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Review

Analysis of Technologies for Carbon Dioxide Capture from the Air

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Abstract: The increase in CO_2 concentration in the atmosphere has prompted the research community to find solutions for this environmental problem, which causes climate change and global warming. CO_2 removal through the use of negative emissions technologies could lead to global emission levels becoming net negative towards the end of this century. Among these negative emissions technologies, direct air capture (DAC), in which CO_2 is captured directly from the atmosphere, could play an important role. The captured CO_2 can be removed in the long term and through its storage can be used for chemical processes, allowing closed carbon cycles in the short term. For DAC, different technologies have been suggested in the literature, and an overview of these is proposed in this work. Absorption and adsorption are the most studied and mature technologies, but others are also under investigation. An analysis of the main key performance indicators is also presented here and it is suggested that more efforts should be made to develop DAC at a large scale by reducing costs and improving efficiency. An additional discussion, addressing the social concern, is indicated as well.

Keywords: atmospheric CO_2; direct air capture; CO_2 reduction; CO_2 removal; key performance indicators; carbon capture technologies

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1. Introduction

Recent estimates report that CO_2 emissions in the world were more than 33 Gton in 2018 [1]. In order to decrease greenhouse gas emissions, several international agreements were signed: the Conference of the Parties (COP21) held at Paris on the 12 December 2015 was a milestone because 197 Countries agreed to keep the temperature increase below 2/1.5 °C above the pre-industrial level by the end of the century [2]. This aim was confirmed by the following Conference of Parties (COP22) held at Marrakesh in 2016, where the national determined contribution (NDC) was defined [3]. However, in order to achieve this objective, CO_2 conventional mitigation, meaning a reduction in CO_2 emissions, might be not enough and the removal of CO_2 might be required, resulting in negative emissions [4,5]. For this reason, negative emissions technologies (NETs) also known as carbon dioxide removal (CDR) technologies, will have a crucial role in the coming years to achieve the CO_2 level defined by the environmental agreements and stabilize the CO_2 concentration between 350 and 440 ppm [6,7].

Negative emissions technologies are defined as the intentional human effort to remove CO_2 emissions from the atmosphere and include the following: afforestation and reforestation (AR), soil carbon sequestration (SCS), biochar (BC), bioenergy with carbon capture and storage (BECCS), direct air capture (DAC), enhanced weathering and ocean alkalinization (EW) and ocean fertilization (OF) [8]. Among these solutions, the research community has been focused for the most part on DAC, due to its advantages [9].

DAC was used for decades to produce CO_2-free air to support life in submarines and spacecraft systems [10,11]; it was presented by Lackner as a GHG mitigation technology only in 1999 [12]. DAC captures CO_2 from the atmosphere to store it as part of a CDR process in the long term (direct air carbon capture and storage—DACCS). Integrated DAC systems have also been studied to supply climate-neutral CO_2 for chemical processes

(power-to-gas (PtG), power-to-liquid (PtL) and power-to-chemical (PtC)), closing the carbon cycle in the short term (direct air carbon capture and utilization—DACCU) [7,13–15].

There are some advantages of DAC. DAC is independent of CO_2 source location, because CO_2 is distributed homogeneously throughout the atmosphere, minimizing or eliminating CO_2 transportation costs when the capture plant is situated near the utilization or storage site [16]; the capture plant can be located in a particular place where the the renewable energy can be exploited at the minimum cost [17]; DAC can tackle emissions from the transport sector and other small sources that constitute about 50% of total emissions; air is ubiquitous, with few contaminants that could cause the degradation of solvents/sorbents (e.g., NO_x, SO_x and particulates) [18]; arable land is not required, avoiding loss of agricultural land [9]; the technology contributes to the achievement of Sustainable Development Goals (SDGs) 13, 9, 6 (by-product water could be used as fresh water in general), 8 (creation of new green jobs), 7 (exploitation of renewable energies), 11 and 12 (production of fuels and materials from atmospheric CO_2) and 3 (positive effect on health) [17]. However, there are also some disadvantages: the long term storage and sequestration of CO_2 are critical (costs, long-term monitoring, potentially induced seismicity and leakage) [19]; low CO_2 partial pressure in the air, about 400 ppm, 350 times lower than coal flue gas so that large volumes of air should be processed to capture a significant amount of CO_2 [7,13,20]; high energy and cost requirements due to the dilute nature of CO_2 in the air, requiring a large volume of air to be treated [21].

DAC technologies include absorption, adsorption, ion exchange resin, mineral carbonation, membrane, photocatalysis, cryogenic separation, electrochemical approach and electrodialysis approaches [6,18,22–26]. Absorption and adsorption technologies are the most analyzed and studied in the literature [18].

DAC technologies are characterized by thermodynamic issues related to the separation of CO_2 from the air, which are more significant than in the separation of CO_2 from the flue gas [27]. Thermodynamic calculation provides the minimum amount of energy for a defined separation depending on the temperature, pressure and initial and final concentrations of the streams. Generally, the minimum required thermodynamic work can be evaluated by the difference in stream exergies, but for isothermal and isobaric processes it can be obtained by the Gibbs free energy, as shown in the following equation and Figure 1 [28–30] (see Equation (1)):

$$W_{min} = RT\left(N_B^{CO2} lny_B^{CO2} + N_B^{B-CO2} lny_B^{B-CO2}\right) + RT\left(N_C^{CO2} lny_C^{CO2} + N_C^{C-CO2} lny_C^{C-CO2}\right) - RT\left(N_A^{CO2} lny_A^{CO2} + N_A^{A-CO2} lny_A^{A-CO2}\right) \quad (1)$$

where W_{min} is the minimum separation work in kJ/mol, R is the universal gas constant 8.314 J/(molK), T is the temperature in K, n_i^{CO2} are CO_2 moles in stream i, n_i^{i-CO2} are the other moles in current i without CO_2, y_i^{CO2} is the CO_2 mole fraction in current i and y_i^{i-CO2} is the mole fraction of the remaining gas without CO_2 in stream i.

Figure 1. Diagram of the CO_2 separation process: CO_2 in the feed stream A is removed, resulting in a product stream B with more CO_2 and a product stream C with a small amount of CO_2. Reproduced with permission from [30].

A first calculation shows that the minimum thermodynamic work needed to separate a stream with 400 ppm of CO_2 into one stream that is poor in CO_2 and a second stream that is mostly CO_2, with a purity of 99%, is 21.86 kJ/molCO_2, while if the feed has a CO_2 concentration of 12%, the minimum thermodynamic work is 7.58 kJ/molCO_2 [31]. Given

this energy difference, it is preferred to capture CO_2 from a concentrated point instead of atmospheric air. Wilcox et al. [32] evaluated the minimum thermodynamic work required to separate CO_2 from the air, natural gas combined cycle flue gas and pulverized coal combustion flue gas. The results are reported in Figure 2 as a function of CO_2 recovery and purity.

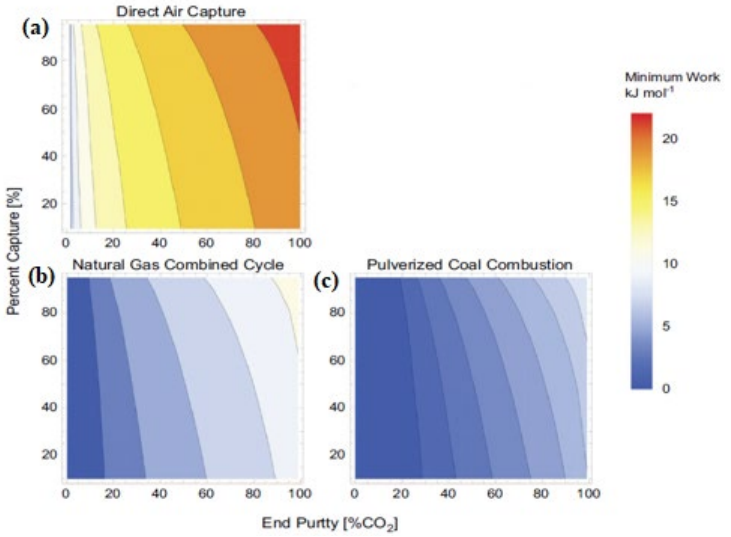

Figure 2. Minimum thermodynamic work of CO_2 separation from (**a**) air, (**b**) natural gas combined cycle flue gas and (**c**) pulverized coal combustion flue gas. Reproduced under the Creative Commons attribution 3.0 license [32].

From Figure 2, it is evident that the minimum thermodynamic work for CO_2 separation from the air is greater than its separation from flue gas, achieving values higher than 20 kJ/molCO_2 for higher CO_2 purities and recoveries. Only for CO_2 purities and CO_2 recoveries lower than 10% and 60%, respectively, is the minimum work for DAC in a range between 8 and 10 kJ/molCO_2, similar to that required for CO_2 separation from power plant flue gas with 90% recovery and 95% purity.

With a higher amount of work required, a higher cost defines DAC systems in comparison with the traditional ones, as has been shown with a Sherwood plot, with costs reported as a function of dilution factor [29]. The Sherwood plot showed that new technologies can have costs 100 times higher than traditional post-combustion capture. However, a deeper economic analysis showed for the near term (within the next 25 years) an optimistic value for DAC costs of approximately 100 \$/ton of CO_2. The pessimistic value was approximately 550 \$/tonCO_2, while the median value was approximately 200 \$/tonCO_2 [33].

Studies in the literature works have mainly been concerned with feasibility analysis of DAC systems, with economic and energetic analyses being undertaken especially for adsorption and absorption [34–37], while the other technologies introduced above require more studies and investigations [22–26,38–40].

This present work aims to provide an interesting and cutting-edge review through a careful analysis of all the DAC systems suggested in the literature. Moreover, after a description and revision of these, attention is focused on DAC companies and key performance indicators (KPIs) in addition to social concerns about this emerging technology.

2. DAC Technologies

In this section, an overview of DAC technologies is set forth. Absorption, adsorption, ion exchange resin, mineral carbonation, membrane, photocatalysis, cryogenic separation, electrochemical and electrodialysis approaches are investigated.

2.1. Absorption

In absorption technology for DAC, water solutions of strong bases containing hydroxide sorbents with a strong CO_2 affinity, such as sodium hydroxide (NaOH), potassium hydroxide (KOH) and calcium hydroxide ($Ca(OH)_2$), are used [3]. The absorption with $Ca(OH)_2$ was proposed by Lackner et al. [12] and it follows the reactions described below [18] (see Equations (2)–(4)):

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad \Delta H_{25\,^\circ C} = -109\ \text{kJ/mol} \tag{2}$$

$$CaCO_3 \rightarrow CaO + CO_2 \quad \Delta H_{900\,^\circ C} = +179.2\ \text{kJ/mol} \tag{3}$$

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad \Delta H^{\circ}{}_{100\,^\circ C} = -64.5\ \text{kJ/mol} \tag{4}$$

The reaction starts with calcium hydroxide and CO_2 to form calcium carbonate ($CaCO_3$). The obtained calcium carbonate is precipitated, accumulated, separated from water, dried and calcined above 900 °C. In this step, calcium oxide (CaO) and CO_2 (concentrated stream) are obtained. Afterwards, calcium oxide is hydrated to produce calcium hydroxide. This reaction scheme allows a closed cycle. However, there are some disadvantages to this process, such as the great amount of lost water, high temperatures and high required energies for the calcination step (179.2 kJ/mol), and the low solubility of calcium hydroxide in water, which limits the hydroxide concentration for CO_2 capture [3,18].

The use of NaOH water solution was proposed by Baciocchi et al. [37] and has a similarity to the Kraft process used in the paper industry to extract cellulose from wood. Compared to $Ca(OH)_2$, NaOH solution allows a strong binding of CO_2 but with a higher solubility of carbonate in water. In this process, there are two cycles working simultaneously. In the first, CO_2 is captured by NaOH to produce sodium carbonate (Na_2CO_3) in the absorber through an exothermic reaction evolving at ambient temperature and pressure (see Equation (5)). In the second cycle, known as the regeneration cycle, NaOH is regenerated in the causticizer/precipitator: Na_2CO_3 reacts with $Ca(OH)_2$ to produce NaOH and $CaCO_3$ (see Equation (6)). From calcium carbonate, CO_2 (concentrated stream) is recovered in the calciner/kiln (see Equation (7)) and receives oxygen (O_2) from an air separation unit. As mentioned above, this step requires a lot of energy, with temperatures above 900 °C to allow the removal of water and decomposition of $CaCO_3$. Afterwards, CaO is hydrated to $Ca(OH)_2$ in the slaker (see Equation (8)) so that it can be sent to the precipitator to be used again [18]. Figure 3 shows the scheme of this process.

$$\textit{Absorber}\ 2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \quad \Delta H_{25\,^\circ C} = -109.4\ \text{kJ/mol} \tag{5}$$

$$\textit{Causticizer}\ Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3 \quad \Delta H_{100\,^\circ C} = -5.3\ \text{kJ/mol} \tag{6}$$

$$\textit{Calciner}\ CaCO_3 \rightarrow CaO + CO_2 \quad \Delta H_{900\,^\circ C} = +179.2\ \text{kJ/mol} \tag{7}$$

$$\textit{Slaker}\ CaO + H_2O \rightarrow Ca(OH)_2 \quad \Delta H_{100\,^\circ C} = -64.5\ \text{kJ/mol} \tag{8}$$

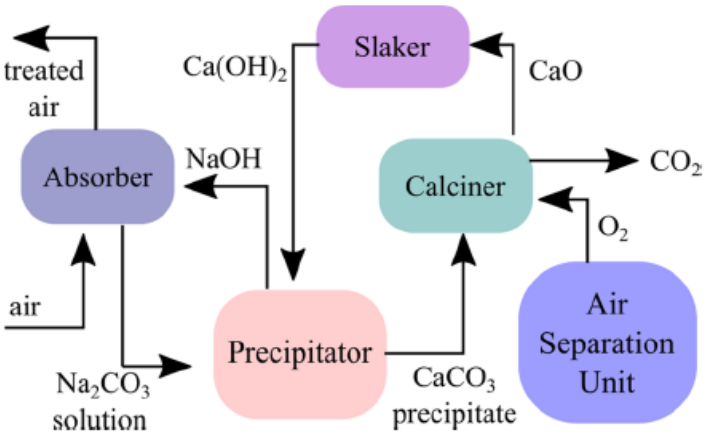

Figure 3. Process scheme for the DAC absorption process with NaOH aqueous solution. Reproduced under the Standard ACS AuthorChoice/Editors' Choice Usage Agreement [18].

An energy calculation showed that the energy for the calcination (179.2 kJ/mol) is well above the calculated thermodynamic minimum for the absorption stage (−109.4 kJ/mol): a high energy requirement is still present [41]. In fact, strong binds are present within the $CaCO_3$ molecules [3]. In addition to this high energy requirement, the water loss (water before calcination in the calciner must be removed) is an additional disadvantage of the process. Zeman [42] estimated that 90 gH_2O/gCO_2 captured are lost. On the other hand, Stolaroff et al. [43] found that water losses can be reduced by increasing the NaOH concentration to 7 M. However, by increasing the NaOH concentration, the solution becomes more viscous and more aggressive, and it is more difficult to handle even if the capture reaction is favored [31].

An alternative to NaOH and $Ca(OH)_2$ solutions is KOH solution, which has lower levels of regeneration, though it is more expensive, so that few studies involving it are present in the literature [18,44]. The choice of a particular solution is a critical point: the solution should be strong enough to capture a significant amount of CO_2 from the dilute air but at the same time weak enough to release CO_2 during the regeneration stage. Enzymes can be added to the solution as catalysts in order to increase the absorption rate of CO_2 [45]. However, problems related to pH, temperature limits and organic decay can occur [46].

This DAC capture technology has important design characteristics. In fact, absorption columns are short and have a large cross section due to the dilute nature of CO_2; they are different from traditional packed towers [47]. Moreover, as a large volume of air is processed, pressure drop should be limited [18]. In addition to packed towers, spray towers or open stagnant pools can be used [44,47]. The spray tower provides a large surface area for air–liquid contact, with a low pressure drop. In this configuration, the costs of large, packed towers are also avoided but the use of a spray causes energy losses [43]. Another problem for this kind of absorber is related to coalescence, which should be reduced by reducing the flow rate and the CO_2 capture rate.

In order to improve the process and overcome its limitations for the regeneration of NaOH, alternative causticization reactions have been suggested, such as autocausticization and direct causticization [18]. In the first case, sodium metaborate ($NaBO_2$) is used, involving the following reactions [18] (see Equations (9)–(12)):

$$2NaBO_2 + Na_2CO_3 \rightarrow Na_4B_2O_5 + CO_2 \quad (9)$$

$$Na_4B_2O_5 + H_2O \rightarrow 2NaOH + 2NaBO_2 \quad (10)$$

$$NaBO_2 + Na_2CO_3 \rightarrow Na_3BO_3 + CO_2 \quad (11)$$

$$Na_3BO_3 + H_2O \rightarrow NaOH + NaBO_2 \quad (12)$$

In this case, the reaction product is water-soluble, removing the need for drying or the movement of solids [48]. However, this requires a lot of energy, as temperatures are higher than 900 °C.

In direct causticization, the reaction product is not water-soluble and these reactions involve titanium dioxide (see Equations (13)–(16)) [18]:

$$7Na_2CO_{3(s)} + 5(Na_2O{\cdot}3TiO_2) \rightarrow 3(4Na_2O{\cdot}5TiO) + 7CO_2 \quad \Delta H_{850\,^\circ C} = 90\ \text{kJ/mol} \quad (13)$$

$$Na_2CO_{3(s)} \rightarrow Na_2CO_{3(l)} \quad \Delta H_{850\,^\circ C} = 25\ \text{kJ/mol} \quad (14)$$

$$7Na_2CO_{3(l)} + 5(Na_2O{\cdot}3TiO_2) \rightarrow 3(4Na_2O{\cdot}5TiO) + 7CO_2 \quad \Delta H_{850\,^\circ C} = 65\ \text{kJ/mol} \quad (15)$$

$$3(4Na_2O{\cdot}5TiO) + 7H_2O \rightarrow 5(Na_2O{\cdot}3TiO_2) + 14NaOH \quad \Delta H_{100\,^\circ C} = 15\ \text{kJ/mol} \quad (16)$$

The disadvantages are that the heat requirement is comparable to that of an aqueous amine-based liquid post-combustion CO_2 capture process (130 kJ/molCO_2) and more processing steps are needed in comparison with the traditional causticizer process [48].

Studies in the literature are mostly concerned with economic and energetic analysis and process design. Regarding energetic analysis, it needs to be underlined that, in addition to heat, electrical energy is required for fans to blow air through the contactor, to spray the aqueous solution and to move the solution between each piece of equipment. Fasihi et al. [49] reported that the electrical energy requirement is in a range between 366 kWh/tonCO_2 and 764 kWh/tonCO_2 (including energy for CO_2 compression), while the thermal energy requirement is in a range between 1420 kWh/tonCO_2 and 2780 kWh/tonCO_2. A process design and an energy evaluation have been carried out by Baciocchi et al. [37] and it was found that 1678 kWh/tonCO_2 was required for the thermal energy, while 440 kWh/tonCO_2 was needed for the electrical energy for the complete absorption process using NaOH. Zeman [41] found that the energy requirement for a packed tower contactor was 555 kWh/tonCO_2, but he suggested that the use of hollow fiber membranes as packing could reduce this to 361 kWh/tonCO_2 (33% lower). A detailed simulation in Aspen Plus of the complete process, shown in Figure 4, was carried out by Keith et al. [34] for the first time. Using a KOH solution, the authors found that to deliver CO_2 at 15 Mpa, 1458 kWh/tonCO_2 of natural gas would be required, in addition to 366 kWh/tonCO_2 of electric energy. A large-scale plant captures about 1 MtonCO_2/year and the levelized cost ranges between 94 and 232 \$/tonCO_2.

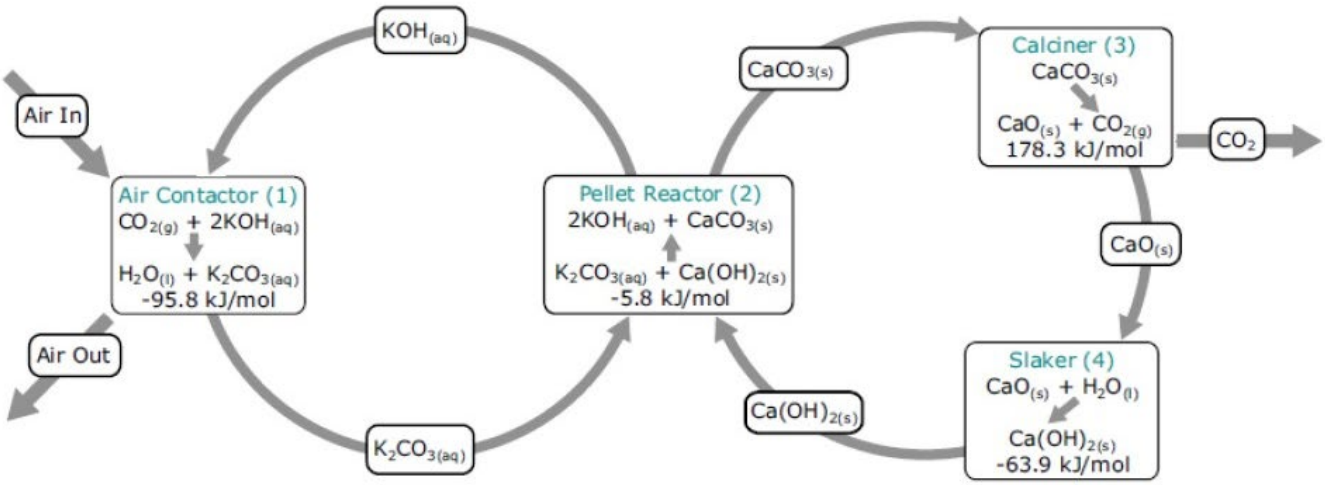

Figure 4. Scheme of the process analyzed by Keith et al. [34] using a KOH solution. Reproduced under a creative commons license.

More specifically, regarding the economic analysis, Holmes and Keith [50] provided an economic analysis of an absorption system using sodium hydroxide to capture CO_2

from the air at a large scale. They found that total costs for the absorber without the regeneration cycle could be in the order of 60 $/ton$CO_2$. Mazzotti et al. [51], comparing different packings, found that the optimized cost ranged from 518 $/t$CO_2$ for M-CC to 568 $/t$CO_2$ for M-250Y, making it a non-competitive mitigation system. A lower cost was found by Stolaroff [52] in studying a complete plant with a contactor using a spray for NaOH solution: the cost range was between 80 $/ton$CO_2$ and 250 $/ton$CO_2$. In the work of Fasihi et al. [49], the expected cost for this kind of technology was reported for the 2040 and 2050. In the first case, costs were in a range between 70 €/tonCO_2 and 90 €/tonCO_2, while, in the second case, costs decreased and were in a range between 55 €/tonCO_2 and 70 €/tonCO_2.

Some experimental works have also been presented. Holmes et al. [53] built an absorber prototype for the Carbon Engineering company to test the cross flow and PVC packing, to evaluate energy requirements and fouling by atmospheric particulates and to assess technical and safety risks.

2.2. Adsorption

While the absorption process mainly uses an aqueous solution of NaOH, KOH or $Ca(OH)_2$, the adsorption process is based on the chemical or physical adsorption of CO_2 with particular sorbents, such as amine-functionalized sorbents, metal organic frameworks (MOFs), zeolites, etc. [6]. Among chemisorbents, amine-functionalized sorbents and solid alkali carbonates sorbents (bulk and supported) have been proposed, while, among physisorbents, MOFs, zeolites and new materials, such as boron nitride nanosheets and nanotubes, have been investigated [18]. Amine-functionalized sorbents have received significant attention for DAC systems due to their stability under humidity, low regeneration temperatures (50–120 °C) and flexibility in the choice of low-cost support [39].

Generally, in the adsorption system, a single equipment unit is used, where adsorption and desorption happen alternately after variations in temperature or pressure or a combination of the two. Generally, pressure swing adsorption (PSA) is not practicable in a real process because a pressure lower than 0.4 mbar is required. At lab scale, the temperature swing adsorption (TSA) is generally used, but the use of an inert gas purge results in a dilute output stream. On the other hand, temperature and vacuum swing adsorption (TVSA) could be used to produce a high-CO_2 purity stream.

Most studies reported in the literature on the adsorption process are on the investigation of sorbents, evaluating adsorption capacities and performances, as discussed below.

2.2.1. Physisorbents

Physisorption occurs between the sorbent surface and CO_2, allowing only a physical interaction. Generally, materials with porosity or nanometric dimensions, such as zeolites, activated carbon, MOFs and new materials, have been considered [54]. Activated carbons are characterized by low cost and high thermal stability, showing an adsorption capacity and selectivity lower than that of zeolites at a low CO_2 partial pressure but higher at a high CO_2 partial pressure [55,56]. For this reason, activated carbons are not a good choice for direct air capture [6].

Factors influencing the CO_2 capture of zeolites are size, charge density and distribution of cations in the porous structure [57]. Humidity has a negative effect on CO_2 capture, and for this reason zeolites are not suggested for direct air capture [6].

MOFs are characterized by flexibility in shape, pore structure, pore size and surface properties [58]. Similar to activated carbons, adsorption capacity and selectivity are lower at low CO_2 partial pressures and in the presence of humidity; MOFs are suitable for CO_2 storage and not for CO_2 separation. However, in recent years, attention has been directed to MOFs (particularly MIL-101(Cr)) functionalized with amine (adsorption of amines onto metal sites or physical impregnation with liquid amines) which provide better performances for CO_2 capture from the air due to their durability under moist conditions [39]. Currently, the high cost of MOFs makes their use in DAC prohibitive [6].

Among novel materials, boron nitride nanosheets [59] and nanotubes [60] have been investigated for the capture of CO_2 from the air. These materials have the ability to capture CO_2 from the air due to the introduction of electrons and to spontaneously desorb CO_2 when electrons are removed.

Generally, adsorption with physisorbents is characterized by a low adsorption capacity due to the dilute concentration of CO_2 in the air and the negative effect of moisture. Some physisorbents are shown in Figure 5, while some data about adsorption capacity are reported in Table 1.

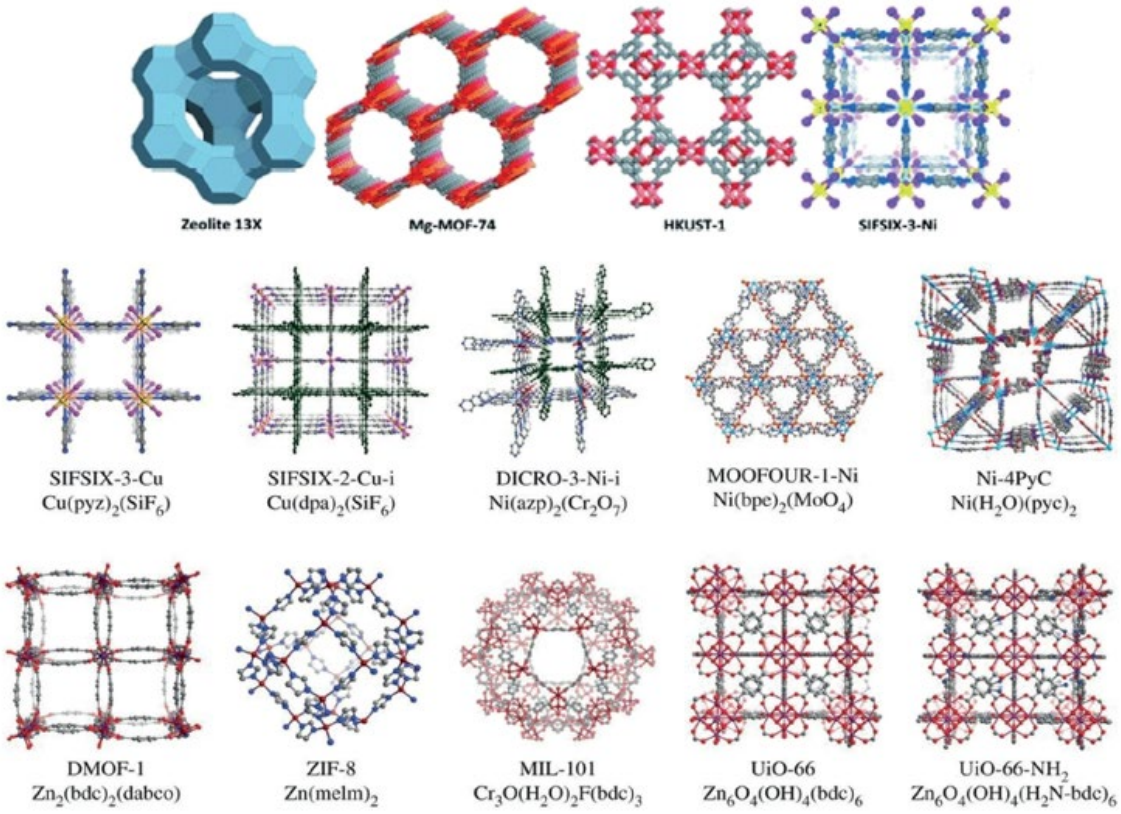

Figure 5. Typical physisorbent materials. Adapted from [6].

Table 1. Adsorption capacity of some physisorbents. Adapted from [6].

Sorbent	Ambient Air (1 atm; 49% RH)		Dry CO_2 (15%)
	CO_2 (mmol/g)	H_2O (mmol/g)	CO_2 (mmol/g)
SIFSIX-3-Ni	0.18	5.17	2.48
HKUST-1	0.05	9.89	1.59
Mg-MOF-74	0.14	9.5	5.34
Zeolite 13X	0.03	8.11	3.18

2.2.2. Chemisorbents

In chemisorbents, a chemical reaction occurs between CO_2 and an amine group on the porous material in what is known as an amine-modified sorbent. Reactions differ depending on whether moisture is present. In dry conditions, primary and secondary amines react with CO_2 to form ammonium carbamate and carbamic acid, respectively [61]. In moist conditions, amines react with CO_2 to produce bicarbonate. Equations (17) and (18) show the reaction between CO_2 and a secondary amine in dry and moist conditions, respectively [18]:

$$CO_2 + 2R_1R_2NH \leftrightarrow R_1R_2NH_2^+ + R_1R_2NHCOO^- \quad (17)$$

$$CO_2 + R_1R_2NH + H_2O \leftrightarrow R_1R_2NH_2^+HCO_3^- \leftrightarrow R_1R_2NH_2^+CO_3^{2-} \quad (18)$$

Amine-functionalized sorbents are divided into three different classes according to the preparation method, as shown in Figure 6 [6,18]. Class I considers all sorbents obtained by the physical impregnation of amines into porous materials. In this case, amines have a low molecular weight and are easily leached during the adsorption and regeneration processes. Class II includes sorbents where amines are chemically grafted onto the surface support. Due to a higher amine content, class I has a higher adsorption capacity than class II. Class III consists of an inorganic support and a chemically grafted polyamine component that is prepared through the in situ polymerization of amine-containing monomers. This class has an adsorption capacity higher than that of sorbents of class II due to the higher number of amines and excellent regeneration capacity. Generally, classes II and III are more suitable for DAC because the amine is chemically bound on the support and this reduces volatilization problems during regeneration and adsorption cycles.

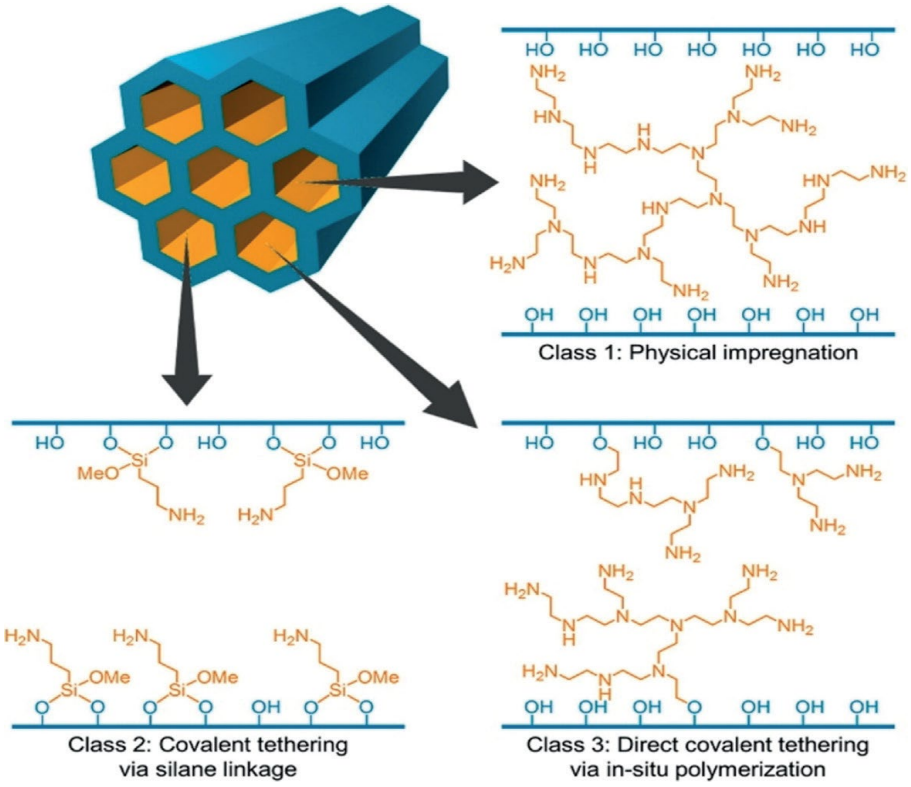

Figure 6. Classification of amine-functionalized sorbents. Reproduced with the permission from [6].

Class I Amine-Functionalized Sorbents

Many works have been presented in the literature about this class of sorbents. Polyethylenimine (PEI) loaded onto a mesoporous silica-based molecular sieve was suggested by Xu et al. [62] for CO_2 capture from the air. It is evident that PEI is the most important amine considered for this class; it can have a linear or branched structure. Moreover, PEI has attracted the attention of researchers due to its high amine content, low volatility and commercial availability [63].

An overview of different works related to class I amine-functionalized sorbents investigated in the literature is shown in Table 2.

Table 2. Class I amine-functionalized sorbents.

Support	Amine	Conditions	Con. CO_2 (ppm)	Adsorption Capacity ($molCO_2/kg_{sorbent}$)	CO_2:N	Method	Reference
Silica (CARiACT® and Davisil®-646) and polymethylmethacrylate® (PMMA, DiaionTM HP-2MG)	Tetraethylenepentamine (TEPA)-38% *w*/*w*	308 K	400	2.5	0.25	TGA	[64]
Commercial silica (CARiACTG10HPV)	Polyethylenimine (PEI)	298 K	400	2.36	0.22	TGA	[65]
Commercial silica (CARiACTG10HPV)	Polyethylenimine (PEI) + (3-aminopropyl)triethoxysilane (APTMS)	298 K	400	2.26	0.21	TGA	[65]
Commercial silica (CARiACTG10HPV)	Polyethylenimine (PEI) + tetrapropyl orthotitanate	298 K	400	2.19	0.21	TGA	[65]
Mesocellular foam (MFC)	Poly(allylamine) (PAA)	298 K	400	0.63	0.11	TGA	[66]
Mesocellular foam (MFC)	Branched Polyethylenimine (PEI)	298 K	400	0.61	0.09	TGA	[66]
Mesocellular foam (MFC)	Linear Polyethylenimine (PEI)	298 K	400	0.44	0.06	TGA	[66]
Zr-SBA-15	Polyethylenimine (PEI) (34.7% *w*/*w*)	298 K	400	0.85	0.1	TGA	[67]
γ alumina	Polyethylenimine (PEI)	298 K	400	1.74	0.16	TGA	[68]
SBA-15	Polyethylenimine (PEI)	298 K	400	1.05	0.11	TGA	[68]
Fumed silica	Polyethylenimine (PEI)-H 33% *w*/*w*	298 K	420	1.18		IR	[69]
Fumed silica	Polyethylenimine (PEI)-H 33% *w*/*w*	298 K, 67% relative humidity	420	1.77		IR	[69]
Fumed silica	Polyethylenimine (PEI)-H 50% *w*/*w*	298 K	420	1.71		IR	[69]
Fumed silica	Polyethylenimine (PEI)-H 50% *w*/*w*	298 K, 67% relative humidity	420	1.41		IR	[69]
SBA-15	Polyethylenimine (PEI)	348 K	400	1.52		TPD	[70]
SBA-15	Polyethylenimine (PEI)	298 K	400	0.77		TPD	[70]
Fumed silica	Polyethylenimine (PEI)PEI+poly(ethylene glycol) (PEG)	323 K	360	0.68	0.07	TGA	[71]
SBA-15	Polyethylenimine (PEI), 67% *w*/*w*	298 K	400	1.92			[72]
Mixed metal oxides (MMO)	Polyethylenimine (PEI), 50% *w*/*w*	298 K	400	1.66			[72]
Mixed metal oxides (MMO)	Polyethylenimine (PEI), 67% *w*/*w*	298 K	400	2.27			[72]
SBA-15	Polyethylenimine (PEI) + poly(ethylene glycol) (PEG) 200	303 K	400	0.79	0.14	TGA	[73]
Fumed silica	Linear Polyethylenimine (PEI)	298 K	400	2.34		IR	[74]
Fumed silica	Branched Polyethylenimine (PEI)	298 K	400	2.44		IR	[74]
Fumed silica	Polyethylenimine (PEI)-M (Mw = 1800)	298 K	400	1.69		IR	[74]
Fumed silica	Polyethylenimine (PEI)-H (Mw = 25,000)	298 K	400	1.67		IR	[74]
Hierarchical bimodal meso/microporous silica	Polyethylenimine (PEI) (Mw = 800)	303 K, 19% relative humidity	400	3.36			[75]
Hierarchical bimodal meso/microporous silica	Polyethylenimine (PEI) (Mw = 800)	323 K	400	2.6		Gravimetric	[75]
Mesoporous carbon	Polyethylenimine (PEI) 55% *w*/*w*	298 K, dry condition	400	2.25			[76]

Table 2. *Cont.*

Support	Amine	Conditions	Con. CO_2 (ppm)	Adsorption Capacity ($molCO_2/kgsorbent$)	CO_2:N	Method	Reference
Mesoporous carbon	Polyethylenimine (PEI) 55% *w*/*w*	298 K, 80% relative humidity	400	2.58			[76]
Mesoporous carbon	Polyethylenimine (PEI) 55% *w*/*w*	298 K	5000	3.34			[76]
Mesoporous γ alumina	Branchd Polyethylenimine (PEI) (Mw = 800)	303 K, 50% humidity	400	1.71		IR	[77]
Alumina monolith	Branched Polyethylenimine (PEI) (Mw = 800) 43–44% *w*/*w*	303 K	400	0.75		Gravimetric	[78]
Non-polar resin (HP20)	Polyethylenimine (PEI) 50% *w*/*w*	343 K	400	2.26			[79]
Microporous polymer	Polyethylenimine (PEI) 20% *w*/*w*	308 K	400	0.2			[80]
SBA-15	Poly(propylenimine) (PPI) prepared by $HClO_4$	303 K	400	0.31			[81]
SBA-15	Poly(propylenimine) (PPI) prepared by HBr	303 K	400	0.25			[81]
SBA-15	Poly(propylenimine) (PPI) prepared by HCl	303 K	400	0.15			[81]
SBA-15	Poly(propylenimine) (PPI) prepared by CH_3SO_3H	303 K	400	0.17			[81]
SBA-15	Tetraethylenepentamine (TEPA)	296 K	400	3.6	0.2		[82]
Nanofibrillated cellulose (NFC)	PEIPolyethylenimine (PEI) 44% *w*/*w*	20% relative humidity	400	0.5		IR	[83]
Nanofibrillated cellulose (NFC)	Polyethylenimine (PEI) 44% *w*/*w*	80% relative humidity	400	2.2		IR	[83]
Mg2(dobpdc)	N,N′-Dimethylethylenediamine (mmen)	298 K	390	2			[84]
Carbon fiber	Polyethylenimine (PEI)	298 K, 100% relative humidity	400	1.3			[85]
MIL-101(Cr)	Polyethylenimine (PEI)	298 K	400	1.35			[86]

An amine-functionalized sorbent made by PEI impregnation onto alumina has been studied in the work of Sakwa Noval et al. [78]. An adsorption capacity of 0.75 molCO_2/kg at a high amine loading, with 303 K and simulated ambient air, was evaluated for a larger extruded monolith sorbent, and it was found to be higher than that of an alumina powder sorbent (0.7 molCO_2/kg). In addition, the authors found that, for the first sorbent, adsorption capacities for two to five cycles were stable but slightly lower than that for one cycle due to minor PEI leaching or rearrangement in the monolith, which has been observed for powder sorbents. The same amine, PEI, was impregnated with a loading up to 21 %wt onto a microporous polymer (PIM-1); an uptake of 0.2 molCO_2/kg at 308 K for simulated air and 1 molCO_2/kg for a flue gas with 14% of CO_2 were measured [80]. However, at a higher amine loading, the CO_2 adsorption capacity was reduced due to the inaccessibility of the amine sites.

Goeppert et al. [74] evaluated how different kinds of PEI impregnated onto fumed silica (linear, branched, with low and high molecular weights, respectively, of 1800 and 25,000 Da) influenced adsorption capacity and found the best uptake for the branched sample with a low molecular weight at a loading of 33 %wt (56 mgCO_2/g). At a higher amine loading (50 %wt), higher adsorption capacities were obtained of up to 107.3 mgCO_2/g for the PEI with an 800 Da molecular weight. However, PEI of lower molecular weight can be more prone to leaching than homologues with higher molecular weights. This could lead to a loss of capacity over time and the possible contamination of downstream equipment.

Chen et al. [79] reported the impregnation of PEI onto non-polar resin HP20, measuring the adsorption capacity for pure CO_2 and simulated air with a CO_2 concentration of 400 ppm. The values for the investigated parameter were, respectively, 4.122 molCO_2/kg and 2.26 molCO_2/kg. This material exhibits promising potential for CO_2 capture from ambient air. Moreover, the authors found that a pore size of 43–68 nm is responsible for diffusion/adsorption phenomena, using a non-local density functional theory. On the other hand, they verified that temperature has a negative effect on adsorption due to exothermic reactions.

Amine mixtures have been investigated. In this context, Brilman and Veneman [64] analyzed the adsorption capacity of a sorbent obtained by the impregnation of silica and polymer supports with tetraethylenepentamine (TEPA) and PEI at different temperatures and CO_2 concentrations. At 308 K and 400 ppm, they measured an adsorption capacity of 2.5 molCO_2/kg, using temperature swing adsorption for regeneration. With a sensitivity study, it was found that regeneration temperatures depend on CO_2 purity and that for the capture of CO_2 from the air a regeneration temperature above 125 °C is needed in order to maintain a reasonable cyclic capacity (above 1.5 molCO_2/kg).

An amine mixture consisting of PEI and poly(ethylene glycol) (PEG) impregnated onto a fumed silica support has been reported in Meth et al. [71] as allowing good CO_2 uptake and at higher temperatures. The experimental results showed that the outside surface area of the support was more important than the inside porosity, offering a more effective surface area and morphology for the distribution of the amine for CO_2 capture without the negative side-effects of agglomeration and stickiness.

Better efficiencies were reported for an amine mixture of PEI and PEG200 loaded onto SBA-15 by Sakwa-Novak et al. [73]; the CO_2 uptake was 0.79 molCO_2/kg. The authors found that the mixture of the two amines provided a way of tuning the sorbent performance and reducing capital costs (via increased amine efficiency), though with increased operating costs.

Generally, silica materials, such as commercial silica, fumed silica, SBA-15, silica fiber and mesocellular foam (MCF), have been widely investigated due to their large surface areas and high pore volumes [72]. In addition, non-silica supports, such as mesoporous carbon and γ-alumina, have been studied, and other interesting supports have been taken into account. Fer example, PEI was loaded onto Mg–Al–CO_3 layered double hydroxide-derived mixed metal oxides (MMOs) in Zhu et al. [72]. At the same amine loading (67% *w*/*w*), the proposed PEI/MMO sorbent showed a higher CO_2 uptake (2.27 molCO_2/kg) than

that obtained with PEI/SBA-15 (1.92 molCO_2/kg) due to the ideal morphologies and nanostructures of their supports. Kinetics and stability were also better for the former, making this sorbent attractive for ultra-dilute CO_2 capture.

Another comparison between two different supports with PEI amines has been reported in Chaikittisilp et al. [68], where SBA-15/PEI and γ-alumina/PEI sorbents were evaluated. The results showed that, under dry conditions at 298 K, the second provided higher CO_2 adsorption capacities and amine efficiencies, making alumina-supported amine materials promising for direct air capture technology. Moreover, the alumina-supported amine sorbent was more stable in short multicycle temperature swing tests and was more robust upon direct contact with steam.

The sorbent SBA-15/PEI has also been investigated by Wang et al. [70], who reported a CO_2 uptake of 0.77 molCO_2/kg at 298 K. However, the best adsorption capacity was obtained at 348 K, with a breakthrough and saturation capacity of 63.1 and 66.7 mg CO_2/g, respectively. The sorbent can be easily and completely regenerated under mild conditions (50–110 °C) and is stable in cyclic operations for at least 20 cycles.

Class I sorbents have poor stability over repeated adsorption/desorption cycles. In order to improve the stability of basic PEIs and CO_2 adsorption kinetics, modified PEIs have been analyzed in Choi et al. [65], who considered 3-aminopropyltrimethoxysilane (A-PEI/silica) and tetraethyl orthotitanate (T-PEI/silica) sorbents in addition to the traditional one, for which there is a stronger bond with silica surfaces. The authors found that this allowed higher adsorption capacity, stability and kinetics until after four temperature swing cycles. In the first cycle, CO_2 uptake was 2.36 molCO_2/kg, 2.26 molCO_2/kg and 2.19 molCO_2/kg for the traditional PEI/silica, A-PEI/silica and T-PEI/silica sorbent, respectively. However, after four cycles, the values for this parameter were, respectively, 1.65 molCO_2/kg, 2.05 molCO_2/kg and 2.16 molCO_2/kg.

In addition to PEI, other amines have been studied. In Sarazen et al. [81], a branched poly(propylenimine) (PPI) was synthetized via cationic ring opening polymerization of azetidine using various acid initiators (HBr, $HClO_4$, HCl and CH_3SO_3H). The results showed that a CO_2 uptake of 0.31, 0.25, 0.15 and 0.17 molCO_2/kg was present for the sorbents prepared using $HClO_4$, HBr, HCl and CH_3SO_3H, respectively. However, HBr and $HClO_4$-initiated composites also showed slightly higher oxidative resistances than those initiated with HCl or CH_3SO_3H.

Pang et al. [87] showed that PPI in a linear and dendritic form and supported in silica has better performance (in terms of CO_2 adsorption capacity) than PEI-based sorbents, a higher resistance to oxidative degradation and that it is less sensitive to oxygen during regeneration, allowing a longer life. The increased adsorption capacity is due to the increased basicity of the amines in PPI and decreased nearest-neighbor interactions. On the other hand, secondary amines linked by propylene spacers still have much of their CO_2 capture capability even after exposure to oxidation conditions relevant to carbon capture, making them less sensitive to regeneration conditions.

Kumar et al. [82] studied TEPA loaded onto an SBA-15 support, an amine-modified mesoporous silicate, and found an adsorption capacity of 3.6 molCO_2/kg. However, the sorbent has problems in terms of degradation over repeated cycling and amine deactivation in the presence of NO_x, SO_x, O_2 and CO.

N,N′-dimethylethylenediamine (mmen) was impregnated onto a MOF, M_2(dobpdc) in the work of McDonald et al. [84], showing an excellent CO_2 capture capacity at low concentrations. A CO_2 uptake of 2 molCO_2/kg was measured at 0.39 mbar in dry conditions. Dynamic gas adsorption/desorption cycling experiments demonstrated that mmen-Mg2(dobpdc) can be regenerated upon repeated exposures to simulated air, with cycling capacities of 1.05 mmol/g after 1 h of exposure.

Poly(allylamine) (PAA) is an alternative to PEI due to the high number of nitrogen groups that are present. In particular, compared to PEI, PAA has a higher density of primary amines and an extra carbon atom in the building unit, which may offer better thermal stability for CO_2 capture. Chaikittisilp et al. [66] compared a sorbent made of silica

mesocellular foam (MCF) impregnated with PAA and two other sorbents with branched and linear PEI. The results showed that at a low amine loading, PAA and branched PEI had an adsorption capacity higher than that of linear PEI in the simulated ambient air due to the very small primary amine loading in linear PEI. For the sorbent with PAA, branched PEI and linear PEI, CO_2 uptakes were, respectively, 0.63 molCO_2/kg, 0.61 molCO_2/kg and 0.44 molCO_2/kg. The authors also found that at higher loadings of PAA the amine sites did not seem to be as accessible, such that CO_2 capacities and amine efficiencies decreased.

Many studies have considered the effect of moisture on adsorption capacity. In Goeppert et al. [69], adsorption capacities of 1.7 molCO_2/kg (dry condition) and 1.41 molCO_2/kg (humid condition) were measured at 298 K with a PEI/fumed silica sorbent. They considered that the adsorbed water blocked access to amine groups, thereby reducing CO_2 capacity. However, an opposite trend was registered for a lower amine loading, achieving a CO_2 uptake of 1.77 molCO_2/kg at 67% relative humidity. The different behavior was due to gas diffusion into the adsorbents. With a lower amine loading, the amine was better dispersed on the support, allowing easier access to amino groups for the incoming gases. On the other hand, at a higher amine loading, the amino group might not be as accessible due to a poorer dispersion on the support's surface and agglomeration of the coated particles.

The positive effect of humidity on CO_2 capture from the air for other sorbents has been reported in several other works. Wang et al. [76] considered a mesoporous carbon support with polyethylenimine in a fixed bed column and found that the CO_2 adsorption capacity was higher with moisture and that an excellent stability was present at a low CO_2 concentration under temperature swing adsorption/desorption cycles, measuring only a 2–5% drop in the sorption capacity after 10 cycles. In fact, 2.25 molCO_2/kg was obtained at an ambient temperature and in dry conditions, while 2.58 molCO_2/kg was measured at 80% relative humidity. On the other hand, after reducing the CO_2 concentration to 5000 ppm, in dry conditions, the adsorption capacity increased to 3.34 molCO_2/kg. The authors developed, also, a first-order kinetic deactivation model based on experimental breakthrough curves in order to study the influence of CO_2 diffusion on the adsorption kinetics.

The positive effect of moisture on adsorption capacity has also been reported in the work of Kwon et al. [75], who considered a PEI-functionalized hierarchical bimodal meso/microporous silica support. At 323 K, they measured 2.6 molCO_2/kg in dry conditions and 3.36 molCO_2/kg at 303 K with 19% relative humidity. This adsorption capacity value is the highest CO_2 uptake value recorded for class I sorbents, to the best of the authors' knowledge, and shows how the presence of water vapor mitigates the kinetic limitations of aminopolymer deposits.

The same effect was found by Sehaqui et al. [83]: the CO_2 adsorption capacity increased from 0.5 molCO_2/kg to 2.2 molCO_2/kg for air with 20% and 80% relative humidity, respectively, for a sorbent composed of oxidized nanofibrillated cellulose (NFC) and a high-molar mass PEI. The authors underlined that the presence of water is also advantageous, as it stabilizes the PEI-based sorbent by inhibiting the formation of urea species.

The effect of steam exposure time was studied by Sakwa-Novak and Jones [77], who examined a PEI-impregnated mesoporous γ-alumina sorbent for which an adsorption capacity of 1.71 molCO_2/kg was measured at 303 K and 50% relative humidity. The authors found that CO_2 adsorption can be reduced by increasing the time of steam exposure due to PEI leaching; after 24 h of steam exposure, a capture reduction of 61.5% was obtained. However, the formation of boehmite on the sorbent surface was not significant with respect to amine efficiency.

Adsorption capacities can be improved by tuning the support, as in Kuwahara et al. [67], where Zr was incorporated onto SBA-15 to this end, changing the acid–base properties of the support. This study showed that Zr also improves regenerability and stability over continued recycling in capturing CO_2 from flue gas and air. The authors reported that an adsorption capacity of 0.85 molCO_2/kg was obtained and verified that the

acid–base properties of the support have a critical, previously unrecognized role in creating more efficient adsorbents, improving thermal stability and adsorbent longevity.

Class II Amine-Functionalized Sorbents

An overview of class II amine-functionalized sorbents is shown in Table 3 [88–102]. Among class II sorbents, Moschetta et al. [97] considered a new synthesis to transform an alkyl halide-functionalized SBA-15 silica containing Br, Cl and I into an amine-functionalized SBA-15 silica through a procedure involving gas-phase post-grafting, using NH_3 at high pressure. The results showed that this route could increase amine loading in aminosilica sorbents without sacrificing amine efficiency and ensuring a CO_2 adsorption capacity of 0.1 molCO_2/kg at 303 K.

The same support was grafted with low amounts of 3-aminopropyltrimethoxysilane in Stuckert and Yang [94], achieving an adsorption capacity of 0.14 molCO_2/kg. Compared with other zeolite sorbents, the authors founds that this amine-functionalized sorbent was able to work in wet conditions but with a lower space velocity of 1500 1/h due to slower uptake rates.

A novel amine-based nanofibrillated cellulose (NFC) sorbent was investigated by Gebald et al. [91]. This support was functionalized by 3-aminopropylmethyldiethoxysilane (APDES), allowing a high CO_2 uptake (2.13 molCO_2/kg) with humidity. The same support was impregnated with N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane (AEAPDMS) in Ng et al. [92], where an adsorption capacity of 1.39 molCO_2/kg was measured at 298 K with 40% relative humidity and the kinetics of CO_2 and H_2O co-adsorption were analyzed. The system showed a good stability over 100 cycles, with a reduction in CO_2 uptake of less than 5%.

The positive effect of moisture has been verified, as well, in Wurzbacher et al. [90], who demonstrated experimentally the stability of temperature vacuum swing adsorption/desorption cycles in a packed bed with diamine-functionalized silica gel sorbents. The CO_2 uptake at 40% relative humidity was 0.44 molCO_2/kg, while in dry conditions it was 0.4 molCO_2/kg.

Higher efficiencies were measured, also, in the work of Didas et al. [93]. Three sorbent materials were obtained by grafting a primary aminosilane (3-aminopropyltrimethoxysilane, APS) to silica SBA-15, varying the degree of surface coverage: SBA-APS-low (a submonolayer surface coverage of amines), SBA-APS-medium (an approximately monolayer coverage of amine) and SBA-APS-high (a dense, multilayer array of amines) [93]. The results showed that the CO_2 adsorption capacity could be increased by increasing the partial pressure of CO_2 and the coverage of amines. At 400 ppm, CO_2 uptakes were, respectively, 0.12, 0.24 and 0.8 molCO_2/kg in dry conditions. However, at low relative humidity, the authors found that the formation of bicarbonate species with low surface amine coverage allowed an increase in amine efficiency. This was the first time that bicarbonate formation, which is known to occur in liquid aqueous amine solutions, was observed for sorbents capturing CO_2 from the air.

Other supports have been studied. In Didas et al. [95], in particular, a comparison between a primary (3-aminopropylsilyl, APS), a secondary (N-methyl-3-aminopropylsilyl, MAPS) and a third (N,N-dimethyl-3-aminopropylsilyl, DMAPS) amine-functionalizing mesocellular foam (MCF) has been reported. The results showed that the primary amine had the greatest potential for CO_2 capture, which at low pressure (100 ppm) was 1 molCO_2/kg. In fact, primary amines possess both the highest amine efficiency for CO_2 adsorption as well as enhanced water affinity (which improves CO_2 adsorption from the air) compared to other amine types.

Table 3. Class II amine-functionalized sorbents.

Support	Amine	Conditions	Con. CO_2 (ppm)	Adsorption Capacity ($molCO_2/kg_{sorbent}$)	CO_2:N	Method	Reference
MCM-41	Triaminesilane (TRI)	298 K	400	0.98	0.12	TGA	[88]
MCM-41	Triaminesilane (TRI)	298 K	300	0.9	0.11	PB	[88]
MCM-41	Triaminesilane (TRI)	298 K, 26% relative humidity	300	1.19	0.15	PB	[88]
MCM-41	Triaminesilane (TRI)	298 K, 67% relative humidity	300	1.4	0.18	PB	[88]
PE-MCM-41	Diethylenetriamino organosilanes (DT)	303 K	400	0.61	0.08	TGA	[89]
PE-MCM-41	Diethylenetriamino organosilanes (DT)	303 K, 73% relative humidity	400	0.54	0.07	TGA	[89]
PE-MCM-41	Diethylenetriamino organosilanes (DT)	281 K–268 K	400	1.16	0.15	TGA	[89]
Silica gel	Diaminosilane (H4N2Si)	298 K	400–440	0.4	0.16	TGA	[90]
Silica gel	Diaminosilane (H4N2Si)	298 K, 40% relative humidity	400–440	0.44	0.18	TGA	[90]
Nanofibrillated cellulose (NFC)	3-aminopropylmethyldiethoxysilane (APDES)	296 K	400	1.11			[91]
Nanofibrillated cellulose (NFC)	3-aminopropylmethyldiethoxysilane (APDES)	296 K, humidity	400	2.13			[91]
Nanofibrillated cellulose (NFC)	N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane (AEAPDMS)	298 K, 40% relative humidity	506	1.39			[92]
SBA-15	3-aminopropyltrimethoxysilane, (APS) low	303 K	400	0.12		IR	[93]
SBA-15	3-aminopropyltrimethoxysilane, (APS) medium	303 K	400	0.24		IR	[93]
SBA-15	3-aminopropyltrimethoxysilane, (APS) high	303 K	400	0.8		IR	[93]
SBA-15	3-aminopropyltrimethoxysilane (APS)	298 K	395	0.14		TGA	[94]
Mesocellular foam (MCF)	3-aminopropylsilyl (APS)	298 K	100	1			[95]
Porous polymer networks (PPNs)	Diethylenediamine (DETA)	295 K	400	1.04			[96]
MIL-101(Cr)	Tris (2-amino ethyl) amine (TREN)	298 K	400	0.35			[86]
SBA-15	NH3	303 K	400	0.1			[97]
Polystyrene	Primary	263 K, dry cold conditions	400	0.8		IR	[36]
Polystyrene	Primary	298 K, fully humidity conditions	400	0.89		IR	[36]
Mesoporous alumina	3-aminopropyltriethoxysilane (APS)	298 K	400	0.15–0.75			[98]
Mg2(dobpdc)	Ethylenediamine (ED)	298 K	390	2.83			[99]
Mg2(dobpdc)	Hydrazine (H_2N_4)	298 K	400	3.89			[100]
Cr-MIL-101-SO3H	Tris(2-aminoethyl)amine (TAEA)	298 K	400	1.12			[101]
Mg/DOBDC	Ethylenediamine (ED)	298 K	400	1.5			[102]

A mesoporous alumina support functionalized by APS has been analyzed in Potter et al. [98] and a CO_2 uptake in the range of 0.15–0.75 molCO_2/kg, according to the amine loading, was measured.

On the other hand, good results were obtained in the work of Lu et al. [96], whose sorbent has great potential to be used in direct air capture technology. The sorbent was PPN-6-CH_2DETA, with a CO_2 uptake of 1.04 molCO_2/kg and an extraordinarily high CO_2 selectivity (3.6×10^{10}). The authors affirmed that low costs could be achieved with this kind of sorbent due to its particular properties.

High CO_2 adsorption capacities were also obtained in the work of Belmabkhout et al. [88], where a TRI-PE-MCM-41 sorbent was suggested (MCM-41 silica with the surface functionalized by a triaminesilane (TRI-PE)). CO_2 was removed from dry and humid air at different CO_2 concentrations. At 298 K, at 400 ppm and 300 ppm of CO_2, adsorption capacities were, respectively, 0.98 molCO_2/kg and 0.9 molCO_2/kg. Moisture had a positive effect on capture. In fact, for the last concentration, a relative humidity of 26% and 67% allowed uptakes of 1.19 molCO_2/kg and 1.4 molCO_2/kg, respectively.

The same support functionalized by a diethylenetriamino organosilanes (DT) amine was used in Wagner et al. [89], allowing, for the simulated air, capacities up to 0.61 molCO_2/kg at 303 K, while lower temperatures ensured an uptake of 1.16 molCO_2/kg. Moreover, in their experiments, the authors found that a decrease in the sorbent's capacity was due to the formation of urea groups, while reactions with atmospheric trace gases or oxygen were neglected.

MOF supports, highly crystalline materials with large surface areas and diverse structures, have also been investigated. In Lee et al. [99], Mg_2(dobpdc) functionalized with ethylenediamine achieved a CO_2 uptake of 2.83 molCO_2/kg. A good stability was obtained during adsorption/desorption cycles; this sorbent is promising for CO_2 capture, with an ultrafast CO_2 adsorption rate when compared with porous materials. The results showed that the adsorption of CO_2 onto this amine led to the formation of carbamic acid and not carbamate.

In Liao et al. [100], the previous amine was replaced by hydrazine (H_2N_4), increasing the adsorption capacity to 3.89 molCO_2/kg. This high CO_2 adsorption capacity, even at low pressure, was due to the ultrahigh concentration of amine groups and the chemisorption of CO_2 associated with carbamic acid formation. Moreover, these good performances could be conserved under mixed gas kinetic conditions and with humidity.

Another MOF, Mg/DOBDC (magnesium dioxybenzenedicarboxylate), modified with ethylenediamine (ED), has been analyzed in Choi et al. [102], ensuring a CO_2 uptake of 1.5 molCO_2/kg after four regeneration cycles. This value was constant after adsorption/desorption cycles.

In Darunte et al. [86], a MIL-101(Cr) material functionalized with tris (2-amino ethyl) (TREN) has been evaluated to capture CO_2 from simulated air. The results showed a CO_2 uptake of 0.35 molCO_2/kg; the sorbent is not suitable for direct air capture systems. Similar results were obtained by Hu et al. (2014) using MIL-101(Cr) loaded with smaller amine molecules, such as DETA and DADPA. The authors found that these sorbents are more suitable for CO_2 capture from flue gas or for CO_2/N_2 separation, thanks to the mild regeneration energy.

In order to improve performances, Li et al. [101] developed a new method based on the Brønsted acid–base reaction to tether alkylamines into Cr-MIL-101-SO_3H for CO_2 capture. The new sorbent was functionalized with tris(2-aminoethyl)amine (TAEA), allowing a CO_2 uptake of 1.12 molCO_2/kg.

An interesting study has been carried out by Elfving et al. [36], considering a polystyrene sorbent functionalized with a primary amine. The analysis was developed in real conditions, such as low partial pressure, low temperature (similar to temperatures in Finland, 273 K and 263 K) and presence of humidity. The results showed that the highest CO_2 uptake (1.06 molCO_2/kg) was achieved at 263 K with humidity.

Class III Amine-Functionalized Sorbents

A few works about class III amine-functionalized sorbents have been published, as shown in Table 4 [18,103–105]. Among these, Chaikittisilp et al. [104] studied, for the first time, a poly(l-lysine) brush–mesoporous silica hybrid to capture CO_2 from the air, under dry conditions at ambient temperature. Comparing the results with other functionalized amine sorbents, they found that the investigated sorbent had a CO_2 capture capacity of 0.6 molCO_2/kg, higher than that of PEI–SBA-15 (0.32 molCO_2/kg) and dimethylamine (DMA)–SBA-15 (0.19 molCO_2/kg), with a slightly higher amine loading. The sorbent was robust during short regeneration tests.

Good performances have been reported in the work of Choi et al. [103], considering hyperbranched aminosilica (HAS) sorbents, for a simulated humidified air with 400 ppm of CO_2. The authors found that, by increasing the amine loading from 2.3 mmolN/g to 9.9 mmolN/g, the CO_2 adsorption capacity increased from 0.16 molCO_2/kg to 1.78 molCO_2/kg. CO_2 was captured reversibly without a significant degradation of performances in short, multicyclic operations.

Functionalized polysilsesquioxane-based hybrid silica materials were studied by Abhilash et al. [105], showing an adsorption capacity of 1.68 molCO_2/kg. Moreover, the authors found a good recycling capability without efficiency losses after 50 cycles of adsorption/desorption in ambient air.

Other sorbents have been proposed and investigated for class III. Diethylenetriamine (DETA) supported on CB-N-g-PCMS-OH^- was obtained from the polymerization of nitrene and showed a CO_2 uptake of 0.14 molCO_2/kg with 95% relative humidity [18].

Faster absorption and desorption rates were obtained using a CB-g-xPCMS-OH^- support (8.6×10^{-3} m^{-1}), although the CO_2 adsorption capacity was the same [18]. These two previous supports were in carbon black functionalized with atom transfer radical polymerization (ATRP) initiators.

Inverse templating is another method used to prepare highly porous polymeric structures [18]. PS-CC and colloidal crystals were functionalized by DETA with a CO_2 uptake of 0.57 molCO_2/kg and 0.36 molCO_2/kg, respectively.

High internal phase emulsion (HIPE)-based materials have also been investigated, achieving an adsorption capacity of 0.5 molCO_2/kg and 0.72 molCO_2/kg [18].

An alternative sorbent of class III has been proposed by Lunn and Shantz [106]. The material was based on the polymerization of Z-protected L-lysine N-carboxyanhydride on an aminopropyl-functionalized SBA-15 support. This approach resulted in polymer brushes tethered to the oxide surface within the mesoporous silica network, yielding a hybrid aminosilica rich in primary amine groups.

Table 4. Class III amine-functionalized sorbents.

Support	Amine	Conditions	Con. CO_2 (ppm)	Adsorption Capacity ($molCO_2/kg_{sorbent}$)	CO_2:N	Method	Reference
CB-N-g-PCMS-OH−	Diethylenetriamine (DETA)	288 K, 95% relative humidity	400	0.14		IR	[18]
CB-gxPCMSOH−	Diethylenetriamine (DETA)	288 K, 95% relative humidity	400	0.14		IR	[18]
PS-CC	Diethylenetriamine (DETA)	288 K, 95% relative humidity	400	0.57		IR	[18]
Colloidal crystal	Diethylenetriamine (DETA)	288 K, 95% relative humidity	400	0.36		IR	[18]
HIPE	Diethylenetriamine (DETA)	288 K, 95% relative humidity	400	0.5		IR	[18]
Pick-20%−silica-2%	Diethylenetriamine (DETA)	288 K, 95% relative humidity	400	0.72		IR	[18]
Mesoporous silica SBA-15	Aziridine	298 K	400	1.78			[103]
SBA-15	Poly(L-lysine)	298 K	400	0.6	0.12	TGA	[104]
Hybrid silica material	3-aminopropyl triethoxysilane (APTMS)	303 K, humidity	400	1.68			[105]

2.3. Comparison between the Absorption and Adsorption Processes

A comparison between adsorption and absorption can be considered. Adsorption technology is characterized by a high modularity and small capture facilities, cyclic steps based on the variation of temperature or pressure or their combination, problems due to the sorbent degradation impacting on costs. However, low energy inputs with low regeneration temperatures can be provided by a low-grade heat, allowing an integration with waste and/or renewable heat. On the other hand, absorption has a higher complexity for the regeneration system, although it works continuously with the absorption cycle and requires a high temperature for regeneration, which is supplied by a high-grade heat source. In the absorption process, packed columns or spray towers are used as air contactors, while, in the adsorption systems, contactors of monolithic, fluidized bed, fixed bed and moving bed designs have been proposed [39]. In addition, while in the adsorption process, water is a by-product, in the absorption system, water is removed and then lost before the calcination step. Another point of comparison for the two technologies is the number of interactions between the solvent/sorbent and CO_2. For the absorption, the solvent may be present up to 30 %wt, limiting the number of interactions with CO_2. On the other hand, for the adsorption, the base is chemically bound on the sorbent such that it is more contained and can therefore be loaded at a much higher weight percent, thereby increasing the number of interactions with CO_2. Another difference between absorption and adsorption is how the material (solvent/sorbent) is packed in the air contactor. In the first case, the solvent flows inside a structured packing material with channel sizes large enough to allow the flow of the liquid but small enough to create sufficient surface area to maximize the number of interactions between CO_2 and the solvent. On the other hand, in the second case, solid sorbents have micro- and mesopores that allow the maximization of surface area and facilitate transport, respectively. As an additional point of comparison, the solvent has a CO_2 loading of about one order of magnitude lower than the sorbent because this last has a higher contact area.

2.4. Ion-Exchange Resin

Ion-exchange resin technology based on moisture swing adsorption was proposed by Lackner [107] to capture CO_2 from the air, providing a solution to the high regeneration costs of amine-functionalized sorbents and replacing the thermal and pressure swing processes. This technique is also known as "artificial trees" because it simulates the process of CO_2 capture from the air as trees do in nature [3]. Essentially, Lackner presented an amine-based exchange resin dispersed on a flat sheet of polypropylene that is able to capture CO_2 when it is dry and release CO_2 when it is wet. Solid resins have the advantages of low degradation rates and fast kinetics, receiving attention for CO_2 capture [108].

Many moisture-swing sorbents are strongly basic ion-exchange resins with quaternary ammonium ions (NR_4^+) acting as a strong base, analogous to Na^+ ions in aqueous solutions. Cations are balanced by anions present in the matrix, such as carbonate (CO_3^{2-}), bicarbonate (HCO_3^-) and hydroxide ions (OH^-). The relative amounts of these anions depend on the amount of CO_2 and moisture, as shown in Figure 7.

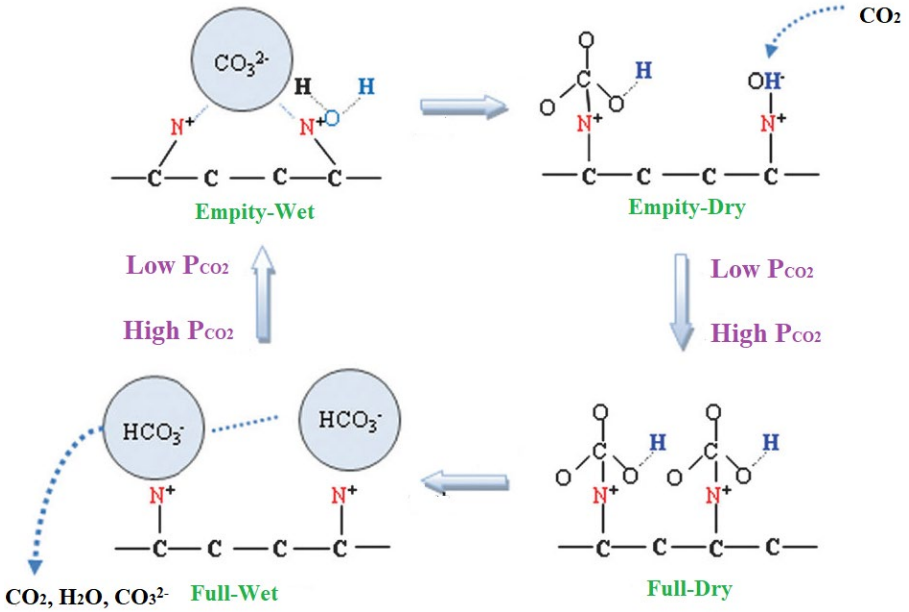

Figure 7. Reaction scheme of CO_2 adsorption/desorption for an anion-exchange resin. Adapted from [109].

In the empty–wet condition, the resin is wet but without CO_2 loading. In this case, positive quaternary ammonium ions are balanced by carbonate ions that are stabilized by the presence of water. In the following step, during the drying, the water content is reduced so that carbonate ions are unstable and cause the splitting of the remaining water to form bicarbonate ions and OH^- ions (empty dry state). OH^- has a strong affinity with CO_2, so that by increasing the loading of CO_2, ions of HCO_3^- are obtained, allowing the capture of CO_2 from the air. In this condition, the resin is completely bicarbonate (fully dry state). After that, by injecting moisture, the resin is wetted; therefore, two HCO_3^- ions react to produce CO_3^{2-}, H_2O and CO_2. This state is called full–wet and after the reaction CO_2 is released (desorbed), resulting in the empty–wet state. The cycle can restart again. During these cycles, the moisture can be provided as liquid water or water vapor in air, and it is estimated that 12–37 mole of water are needed per mole of CO_2 [109,110].

The main reactions involved in this capture technique are the following [111] (see Equations (19)–(22)):

$$H_2O \leftrightarrow H^+ + OH^- \quad (19)$$

$$CO_3^{2-} + H^+ \leftrightarrow HCO_3^- \quad (20)$$

$$OH^- + CO_2 \leftrightarrow HCO_3^- \quad (21)$$

$$HCO_3^- + HCO_3^- \leftrightarrow CO_3^{2-} + CO_2 + H_2O \quad (22)$$

There are several advantages to moisture swing adsorption, such as the following:

- The use of water as an energy source for the adsorption and desorption stages reduces energy costs due to a low energy consumption of about 50 kJ/molCO_2 [107];
- Absorbed water and CO_2 on the sorbent moves in opposite directions: energy penalties for the absorption and desorption of water are completely eliminated (for other sorbents, water binds more strongly than CO_2, and, considering that it is present at concentrations 10–50 times higher than those of CO_2, there is a high energy penalty for desorbing water and CO_2);
- Heating and cooling of sorbents are avoided;
- Higher efficiencies can be obtained by introducing temperature and pressure variations.

However, one disadvantage is that performances are highly weather- and geography-dependent [3]. Moreover, the used water must be relatively clean to avoid contamination

with the resin (contaminations can be minimized by using vapor water instead of liquid water). Another disadvantage is that a huge amount of water is required: 10 Gton of CO_2 could need about 100 km^3 of water, while world water consumption is 3600 km^3 [112]. In addition, the output stream is characterized by low CO_2 purity and CO_2 at a partial pressure of about 8 kPa. This low value suggests integration with utilization processes, such as algae production for biofuel and enhanced mineral carbonation, or the need of additional compression steps for other CO_2 utilization and storage options [109]. Moreover, the process is actually limited to theoretical conceptualization and laboratory scale prototypes [113].

Few works have been presented in the literature about this way of capturing CO_2 from the air. Wang et al. [109] provided a thermodynamic analysis and found that the Langmuir isothermal model describes the process better. Molecular dynamics (MD) and quantum mechanics (QM) are the methodologies used by Shi [111], which are said to allow better comprehension of this technology. The influences of pore size, spacing of cations, surface hydrophobicity and temperature on CO_2 capture efficiency were there elucidated. Yang et al. [114] studied moisture swing adsorption with the nuclear magnetic resonance (NMR) technique, finding that CO_2 is adsorbed at a low humidity, but these results are questionable because their data were taken below the freezing point of water.

2.5. Electrochemical Method

The first application of an electrochemical method was in the early 1970s to capture CO_2 in spacecraft cabins [115,116]. In Wynveen et al. [115], the system was able to capture 1.9 $kgCO_2$/day without signs of deterioration after 260 days of working. Other studies have been reported in Winnick et al. [117] and Kang et al. [118], considering a molten carbonate fuel cell at high temperatures.

Substantially, in this method, CO_2 is captured using electrochemical reactions and an electrochemical cell operating in a fuel cell mode if electricity is provided or in a driving mode if electricity is consumed [119]. A fuel cell concentrator has been suggested by Eisaman [23], as shown in Figure 8. In this system, hydrogen is used as the energy source to capture CO_2 and release it at a higher concentration. In addition, a filter-paper membrane is sandwiched between two gas diffusion electrodes (coated with carbon particle-support platinum catalyst) and is wetted by an electrolyte solution (a room-temperature ionic liquid) to support the transfer of ions between the electrodes, electrically connected with a variable resistive load. The stainless-steel current collector plates of the anode and cathode serve as gridded gas flow fields that deliver gases at known flow rates to the electrodes: H_2 at the anode and a combination of N_2, O_2 and CO_2 at the cathode. In the process, the cell temperature is kept at 298 K by using cooling water.

The reactions that occur at the anode side are the following (see Equations (23)–(25)):

$$H_2 \rightarrow H^+ + 2e^- \tag{23}$$

$$HCO_3^- + H^+ \rightarrow H_2O + CO_2 \tag{24}$$

$$CO_3^{2-} + 2H^+ \rightarrow H_2O + CO_2 \tag{25}$$

while at the cathode side the following reactions occur (see Equations (26)–(28)):

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow OH^- \tag{26}$$

$$CO_2 + OH^- \rightarrow HCO_3^- \tag{27}$$

$$HCO_3^- + OH^- \rightarrow H_2O + CO_3^{2-} \tag{28}$$

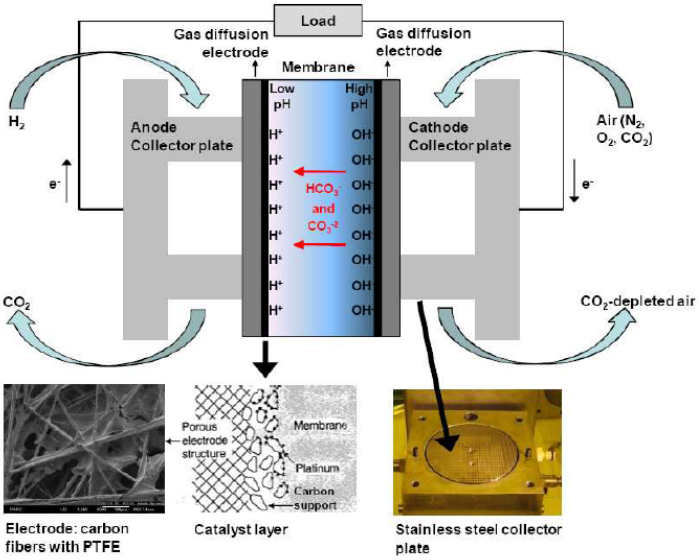

Figure 8. Fuel cell concentrator scheme. Reproduced under the techconnect license [23].

Essentially, the CO_2 provided at the cathode side reacts with OH^- to form bicarbonate (HCO_3^-) (Equation (27)) and carbonate (CO_3^{2-}) ions (Equation (28)). After the diffusion of carbon ions at the anode side, these react with H^+ to produce more concentrated CO_2 and water.

The Faradaic efficiency (the number of CO_2 molecules transferred over the total number of electrons transferred) and the energy consumption are, respectively, 23% and 350 kJ/molCO_2 [119].

Some disadvantages are present for this technology. As it is possible to see, the application of the electrochemical approach to CO_2 capture from the air has high energetic costs to deliver a large amount of air to the cell, due to the low CO_2 concentration, limitations in applicable current density and difficulties in generating a pure CO_2 stream [119]. However, some advantages of this methodology are the possibility of separating CO_2 in a single step; the continuous development; the lack of energy waste during the heating of the solvent or pressuring a gas feed, respectively, in the absorption and adsorption processes; the modularity able to capture CO_2 at different scale; and integration with a future electrified industry.

Other studies have investigated the electrochemical approach. In recent years, Voskian and Hatton [120] have suggested a new kind of electrochemical method to capture CO_2 from the air or other gases, based on passing these on electrochemical plates working in charging and discharging modes and forming an interesting battery. The process is known as Faradaic electro-swing reactive adsorption for CO_2 capture. It works as an electro-swing adsorption (ESA) process; a schematic representation is shown in Figure 9. The cell is composed of two cathode electrode substrates coated with a CO_2-binding quinone–carbon nanotube (Q-CNT) composite, sandwiching an anode electrode substrate coated with a ferrocene–carbon nanotube (Fc-CNT) composite, with separator membranes between the electrodes. The first one can capture CO_2 through a redox reaction via carboxylation of quinone, while it can release CO_2, reversing the polarity. On the other hand, the electrode with ferrocene acts as an electron source and sink for quinone reduction and oxidation, respectively, to regulate the uptake and release of CO_2. A room-temperature ionic liquid on the electrode substrates allows the passage of ionic currents through the electrolyte for the activation and deactivation of the electrodes and the diffusion of CO_2 into the electrolyte-wetted cathode during the capture. Any reactions between quinone and oxygen (causing the oxidation of reduced quinones) are avoided by tuning the electron density of the quinone polymer.

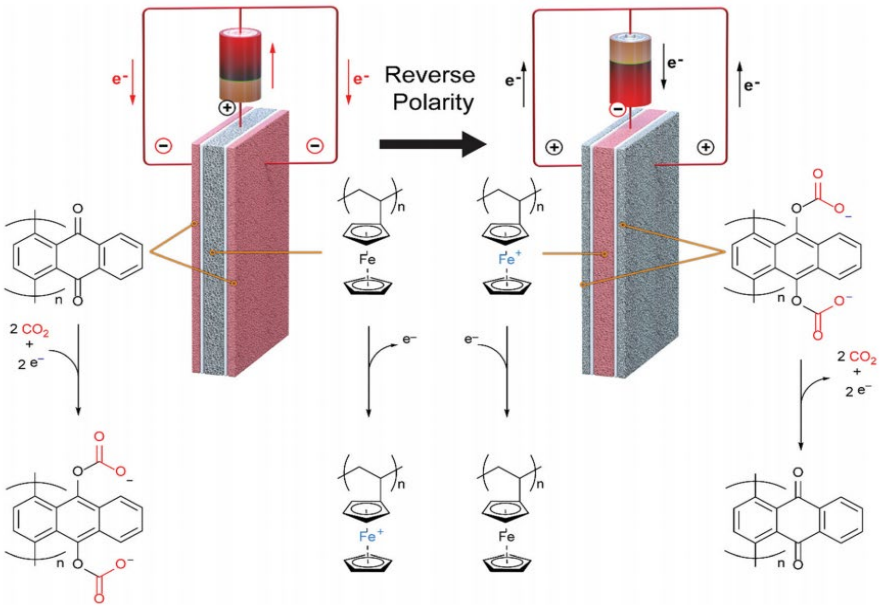

Figure 9. Schematic of a single electro-swing adsorption electrochemical. Reproduced under the Creative Commons attribution noncommercial 3.0 unported licence [120].

During the battery charging, when electricity runs into the battery, an electrochemical reaction occurs at the surface of each electrode, which, with high natural affinity for CO_2, capture this gas. During the battery discharging, CO_2 is released. The particularity of this system is the binary nature of the electrode affinity to CO_2, depending on the charging or discharging mode. In fact, electrodes have a high affinity and no affinity to CO_2 if these are in the charging or discharging phase, respectively.

The suggested system eliminates parasitic energy losses by using redox carriers, ensuring a Faradaic efficiency higher than 90% and with an energy consumption of 40–90 kJ/molCO_2 for CO_2 molar concentrations between 0.6% and 10%. The authors plan to develop a pilot-scale plant within a few years and estimate a cost between USD 50 and USD 100 per ton of CO_2 captured.

Among electrochemical methods, an interesting suggestion has been proposed by Shu et al. [121], demonstrating experimentally simultaneous alkaline solution regeneration and CO_2 desorption using an H_2 recycling electrochemical cell. As shown in Figure 10, the process is based on an H_2-recycling electrochemical system (HRES) connected to a membrane contactor. The HRES is composed of three compartments: an anode, an "acidifying" and a cathode compartment. During the operation, protons (H^+) are obtained through the H_2 oxidation at the anode and are transported towards the "acidifying" compartment that is also fed by the spent solution coming from the air contactor, decreasing the pH and converting (bi)carbonate ions into carbonic acid. Once the solution is saturated with carbonic acid, a further pH decrease allows the desorption of CO_2, for which gas–liquid separation occurs in the membrane contactor. On the other hand, the alkaline solution is regenerated at the cathode side due to the production of OH^- and is sent again to the air contactor. The authors find that the experimental energy consumption was 374 kJ/molCO_2, while 164 kJ/molCO_2 was obtained in a simulation of the system.

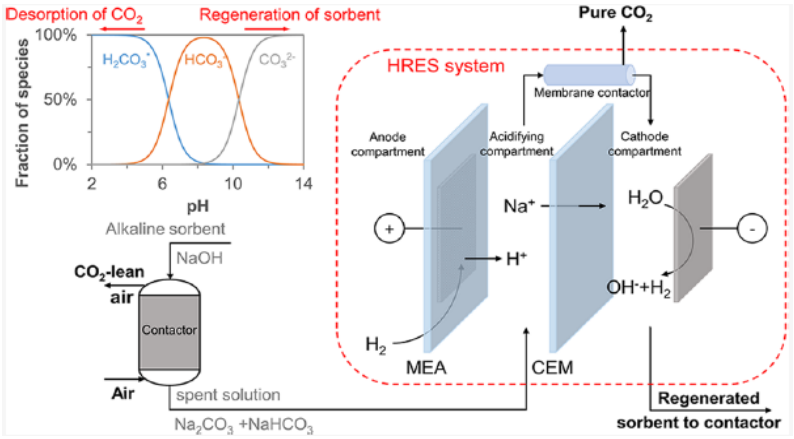

Figure 10. Scheme of the experimental process (MEA = membrane electrode assembly, CEM = cation exchange membrane). Reproduced under the ACS AuthorChoice/Editors' Choice via CC-BY-NC-ND Usage Agreement [121].

Nevertheless, the electrochemical approach requires more studies and development.

2.6. Electrodialysis

The electrodialysis methodology using a bipolar membrane electrodialysis (BPMED) stack has been described in the literature for CO_2 capture from the air, although it has not been deployed at industrial or even at pilot scale yet. A process scheme for CO_2 capture based on this technology was proposed by Sabatino et al. [22], as in Figure 11. CO_2 is captured from the air through an air contactor using an aqueous solution of KOH. In this capture reaction, K_2CO_3 and $KHCO_3$ are produced, present in waste as K^+ and CO_3^{2-}/HCO_3^-. The regeneration of KOH solution is carried out using a bipolar membrane electrodialysis stack, the scheme for which is shown in Figure 12.

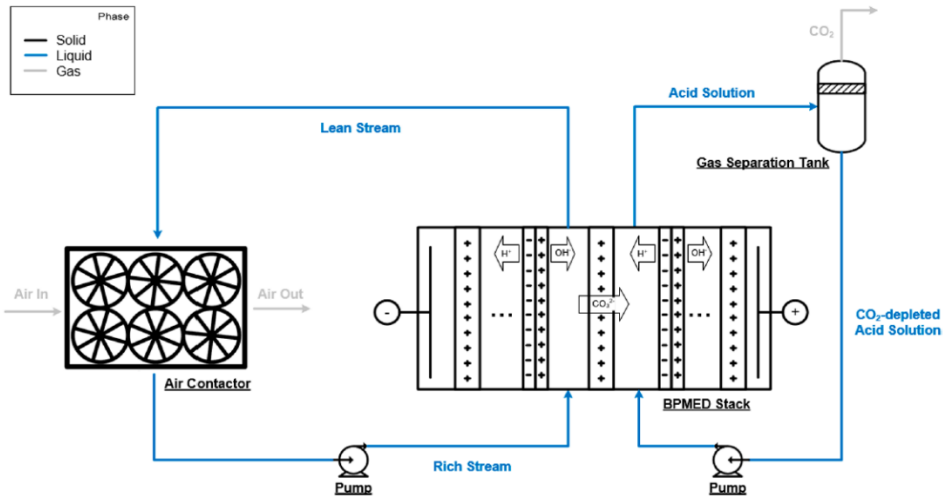

Figure 11. Process scheme for CO_2 capture from the air using bipolar membrane electrodialysis. Reproduced under the ACS AuthorChoice/Editors' Choice via CC-BY-NC-ND Usage Agreement [22].

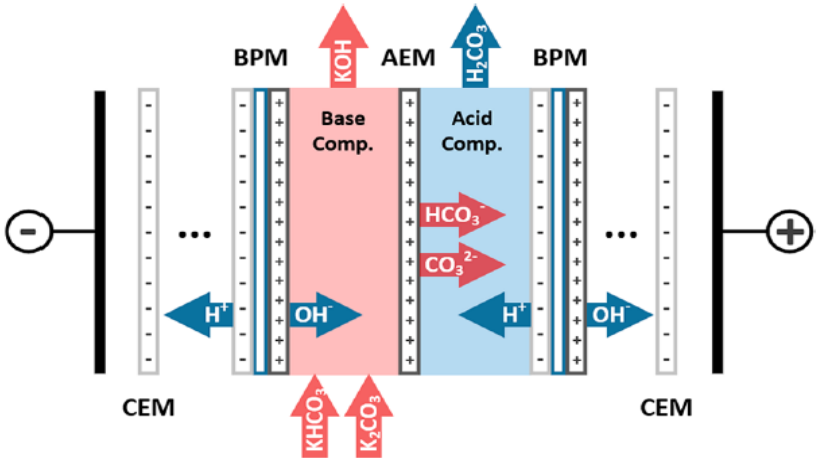

Figure 12. Configuration of BPMED cell (AEM = anion-exchange membrane, CEM = cation exchange membrane, BPM = bipolar membrane). Reproduced under the ACS AuthorChoice/Editors' Choice via CC-BY-NC-ND Usage Agreement [22].

The cell is divided by an anion-exchange membrane (AEM) into acidic and basic comportments: the stream with K_2CO_3 and $KHCO_3$ is sent to the basic comportment, while into the acid comportment a buffer solution flows. At the extremity, the bipolar membrane (BPM) has cation-exchange and anion-exchange layers with ion-selective properties. When an electric current is passed through them, BPMs splits water in H^+ and OH^-, and in the basic comportment K^+ and OH^- react to form KOH (see Equation (29)) [22].

$$K^+ + OH^- = KOH \tag{29}$$

The CO_2-based ions diffuse through the AEM to the acid compartment, where they react with H^+ to produce dissolved carbon dioxide (see Equations (30)–(31)) [22].

$$CO_3^{2-} + H^+ = HCO_3^- \tag{30}$$

$$HCO_3^- + H^+ = H_2CO_3 \tag{31}$$

The CO_2 solubility in the acid solution is low, then bubbles are generated so that the biphasic solution is sent to a vessel to separate the gaseous CO_2 from the acid buffer solution. In this way, pure CO_2 is released, while the CO_2-depleted acid stream is re-pressurized and sent to the electrodialysis unit. On the other hand, the aqueous solution of KOH, the lean stream, is sent to the air contactor.

The authors considered a techno-economic analysis of the process, finding an energy consumption of 236 kJ/molCO_2 and a cost of 773 \$/tonCO_2, (the bipolar and ion-exchange membranes have the highest cost). In the economic analysis, a membrane lifetime of 5 years was supposed, with an area of 1.785 m^2 and 2400 cells. The electricity cost was fixed to 0.06 \$/kWh, while the stack unit costs 0.75 M\$/unit and the anion-exchange membrane costs 70 \$/m^2 and the BPM 750 \$/m^2. From these results, it is evident that this new proposed regeneration method requires an amount of regeneration energy (that is only electrical energy) lower than that of the Carbon Engineering plant and avoids solid handling but has higher costs (about three time more expensive than the Carbon Engineering plant).

The authors suggested that other studies should be focused on optimizing the electrolyte compositions, aiming to decrease the transport losses in the system and provide more insights into the reaction kinetics.

Other works in the literature have investigated this technology. An integration of this kind of system in a process for producing methanol by exploiting the electrical energy produced by photovoltaic panels has been suggested in Smith et al. [122]. Bipolar membrane electrodialysis has also been analyzed in the work of Eisaman et al. [23], suggesting a high-pressure, high-current density operation with an optimum pH controller in order to reduce

energy consumption. The required energy for CO_2 capture from the air was estimated to be 62 kJ/molCO_2, with 85% current efficiency and 100 mA/cm^2. Overall, research and development are continuing to allow the implementation of this technology at an industrial scale.

2.7. Additional Technologies for CO_2 Capture from Air

In this section, other technologies for CO_2 capture from the air are described. These include membrane separation, carbon mineralization, photocatalysis and cryogenic separation.

A few studies have been reported about membrane separation for CO_2 capture from the air, although they are promising for CO_2 separation from more concentrated sources [38,123,124]. Keith et al. [45] reported that a DAC based on membrane is implausible due to the very low driving force (the driving force for CO_2 permeation from the air is about 40 kPa, three to four orders of magnitude lower than that required for a capture that is economically feasible) and large volume of sweep gas that is required. Another disadvantage is the trade-off between permeability and selectivity, limiting the general utility, especially when high performances are needed. In the work of Jindaratsamee et al. [123], an amine liquid membrane with several glycol compounds was considered to capture CO_2 from the air, evaluating the effect of membrane durability, amine concentration and the molecular structure of amine compounds on CO_2 permeability. Diffusion phenomena were described in the work of Rahaman et al. [38]: N_2 gases have a solution–diffusion mechanism, while CO_2 gases have a facilitated transport mechanism. Moreover, considering a membrane with 6% of PEI, the authors found a great CO_2/N_2 selectivity (about 300). A simulation has been developed in Fujikawa et al. [124]. Three stages of a polymeric membrane were used to concentrate CO_2 from 0.04% to 40%, with a competitive energy consumption (14.2 kWh/kgCO_2/day). Other studies showed that high-performance materials (not commercialized and inorganic) could achieve a CO_2 concentration of 12% in a single stage and up to 99% with two stages [39]. However, the costs of systems with two stages were estimated to be in the order of 1000–10,000 \$/tonCO_2, with an energy consumption of about 10 GJ/tonCO_2.

In mineral carbonation or mineralization, metal oxides (mainly CaO and MgO) present in geological formations, such as "ultramafic rocks" (mainly olivine, serpentine, brucite and/or wollastonite), react with atmospheric CO_2 to produce thermodynamically stable mineral carbonates, resulting in a permanent form of CO_2 storage [18]. This is an irreversible chemical reaction, ensuring storage of CO_2, as described in the following reactions (see Equations (32)–(36)) [24]:

$$CaSiO_3 + CO_2 \leftrightarrow CaCO_3 \quad (32)$$

$$Mg_sSiO_4 + 2CO_2 \leftrightarrow 2MgCO_3 + SiO_2 \quad (33)$$

$$CaMgSi_2O_6 + 2CO_2 \leftrightarrow CaMg(CO_3)_2 + 2SiO_2 \quad (34)$$

$$Mg_3Si_2(OH)_4 + 3CO_2 \leftrightarrow 3MgCO_3 + 2SiO_2 + 2H_2O \quad (35)$$

$$Mg(OH)_2 + CO_2 \leftrightarrow MgCO_3 + H_2O \quad (36)$$

Overall, these are thermodynamically favored and natural spontaneous reactions that occur during weathering, according to which CO_2 in air reacts with Mg^- and Ca^- rich rocks to produce solid carbonates. This technology is called weathering and occurs slowly on a geological time scale [125]. The benefits of this capture route were suggested by Neeraj and Yadav [126] and Dabirian et al. [127] as the following: its being environmentally safe, the exothermic reactions reducing energy consumption, the abundance of feedstock, permanent CO_2 storage, no monitoring requirements, the generation of products that are thermodynamically stable and large potential sequestration capacity (CO_2 uptake values: 0.62 tons of CO_2/ton of olivine, 0.76 tons of CO_2/ton of brucite and ~0.4 to 0.5 tons of CO_2/ton of pyroxene, serpentine and wollastonite [24]). On the other hand, the main disadvantage of this capture route is that the process is very slow, such that many methods have been proposed to accelerate it [18].

The photocatalytic process uses an engineered photocatalyst to artificially mimic photosynthesis and reduce CO_2 into solar fuels, increasing overall process efficiency. Photocatalysts are semiconductors with a relatively low bandgap energy. By providing electromagnetic radiations, such as solar energy, with an energy equal or higher than that of the bandgap, valence electrons are excited into the conduction band, creating positively charged holes in the valence band. The promoted valence electrons are able to reduce atmospheric CO_2 to valuable fuels. On the other hand, holes in the valence band promote the oxidation of water, generating H_2 [18]. A deep description of the photocatalytic process has been provided in Adamu et al. [26]. Limitations of this route include the following: low yield, low selectivity, the use of batch photoreactors with low surface area–volume ratio and poor mixing systems, as well as present economic non-feasibility [18].

Cryogenic separation is a physical process that separates CO_2 under extremely low temperatures (about −160 °C at 400 ppm). A scheme for cryogenic separation is shown in Figure 13 [25]. In this process, ambient air enters the unit (point 1) and is cooled in a precooler stage (point 2). The cooled stream (point 3) enters a CO_2 deposition chamber (point 4), where additional cooling takes place. This additional cooling is performed by a cryogenic refrigeration cycle. After CO_2 deposition, the bulk of the air (point 5) is cycled back through the precooler (point 6), where it absorbs thermal energy from the incoming ambient air before being exhausted (point 7). The precooler is composed of two functional components: a heat exchanger and a radiative cooler to further remove heat from the ingested air. A disadvantage is that the cryogenic separation is expensive due to the very low temperature needed for refrigeration, requiring about 10–100 GJ/tonCO_2—a value higher than other methods [45]. However, this technology can achieve percent of capture (about 99.99%) and purity (99.99%) levels higher than those of other processes without requiring additional chemicals, and the obtained CO_2 is suitable for geological storage [39].

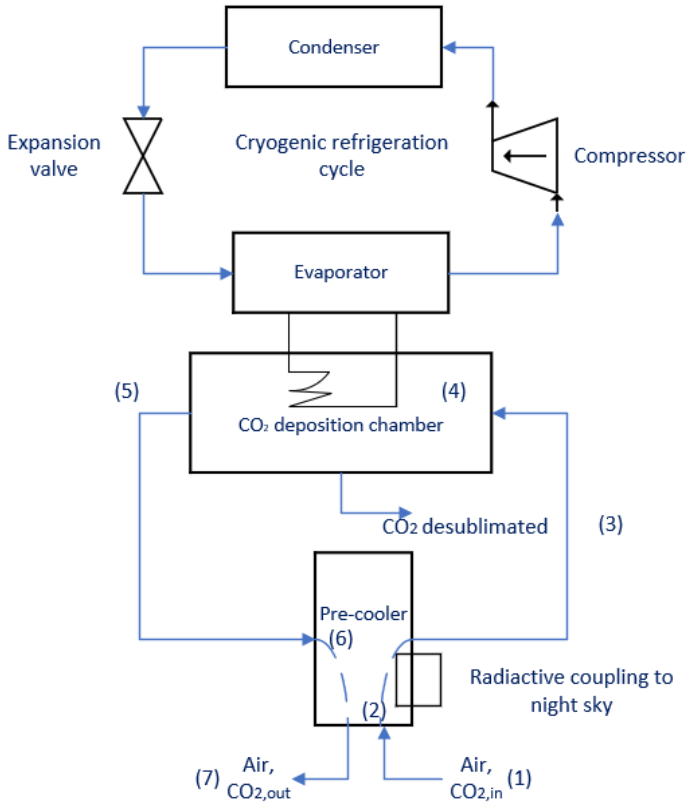

Figure 13. CO_2 cryogenic separation process scheme. Adapted from [25].

3. DAC Companies

Several companies have developed direct air capture technology, such as Carbon Engineering, Climeworks, Global Thermostat, Hydrocell, Skytree and Infinitree.

Carbon Engineering is a Canadian company led since 2009 by David Keith, a professor at Harvard University [3]. The company's approach is based on the use of absorption technology with KOH aqueous solution, as shown in Figure 4 and discussed in Section 2.1. It is the only solvent-based company in the market. Carbon Engineering constructed the first pilot plant in British Columbia (Canada) in 2015, and spent the years between 2019 and 2021 constructing and designing a demonstration DAC plant. Currently, they have a commercial plant under construction in Parmian Basin (TX, USA), as shown in Figure 14, which has a capture capacity of 1 MtonCO_2/year, the captured CO_2 being used for enhanced oil recovery [128].

Figure 14. Carbon Engineering plant in *Texas*. Reproduced under a Creative Commons license [34].

The main features of this process are the air contactor design (instead of the convectional absorption column) and the pellet reactor (instead of a convectional precipitator). The first is an open-air contactor with a cross-flow and slab geometry: the aqueous solution flows downward along the PVC structured packing, while air is pushed horizontally and orthogonally to the solution with a velocity of 1.3 m/s, in order to achieve a trade-off between the operative (fan power) and capital (size of absorber) costs. The overall configuration differs from that of traditional closed counter-flow towers and reduces the total cost. The pellet reactor is used instead of the traditional precipitator, and $CaCO_3$ pellets are suspended in a solution flowing upward, while a slurry made of 30% $Ca(OH)_2$ is fed at the bottom. In this way, $CaCO_3$ pellets, rather than lime mud, are able to precipitate, reducing energy consumption and increasing the thermal efficiency to 78% [3]. Since the process uses natural gas for heating (the regeneration temperature is set to 1173 K), 0.48 tons of CO_2 are released per ton of captured CO_2 and are captured in a following step. The purity of the obtained CO_2 is 97.1% [129].

Another process was proposed by Carbon Engineering; it is called "thermo-catalysis". In this process, which will be used in the future, the captured CO_2 reacts with renewable hydrogen obtained by water electrolysis to produce synthetic fuels, such as gasoline, diesel and jet fuel [130]. A pilot plant for this kind of process is located in Squamish, British Columbia (Canada). Moreover, the company is proposing a purely electrical process, in which high-temperature electrical heating will provide thermal energy for calcination [49].

Another important company is Climeworks, a Swiss company that is a spin-off of ETH Zurich, founded by the engineers Christoph Gebald and Jan Wurzbacher in 2009 [3,49]. The company developed their first prototype in 2013. Currently, they have the first commercial plant in the world, located in Hinwil (Switzerland), with a capture capacity of 900 tonCO_2/year. In contrast to that of Carbon Engineering, the plant is scalable and modular, and it consists of a single collector that is able to capture 135 kgCO_2/day, as in Figure 15 [3,131].

Figure 15. The Climeworks plant in Switzerland. Reproduced with permission granted by Climeworks AG [131].

Climeworks uses an amine-functionalized sorbent of class II, such as the 3-aminopropy lmethyldiethoxysilane (APDES), loaded onto nanofibrillated cellulose (NFC) (APDES-NFC-FD) (Wurzbacher, 2015). Regeneration is achieved by temperature vacuum swing adsorption (TVSA) and at a temperature of 373 K, exploiting the waste heat from a local incinerator. A full cycle has a duration of 4–6 h [129]. The CO_2 obtained with a purity of 99.9% is used to supply a greenhouse.

Another commercial plant of this company is located in Hellisheidi (Iceland), called Orca, and it is able to capture and store CO_2 at 700 m underground, with a capacity of 4000 tonCO_2/year. The captured CO_2 is mixed with water and pumped underground, where, through mineral carbonation, it reacts with basalt rocks. For mineralization, Climeworks partners with the Iceland company Carbfix, an expert on rapid underground mineralization of CO_2. Renewable geothermal energy with a geothermal power plant is used for the regeneration stage of the adsorbent bed.

Climeworks has two pilot plants, one in Troia (Italy) and the other in Dresden (Germany) (Climeworks, 2020 [129]). In the first pilot plant, CO_2 is used to produce methane and captures up to 150 tonCO_2/year [132]. The pilot plant in Dresden is aiming to capture CO_2 to produce carbon-neutral fuels (mainly diesel), exploiting renewable energies for hydrogen production and creating a closed carbon cycle [129].

Overall, Climeworks has 14 pilot plants (with a net removal capacity of 2000 tonCO_2/year) across Europe, using renewable energy as an energy source and using the captured CO_2 for fuel, food and beverage production. This company aims to remove 225 MtonCO_2 (about 1% of total worldwide emissions) by 2025 [133].

Global Thermostat was founded by Peter Eisenberger, a professor from Columbia University in 2010 in New York (USA) [3]. This company has a pilot plant at the Stanford

Research Institute (SRI) International in Menlo Park (California) based on the adsorption process, as shown in Figure 16 [49]. As with Climeworks, the plant is modular, with a capacity of 1000 tonCO_2/year [134].

Figure 16. Global Thermostat plant [3].

The adsorption system uses an amine-functionalized sorbent of class I: an amino-polymer bonded on a porous ceramic honeycomb monolith structure [134]. The regeneration is based on temperature vacuum swing adsorption, using the residual heat from industry and has a desorption temperature of 358–368 K and a desorption pressure of 0.5–0.9 bar [129]. The full cycle has a duration lower than 30 min [129]. The plant produces CO_2 with a purity higher than 98.5% for global food and beverage companies. Global Thermostat has other pilot plants in Magallanes (Chile) and Oklahoma (USA), where the captured CO_2 is used for fuel production. In the future, they want to expand their technology into a facility capturing 1 MtonCO_2/year, with ExxonMobil as partner [133].

Hydrocell is a Finnish company founded in 1993 [135]. The process used by the company consists of a standard shipping container, fully portable, that is able to capture 1.387 tonCO_2/year. TVSA is used for regeneration, with a temperature range between 343 K and 353 K (the lowest value among the other systems considered) [129].

Skytree and Infinitree are additional small companies developing DAC technology, with, however, little information available on their operations. Skytree was founded in 2008 in Amsterdam (The Netherlands) as a spin-off of the European Space Agency [136]. The capture process is based on electrostatic absorption and moisturizing desorption at 353–363 K, exploiting low-grade heat [129]. This company's system is characterized by smaller modules compared to the systems of the previously discussed companies, and the captured CO_2 is used for algal growth enhancement in an aquarium.

The other small company, Infinitree, was founded in 2014 in Huntington, New York [137]. The capture process is based on moisture swing adsorption using an ion-exchange sorbent, with a capture capacity of 100 tonCO_2/year. As with Skytree, the CO_2 captured is used to enhance plant growth.

Overall, there are 19 plants operating worldwide, capturing 10,000 tonCO_2/year [40]. However, in order to meet the global goals defined in the international agreements (aiming at the removal of 1000 GtonCO_2 by 2100), it has been estimated that about 13,000 DAC plants with a capture capacity of 1 MtonCO_2/year are required [138].

4. Key Performance Indicators

The most important KPIs, such as thermal and electrical energy consumption, operating costs (OPEX) and capital costs (CAPEX) (or general total costs), land use, water demand, technology readiness level (TRL) and environmental impact, are analyzed in this section.

These KPIs are important because they are related to the potential development and realization of these processes. Energy consumption, costs, land use, environmental impact and water demand are all important factors in the construction of a plant and its operation.

Data about energy consumption in terms of thermal and electrical energies are provided in Table 5 for the main DAC companies described in Section 3. The Carbon Engineering company can achieve a thermal energy value of 366 kWh_{el}/tonCO_2.

Table 5. Energy consumption for the main DAC companies [129].

Company	Thermal Energy ($kWh_{th}/tonCO_2$)	Electrical Energy ($kWh_{el}/tonCO_2$)
Carbon Engineering	1458 (by natural gas)	366 (air separation unit for oxy-fuel + compressor + fan)
Climeworks	1500–2000 (by waste heat)	200–450 (fans + control)
Global Thermostat	1170–1410 (by steam)	150–260 (fans + control)

Energy consumption in DAC processes investigated in the literature has been reported on in the work of Fasihi et al. [49]. For the absorption process, thermal energy use is in the range of 1420–2450 $kWh_{th}/tonCO_2$ [34,41], while electrical energy use is in the range of 440–2790 $kWh_{el}/tonCO_2$ [37,139]. For the adsorption processes studied in the literature, on the other hand, thermal energy consumption is 1656 $kWh_{th}/tonCO_2$ in the work of Kulkarni and Sholl (2012), while 218 $kWh_{el}/tonCO_2$ is the required electrical energy level. Higher values of electrical energy are needed for adsorption with metal organic frameworks, such as the value of 1420 $kWh_{el}/tonCO_2$ reported in Sinha et al. (2017). Lower values of electrical energy are suggested in adsorption processes using ion-exchange resin: 316 $kWh_{el}/tonCO_2$ [107], 423–631 $kWh_{el}/tonCO_2$ [140] and 333 $kWh_{el}/tonCO_2$ [141].

Cost estimation presents a more difficult problem. Fuss et al. [8] estimated a DAC cost of up to 1000 $/tonCO_2$, this could decrease to 100–300 $/tonCO_2$ in 2050, while House et al. [29] suggested a range of 35–1000 $/tonCO_2$. These costs are certainly higher than those of CO_2 capture from flue gas that are in the order of 30–100 $/tonCO_2$ [18]. The high initial cost is due to the upfront expenses and the lack of experience with this technology. Table 6 shows the costs which are available for the main DAC companies, such as Carbon Engineering, Climeworks and Global Thermostat. The economic data for the first company (94–232 $/tonCO_2$) was obtained by a design in Aspen Plus [34,113]. A different situation obtains for Climeworks, for which the first commercial plant has an actual cost of 600 $/tonCO_2$, which is expected to be reduced in the future to 200 $/tonCO_2$ and 100 $/tonCO_2$, respectively, in 2025 and 2030 [3,113]. Lower costs are given for Global Thermostat (50 $/tonCO_2$), which could be further reduced to 15–50 $/tonCO_2$ depending on how long the amine surfaces last [142]. This small value can be obtained considering that the steam needed for the process comes from waste heat at low or even no cost. However, it is a very optimistic cost, without any transparency in the economic analysis and is presented in order to have a more competitive plant from an economic point of view operating in the market.

Table 6. Costs of the main DAC companies.

Company	Time Period	Total Cost ($/tonCO_2$)	Reference
Carbon Engineering	2018	94–232 (levelized)	[34]
Climeworks	2018	600	[113]
	2025	200	[3]
	2030	100	[3]
Global Thermostat	2017	50	[141]
	future	15–50	[141]

In the literature, there are other cost analyses for CO_2 capture processes from the air, based on absorption and adsorption. A real comparison between these costs cannot be conducted due to the lack of transparency in economic analyses and due to different and undefined assumptions. A range of cost values have been reported, as shown in Figure 17, for adsorption and absorption processes. In this analysis, the capital cost has the highest influence on the total cost, with a value of 1000 $/tonCO_2$ for the solid sorbent process. However, a low value of about 14 $/tonCO_2$ has also been obtained in this case. The capital cost for the liquid sorbent system is between 80 $/tonCO_2$ and 150 $/tonCO_2$. Lower values are given for the operating costs for both processes: a range of 40–80 $/tonCO_2$ for the absorption plant, and a range of 4–48 $/tonCO_2$ for the adsorption system. Overall, it is

possible to underline that the wide range of costs is due to the emerging technology, the process boundaries considered and approaches to economic assessment.

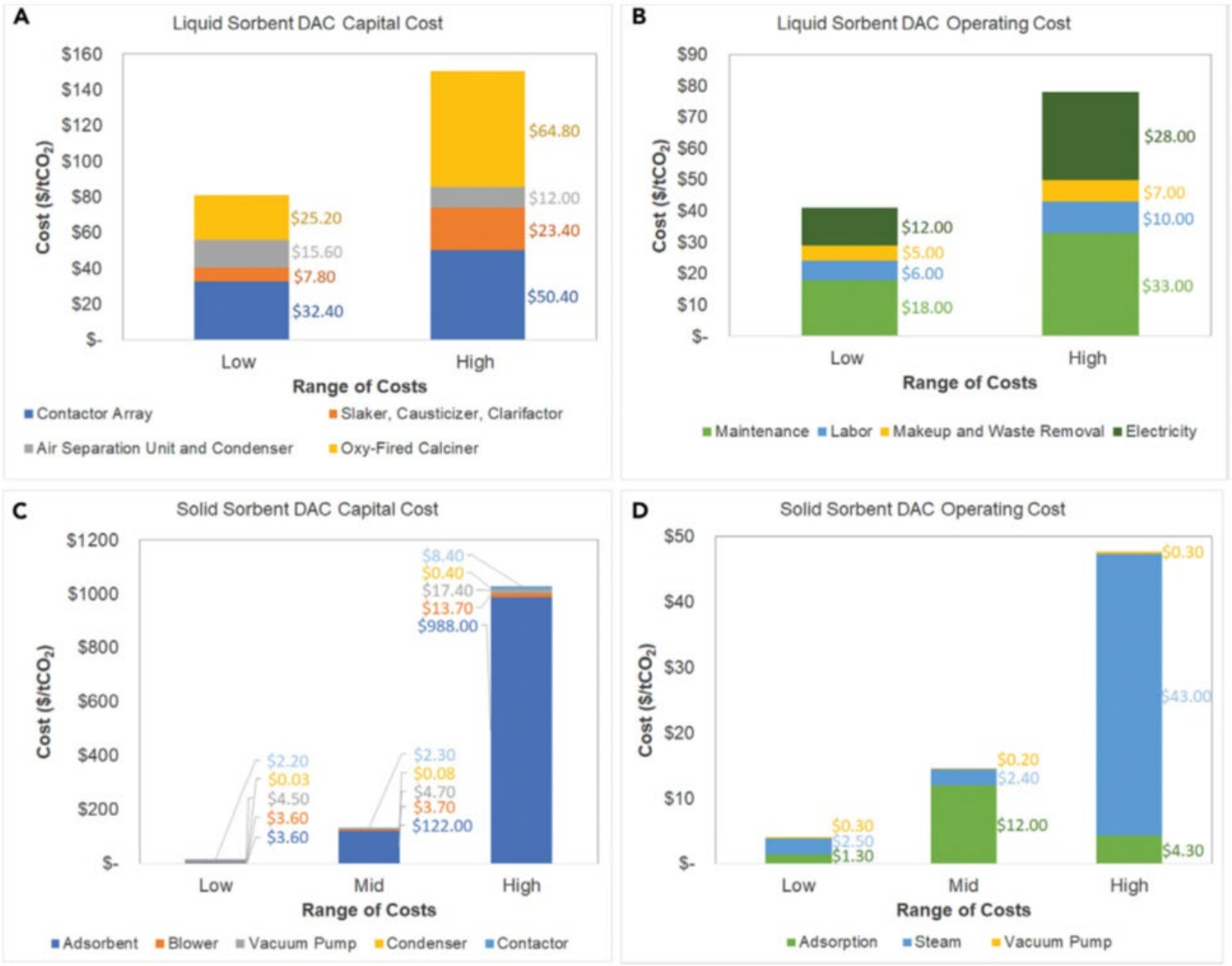

Figure 17. DAC cost breakdown and comparison: (**A**) liquid solvent SAC capital costs; (**B**) liquid solvent DAC operating costs; (**C**) solid sorbent DAC capital costs; (**D**) solid sorbent DAC operating costs. Reproduced with permission from [40].

Another KPI is land use. To have an idea of this indicator, respective values for Carbon Engineering, Climeworks and Global Thermostat have been reported as follows: 0.2 km^2 for 1 $MtCO_2$/year (plant in Texas), 0.1 km^2 for 1 $MtCO_2$/year (plant in Switzerland), 0.0008 km^2 for 1 $MtCO_2$/year (plant in Iceland) and 0.05–0.002 km^2 for 1 $MtonCO_2$/year [40]. Data are reported in the literature for the land use for different combinations of DAC systems and energy sources, as reported in Table 7 [143]. For the absorption process, land use ranges between 0.4 and 14 km^2 for 1 $MtonCO_2$/year, while for the adsorption system, land use is between 0.5 and 66 km^2 for 1 $MtonCO_2$/year. It is evident that, if renewable energy is used, a higher portion of land is needed.

Table 7. Land use for different combinations of DAC systems and energy sources. NG: natural gas, PV: photovoltaic, CCS: carbon capture and storage [142].

DAC System and Energy Source	Total Area for 1 $MtonCO_2$/Year Plant (km^2)
Solvent: NG with CCS	0.4
Solvent: NG with CCS + solar PV	7.5
Solvent: NG with CCS + geothermal	1.9
Solvent: NG with CCS + wind	14
Sorbent: NG with CCS	0.5
Sorbent: solar PV	34.7
Sorbent: geothermal	7.5
Sorbent: wind	66

It is interesting to underline the total area required to meet the global goal set in the international agreements that aims to remove 1000 $GtonCO_2$ by 2100. Supposing that 13,000 Carbon Engineering-type plants are needed, a total land area of about 6.6 times the size of New York city will be required [137].

Water can be lost in absorption processes capturing CO_2 from the air but can be produced in adsorption processes. Stolaro et al. [43] reported that for an absorption process using an aqueous NaOH solution, water losses would be 20 mol H_2O/mol CO_2. For Broehm et al. [33] water losses can be in a range between 0 and 50 tons per ton of captured CO_2. This loss depends on several factors, including the humidity and ambient air temperature and the solution concentration. For the Carbon Engineering company, 4.7 tons of water are lost per ton of captured CO_2 [129]. On the other hand, for Climeworks, water is produced as a by-product in an amount of 0.8–2 tons per ton of captured CO_2 [129]. This water can be used to produce H_2 and fuels.

Regarding TRL, the highest value of 9 was given to the Climeworks process, while a value between 7 and 8 was assigned for the Carbon Engineering plant. Lower values of TRL are assigned for other technologies, such as 2–4 for cryogenic separation, 2–3 for membranes and 3–4 for electrodialysis [39].

Climate change is the parameter considered for environmental impact and a very few studies have been reported in the literature on this kind of analysis. Higher CO_2 removal efficiencies have been obtained for the adsorption process, achieving a value up to 93.1% in Deutz and Bardow [144] for the Climeworks plant in Iceland. A negative value of climate change (−98.7 $kgCO_{2eq}$/tonne CO_2 captured and stored) was reported by Leonzio et al. [145] for the Climeworks plant in Switzerland, according to a cradle-to-grave analysis. For the absorption system, a carbon removal efficiency of 62% was reported in de Jonge et al. [146].

5. Social Concerns

Many stakeholders have not yet developed a coherent position towards DAC, as the main concern is cost. Even though economies of scale are expected with upscaling, currently, the limited number of large-scale plants and uncertainties in cost analysis determine strong disincentives for potential investors [39]. However, proponents of this new emerging technology underline some advantages, in comparison with other negative emissions technologies, that could help to overcome cost concerns. At first, a DAC plant might be located near the storage site or renewable energy facilities in order to reduce CO_2 transport costs. Moreover, the captured CO_2 could be used in the food industry, for fuel production or for other applications. Another attraction of DAC is that it can avoid some critical resource pressures and side-effects associated with other NETs [39]. Important, also, is the creation of new job opportunities: 1 $MtonCO_2$ captured in a DAC plant can ensure about 3500 jobs. For these reasons, as DAC spreads, governments will have to incentivize this new technology, reducing its costs. In this context, Daggash and MacDowell [147] have proposed a negative emissions credit for each ton of CO_2 removed.

6. Conclusions

The stringent environmental agreements urge not only CO_2 mitigation technologies but also the removal of CO_2 from the atmosphere through NETs. One of these is DAC. In this process, CO_2 is captured from the atmosphere using several systems, such as absorption, adsorption, ion-exchange resin, mineral carbonation, membrane, photocatalysis, cryogenic separation, electrochemical and electrodialysis approaches, and is put in storage or used in other chemical processes, closing the carbon cycle (as a human-controlled carbon cycle).

In this work, an extensive review of the above-mentioned DAC processes reported in the literature in recent years has been presented. Each DAC system, at commercial and lab scale, has advantages and disadvantages that underline the need for an integrated portfolio of solutions to satisfy climate goals.

Absorption, using an aqueous solution of strong base, and adsorption, mainly based on chemisorbents with amine-functionalized sorbents, are the most intensively investigated and mature systems used by the principal companies that have emerged in this field. Among these, only one—Climeworks—has the first commercial plant in operation.

As an interesting feature of the present work, KPIs are proposed as a way to compare DAC technologies. Thermal and electrical energy consumption, OPEX and CAPEX (or general total costs), land use, water demand, TRL and environmental impact are the most important factors to consider. It is worth pointing out how costs and energy consumption are higher than those required by CO_2 capture from flue gas, and the TRL is not at industrial scale for all technologies. Moreover, a wide range of cost and energy consumption values have been suggested in the literature due to the fact that it is a new emerging technology, and more efforts are needed to concretize all of the research presented in this work. An independent and accurate economic and energetic analysis is required for this new process and should be developed in future research, as has already been conducted by Leonzio et al. [148].

Overall, the objective of researchers and companies is to decrease costs and energy consumption while increasing the amount of captured CO_2. To achieve this objective, some suggestions can be provided, such as to consider a trade-off between the energy required for regeneration and how tightly the sorbent/solvent binds CO_2, in order to reduce the energy consumption. Moreover, it is possible to supply low-carbon heat energy and exploit renewable energy and waste heat, as well as reduce capital costs, through optimal design of air contactors. It is suggested that an optimal location be found which has low-carbon heat and power availability, favorable air conditions with low levels of moisture that can reduce the amount of captured CO_2, favorable temperature to reduce the heat energy required for regeneration and favorable wind to reduce fan power consumption.

In the near term, in order to reduce total costs, government support, e.g., through grants, tax credits and public procurement of CO_2 removal, should be provided for this emerging technology. In the long term, actions related to CO_2 pricing mechanisms and accounting frameworks that recognize and value the negative emissions associated with storing captured CO_2 should be adopted.

Future research should be focused on the development of an optimal sorbent with a low regeneration energy, high CO_2 selectivity, fast reaction time, long stability and low degradation rates. For air contactors, attention should be put on increasing the contact area while minimizing pressure drop and the energy requirement for air movements. The systems should minimize sorbent/solvent losses and increase capture capacity.

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