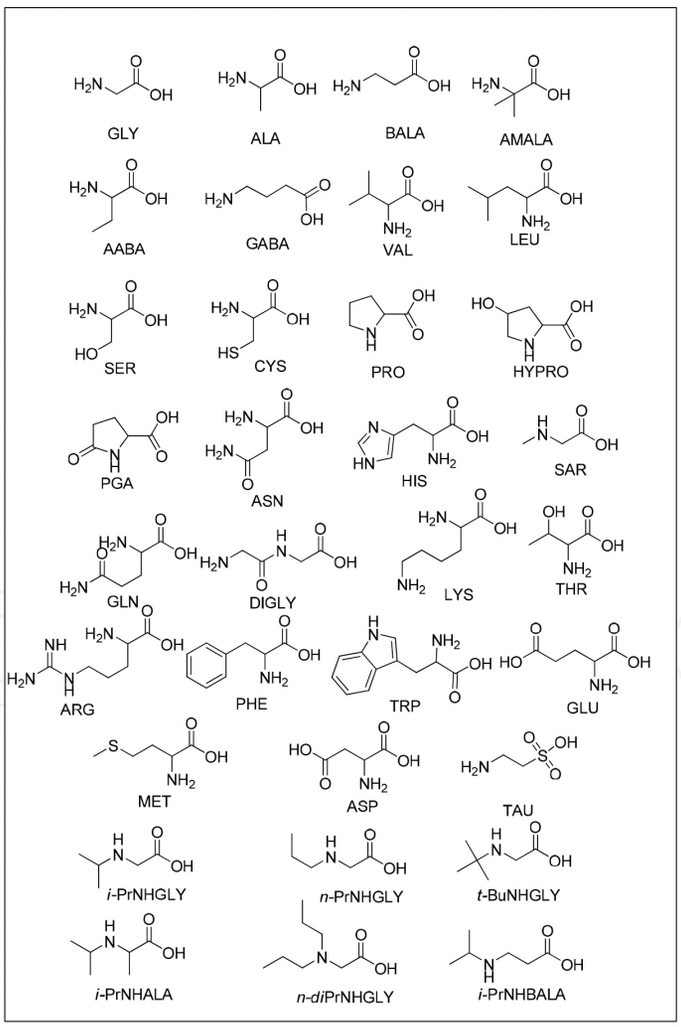

Figure 4. Amino acids used in CO_2-capture studies, and presented along this chapter.

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Amino acid system	Solvent / Concentration of the capture agent	P, T_{abs}, T_{desorp} (kPa, K, K)	Absorpt method	Initial rate absorpt (mol CO_2 mol amine^{-1} min^{-1})	Initial rate desorpt (mol CO_2 mol amine^{-1} min^{-1})	CO_2 uptake (mol CO_2 mol amine^{-1})	pKa, parent amine / amino-acid
Reference MEA [6]	1 M aqueous	15, 313, 353	Bulk sol.	3.84×10^{-2}	2.00×10^{-2}	0.736	9.5
[K]GLY [6]	1 M aqueous	15, 313, 353	Bulk sol.	3.93×10^{-2}	1.84×10^{-2}	0.738	2.34, 9.6
[K]ALA [6]	1 M aqueous	15, 313, 353	Bulk sol.	3.16×10^{-2}	1.98×10^{-2}	0.670	2.35, 9.69
[K]BALA [6]	1 M aqueous	15, 313, 353	Bulk sol.	3.65×10^{-2}	1.80×10^{-2}	0.721	3.60, 10.19
[K]AABA [6]	1 M aqueous	15, 313, 353	Bulk sol.	3.76×10^{-2}	1.87×10^{-2}	0.728	2.65, 9.6
[K]GABA [6]	1 M aqueous	15, 313, 353	Bulk sol.	3.87×10^{-2}	1.54×10^{-2}	0.749	4.23, 10.43
[K]AMALA [6]	1 M aqueous	15, 313, 353	Bulk sol.	2.43×10^{-2}	1.20×10^{-2}	0.750	2.36, 10.21
[K]SER [6]	1 M aqueous	15, 313, 353	Bulk sol.	3.16×10^{-2}	2.26×10^{-2}	0.619	2.21, 9.15
[K]CYS [6]	1 M aqueous	15, 313, 353	Bulk sol.	3.18×10^{-2}	2.46×10^{-2}	0.485	1.92, 8.37, 10.70
[K]PRO [6]	1 M aqueous	15, 313, 353	Bulk sol.	4.26×10^{-2}	1.48×10^{-2}	0.746	1.99, 10.96
[K]HYPRO [6]	1 M aqueous	15, 313, 353	Bulk sol.	4.03×10^{-2}	1.55×10^{-2}	0.655	1.82, 9.65
[K]PGA [6]	1 M aqueous	15, 313, 353	Bulk sol.	2.41×10^{-2}	0.38×10^{-2}	0.224	−1.76, 3.48, 12.76
[K]ASN [6]	1 M aqueous	15, 313, 353	Bulk sol.	2.79×10^{-2}	2.34×10^{-2}	0.573	2.02, 8.80
[K]GLN [6]	1 M aqueous	15, 313, 353	Bulk sol.	3.06×10^{-2}	$2.08 \times 10–^{2}$	0.600	2.2, 9.1
[K]DIGLY [6]	1 M aqueous	15, 313, 353	Bulk sol.	2.99×10^{-2}	2.18×10^{-2}	0.510	-
[K]ARG [6]	1 M aqueous	15, 313, 353	Bulk sol.	3.56×10^{-2}	2.19×10^{-2}	1.107	1.82, 8.99, 12.48
[K]TAU [6]	1 M aqueous	15, 313, 353	Bulk sol.	3.17×10^{-2}	2.26×10^{-2}	0.573	1.5, 9.06
[Na]GLY [7]	PEG_{150} 3 mmol/ 15 mmol sol.	100, 298, 313	Bulk sol.	-	-	0.43 (20 min)	2.34, 9.6
[Na] *i*-PrNHGLY [7]	PEG_{150} 3 mmol/ 15 mmol sol.	100, 298, 313	Bulk sol.	-	-	0.91 (25 min)	-
[Na]*n*-PrNHGLY [7]	PEG_{150} 3 mmol/ 15 mmol sol.	100, 298, 313	Bulk sol.	-	-	0.59 (30 min)	-
[Na]*t*-BuNHGLY [7]	PEG_{150} 3 mmol/ 15 mmol sol.	100, 298, 313	Bulk sol.	-	-	0.85 (25 min)	-
[Na]*i*-PrNHAla [7]	PEG_{150} 3 mmol/ 15 mmol sol.	100, 298, 313	Bulk sol.	-	-	0.73 (30 min)	-
[Na] *n*-*Di*PrNHGLY [7]	PEG_{150} 3 mmol/ 15 mmol sol.	100, 298, 313	Bulk sol.	-	-	0.48 (30 min)	-
[Na] *i*-PrNHBALA [7]	PEG_{150} 3 mmol/ 15 mmol sol.	100, 298, 313	Bulk sol.	-	-	0.65 (15 min)	-

Table 1. CO_2 absorption and desorption properties of amino acid-based systems.

Diverse potassium salts of amino acids from chiral pool dissolved in aqueous media were tested [6] (**Table 1**). Glycine (GLY) salt presents similar performances as conventional MEA solutions. Differently, alanine (ALA) is identified by a different reaction profile with CO_2, the level of CO_2 incorporation and the associated initial rate of absorption are lower. Nevertheless, the rates of CO_2 release at moderate temperatures are higher. The reason for such behaviour are the bulkiness of the associated substituent group and the moderate pKa of the amine functionality, contributing to the mitigated propensity of CO_2 to be chemically captured, either in the form of carbamate (amino acid as nucleophile) or of bicarbonate (alanine as base).β-Alanine (BALA) is an extended amino acid with concomitant bulkiness and high pKa of its amine functionality, contributing to lower CO_2 absorption and desorption performances with respect to GLY, nevertheless, BALA presents improved CO_2 absorption and poorer desorption performances when compared with Alanine. With α-aminobutyric acid (AABA), the amine functionality should act preferably as base, due to probable 5-element-ring-hydrogen bond interaction between carboxyl and amine functionalities owing to the size of the linear substituent group, leading to a more favourable incorporation of CO_2 in the form of hydrogencarbonate after reaction with water. Improved incorporation with a factor of two, with respect to carbamate leads to improved absorption performances when compared with Alanine.

The performance of γ-aminobutyric acid (GABA) in terms of CO_2 uptake is higher than the previously mentioned amino acids, the high pKa leads to the formation of hydrogencarbonate, which is a slower reaction than the formation of carbamate. This information is in line with the lower initial ratio of CO_2 absorption obtained when compared with GLY. α-Methyl alanine (AMALA) presents two methyl groups in the α-position and a high pKa of the amine functionality which, similar to AABA, acts as enhanced base by hydrogen-bond stabilization of the protonated base by the carboxyl group of the amino acid. AMALA is characterized by the highest value of CO_2 uptake among the presented amino acids; nevertheless, it presents the lowest initial rate of CO_2 absorption. These results are compatible with the preferential formation of hydrogencarbonate instead of carbamate. Serine (SER) and cysteine (CYS) are hydroxyl and thio-functionalized amino acids, respectively, that may create destabilization as hydrogen donors when the protonated amine functionality is interacting with the carboxyl group of the amino acid. Considering this aspect, the formation of carbamate should be predominant with respect to the hydrogencarbonate counterpart, and the CO_2 uptake is low. The initial rate of desorption associated with these two amino acids is high due to the steric repulsion between the formed carbamate and the bulky hydroxyl or thiol functionalities.

Proline (PRO), 4-hydroxy proline (HYPRO) and pyroglutamic acid (PGA) are cyclic, secondary amino acids, with PRO presenting high pKa and, possibly due to stabilization of protonated amine by the carboxyl group, may lead to enhanced CO_2 uptake, the highest pKa among the presented amino acids, leading to a higher hydroxide/water ratio and an enhanced kinetics for CO_2 uptake. The amine functionality of HYPRO presents lower pKa than PRO-equivalent, leading, possibly, to a less favourable hydrogencarbonate/carbamate ratio and low CO_2 uptake. PGA presents an electro-tractor carbonyl group conjugated with the amine functionality hampering its performance either as a nucleophile or base, leading to a low level of CO_2 incorporation.

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Asparagine (ASN) and Glutamine (GLN) are linear amide-functionalized amino acids, presenting low pKa associated with the corresponding amine functionalities, leading to low levels of CO_2 uptake. Due to steric repulsion, the ratio of the kinetics of CO_2 uptake/desorption is mitigated. Diglycine (DIGLY) leads to a low level of carbon dioxide incorporation due to inherent bulkiness associated to the chemical structure. Arginine (ARG) presents highly basic guanidine functionality and a not so basic amine group. The combination of both functionalities leads to the highest level of CO_2 incorporation, despite the presence of both functionalities. Taurine (TAU) amine group presents low pKa, considering this; the ratio carbamate/hydrogencarbonate should be high.

In another study, [7] mostly secondary but also tertiary bulky amines in PEG_{150} solvent are tested. With [Na] *i*-PrNHGLY (**Figure 4**, **Table 1**), the level of CO_2 incorporation was near 100% with respect to the amine unit. The main reason for such result is the formation of carbamic acid instead of carbamate leading to a nearly full use of the amine functionality to capture CO_2 instead of half (in the carbamate/ammonium salt). To this result contributes the stabilization of the carbamic acid functionality by the carboxyl group, the steric repulsion associated with the amine substituents, avoiding deprotonation of the carbamic functionality, and the type of chemical environment [7]. The carbamic acid reaction profile and steric hindrance lead to low energy requirements for CO_2 desorption (313 K). An interesting work was carried out by Wang et al. [17], where, from a diverse set of amino acid sodium salts (aqueous solutions) was possible to observe with Alanine, a phase-split between a CO_2-rich and a CO_2-lean phase. The CO_2-rich phase was composed of carbamate and hydrogencarbonate. The decrease on the volume of solution leads to a significant decrease in energy input for the CO_2 strip.

In a different study [19], (**Figure 4**, **Table 2**) a diverse set of amino acid ionic liquids (neat) for CO_2 capture was tested. The best performance was obtained with $[N_{66614}]$ LYS, leading to nearly two equivalents of CO_2 reacting with the two amine functionalities existing in lysine. The reason behind this outstanding result relies on the formation of carbamic acid (as in Ref. [7]). One additional point is addressed to the catalytic effect of the carboxyl group, promoting the proton transfer, starting from zwitterionic structure (after nucleophilic attack to CO_2) to the carbamic acid end product. In this work the effect of the cation in the CO_2 uptake was checked. $[N_{66614}]$ and $[P_{66614}]$ were tested in combination with the LYS anion. It was observed that the initial rate of absorption was higher with $[P_{66614}]$, nevertheless $[N_{66614}]$ lead to high CO_2 uptake (**Table 2**). $[N_{66614}]$LYS is associated with stronger hydrogen-bond interactions after chemisorption of CO_2 leading to an increment of viscosity and poorer kinetics. Due to the different stabilized-arrangement of this ionic liquid, after incorporation of CO_2, nearly all the amine groups are converted to carbamic acid functionalities. $[P_{66614}]$LYS presents another configuration after CO_2 uptake with concomitant half of the amine groups presented as carbamic acid functionalities, ¼ as carbamate and the remaining ¼ as ammonium.

A conceptual study was carried out in our laboratories [20] concerning the preparation of reversible ionic liquids using GLY, ALA, valine (VAL), leucine (LEU), phenylalanine (PHE) and tryptophan (TRP) that activated by an organic superbase, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or 1,1,3,3-tetramethylguanidine (TMG), react with CO_2 to obtain carbamate-based ionic liquids. The system can revert back to the early configuration upon heating at an

appropriate temperature. It was possible to observe for the DBU series a decrease in the temperature associated with CO_2 release when the bulkiness of the substituent group of the amino acid increases. A similar order was observed with the TMG set, however not completely defined.

Amino acid system	Solvent / Concentration of the capture agent	P, T_{abs}, T_{desorp} (kPa, K, K)	Absorpt method	Initial rate absorpt (mol CO_2 mol amine^{-1} min^{-1})	Initial rate desorpt (mol CO_2 mol amine^{-1} min^{-1})	CO_2 uptake (mol CO_2 mol amine^{-1})	pKa, parent amine /amino – acid
[N_{66614}]LYS [19]	neat	100, r.t, 353	-	-	-	2.1 (24 h)	2.18, 8.95, 10.53
[N_{66614}]ASN [19]	neat	100, r.t, 353	-	-	-	2.0 (48 h)	2.02, 8.80
[N_{66614}]GLN [19]	neat	100, r.t, 353	-	-	-	1.9 (48 h)	2.2, 9.1
[N_{66614}]HIS [19]	neat	100, r.t, 353	-	-	-	1.9 (48 h)	1.80, 9.33, 6.04
[N_{66614}]ARG [19]	neat	100, r.t, 353	-	-	-	1.3 (48 h)	1.82, 8.99, 12.48
[N_{66614}]MET [19]	neat	100, r.t, 353	-	-	-	1.2 (24 h)	2.28, 9.21
[P_{66614}]LYS [19]	neat	100, r.t, 353	-	-	-	1.6 (48 h)	2.18, 8.95, 10.53

Table 2. CO_2 absorption and desorption characteristics of amino acid-based systems.

Other studies concerning the application of amino acid-based ionic liquids in CO_2 capture are presented here. Lv et al. [21] tested 1-aminopropyl-3-methylimidazolium glycinate aqueous solution and could achieve 1.23 mol of CO_2 loading per mol of ionic liquid. The reaction was followed by ^{13}C-NMR and it comprised two steps: (1) initial formation of carbamate, followed by (2) hydrolysis of this functionality to obtain hydrogencarbonate. The same author [22], reported the use of [C_2OHMIM] GLY aqueous solution to 0.575 mol of CO_2 uptake/mol ionic liquid. In that study the effect of O_2 on the absorption performances was determined, which were better than in the case of MEA solution. In another study, Li et al. [23], tested [P_{4444}] salts of GLY, ALA and PRO, in combination with PEG solvents, on the design of membranes for CO_2/H_2 separation. In a different framework, amino acids are combined with inorganic bases (mainly carbonate salts) in aqueous solutions to promote kinetics and capacity of CO_2 uptake. GLY, sarcosine (SAR), PRO [24] and ARG, as well, were used in that context [25].

Finally, as an example for the promoting effect of adding the conventional alkanolamines to amino acid systems, Gao et al. [26] combined MDEA aqueous solution with [N_{1111}] GLY. The

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reason behind this option relies on the fact that MDEA, a tertiary amine, acts as base in the considerable slow reaction between water and CO_2 to obtain hydrogencarbonate, leading to high CO_2 uptake. The GLY-based amino acid presents good kinetic performances, however low CO_2 incorporation in the form of carbamate. Considering the reaction of carbamate hydrolysis and the complementary reactive profiles of MDEA and [N_{1111}] GLY, such systems are presented here as an alternative to conventional frameworks.

2.1.2. Saccharides and related bio-polymers

The use of saccharides and related bio-polymers (**Figure 5**) constitute natural and abundant alternatives for CO_2 fixation, chemisorption and adsorption. Concerning fixation, Sun et al. [27] developed a superbase/cellulose catalytic system to obtain cyclic carbonates from epoxides and CO_2. Cellulose acts as a hydrogen bond donor and the superbase as the nucleophile in the activation of the epoxide. High conversions and selectivities are associated with DBU/cellulose. In a different study, Tamboli et al. [28], reported the use of chitosan/DBU dissolved in 1-mesyl-3-methylimidazolium (mesylMIM)-based ionic liquids for preparation of dimethyl carbonate (DMC) from methanol and CO_2. From the chemisorption perspective, it was tested in our laboratories [29] the use of monosaccharides, oligosaccharides or a polysaccharide-activated, by combination with adjustable proportion of liquid DBU or TMG as organic superbases, for CO_2 capture. Of course, it is necessary to consider that low ratios of superbase lead to highly viscous solutions with hampered capacity for CO_2 mass transfer and concomitant poor performances in the capture of this GHG. In a different perspective, an excess of the superbase would lead to high dilution of the capture agent with associated limitation on the wt% of CO_2 uptake. It was necessary to carry out an optimization for maximal performances (D-Mannose:DBU —0.625/1 in equivalents leading to 13.9 wt% of CO_2 uptake and 3.3/5 alcohol functionalities converted to carbonates). It is also important to consider an effective stirring to overcome the increase of viscosity with the progress of reaction, which limits CO_2 uptake.

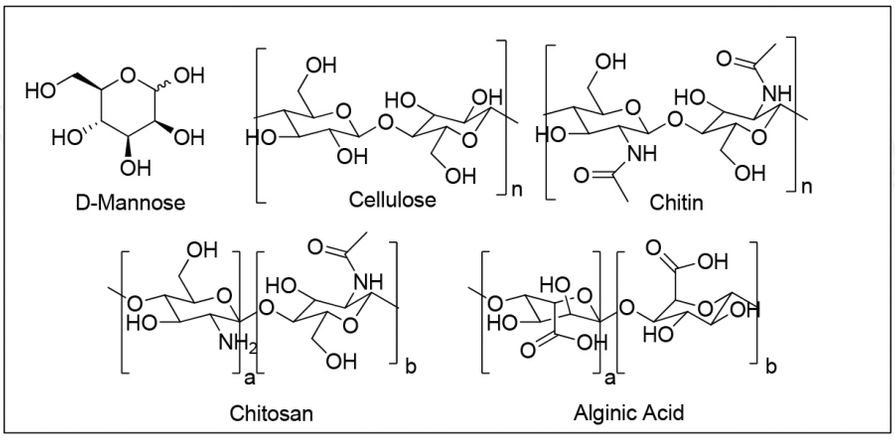

Figure 5. Examples of mono-saccharide and related biopolymers.

In a different study, Eftaiha et al. [30] used chitin acetate in DMSO for CO_2 capture. The mechanism involves activation of the alcohol groups by DMSO followed by conversion into

carbonates which are stabilized by the ammonium groups available in chitin acetate. A very interesting concept was reported by Sehaqui et al. [31] and used in the preparation of cellulose-polyethyleneimine foams and study of its properties on CO_2 capture from air. To this end, it is essential a high relative humidity for optimal CO_2 uptake. The confined/activated water might have a crucial role in the mode of action of this system. There are other studies that deal with carbon dioxide chemisorption by the use of chitin or chitosan dissolved in ionic liquids such as the one reported by Xie et al. [32]. The use of saccharide-based polymers is also associated with adsorption systems. In this context, carbon spheres were prepared from alginate and chitosan, after thermal treatment between 673 and 1073 K, leading to an excellent capacity for CO_2 adsorption. The high conductivity presented by alginate-based spheres was crucial for the development of an adsorption/desorption system based on the use of electric power as a "switch" with low energetics associated with CO_2 capture and release.

2.2. Enzymatic

CO_2 fixation and conversion catalysed by enzymatic-cellular systems is essential in the recycling processes inherent to life. Six major routes [33] are available (**Figure 6**):

1. Calvin cycle: it is one of the most important processes in nature, being the major route for carbon dioxide conversion. It is present in a great majority of photosynthetic organisms and besides the CO_2 fixation (thermodynamically favourable), catalysed by 1,5-ribulose bisphosphate carboxylase (RuBisCO), in each cycle are produced saccharides, fatty acids and amino acids.
2. Reductive citric acid cycle: this cycle, comprising four carboxylation steps exists, basically, in the conversion of CO_2 and water into carbon compounds. It is found mainly in some thermophilic bacteria that grow on H_2, and bacteria that reduce sulphate. The first carboxylation step, the conversion of succinyl CoA into 2-oxoglutarate is thermodynamically unfavourable ($\Delta G°' = 19$ kJ/mol), such as the conversion of 2-oxoglycerate into isocitrate ($\Delta G°' = 8$ kJ/mol) and the production of pyruvate from acetyl CoA ($\Delta G°' = 19$ kJ/mol). The fourth carboxylation step, the conversion of phosphoenolpyruvate into oxaloacetate is thermodynamically favourable ($\Delta G°' = -24$ kJ/mol) and due to its incorporation into this cycle the promotion of the three previous carboxylation steps is assured.
3. Reductive acetyl CoA route: it is a non-cyclic route, existing in some acetogenic and methanogenic micro-organisms. This process includes the conversion of CO_2 into formic acid ($\Delta G°' = 22$ kJ/mol) catalysed by formate dehydrogenase. The other fixation step comprises the conversion of carbon dioxide into CO ($\Delta G°' = 0$ kJ/mol).
4. The 3-hydroxypropionate cycle was found in *Chloroflexaceae*, a phototrophic bacterium and comprises two favourable CO_2 conversion steps, from the thermodynamic point of view. Malonyl CoA from acetyl CoA ($\Delta G°' = -14$ kJ/mol) and conversion of propionyl CoA into methylmalonyl CoA ($\Delta G°' = -11$ kJ/mol) are the two CO_2 conversion steps.
5. A recently found cycle is the 3-hydroxypropionate/4-hydroxybutyrate cycle existing in *Metallosphaera* and includes three CO_2 conversion steps, existing in the (2) reductive citric acid cycle and (4) 3-hydroxypropionate cycle (**Figure 6**).

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6. Finally the dicarboxylate/4-hydroxybutyrate cycle is found in *Thermoproteales* and *Desulfurococcales* and comprises two carbon dioxide conversion steps, (2a) and (2b), existing in the reductive citric acid cycle (**Figure 6**).

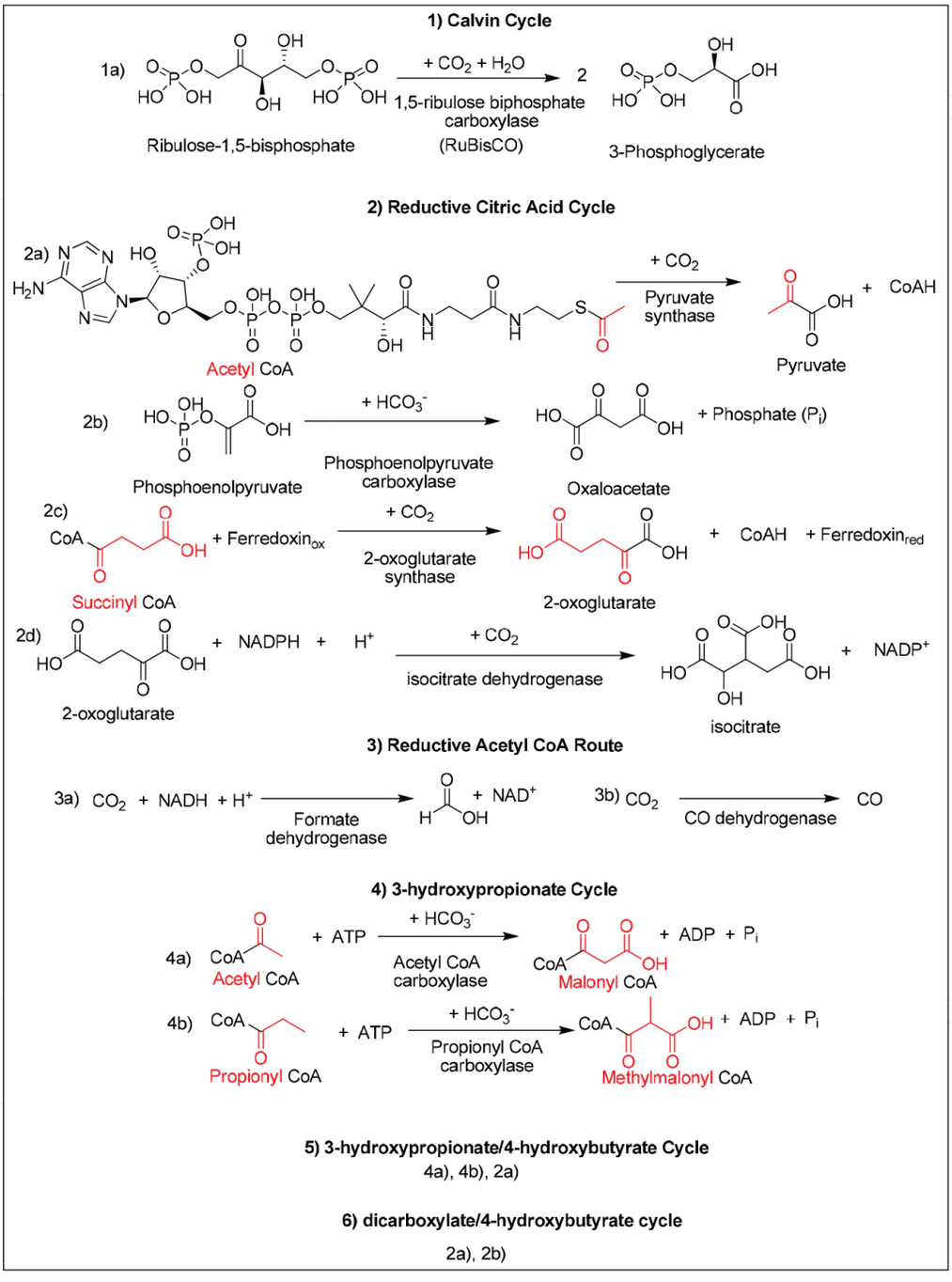

Figure 6. Enzymatic-catalysed reactions of CO_2 incorporation involved in the six main cellular metabolic routes [33].

In all the conversion steps (**Figure 6**) the source of the C_1 synthon is either CO_2 itself or HCO_3 as the intermediate. The preparation of HCO_3 is catalysed by the ubiquitous enzyme carbonic anhydrase (CA):

This enzyme, one of the fastest enzymes known, has a diversity of structures and is catalogued in five different families (α, β, γ, δ and ζ). As an illustrative example, a typical mechanism of a α-CA, which contains in the active site, a Zn(II) centre coordinated with three HIS and one water molecule forming hydrogen bond with the hydroxyl group of THR (activated by GLU) will be described. This concerted interaction, convert water/hydroxide to an enhanced nucleophile towards CO_2, leading to the formation of hydrogencarbonate. Afterwards a new water molecule replaces HCO_3 in the Zn(II) coordination site and a new cycle is initiated [34]. Considering the diverse enzymatic reactions available (**Figure 6**) and the specific instance of CA (**Figure 7**), some concerns should be addressed. From the presented enzymatic-catalysed reactions (**Figure 6**) only a parcel can be used *in vitro* for conversion of CO_2, which is not the case of the reactions involving coenzyme A (CoA), that lead to uncommon/useless products. Other reactions are thermodynamically unfavourable under standard conditions, and pH, ionic strength or temperature tuning should be carried out [35]. It is important to highlight that the possibility of tuning reaction parameters is restrained due to possible inactivation/denaturation of enzyme under specific reaction conditions.

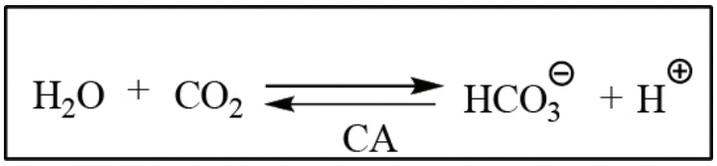

Figure 7. CO_2 conversion to HCO_3 catalysed by carbonic anhydrase.

Other option is the coupling of reactions leading to a net thermodynamic feasible transformation [36]; however, as the reaction system becomes more complex, acceptable operational conditions become usually narrower. Due to the efficiency of CA, the enzymatic reaction associated is, by far, the most represented reaction of CO_2 incorporation in the literature, usually associated with the direct sequestration of CO_2 in the form of solid calcium or magnesium carbonates [34, 37], separation operations [38] and even coupled to other enzymatic CO_2 incorporation reaction in order to increase drastically the concentration of the C_1 synthon in the form of hydrogencarbonate in water and improve the reaction outcome [39]. The high temperatures and inhibitors produced during combustion processes and high commercial value associated with this enzyme, limit the efficiency of CA, nevertheless diverse frameworks were developed in order to overcome operational constraints such as: direct use of carbonic anhydrase mimics [40], support immobilization of the enzyme [41], (to avoid denaturation under harsh conditions), and combination with motion [42] generated by a chemical-engine (to overcome the diffusion constraints associated with immobilization) appear as useful frameworks. Testing carbonic anhydrase from thermophiles [43] and its genetic edition with overexpression in *Escherichia coli* are other alternatives [44].

2.3. Biological

The concluding topic comprises the use of micro-organisms as productive units of added-value products from CO_2 (sequestration and/or utilization). Diverse concepts were explored

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in the literature such as: (1) microbial electro-synthesis [45, 46], where electrons are supplied from a cathode to micro-organisms, which converts CO_2 into added-value products, usually methane and/or acetate. The electrons are provided by electric current, preferentially from renewable resources. Another framework is (2) microbial carbon capture cell [47], where, different from microbial electro-synthesis, the source of electrons comes from the microbial-assisted degradation of organic compounds from wastewater in the anode with formation of protons, electrons and CO_2. Usually the anode and the cathode are separated by an ion exchange membrane. The cathode receives the generated electrons and, assisted by micro-organisms, converts CO_2 into useful chemicals. Another option available is, (3) microbial electrolytic carbon capture, which similar to microbial electro-synthesis, is used as an external electric power source to increase the potential generated by degradation of organic compounds in the anode assisted by micro-organisms. H_2 and OH^- are generated in the cathode with the anion reacting with CO_2 to obtain hydrogencarbonate [48]. Usually, depending on the microbial cultures on the cathode, it is possible to obtain methane, acetate and other compounds. When acetate is required acetogens are used, nevertheless there is competition associated with the formation of methane, which is inhibited by the addition of compounds, such as 2-bromoethanesulfonate. Other systems available are based solely on the application of light in photo-reactors in order to photosynthetic micro-organisms produce added value compounds. All these options should be optimized in order to be effectively used in real situations.

3. Conclusions and challenges

While renewable sources of energy do not definitely replace conventional fuels, the use of bio-inspired systems for CO_2 capture, sequestration and utilization, constitutes an already open window of opportunity in the context of mitigation of environmental effects associated with excessive anthropogenic GHG emissions. Characteristics such as abundance, low corrosion, biodegradability and possibility to tune interaction with CO_2, constitute clear advantages of the described bio-inspired systems. With bio-molecular frameworks, it is important to overcome the kinetic constraints associated with increase of viscosity when CO_2 is captured. Simultaneously the conception of robust systems requiring low energetics for CO_2 release is important. Additionally, the straightforward use of the specific functionalities of amino acids, saccharides and related bio-polymers on the enhancement of the levels of fixation and utilization of CO_2 is essential. Concerning enzymatic systems is of extreme importance, for stand-alone and especially multi-enzymatic systems, the design/optimization of the system configuration to obtain the target product in high yields or simply sequester CO_2 as a solid. Additional attention should be devoted to the design of robust systems compatible with the real conditions of combustion/processing of gases, addressed to immobilization, design of enzymatic mimics and genetic engineering. Finally, the biological systems available should be improved with application studies in order to overcome robustness and selectivity constraints associated with electro/photochemical systems.

Abbreviations

AABA:	α-Aminobutyric acid
ADP:	Adenosine Diphosphate
AFOLU:	Agriculture, Forestry and Other Land Use
ALA:	Alanine
AMALA:	α-Methyl Alanine
ARG:	Arginine
ASN:	Asparagine
ATP:	Adenosine Triphosphate
BALA:	β-Alanine
t-BuNHGLY:	N-*t*-butylglycine
[C_2OHMIM]:	1-(2-hydroxyethyl)-3-methylimidazolium
CA:	Carbonic Anhydrase
CoA:	Coenzyme A
CYS:	Cysteine
DBU:	1,8-Diazabicyclo[5.4.0]undec-7-ene
DEA:	Diethanolamine
DIGLY:	Diglycine
n-DiPrNHGLY:	N-*n*-dipropylglycine
DMC:	dimethyl carbonate
GABA:	γ-Aminobutyric acid
GHGs:	Green House Gases
GLN:	Glutamine
GLU:	Glutamate
GLY:	Glycine
HIS:	Histidine
HYPRO:	4-hydroxy proline
IPCC:	Intergovernment Panel on Climate Change
LEU:	Leucine
LYS:	Lysine
MDEA:	Methyldiethanolamine
MEA:	Monoetanolamine
[MesylMIM]:	1-mesyl-3-methylimidazolium
MET:	Methionine
[N1111]:	Tetramethylammonium
[N66614]:	trihexyltetradecylammonium
NADP:	Nicotinamide Adenine Dinucleotide Phosphate
[P4444]:	Tetrabutylphosphonium
[P66614]:	trihexyltetradecylphosphonium
PEG:	Polyethyleneglycol
PGA:	Pyroglutamic acid
PHE:	Phenylalanine
i-PrNHAla:	N-*i*-propylalanine
i-PrNHBALA:	N-*i*-propyl-β-Alanine
i-PrNHGLY:	N-*i*-propylglycine

n-PrNHGLY:	N-*n*-propylglycine
PRO:	Proline
RuBisCO:	1,5- Ribulose Bisphosphate Carboxylase
SAR:	Sarcosine
SER:	Serine
TAU:	Taurine
THR:	Threonine
TMG:	1,1,3,3-tetramethylguanidine
TRP:	Tryptophan
VAL:	Valine

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References

[1] World population clocks – http://www.worldometers.info/world-population/ (accessed on 21/07/2016)

[2] Intergovernmental Panel on Climate Change – Climate Change 2014, Mitigation of Climate Change http://www.ipcc.ch/pdf/assessment-report/ar5/wg3/ipcc_wg3_ar5_full.pdf (accessed on 20/07/2016)

[3] M. K. Mondal, H. K. Balsora, P. Varshney, "Progress and trends in CO_2 capture/separation technologies: A review", *Energy*, 2012, 46, 431–441.

[4] M. S. Shannon, J. E. Bara, "Reactive and reversible ionic liquids for CO_2 capture and acid gas removal", *Separation Sci. Technol*., 2012, 47, 178–188.

[5] D. J. Heldebrant, C. R. Yonker, P. G. Jessop, L. Phan,"Organic liquid CO_2 capture agents with high gravimetric CO_2 capacity", *Energy Environ. Sci*., 2008, 1, 487–493.

[6] H. J. Song, S. Park, H. Kim, A. Gaur, J-W. Park, S-J. Lee, "Carbon dioxide absorption characteristics of aqueous amino-acid salt solutions", *Int. J. Greenhouse Gas Control*, 2012, 11, 64–72.

[7] A. H. Liu, R. Ma, C. Song, Z-Z. Yang, A. Yu, Y. Cai, L-N. He, Y-N. Zhao, B. Yu, Q-W. Song, "Equimolar CO_2 capture by N-substituted amino acid salts and subsequent conversion", *Angew. Chem. Int. Ed*., 2012, 51, 11306–11310.

[8] D. Guo, H. Thee, C. Y. Tan, J. Chen, W. Fei, S. Kentish, G. W. Stevens, G da Silva, "Amino acids as carbon capture solvents: Chemical kinetics and mechanism of the glycine + CO_2 reaction", *Energy Fuels*, 2013, 27, 3898–3904.

[9] S. C. C. Wei, G. Putxy, P. Feron, "Amino acid salts for CO_2 capture at flue gas temperatures", *Energy Procedia*, 2013, 37, 485–493.

[10] S. Yan, Q. He, S. Zhao, H. Zhai, M. Cao, P. Ai, "CO_2 removal from biogas by using green amino acid salts: Performance evaluation", *Fuel Process. Technol*., 2015, 129, 203–212.

[11] S. Mazinani, R. Ramazani, A. Samsami, A. Jahanmiri, B. Van der Bruggen, S. Darvishmanesh, "Equilibrium solubility, density, viscosity and corrosion rate of carbon dioxide in potassium lysinate solution", *Fluid Phase Equilibria*, 2015, 396, 28–34.

[12] S. Shen, Y. n Yang, Y. Wang, S. Ren, J. Han, A. Chen, "CO_2 absorption into aqueous potassium salts of lysine and proline: Density, viscosity and solubility of CO_2", *Fluid Phase Equilibria*, 2015, 399, 40–49.

[13] N. A. Rahim, N. Ghasem, M. Al-Marzouqi, "Absorption of CO_2 from natural gas using different amino acid salt solutions and regeneration using hollow fiber membrane contactors", *J. Nat. Gas Sci. and Eng*., 2015, 26, 108–117.

[14] Z. W. Chen, R. B. Leron, M-H. Li, "Equilibrium solubility of carbon dioxide in aqueous potassium L-asparaginate and potassium L-glutaminate solutions", *Fluid Phase Equilibria*, 2015, 400 20–26.

[15] W. Li, X. Zhang, B. Lu, C. Sun, S. Li, S. Zhang, "Performance of a hybrid solvent of amino acid and ionic liquid for CO_2 capture", *Int. J. Greenhouse Gas Control*, 2015, 42 400–404.

[16] S. Shen, Y. n Yang, Y. Bian, and Y. Zhao, "Kinetics of CO_2 absorption into aqueous basic amino acid salt: Potassium salt of lysine solution", *Environ. Sci. Technol*., 2016, 50, 2054–2063.

[17] X. Wang, N. G. Akhmedov, D. Hopkinson, J. Hoffman, Y. Duan, A. Egbebi, K. Resnik, B. Li, "Phase change amino acid salt separates into CO_2-rich and CO_2-lean phases upon interacting with CO_2", *Applied Energy*, 2016, 161, 41–47.

[18] A. P. Hallenbeck, A. Egbebi, K. P. Resnik, D. Hopkinson, S. L. Anna, J. R. Kitchin, "Comparative microfluidic screening of amino acid salt solutions for post-combustion CO_2 capture", *Int. J. Greenhouse Gas Control*, 2015, 43, 189–197.

[19] S. Saravanamurugan, A. J. Kunov-Kruse, R. Fehrmann, A. Riisanger, "Amine-functionalized amino acid-based ionic liquids as efficient and high-capacity absorbents for CO_2", *ChemSusChem*, 2014, 7, 897–902.

[20] G. V. S. M. Carrera, N. Jordão, M. M. Santos, M. Nunes da Ponte, L. C. Branco, "Reversible systems based on CO_2, amino acids and organic superbases", *RSC Adv*., 2015, 5, 35564–35571.

[21] B. Lv, G. Jing, Y. Qian, Z. Zhou, "An efficient absorbent of amine-based amino acid-functionalized ionic liquids for CO_2 capture: High capacity and regeneration ability", *Chem. Eng. J*., 2016, 289, 212–218.

[22] B. Lv, Y. Xia, Y. Shi, N. Liu, W. Li, S. Li, "A novel hydrophilic amino acid ionic liquid [C_2OHMIM][Gly] as aqueous sorbent for CO_2 capture", *Int. J. Greenhouse Gas Control*, 2016, 46, 1–6.

[23] J. Li, Z. Dai, M. Usman, Z. Qi, L. Deng, "CO_2/H_2 separation by amino-acid ionic liquids with polyethyleneglycol as co-solvent", *Int. J. Greenhouse Gas Control*, 2016, 45, 207–215.

[24] H. Thee, N. J. Nicholas, K. H. Smith, G. da Silva, S. E. Kentish, G. W. Stevens, "A kinetic study of CO_2 capture with potassium carbonate solutions promoted with various amino acids: Glycine, sarcosine and proline", *Int. J. Greenhouse Gas Control*, 2014, 20, 212–222.

[25] S. Shen, X. Feng, S. Ren, "Effect of arginine on carbon dioxide capture by potassium carbonate solution", *Energy Fuels*, 2013, 27, 6010–6016.

[26] Y. Gao, F. Zhang, K. Huang, J-W. Ma, Y-T. Wu, Z-B. Zhang, "Absorption of CO_2 in amino acid ionic liquid (AAIL) activated MDEA solutions", *Int. J. Greenhouse Gas Control*, 2013, 19, 379–386.

[27] J. Sun, W.Cheng, Z. Yang, J. Wang, T. Xu, J. Xin, S. Zhang, "Superbase/cellulose: An environmentally benign catalyst for chemical fixation of carbon dioxide into cyclic carbonates", *Green Chem*., 2014, 16, 3071–3078.

[28] A. H. Tamboli, A. A. Chaugule, H. Kim, "Highly selective and multifunctional chitosan/ionic liquids catalyst for conversion of CO_2 and methanol to dimethyl carbonates at mild reaction conditions", *Fuel*, 2016, 166, 495–501.

[29] G. V. S. M. Carrera, N. Jordão, L. C. Branco, M. Nunes da Ponte, "CO_2 capture systems based on saccharides and organic superbases", *Faraday Discuss*., 2015, 183, 429–444.

[30] A. F. Eftaiha, F. Alsoubani, K. I. Assaf, W. M. Nau, C. Troll, A. K. Qaroush, "Chitin-acetate/DMSO as a supramolecular green CO_2-phile", *RSC Adv*., 2016, 6, 22090–22209.

[31] H. Sehaqui, M. E. Gálvez, V. Becatinni, Y. C. Ng, A. Steinfeld, T. Zimmermann, P. Tingaut, "Fast and reversible direct CO_2 capture from air onto all-polymer nanofibrillated cellulose-polyethylenimine foams", *Environ. Sci. Technol*., 2015, 49, 3167–3174.

[32] H. Xie, S. Zhang, S. Li, "Chitin and chitosan dissolved in ionic liquids as reversible sorbents of CO_2", *Green Chem*., 2006, 8, 630–633.

[33] J. Shi, Y. Jiang, Z. Jiang, X. Wang, X. Wang, S. Zhang, P. Han, C. Yang, "Enzymatic conversion of carbon sioxide", *Chem. Soc. Rev*., 2015, 44, 598–6000.

[34] B. K. Kanth, J. Lee, S. P. Pack, "Carbonic anhydrase: Its biocatalytic mechanisms and functional properties for efficient CO_2 capture process development", *Eng. Life Sci.*, 2013, 13, 422–431.

[35] S. Xia, B. Frigo-Vaz, X. Zhao, J. Kim, P. Wang, "Biocatalytic carbon capture via reversible reaction cycle catalyzed by isocitrate dehydrogenase", *Biochem. Biophys. Res. Comm.*, 2014, 452, 147–150.

[36] S. Xia, X. Zhao, B. Frigo-Vaz, W. Zheng, J. Kim, P. Wang, "Cascade enzymatic reactions for efficient carbon sequestration", *Biores. Technol.*, 2015, 182, 368–372.

[37] I. M. Power, A. L. Harrison, G. M. Dipple, "Accelerating mineral carbonation using carbonic anhydrase", *Environ. Sci. Technol.*, 2016, 50, 2610−2618.

[38] L. A. Neves, C. Afonso, I. M. Coelhoso, J. G. Crespo, "Integrated CO_2 Capture and enzymatic bioconversion in supported ionic liquid membranes", *Separat. Purific. Technol.*, 2012, 97, 34–41.

[39] Y. Wang, M. Li, Z. Zhao, W. Liu, "Effect of carbonic anhydrase on enzymatic conversion of CO_2 to formic acid and optimization of reaction conditions", *J. Mol. Catal. B: Enzymatic*, 2015, 116, 89–94.

[40] J. H. Satcher, Jr., S. E. Baker, H. J. Kulik, C. A. Valdez, R. L. Krueger, F. C. Lightstone, R. D. Aines, "Modeling, synthesis and characterization of zinc containing carbonic anhydrase active site mimics", *Energy Procedia*, 2011, 4, 2090–2095.

[41] M. Vinoba, M. Bhagiyalakshimi, S. K. Jeong, S. C. Nam, Y. Yoon, "Carbonic anhydrase immobilized on encapsulated magnetic nanoparticles for CO_2 sequestration", *Chem. Eur. J.*, 2012, 18, 12028–12034.

[42] M. Uygun, V. V. Singh, K. Kaufmann, D. A. Uygun, S. D. S. de Oliveira, J. Wang, "Micromotor-based biomimetic carbon dioxide sequestration: Towards mobile microscrubbers", *Angew. Chem. Int. Ed.*, 2015, 54, 12900–12904.

[43] M. E. Russo, G. Olivieri, C. Capasso, V. De Luca, A. Marzocchella, P. Salatino, M. Rossi, "Kinetic study of a novel thermo-stable α-carbonic anhydrase for biomimetic CO_2 capture", *Enzyme Microb. Technol.*, 2013, 53, 271–277.

[44] B. H. Jo, J. H. Seo, H. J. Cha, "Bacterial extremo-α-carbonic anhydrase from deep-sea hydrothermal vents as potential biocatalysts for CO_2 sequestration.", *J. Mol. Catal. B: Enzymatic*, 2014, 109, 31–39.

[45] S. A. Patil, J. B. A. Arends, I. Vanwonterghem, J. van Meerbergen, K. Guo, G. W. Tyson, K. Rabaey, "Selective enrichment establishes a stable performing community for microbial electrosynthesis of acetate from CO_2", *Environ. Sci. Technol.*, 2015, 49, 8833−8843.

[46] C. W. Marshal, D. E. Ross, E. B. Fichot, R. S. Norman, H. D. May, "Long-term operation of microbial electrosynthesis systems improves acetate production by autotrophic microbiomes", *Environ. Sci. Technol*., 2013, 47, 6023–6029.

[47] X. Hu, J. Zhou, B. Liu, "Effect of algal species and light intensity on the performance of an air-lift-type microbial carbon capture cell with an algae-assisted cathode", *RSC Adv*., 2016, 6, 25094–25100.

[48] L. Lu, Z. Huang, G. H. Rau, Z. J. Ren, "Microbial electrolytic carbon capture for carbon negative and energy positive wastewater treatment", *Environ. Sci. Technol*., 2015, 49, 8193–8201.

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