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# $CO_2$ DIRECT AIR CAPTURE TECHNOLOGIES FOR A LONG TERM STRATEGY TOWARDS A NET ZERO EMISSIONS ECONOMY

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# SUMMARY

# 1 INTRODUCTION

## 1.1 Climate change and $CO_2$ anthropic emissions

### 1.1.1 Global warming: EU Climate strategies & targets

Climate change mitigation is one of the most delicate issues of the moment, as climate change affects regions all over the world, causing phenomena like polar ice melting, rising of sea level and extreme weather events, which lead to human health and wildlife damages, and huge economic losses too (1).

The main driver of climate change, due to global warming, is recognized to be the greenhouse effect, caused by anthropic greenhouse gases (GHGs) emissions, widely exceeding their natural occurrence. Among these gases, particular attention is given to methane ($CH_4$), released in large quantities by intensive livestock farms, nitrous oxide ($N_2O$), mostly derived from nitrogen fertilisers use, and fluorinated hydrocarbons (HFCs). However, by far the most relevant is carbon dioxide ($CO_2$), which comes from the exploitation of fossil resources, strictly coupled with economic growth, for almost any kind of use. Carbon dioxide is released in the atmosphere in an amount around 37 Gt/year (2) and its concentration has increased from 280 ppm in the pre-industrial era to 413 ppm in 2020, with an annual growth rate of about 2 ppm (3).

The growing $CO_2$ concentration in the atmosphere enhances greenhouse effect and is directly responsible for global warming phenomenon, which led to a global average temperature 1.1 °C above pre-industrial levels in 2019 and is currently increasing at a rate of 0.2 °C per decade. Being a total increase of 2 °C, compared to the pre-industrial value, associated with serious negative impacts, linked to a much higher risk that dangerous and possibly catastrophic changes in the global environment will occur, the international community has recognised the need to keep warming well below this value and pursue efforts to limit it to 1.5 °C (1).

For these reasons, at the heart of the European Green Deal and in line with the EU's commitment to global climate action under the Paris Agreement, the EU aims to be climate-neutral by 2050, achieving an economy with net-zero greenhouse gas emissions (NZE scenario) in 2100. The transition route to a "green" economy and its stages are outlined in the EU's climate strategies & targets; in particular, at least 40% cuts in greenhouse gases emissions, compared to 1990 levels, 32% share for renewable energy and 32.5% improvement in energy efficiency by 2030 are required in order to achieve a NZE in 2050. To meet this ambitious vision, the need of a multisectoral approach is pointed out, still keeping view of the effects of each sub-system variation on the hole global system (4).

Categorizing different national economies across the world, a strong dependence of the gross domestic product (GDP), representative for economic growth, on the energy and matter availability is highlighted, almost regardless to social conditions. Furthermore, the inconsistence of "dematerialized" economies, based on services, is shown (5). It results clear that, to sustain economic growth, energy and matter are needed and the environmental impacts are determined by the way in which their extraction and use are carried out. These activities are mainly based on fossil fuels consumption and proportional $CO_2$ emissions, but new technologies allow the exploitation of renewable energy sources (RES), defined by the European Environmental Agency as energy sources that do not rely on fuels of which there are only finite stocks, provided by natural cycles (e.g. wind, rain, forests growth…) and substantially powered by solar radiation.

The only feasible solution for economy "decarbonization", which could allow the transition to a safer zero climate impact economy, is to further develop these technologies and design systems in order to maximize the RES extraction and their use efficiency. However, to achieve this ambitious goal, more efforts are needed and, at the moment, global energy is still provided by the use of fossil fuels for more than 80% (6). Environmental policies are aimed to reduce GHG emissions in the perspective to neutralize them, but this cannot be done immediately without carrying dramatic economic and social impacts. The use of fossil resources is already discouraged, in particular keeping in account the carbon intensity of each resource, and while coal use is going to be left in the EU28 region, natural gas is expected to support the oncoming energetic transition, at its different stages. To mitigate the impacts during the transition and accomplish neutral or negative greenhouse gas emission energy systems, negative $CO_2$ emission technologies (NETs), which allow its removal from the atmosphere, are required too.

### 1.1.2 IPCC carbon budgets and decarbonization pathways

The Intergovernmental Panel on Climate Change (IPCC) has introduced the concept of carbon budgets, representing the quantity of $CO_2$ that can be emitted across the remainder of the century to keep warming below a given temperature, through the assessment of 900 mitigation scenarios from about 30 Integrated Assessment Models (IAMs). In 2011, a budget of about 1000 $GtCO_2$, for a 66% probability of meeting the 2 °C Paris Agreement target, was estimated using data referred to 76 scenarios from 5 IAMs (7).

NETs are involved in the majority of consistent scenarios to achieve Paris Agreement targets, and their technical, economic and social viability is supposed to be achieved in the future. Among these, the inclusion of technologies capable of removing $CO_2$ directly from the atmosphere allows to choose a less challenging emissions reduction pathway, in which continued emissions in excess of natural sinks to 2100 and beyond are compensated by a hypothetical technology that removes the excess $CO_2$, owing to an inability to adequately constrain emissions. Following this pathway, net emissions will be reduced sufficiently and become negative after 2070 only by applying NETs at increasingly high rates after 2035-2040 (8), as shown in Figure 1.

This assumption is an issue of risk; the promise of future and cost-optimal negative-emission technologies is more politically appealing than the prospect of developing policies to deliver rapid and deep mitigation now, but the weakening of near-term mitigation actions and the failure of future NETs implementation could lead to rapid temperature rises similar to the 4 °C "business as usual" pathway feared before the Paris Agreement, mainly affecting low-emitting communities that are geographically and financially more vulnerable to climate change (9).

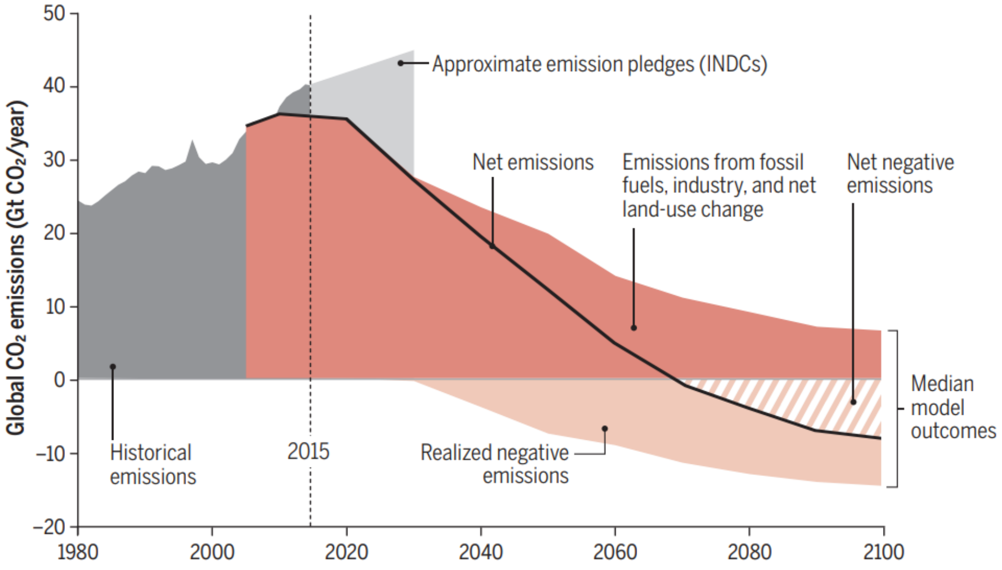

*Figure 1: Schematic representation of carbon budget management in the decarbonisation pathway drawn to achieve climate neutrality by 2050 and net-zero emissions by 2100.* (9)

Recent modelling results suggested that in the considered mitigation scenarios a removal capacity of 3.3 GtC, equivalent to 12.1 $GtCO_2$ should be achieved by NETs in 2100. However, while many IAMs take in account massive deployment of NETs in the future, there is none of these currently available that could be implemented to meet the 2 °C target without significant impact on either land, energy, water, nutrient, albedo or cost, as most of them are only at early stages development and need further research before their large-scale application. Moreover, the delayed reduction of GHG emissions, and the consecutive atmospheric $CO_2$ concentration further rising in the near-term, could emphasize global warming effects forcing climate balances and inducing amplifying feedbacks. The temperature increase could turn Earth's climate to a condition similar to paleoclimate, when it was less than 1 °C warmer than today, sea levels were more than 6 m higher and evidence of extreme storms was found, so a 2 C global warming above the preindustrial level is seriously thought to be dangerous (10).

These observations imply that a large cut in GHG emissions should not be postponed but, doing this, much more attention must be paid to NETs, taking immediate actions, both on technical and political aspects, to assure their massive deployment and application. The role of NETs in the near-term could result crucial to follow a safe decarbonisation pathway, without exceeding critical $CO_2$ levels, as a mitigation agent for anthropic emissions from fossil resources during the transition.

## 1.2 Negative $CO_2$ Emission Technologies (NETs)

The various NETs, currently under development, are all aimed to carbon sequestration, through the capture of $CO_2$ from the atmosphere, and its transfer and storage in another environmental matrix, as highlighted in Figure 2 at the end of this section.

### 1.2.1 Environmental engineering approach

Different environmental engineering approaches are taken in exam as they could represent a relatively low-cost solution, exploiting natural processes, but a better knowledge on these processes has to be acquired because they are difficult to control and the wide involved areas could lead to adverse effects of the same size.

#### *1.2.1.1 Afforestation and reforestation (AR)*

Afforestation and reforestation (AR) are based on the absorption of $CO_2$ through plant growth and consist of planting trees and restoring or growing new forests, without logging, to fix carbon as biomass in the land matrix. The global carbon removal potential of AR has been estimated around 1.1 GtC/year by 2100 and could even reach 3.3 GtC/year, for a very large scale deployment, implying the use change of 20% to 60% of the total arable land (11); these are already existing and low-cost technologies, feasible in the short-term, but their hypothetic massive application in the future poses several issues.

Firstly, AR large land requirements should not lead to a competition with land for food; in addition, trees planting could cause the release of carbon fixed in the soil and fertilisation activities are linked to increased nitrous oxide emissions, which heavily affect the net equivalent $CO_2$ balance, even leading to a negative environmental performance. Moreover, nutrients and water availability vary greatly across different geographical areas and replanting to generate dense forests with high carbon stocks rather than the sparse, low plantations observed in many areas requires more work to identify suitable environments for future afforestation to sequester carbon, prevent soil degradation and enhance biodiversity (12).

Another not negligible concern is about alterations in the physical characteristics of Earth's surface, due to changes in land use, such as increased evapotranspiration and cloud cover in the tropics. Albedo, which is the reflectance of solar energy by the Earth's surface, in areas where shorter vegetation may be persistently covered by highly reflective snow in winter, could be reduced by the presence of tall coniferous trees, which remain exposed and therefore much less reflective (13); this effect is large enough to mean that AR in northerly latitudes may have a neutral or net warming effect, larger than the carbon sink provided by the vegetation, and to further restrict the exploitable areas for this NET.

Despite some examples of afforestation and reforestation can already be seen in the EU with a net increase in forest carbon stock of 756 million tonnes of carbon annually in recent years, and a major replanting programme in China to increase forest cover by 434,000 km$^2$ (12) , the issues presented above suggest that AR future deployment as NET would be limited and too low to achieve a NZE scenario alone, but would be a useful contribution, in particular in the short-term.

#### *1.2.1.2 Land management to increase carbon in soils*

Land management to increase carbon in soils includes soil carbon sequestration (SCS), realised by the addition of organic matter, and soil amendment with biochar, which are currently not included in IAMs but could represent a valuable opportunity. The main advantage is offered by the fact that there is no competition for land, as SCS and biochar addition can be applied to all managed land without changing its current use; moreover, biochar, commonly obtained from biomass pyrolysis as a by-product, could be implemented in combination with bioenergy (BE) and bioenergy with carbon capture and storage (BECCS) (14). The global carbon removal potential has been estimated around 0.7 GtC/year, with the technical possibility to reach about 1.3 GtC/year, for both

SCS and biochar application. Given that biochar application rates to soil can be high and that it is more recalcitrant than soil organic matter, land requirements are lower than for SCS. Both methods may have positive impacts on the managed land, as they could enhance soil water holding and crops productivity; biochar, darkening the land surface, could also slightly decrease albedo.

Limitations of soil carbon sequestration as a NET centre around issues of sink saturation and reversibility. SCS potential is large at the outset, but decreases as soils approach a new, higher equilibrium value, such that the potential decreases to zero when the new equilibrium is reached; moreover, practices need to be maintained, even when the sink is saturated and the emission potential has reduced to zero. Sink saturation occurs after 10 to 100 years, depending on the SCS option, soil type and climate zone (slower in colder regions), with IPCC using a default saturation time of 20 years while these issues are less pronounced for biochar, as it is more recalcitrant and equilibrium, if it occurs, would be expected to take much longer (14).

Land management to increase carbon in soils, considering its current level of technical development, application requirements and potential impacts, seems to be an excellent NET for mitigation in the short term. However, given the uncertainty in the relationships between these techniques and soil $CH_4$ and $N_2O$ emissions, limited maximum capacities and the issues of sink saturation SCS and biochar addition cannot certainly be applied alone and the deployment of other NETs still remains urgent, in particular if they are implemented for mitigation relatively soon and may no longer be available, or will be less effective (15).

#### *1.2.1.3 Enhanced weathering (EW) and ocean fertilisation (OIF)*

Enhanced weathering (EW) consists of improving the slow rates of geochemical processes that naturally absorb $CO_2$ by some physical or chemical mechanism. This technique could involve spreading finely ground carbonate or silicate minerals, such as olivine and basalt, both over large areas of land, as is already done in some cases to reduce the acidity of soils for agriculture, and over oceans. When silicate or carbonate minerals dissolve in rainwater, the absorbed $CO_2$ is drawn into the solution from the atmosphere and accumulates in carbonate formations. Recently some field studies have started on the potential of using basalt in agriculture to increase carbon uptake while at the same time improving agricultural productivity; however, no pilot or demonstration processes are currently underway to determine the scientific, technical and negative emission advantages and disadvantages of EW. The carbon removal potential has been estimated to be perhaps 1 GtC/year by 2100, with a median value of 0.2 GtC/year, much lower than other NETs, and the associated mining, transport and grinding of about 1 to more than 3 gigatonnes of minerals for each gigatonne of removed carbon could result in the main disadvantage of this technique (8, 10).

Ocean fertilisation refers to the addition of micronutrients which should stimulate planktonic algae growth; these and other microscopic plants take up $CO_2$ and convert it to organic matter through photosynthesis, some of which sinks as detritus and is sequestered in the deep ocean. This process is thought to be able of affecting atmospheric $CO_2$ concentrations significantly over several decades to centuries by as much as tens to over 100 ppm. However, a very large increase of plankton production is required to achieve significant amounts of sequestration, because most of the carbon fixed is released when the plankton decays or is consumed, and only a small proportion reaches the deep ocean and the sequestration potential is therefore unlikely to exceed 1 GtC per year. and OIF is thus associated with very high levels of uncertainty and ecological risks for a relatively small sequestration.

The most promising micronutrient examined to date is iron because of the large ratios of carbon to iron in plankton (OIF: ocean iron fertilisation); OIF should ideally promote the formation of plankton with larger cells that may encourage more rapid sinking, but several possible drawbacks have been identified. This phenomenon may affect higher trophic levels, including fish, seabirds and marine mammals, bringing possible ecological impacts on the marine food web and fisheries, and downstream effects on nutrient supply, productivity and food web dynamics, in unpredictable ways. Moreover, the types of plankton cannot be controlled and will depend on other environmental factors, so iron addition may also stimulate the growth of diatom species, some of which are associated with toxic algal blooms. For these reasons OIF is thus associated with very high levels of uncertainty and ecological risks for a relatively small sequestration potential (16).

## 1.2.2 Industrial process approach

Industrial approaches are based on NETs implementation from currently existing technologies, as $CO_2$ separation from gaseous streams, both for supplying and removal, is involved in many industrial processes. The main issue is the management of the separated $CO_2$, as its industrial consumption of about 230 Mt/year represents a minimal fraction of the global production and emission. The excess of $CO_2$ must be captured and stored or used in some way; NETs developed as industrial plants are currently designed to store the $CO_2$ underground subsequently its removal (CCS) but, the creation of a market for its use, could also lead to $CO_2$ direct utilisation (CCU). The description of different industrial NETs is focused on what concerns the approaches of $CO_2$ capture while its storage method and utilisation opportunities are treated below with more detail.

### *1.2.2.1 Bioenergy with carbon capture and storage (BECCS)*

Bioenergy with carbon capture and storage (BECCS) is substantially the combination of two existing technologies; bioenergy (BE), which allows to reduce $CO_2$ net emissions, close to 0, through the exploitation of biomass instead of fossil resources, and CCS, which makes emissions negative, removing the $CO_2$ produced by the energetic conversion at plant (17). BE, in general, is already at a good development level and strong reductions of emissions could be obtained by biomass utilisation, taking in account that it fixes atmospheric $CO_2$ during its growth. BE plants are usually aimed to the cogeneration of heat and power (CHP) and based on a gasification process through air, which converts biomass to syngas, mainly composed by hydrogen and carbon monoxide in different proportions, in a similar way to coal; the outlet gas is than cleaned, before its combustion in gas turbines (GT), boilers for steam turbines (ST), internal combustion gas engines (ICE) or fuel cells (FC), which could offer a cleaner exhaust gas, associated with high purity syngas requirements, and are still under study (18, 19).

Many bioenergy CHP plants working in the world have good levels of electrical and thermal efficiency, which could be further improved, but the net emissions reduction is affected by the processes of biomass extraction, transport and treatment, still relying on fossil fuels. As improving efficiencies could lead to lower emissions, due to the lower quantity of matters consummated for the same energy output, to reach net negative emissions CCS units must be added to BE plants; in this way a large amount of the $CO_2$ sequestrated by biomass growth, released during its exploitation, is captured from exhaust gases and stored underground, globally subtracting it to the atmosphere (20).

Recently, more interest has been given to pyrolysis processes as they are carried out without additional air feeding, at lower temperature, and leave a larger amount of residual char, reducing the carbon content in syngas and its emission as $CO_2$ after combustion, also considering that the retained char could be allocated to biochar soil amendment technologies. Moreover, BE and BECCS could be integrated with afforestation and reforestation, keeping in account though that the obtainable benefits are shared by the different NETs involved in these systems, on the basis of the biomass consumption and growth rates, and are non-addictive (17).

However, BECCS is one of the most advanced developing NETs, with some existing demonstration projects, and for this reason is considered as a principal or unique NET in the majority of IAMs used to assess scenarios consistent with Paris Agreement target. This technology should be able to achieve a global carbon removal potential of 3.3 GtC/year, adequate for a NZE scenario, but impacts on other environmental aspects could be relevant and, to reach this result, the implementation of a CCS framework, first of all solving the issues related to its safety and the availability of disposal sites, is essential (20, 21).

Deployment of BECCS at that scale would have very large land requirements, of about 1 to 1.7 hectares for each tonne of carbon equivalent removed each year for forest residues, 0.6 hectares for agricultural residues, and 0.1 to 0.4 hectares when purpose-grown energy crops are used, potentially competing or overlapping with land availability for AR, as well as for food production, and causing dramatic changes to ecosystems, if protection measures are lacking. Moreover, productivity and resource requirements differ greatly between types of land and biomass, and impacts on the pre-existing carbon stocks can reduce or even reverse the carbon removal potential. BECCS may also be limited by nutrient demand, or by increased water use, particularly if feedstocks are irrigated and considering the additional water required for CCS. BECCS application thus needs to be evaluated on a case-by-case basis and cannot be seen as a primary NET; considering its layout and the obtainable benefits and adverse effects, massive deployment of this technology seems to be useful only after fossil fuel use is restricted and all fossil fuel power is already treated with CCS (22).

#### 1.2.2.2 $CO_2$ direct air capture (DAC)

$CO_2$ direct air capture (DAC) is aimed to its collection from ambient air through fully chemical processes, with difference to BECCS, which involves the use of biomass and so relies on biological processes too. DAC uses a solid or liquid sorbent to bind the $CO_2$ and is similar to the capture stage of CCS basis technology, which can be applied also to fossil fuels power and industrial plants, as a mitigation solution only; there are, however, some important differences due to the low concentration of $CO_2$ in air versus the concentration in flue gases. For this reason, while CCS needs to be coupled with processes offering a high $CO_2$ content outlet stream, DAC, anyway flanked by a storage technology (DACCS), may be located in principle anywhere, for instance, close to storage sites, even on offshore platforms, thereby minimising transport costs, but its external energy supply needs, which should be accomplished by a carbon-neutral source, limits the choice of a suitable location (23).

DAC technologies are mainly based on absorption or adsorption, but some other approaches are under evaluation. Absorption techniques involve strong base solutions, which capture $CO_2$ as carbonates, $CO_2$ extraction and solution recovery are carried out through a calcination process, which requires high temperature heat supply. Adsorption is realised on solid sorbents, featured by a high selectivity for $CO_2$ even in presence of water vapour, commonly adopting a temperature swing adsorption (TSA) or pressure swing adsorption (PSA) layout, or their combination, for sorbent regeneration, offering the possibility of using low-grade waste heat (24).

DAC could be considered the most safe and reliable NET, as it has almost negligible environmental impacts, linked to a small direct land footprint, which also make plants deployable on unproductive land that supplies few ecosystem services, and low water requirements compared to other NETs, especially using solid sorbents. The only limit to carbon removal potential could be due to the needed technical and financial efforts, indeed, the main issues of DAC are the low-cost availability of high-performance $CO_2$ removal technologies and energy supply. The latter also poses additional environmental concerns as the land footprint could be remarkable if solar photovoltaic panels or wind turbines were used to provide the energy required. Moreover, recent studies concluded that even with a large-scale deployment of a hypothetical and successful BECCS, the Paris targets would not to be met, so a substantial deployment of DACCS would be necessary to solve this issue (25).

For their additional limitations, like BECCS, DACCS could become worthwhile after any remaining point sources had already been fitted with CCS; however, the possibility of generating the $CO_2$ directly where it is used makes DAC particularly suitable for utilisation applications (CCU). Even though this does not lead to negative emissions, it is an important driving force for the development of DAC technology as at the current stage of deployment, in addition to academic research, commercial operation is focusing on $CO_2$ utilisation instead of storage (22, 23).

In Figure 2 the described NETs, other mitigation solutions and power generation technologies are schematised, to resume and make easily comparable the involved carbon flows between environmental matrices.

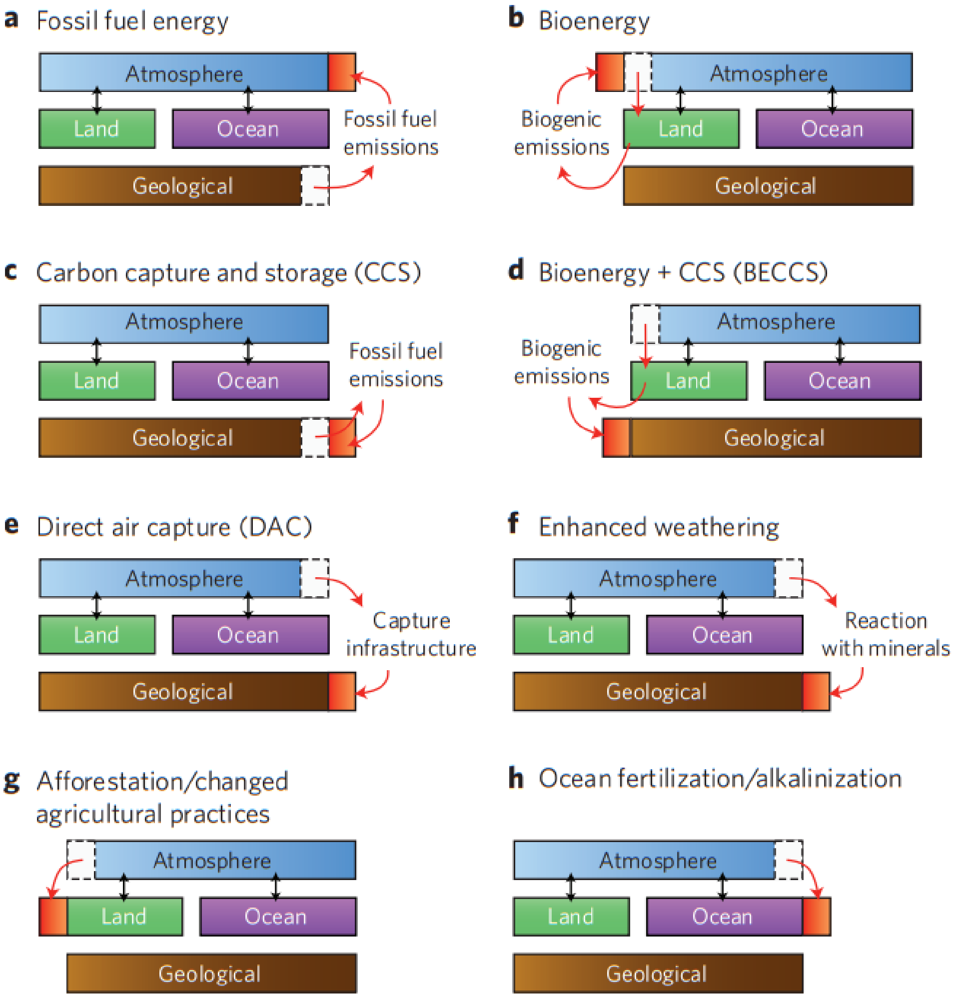

*Figure 2:Schematic representation of carbon flows among atmospheric, land, ocean and geological reservoirs involved by different technologies. (10)*

# 2 $CO_2$ CAPTURE, STORAGE AND UTILISATION (CCS/CCU)

The deployment of $CO_2$ capture technologies, both at plants and directly from the atmosphere, as mentioned before, strongly relies on the assessment of a storage framework (CCS), eventually accompanied by the consolidation of utilisation pathways (CCU).

## 2.1 Carbon capture and storage (CCS)

CCS implementation could allow the reduction of $CO_2$ emissions from power generation and from energy-intensive industrial processes, like those involved in cement, iron and steel, aluminium, pulp and paper, and refinery sectors; furthermore, geological storage technologies are also essential for an effective large-scale deployment of BECCS and DACCS, considered the most reliable NETs to achieve climate neutrality in 2100. By the moment, CCS offers promising perspectives and some commercial applications in power generation, or even in purified hydrogen production; in 2019 the Global CCS Institute reported more than 50 large-scale facilities, mainly located in USA and EU, based on oxy-fuel combustion, pre-combustion and post-combustion capture, which are depicted in Figure 3. Despite a recorded capture capacity of only 96 $MtCO_2$ annually, CCS deployment is ongoing, and many new commercial projects are arising (26, 27).

### 2.1.1 Capture strategies

Post-combustion capture, in which the product $CO_2$ is collected from the process flue stream after fuel combustion with air has taken place, is the most adopted layout, as it is linked to traditional power generation technologies and easily retrofittable to existing plants; however, other methods are attracting more interest, given by the fact that in these ways $CO_2$ can be more effectively removed from non-diluted streams (28). Among these, oxyfuel combustion involves the use of oxygen, instead of air, for burning the fuel, avoiding inert nitrogen addition and hence yielding a flue stream that is highly concentrated in $CO_2$; this practically eliminates the need for post separation operations but actually introduces drawbacks related to pure oxygen, often supplied by an air separation unit (ASU) (29). Otherwise, chemical looping combustion (CLC) could allow delivering the oxygen for combustion through a suitable metal oxide carrier, which is reduced upon reaction with the fuel and is then recycled and re-oxidized into an air reactor; however, this is an emerging technology as oxidation and reduction rates are primarily governed by the defect chemistry and defect transport rates in the crystal lattice of the particular metal oxide carrier employed (30).

Pre-combustion capture is another approach which involves gasification of the fuel, referred to as steam reforming if it is natural gas, by reacting it with steam and oxygen or air, and the $CO_2$ separation from the syngas, or hydrogen by a further water-gas shift reaction step, before its combustion with air in a gas turbine to generate electricity; this is the currently adopted method in integrated gasification combined cycle (IGCC) plants, often fed by coal, or even by woody biomass for BECCS (29, 31). This layout offers a good balance between post-combustion and oxy-combustion benefits due to high $CO_2$ concentration in the reformed gas and the possibility to use air for combustion of a decarbonized stream, obviously still maintaining an unit, in example of selective catalytic reduction (SCR), for the abatement of nitrogen oxides ($NO_x$), formed at high temperature, in the flue gas. Moreover, the possible use of air for partial oxidation too, would make an ASU not necessary, anyway keeping a lower inert fraction in the stream undergoing $CO_2$ capture than in post-combustion technology. Pre-combustion capture also offers the opportunity to easily develop the co-production of hydrogen, as well as chemicals and fuels, achievable subsequently via the Fischer-Tropsch (F-T) synthesis process, via gasification, which is a large and mature industry, softening its carbon footprint.

The coupling of gasification processes, fed by pure oxygen or eventually through CLC, to avoid nitrogen presence, with solid oxides fuel cells (SOFC) for the hydrogen or syngas combustion is under development as it would improve the overall system efficiency (32). Moreover, the realisation of appropriate electrochemical cells, aimed to direct conversion of either solid or gaseous hydrocarbons, known as carbon fuel cells (CFC), direct carbon fuel cells (DCFC) or carbon-air fuel cells (CAFC), offers product streams featured by the substantial presence of only $CO_2$ and steam, avoiding the need of an ASU.

Indeed, air is directly fed to the cell cathode and only oxygen is adsorbed and flows to the anode after reduction, typically by selective transport through an ionically conducting dense solid electrolyte, like yttria-stabilized zirconia (YSZ). These cells are often designed as solid oxides fuel cells (SO-CFC) but molten carbonates (MC-CFC) and hybrid solutions are under development, in particular for solid fuels conversion (33).

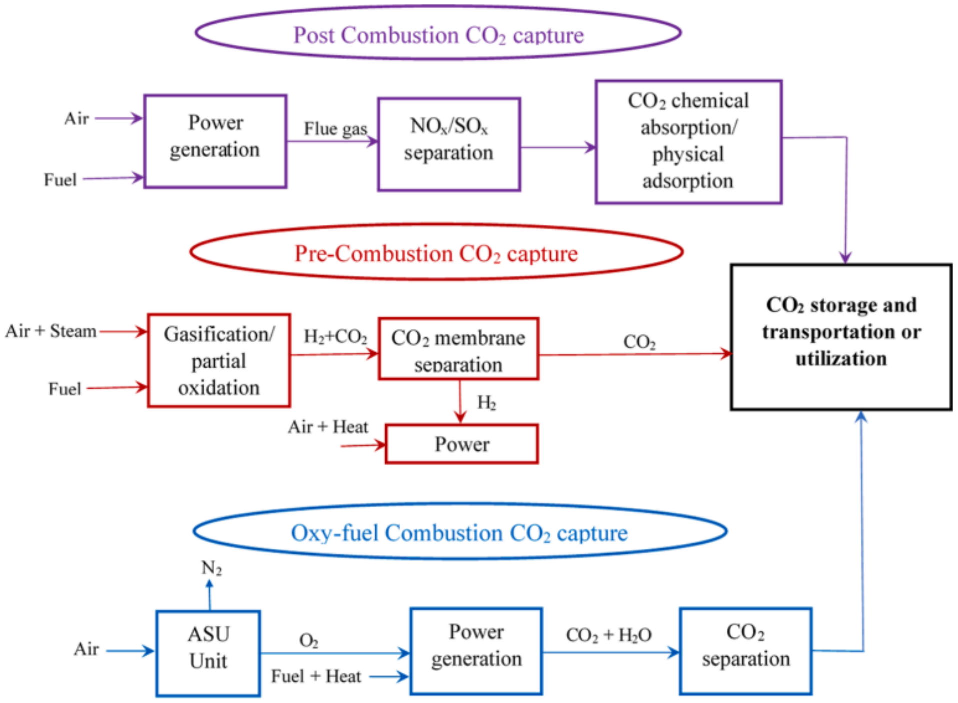

*Figure 3: Schematic block flow diagram (BFD) of the main $CO_2$ capture strategies applied to power generation. (31)*

### 2.1.2 Storage technologies

Permanent sequestration of $CO_2$ is the last essential step in the CCS chain and can be implemented using a variety of strategies; however, despite $CO_2$ storage being a technically proven technology, further deployment is delayed by some uncertainties and challenges. In the CCS framework, the potential options for $CO_2$ sequestration are underground geological storage, deep ocean storage, and mineral carbonation; the former comprising itself several options including saline aquifers, depleted oil and gas reservoirs, unmineable coal seams, hydrate storage, and $CO_2$ within enhanced geothermal systems (34, 35).

Different underground geological storage methods, summarized in Figure 4, which could be placed on-shore as well as off-shore, are based on the compression and injection of supercritical $CO_2$ and often borrow knowledge and part of the facilities from the oil and gas extraction sector and, in some cases, can also complement it.

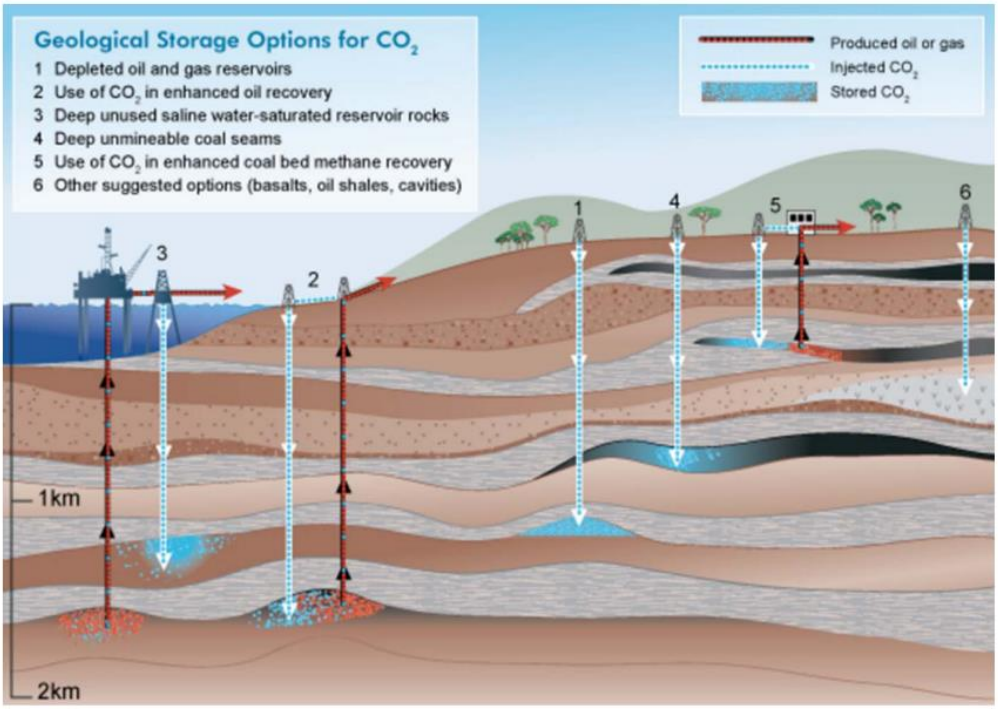

*Figure 4:Representation of different geological storage options for $CO_2$. (35)*

### 2.1.2.1 $CO_2$ storage coupled with fossil resources recovery

$CO_2$ storage in depleted oil and gas reservoirs is one of the most considered storage options as these sites have been extensively studied before and during the hydrocarbon exploration stage, including the storage capacity, the surface and underground existing infrastructure can be utilised for the storage purpose, either without or with only minor modifications, and the injection of gases for EOR has already been widely known and employed. In addition, oil and gas reservoirs are valuable hydrocarbon-containing analogues that can be used to demonstrate the effectiveness of caprock or seal over geological periods, reducing concerns on safety issues (36). Depleted oil and gas reservoirs can also be considered for EOR, which makes them economically more favourable leading to an additional production of oil. The main requirements for deployment of this kind of projects are the additional characterisation of storage site regarding caprock integrity and abandoned wells, enhanced monitoring and field surveillance and measurements of fugitive and venting emissions from any surface processing facilities to evaluate the risk of leakage and its rate, taking actions to ensure any components of the well can withstand effects of corrosion (37).

Still corrosion is the main associated concern with the type and level of impurities, such as CO, $NO_2$, $SO_2$, $H_2S$, $Cl^-$, in $CO_2$ streams, which can significantly impact the transport and injection facilities and needs to be critically characterised prior to a $CO_2$- EOR project. The impurities in the $CO_2$ stream depend on the point source of $CO_2$ and its corresponding capture technologies and the typical minimum purity of $CO_2$ streams is around 90%vol (29). Higher levels of impurities could also imply higher operating pressures to maintain the $CO_2$ in its dense phase, due to possible shifts in its phase diagram boundaries, and, if non-condensable, a strong reduction in the storage capacity of the reservoir. While safety concerns for flammability are usually not posed, the presence of $O_2$ can trigger microbial activity in the reservoir and can affect efficiency of the $CO_2$-EOR process, leading to injection blockage, oil degradation, and oil souring (39).

Another storage option could be provided by unmineable coal seams; the presence of cleats within the coal matrix provides some permeability to the system and its very large number of micro-pores makes it capable of adsorbing significant amounts of gases. The trapping mechanism is based on the higher affinity of coal towards gaseous $CO_2$ than methane; this provides the opportunity of storing large amounts of $CO_2$ while still improving the profitability and efficiency of commercial operations of coalbed methane (CBM), in particular accelerating its rate (38). Although $CO_2$-EOR is an established approach in the oil industry, utilisation of $CO_2$ for enhanced coalbed methane (ECBM) is yet to be well understood, but many of the uncertainties in ECBM recovery can be addressed based on the existing knowledge of the $CO_2$-EOR process and existing technologies from the oil industry could be utilised with slight modification.

#### 2.1.2.2 $CO_2$ storage in saline aquifers and basalt formations

$CO_2$ storage in saline aquifers is one of the most feasible technology deployment options, as it provides the largest potential storage volume and the majority of saline aquifers are currently not suitable for other applications, including nuclear wastes disposal, natural gas reserves to allow delayed consumption and "low-space-consuming" renewables as geothermic, particularly in the framework of densely populated countries (40). However, from an economic aspect, saline aquifers are less desirable as a storage option then depleted oil and gas reservoirs, due to the absence of necessary infrastructure, such as injection wells, surface equipment and pipelines, and the associated capital cost. Almost all deep-seated (> 1 km) saline aquifers are located within sedimentary basins, that can host enormous quantities of $CO_2$ due to their large pore volume and high permeability, minimising the number of necessary injectors and favouring pressure dissipation. The density of supercritical $CO_2$ in saline reservoirs is about 0.6–0.7 $g/cm^3$, which is lower than the density of saline formation water, thus causing $CO_2$ to rise towards the caprock due to buoyancy force. To assure long-term $CO_2$ storage, the host basin must be considerably large and the caprock must possess a good sealing capacity. This low permeability caprock, and the absence of fracturing or faulting, are essential to prevent $CO_2$ migration out of the storage reservoir and leakage (35).

$CO_2$ can be securely stored by four trapping mechanisms; the most dominant is structural or stratigraphic trapping which consists of the storage of a high-density free phase, that is unable to enter the pore space of the caprock, and remains below an impermeable top seal, after rising up to the top of geological structures. Solubility trapping involves $CO_2$ dissolution in brine which reduces the volume of the free-phase and increases the brine density, also accelerating the transfer of injected $CO_2$ to $CO_2$-lean brine through a gravitational instability effect. Mineral trapping refers to geochemical reactions of $CO_2$ with saline water and minerals in host rock, leading to the precipitation of carbonate phases that effectively lock up the carbon in immobile secondary phases, however this process is slower than solubility trapping and takes place over a longer geologic timescale. Residual trapping only happens where water drainage occurs during

$CO_2$ injection; the fluid is displaced by the injected $CO_2$, as it progresses through the porous rock, and then returns and disconnects the remaining $CO_2$, trapping it within pore spaces (41).

$CO_2$ storage in deep basalt formations results an attractive solution as their high reactivity and abundance of divalent metal ions can potentially fix $CO_2$ for geological timescales and basalt rocks offer a high storage potential, forming about 8% of the continents and much of the ocean floor. On the other side, permeability and porosity of the matrix are highly heterogeneous so only some zones are effective for the storage and the hindering of carbonation and hydration of the basalt by water pore displacement could require the $CO_2$ injection in water solution (42). Injection in deep sea basalt provides enough depth to allow denser $CO_2$ liquid to sink, facilities the formation of stable carbonates in relatively short time and stops upward migration through an impermeable sediment cover. Despite sparse and rare $CO_2$ leakage does not necessarily affect the sea bottom environments, this could be avoided by the fast formation of forms stable hydrate at deep ocean conditions. The main issues on this method are related to the volume variation of the formed secondary phase, commonly increasing, which affects maximum storage capacity and may even influence further activities acting on rock pores availability.

#### *2.1.2.3 $CO_2$ storage based on secondary phases formation*

On the principle of fast hydrate formation under adequate conditions another possible storage mechanism have been pointed out; the $CO_2$ hydrate storage involves the liquid $CO_2$ injection into deep-water or sub-permafrost sediments, beneath the $CO_2$ hydrate stability zone, where an impermeable cap is formed, through the precipitation of $CO_2$ hydrates within rock pore spaces, over a large amount of buoyancy-driven migrating liquid $CO_2$, blocking its further rising. However, the specific conditions needed to assure the cap formation, $CO_2$ hydrate storage applicability is limited to a few environments and requires deep preliminary studies on each site (43). Alternatively, to improve economic benefits in a similar way to EOR and ECBM an enhanced gas recovery ($CO_2$-EGR) strategy was proposed, aimed to release the methane, through $CO_2$ injection into methane hydrate-bearing sediments, and subsequently form CO2 hydrates instead. However, additional concerns are associated to this technique as the possibility of mixing the injected $CO_2$ with existing methane in turn may degrade the resources and drilling activities may destabilise the hydrate-bearing sediments.

Still relying on the deep interactions between $CO_2$ water and rocks to form carbonate minerals, the application of supercritical $CO_2$ as a working fluid for geothermal applications offers many advantages, respect to water, including being a potential underground storage solution. Indeed, the lower viscosity makes $CO_2$ capable of accessing the rock mass in enhanced geothermal systems (EGS) and this also leads to its partial loss underground; while using water in the circuit could bring adverse environmental impacts, in this way a consecutive benefit is obtained too. (44) Moreover, if geothermal is applied to high temperature gas reservoirs (HTGR), $CO_2$-EGR could be applied as the gas recovery is also useful to reduce its concentration below 10% in $CO_2$ and keep good thermal properties of the fluid. Main uncertainties on geothermal approach are related to the sealing effectiveness and to possible competing uses in densely populated areas.

#### 2.1.2.4 Deep ocean sequestration

An alternative to geological storage could be $CO_2$ deep ocean storage, achieved through its direct discharge to the seafloor, as a liquid, to form rising droplet plumes which consequently dissolve into seawater, or injecting it into a column, where it can react with seawater, at a controlled rate, to form hydrate; in this way $CO_2$ accumulates in cold and deep waters, which move slowly, and can remain isolated from the atmosphere for millennial timescales. This solution may have a great potential, as oceans cover 70% of the earth's surface and have absorbed almost a third of cumulative anthropogenic $CO_2$ emission over the industrial period, so many modelling simulations have been conducted to evaluate the efficiency of oceanic sequestration in different sites, mainly focusing on injection depth, residence time and distribution of $CO_2$ concentration. In this way, possible environmental drawbacks, due to water acidification near the injection zones, can be took in account for the site selection and different injection procedures effects can be assessed; in particular, continuous injection resulted to cause a source of leakage of more than 10%, after about 50 years. However, to apply deep ocean sequestration as a safe and reliable solution more detailed evaluations are needed, starting from the improvement of the current numerical model by including an air-sea $CO_2$ exchange mechanism and considering in more detail the viability of transporting large amounts of $CO_2$ in the ocean (45).

#### 2.1.2.5 Mineral carbonation processes

Mineral carbonation, among the described storage options, could be regarded as the less hazardous respect to releases, practically free of leakage, as $CO_2$ mineralisation reaction with alkaline earth metal oxides or hydroxides lead to the formation of more stable carbonates. This could happen *in-situ*, when the $CO_2$ is injected in suitable rocks underground and reaction conditions are provided by the location, in a similar way to other geological storage mechanisms, or *ex-situ*, when minerals are mined and reacted in industrial plants. The former solution needs acquisition of knowledge on geological characterisation and underground processes kinetics, while the latter poses issues linked to the impacts of extraction and transport of minerals, resembling to enhanced weathering, and to the energy requirements for maintaining reaction conditions (46). *Ex-situ* mineralisation could be achieved directly, reacting gaseous $CO_2$ with minerals at temperatures above 650°C, or through an aqueous solution and the use of various industrial wastes as a feedstock, rather than minerals, allows to reduce impacts and develop circular economy pathways. Despite these solutions seem to be inconvenient for a large deployment and need further improvements, a strategic small-scale deployment could result crucial in reaching emissions mitigation targets (47).

#### 2.1.2.6 Storage sites affordability

Many of the storage options face multiplicity of technical, economic, geographical, social and regulatory hurdles; however, to support the oncoming massive deployment of CCS technologies an effective storage framework has to be realised. The most promising and technical consolidated methods, based on underground injection, have their major concerns in possible catastrophic $CO_2$ releases and geological events, due to pressure and volume variations induced by the stored material, while deep ocean sequestration deployment presents high uncertainties on long-term effectiveness and chronic environmental effects and a wide application of mineralisation processes would difficultly become affordable.

However, low risk strategies and technologies currently available are limited by cost and fall short of removing climatically significant quantities of $CO_2$, while several estimations on the global capacity for geological storage revealed huge potential for these techniques, offering the opportunity to assess their application for the selection of adequate locations. The main aspects to be further investigated are associated with estimation of actual storage capacity, tracking, verification and monitoring of $CO_2$ during and after injection, characterisation of potential injection-induced seismicity, standardisation of storage evaluation criteria, and effective ethic mechanisms, to fully understand and anticipate the potential drawbacks (34).

Global estimates reflected total available sizes, but the actual accessible or usable capacities that are economically and technically feasible may be much less; the practically accessible global capacity for geologic sequestration of CO2 have been recently estimated to range between 8000 and 55,000 GtCO2 (48). A geographic distribution of potential $CO_2$ storage reservoirs is illustrated in Figure 5; this could assist the deployment of different mitigation solutions through site specific evaluations and an effective facilities distribution, aimed to reduce the cost, logistic and technical challenges of $CO_2$ transportation.

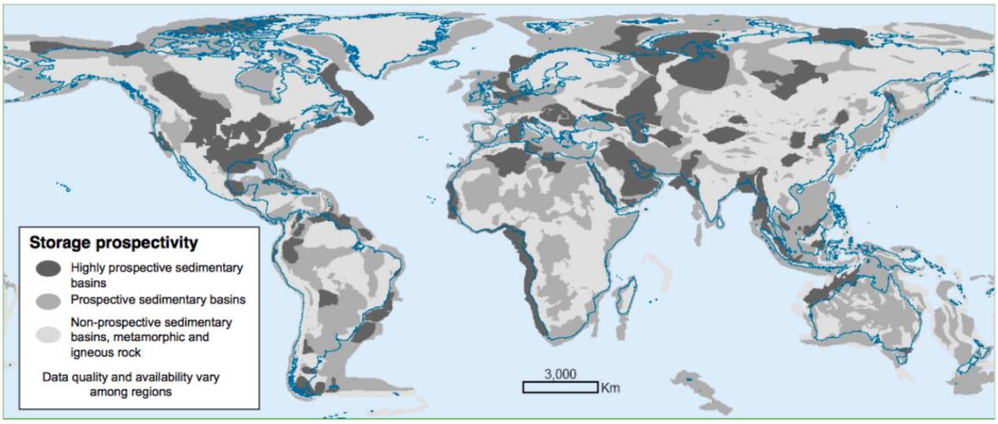

*Figure 5: Global distribution of potential $CO_2$ storage sites.* (49)

For large-scale $CO_2$ storage, the proximity of the sequestration site to point sources is an important consideration, and this could be achieved matching large-scale fossil fuel power plants with onshore potential $CO_2$ storage sites. Off-shore locations, indeed, would be more adequate to store $CO_2$ from other sources than power generation and would be even coupled with other activities like EOR, to make them cost-competitive; in this context, for the reduction of $CO_2$ supply duties, DAC could represent the best available technology.

## 2.2 Carbon capture and utilisation (CCU)

CCU, which consists of developing $CO_2$-derived products and services together with related technologies to use $CO_2$ as a feedstock rather than releasing it to the atmosphere, can complement CCS, but is not an alternative, as the large quantity of $CO_2$ to be captured cannot certainly be fully absorbed by any CCU scenario. Indeed, by the moment only a minimal fraction of the anthropogenic emissions, of about 230 $MtCO_2$, is yearly used for industrial purposes, such as urea manufacturing, and a lot of commercial applications currently involve its direct use, in example as a working fluid or solvent, for enhanced oil recovery (EOR), in food and beverage production and for stimulating plant growth in greenhouses. Anyway, to contribute to its circular economy development and to the climate mitigation objectives achievement, CCU implementation would be aimed at using $CO_2$ as a feedstock and converting it into value-added products such as polymers, building materials, chemicals and synthetic fuels. The main drawback of $CO_2$ chemical use is the large amount of energy necessary to feed its the strongly disadvantaged reactions, as it is a highly stable compound, having a standard formation enthalpy of about -393.5 kJ/mol. (50, 51).

### 2.2.1 Building sector

$CO_2$ utilisation in building materials could be regarded as a hybrid solution between use and storage, as it is converted to minerals which will be almost permanently stored in new buildings. Calcium-silicate-based binders, such as Portland cement and its lower energy alternatives, experience very rapid hardening when adequately moistened and exposed to high concentrations of $CO_2$. Carbonation curing of concrete involves the introduction of gaseous $CO_2$

which reacts with the calcium silicates in cement and forms a highly densified surface layer by the precipitation of calcium carbonates, resulting in improved physical performance and better overall resistance to freeze-thaw cycles, sulphate salts, and acids. While natural carbonation is undesirable as it lowers the pH, leading to corrosion in reinforced concrete, a curing process carried out under adequate conditions would overcome that issue. In addition to binder activation, artificial carbonate aggregates could be produced from suitable industrial waste, such as steel slag and bauxite residue, optimally activated by $CO_2$, also for the purpose of waste recycling into raw building materials, yielding a final $CO_2$-impregnated material suitably hardened and graded to replace natural aggregates in concrete. Anyway, this kind of approach would result more adequate to mitigate the high $CO_2$ emissions of building sector, rather than an effective mitigation solution for emissions from other sources (52, 53).

### 2.2.2 Polymers and specialty chemicals

Chemicals and polymers production are other processes which could represent growing $CO_2$ utilisation pathways as this compound is already used, even though in low quantities, by many industrial processes. As mentioned before, the largest amount of $CO_2$ is currently used in the synthesis of urea, forming C-N bonds with ammonia. Many other high-added-value compounds, including carbamates, isocyanates and ureas, used as pharmaceuticals, agrochemicals, fuel additives and polymers, can be manufactured at the same manner, avoiding the use of highly toxic phosgene (54). A phosgene-less synthesis route can be also adopted for organic carbonates, obtained by alcohols through the formation of C-O bonds, which are widely used for the synthesis of polymers, such as various polycarbonates and polyurethanes, surfactants and plasticizers. To achieve high yields, however, this kind of reactions need the forcing of equilibrium by the removal of side product water. $CO_2$ can be also used to form C-C bonds, as direct or indirect carboxylating reagent, for the preparation of carboxylic and dicarboxylic acids. The latter would have an important role in the bio-based polymer industry, as they are used both as monomers and additives and could be obtained by sugars (55).

These pathways, offer the advantage of requiring little energy input, because $CO_2$ is converted into carbonate, with an even lower energy state, and, particularly for polymer processing, would even result a more cost-effective solution than their fossil counterparts. However, these products are by the moment almost specialty chemicals and, despite offering high value-added products, would difficultly cope with the large amount of $CO_2$ to be used, while the global market volume for hydrocarbon fuels is nearly two orders of magnitude larger than that for chemicals, making $CO_2$-to-fuels is an attractive perspective. Indeed, as a large amount of the global $CO_2$ emissions is raised by the exploitation of fossil fuels, this would result a more actual solution to accomplish a closed material cycle for carbon, even carbon neutral if the energy supplied to the system comes from nuclear or renewable sources (50, 56).

### 2.2.3 $CO_2$-to fuels

$CO_2$-to-fuels conversion would also offer an effective means for large-scale energy storage, as power-to-X (P2X), including power-to-gas and power-to-liquid technologies are based on the production of hydrogen, commonly through an electrolyser, and its subsequent reaction with $CO_2$, obviously captured from some source, to form both gaseous and liquid hydrocarbons. These processes are regarded with interest to balance renewable power extraction flotation because of the high energy density of hydrocarbons, especially of liquid fuels, which can offer significant advantage to battery storage; moreover, $CO_2$-derived fuels may notably be used in sectors for which few low-carbon alternatives exist, such as aviation (57).

The most mature conversion pathways, depicted in Figure 6, are direct conversion of $CO_2$, by hydrogenation and indirect conversion, via reverse water-gas shift (r-WGS), forming CO to be added to syngas mixtures. The former allows to produce light compounds, such as methane, ethane and their alcohols, while syngas can be converted to higher hydrocarbons relying on the well-known Fischer-Tropsch (F-T) process. In addition, both the methods would be aimed at the synthesis of methanol, of which the role in decarbonised energy conversion have long been regarded with interest. Indeed, it is a key intermediate for many other consolidated processes, that were initially developed to build chemicals by coal, but are also suitable for $CO_2$ utilisation (58).

Being $CO_2$ a very stable and non-reactive molecule, in a strongly oxidised state, the large amounts of external energy to convert it into an energy-rich fuel is chemically supplied by the high reduction power of hydrogen molecule, so the effectiveness of the carbon recycling process would be strongly affected by the source of energy used to produce it. Indeed, hydrogen is currently available in different "shades"; namely, grey hydrogen, which is produced by reforming natural gas, emitting $CO_2$, blue hydrogen, obtained in the same way, but applying CCS with a similar layout to pre-combustion capture, and green hydrogen, delivered by RES extraction, by water hydrolysis. While by the moment grey hydrogen is the most affordable, green shade has attracted increasing interest in recent years, due to great cost reductions in solar PV and wind energy technologies and to the fact that environmental regulations will make the two colours cost follow opposite trends. For the same reason, as a decline in fossil fuels use and a wide deployment of CCS are expected, the $CO_2$ used must increasingly be sourced from biomass or through direct air capture (DAC), which can truly support a carbon-neutral life cycle (50, 59).

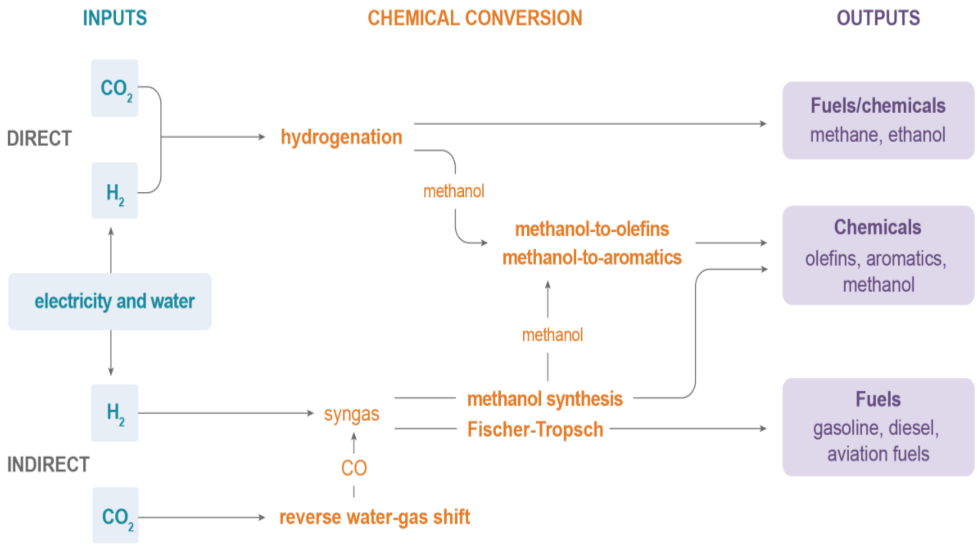

*Figure 6: Scheme of main chemical conversion pathways involved in $CO_2$ use as a feedstock. (50)*

Despite the catalytic thermal routes are the most employed, several promising alternatives could be represented by photocatalytic, electrochemical or photoelectrochemical pathways, that both would allow avoiding hydrogen provision. Photocatalytic systems, indeed, are designed to simulate natural photosynthesis coupling $CO_2$ reduction with $H_2O$ oxidation, powered by sunlight on adequate catalysis conditions, but offer still limited yields. More improvements on electrocatalysis materials and process conditions are too required for electrochemical approaches, which are based on the uptake of hydrogen from water, in a similar manner to electrolysers, but would carry out the hole $CO_2$-based fuel synthesis in a single step (60).

## 2.3 $CO_2$ transport

Transport is the stage of carbon capture, utilisation or storage that links $CO_2$ sources with production or storage sites; as mentioned above, this could result one of the most critical aspects to be considered outlining a CCUS framework. The four basic options for $CO_2$ are pipeline, waterborne, rail, and road transport, which all involve bringing $CO_2$ in the supercritical or the liquid state, at pressures ranging over 50 to 100 atm (5-10 Mpa) (49).

Before this stage, the captured $CO_2$ usually needs to be purified, in order to avoid troubles in the subsequently compression and liquefaction, and even in its storage. In particular, non-condensable gases like $N_2$ and $O_2$, present in the air and still abundant in post-combustion flue gases, affect the viscosity, compressibility, and fluid dynamics properties of the $CO_2$, $H_2$, mainly from pre-combustion syngas clean-up step, could lead to embrittlement of the transport vessel or pipeline. while pollutants like $NO_x$ and $SO_x$, from fossil fuels, are commonly removed upstream the capture unit. Moreover, moisture, contained in each type of $CO_2$ stream to be captured, has a significant role, as their mutual solubility at transport conditions would allow the formation of a high corrosive aqueous phase saturated with $CO_2$, having an acidic pH around 3. Hence $CO_2$ is almost always dried before transport, as if containing less than 10 ppmv $H_2O$ it results non-corrosive to pipelines and vessels made of carbon-manganese and other low expensive steels (61).

In the context of long-distance movement of large quantities of $CO_2$, pipeline transport is part of current practice, as pipelines are already widely used for natural gas, oil, condensate and water transport, both on land and in the sea. $CO_2$ pipelines, as well, are not new, however, their deployment is currently at small scale, for the lacking in storage facilities and utilisation pathways, and in Europe there are few $CO_2$ pipelines today (61). $CO_2$ pipelines are usually operated under supercritical conditions, at pressures between 8.5 and 15 MPa, and temperatures between 13 °C and 44 °C, in order to maintain the stable single-phase flow of $CO_2$, avoiding liquid-vapour equilibrium region.

Despite pipelines technical advantages, for short distances between the $CO_2$ source and storage or small volumes road and rail transport may result more cost-effective, while for distances significantly longer than 1000 km, and even for some offshore applications, ship tankers offer better economics and are generally preferred. These methods refer to the routine operations of liquefied natural gas and petroleum gases transport by marine tankers, on a large scale, and even by rail and road tankers. In the same way $CO_2$, still after purification, is commonly carried in liquid form, keeping it near above its triple point to achieve a high density; however, this solution exhibits a high energy requirement, mostly due to the liquefaction process (62).

## 2.4 $CO_2$ pricing and sharing

To encourage the deployment of mitigation measures, environmental policies are implemented aiming at an adequate balance among taxation and incentives on $CO_2$ emissions management. Carbon pricing is view as the most suitable tool to promote investment and accelerate progress in decarbonizing the global energy systems. Currently, carbon pricing is implemented at different levels across the world, under Kyoto Protocol guidelines, with the main goal of achieving a fair distribution of pro-capita $CO_2$ emissions (63).

Economic policy approaches could be based on carbon taxation, which would force cuts in fossil resources use and consequent emissions through the application of direct technical measures, or on emission trading scheme (ETS), including both cap-and-trade and baseline-and-credit systems. Those indirect solutions would rise a market share for $CO_2$, offering potential economic benefits for mitigation initiatives aimed at its consumption, even if decoupled by its production and/or release. NETs deployment and CCU pathways implementation would so result more attractive options and more effective management and sharing mechanisms of infrastructures, such as piping and storage facilities, could be established (64).

European countries, leading the green economy transition, have already well implemented carbon pricing through EU-ETS, which is a cap-and-trade system with international credit exchange flexible mechanisms. European Unit Allowances (EUAs), equivalent to 1 ton$CO_2$eq, are yearly assigned to each country and distributed among $CO_2$ emitters, in a decreasing amount to suite the established emission reduction pathway; these credits can then be exchanged on international platforms on basis of actual emissions, paying for the excess or gaining by the reductions. The EU ETS is currently the world's largest carbon market and the biggest source of demand for international credits, making it the main driver of the international carbon market and the main provider of clean energy investment in developing countries and economies in transition. Anyway, as pricing carbon work well for large volume point source emissions sectors, such as electric power generation, fertilizer production and cement or steel manufacturing, while it is more difficult to implement for the transportation sector and agro-food industries, only about 21.5% of the global GHG emissions is currently regarded by carbon pricing initiatives (63, 65).

While a high $CO_2$ price would be advisable by an environmental point of view some main drawbacks have to be kept in account. Indeed, as industries subject to regulations would drop the additional cost downstream on consumers, low-income population of advanced countries would be the most economically affected and possible detrimental effects on the economic growth could affect the expected payback, consequently bringing to loss of interest, for technological development activities. Moreover, geographical differences on pricing to allow less advanced countries to develop would rise the risk that some emitters may get a free ride on the sincere mitigation efforts of others, or heavy polluters may relocate to regions where the carbon price is low. To meet the target set by the

2015 Paris Agreement, the 2017 Report of the High-Level Commission on Carbon Prices recommended implementing a price of \$40/t$CO_2$ to \$80/t$CO_2$ by 2020, and \$50/t$CO_2$ to \$100/t$CO_2$ by 2030; anyway, by the moment most of the prices lie below \$25/t$CO_2$, and many are even considerably lower, at around \$10/t$CO_2$ to \$15/t$CO_2$, failing to provide a strong incentive and motivation to capture $CO_2$ emissions (64). Certainly, the price of carbon should be urgently increased but, to serve as an effective deterrent to unnecessary emissions, more detailed procedures for the allocation of costs, socio-economic dampen mechanisms and global incentives to NETs deployment are needed.

# 3 $CO_2$ CAPTURE TECHNOLOGIES

The technologies aimed at the capture of $CO_2$, even directly from the air, are based on the improvement and adaptation of the more common point source capture and separation methods. Indeed, the recovery of $CO_2$, though not yet employed on a large scale, is a well-developed procedure and the separation of $CO_2$ from gas streams can be achieved by a range of known separation techniques depending on the conditions. Among these, the selection and improvement of case specific technologies is necessary to assure a sustainable capture way, as the separation of $CO_2$ is estimated to represent about 75% of the total cost associated with CCS operations, and even more for DAC (68). In example, while pre-combustion and oxyfuel streams could be almost $CO_2$ and moisture, post-combustion flue gas $CO_2$ concentrations are typically low due to nitrogen dilution, varying between 5 and 15% by volume, and further variations are applied to DAC as the tenor of $CO_2$ is much lower, ranging around 400 ppm, but high temperatures and presence of contaminants, typical of flue gas, are not involved (29).

## 3.1 Absorption in liquid systems

Absorption processes, either chemical and physical, rely on the interfacial equilibrium between the gas stream stripped by the absorbent liquid phase in an absorption tower, often realised as a packed bed, a spray column, or a bubble column. After that step, solvent is recovered removing the $CO_2$ in a coupled regeneration tower, where higher temperatures and/or lower pressures are applied, leaning on the solubility behaviour of gasses in liquids. For effective capture of $CO_2$ from massive volumes of gasses, in example from power plants, exceptionally large interfacial contactor areas are required to overcome the mass transfer resistance at the gas / liquid interface; moreover, low concentrations of $CO_2$ in the gas even require the use of large absorption towers, consequently affecting capital and energy costs. Therefore, in recent years many efforts have also been focused on the development of alternative processes for $CO_2$ capture, such as adsorption onto suitable solids, cryogenic separation and permeation through membranes (68, 69).

Another possible approach, aimed at the reduction of the absorption utilities size, improving the gas / liquid contact, is the adoption of a rotating packed bed (RPB) layout, also denoted as Higee technology, already used in many industrial unit operations. In this kind of towers, the liquid, fed in countercurrent flow or cross flow, contacts the gas on the surface of packing under high centrifugal field, so that it is split into small droplets and thin film during it passes through the packing (70).

## 3.1.1 Chemical absorption

### *3.1.1.1 Alkanolamines aqueous solutions*

Absorption is commonly achieved through chemical reaction between $CO_2$, acting as an acid, by reaction (1), and a basic compound in aqueous solution. Main post-combustion capture technologies consist of absorption into liquid amine solutions, that have been previously used industrially for more than half a century and are presently still one of the most suitable and widely employed technologies for high volume flue gas stream treatment. The commonly used absorbents are typically 25–30 wt% aqueous solutions of alkanolamines, such as monoethanolamine (MEA), diethanolamine (DEA), and N-methyldiethanolamine (MDEA), containing at least one hydroxyl and amine group, which capture $CO_2$ following the reactions (2), (3), (4), listed below (71).

Despite their proven efficacy in capturing $CO_2$, absorption processes still entail major drawbacks related to the corrosive properties of liquid amines and the energy losses, mainly influenced by chemical reactions in absorber column, and finite temperature differences in heat exchangers. Moreover, the amine losses incurred during the operation, due to thermal and chemical degradation, by $O_2$ or pollutants like $NO_x$ and $SO_x$, have a not deniable impact, due to their large production $CO_2$ footprint and costs (69).

Solvent regeneration commonly an intense stripping with steam at temperatures of about 120 to 140 °C, higher than those of 40 to 60 °C involved for the absorption step; some solutions have been attempted using polyethylene glycol (PEG) as a solvent, to reduce the energy duty of the process, relying on its much lower heat capacity than water. This could also represent a good solution to corrosion issues; however, its actual applicability is limited by a low temperature resistance, leading to undesirable weight losses during operation (73).

(1) $$CO_2 + H_2O \rightleftarrows H_2CO_3 \rightleftarrows H^+ + HCO_3^-$$

(2) $$2\,R_1R_2NH + CO_2 \rightleftarrows R_1R_2NCOO^-R_1R_2NH_2^+$$

(3) $$R_1R_2NCOO^- + H_2O \rightleftarrows R_1R_2NH + HCO_3^-$$

(4) $$R_1R_2R_3N + CO_2 + H_2O \rightleftarrows R_1R_2R_3NH^+ + HCO_3^-$$

The reactivity of alkanolamines towards $CO_2$ decreases with amine ranking, in example from 7000 $m^3/(s\cdot kmol)$ for MEA, to 1200 $m^3/(s\cdot kmol)$ for DEA, and to 3.5 $m^3/(s\cdot kmol)$ for MDEA, at 25 °C, while the $CO_2$ capacity follows an opposite trend, being about 1 mol$CO_2$/mol for tertiary amines, near to the double of the average $CO_2$ capacity of primary and secondary amines, as the latter form carbamates while the former lead to bicarbonates production (69).

For these reasons mixed amines have been proposed to enhance $CO_2$ capture efficiency and reduce regeneration cost; enhancement of the $CO_2$ equilibrium loading capacity could be also achieved using steric hindrance amines, such as 2-amino-2-methyl-1-propanol (AMP), to reduce the stability of the formed carbamate, that undergoes hydrolysis, releasing bicarbonate and free amine molecules for further reaction. Moreover, the cyclic diamine piperazine (PZ), and its derivatives, act as promoters for $CO_2$ capture because of the rapid formation of carbamate; however, PZ advantages on the resistance to oxygen and thermal degradation, to a temperature up to 150°C, are balanced by a lower solubility and a higher vapor pressure respect to the traditional alkanolamines (74).

An alternative pathway to reduce the energy burden of the regeneration step, resulting in overall energy savings of 10% to 45%, involves the replacement of thermal regeneration with capacitive deionization (CDI). Here charged species in the solution, formed by absorption chemical reactions are collected by electrosorption, either on the anode and the cathode surfaces; in this way, the regenerated ion-free amine solution is then fed back to the $CO_2$ absorber, and only the reacted sorbent, in concentrated solution, is recovered by heating (75).

#### 3.1.1.2 Ammonia aqueous solutions

Chemical absorption could be also achieved through basic solutions of ammonia, or other inorganic substances, in attempt to overcome some of the technical limitations of amine-based scrubbing. In the "chilled" ammonia process the gas reacts with the aqueous ammonia solution in a wet scrubber to form ammonium bicarbonate ($NH_4HCO_3$) or carbonate ($(NH_4)_2CO_3$), then regenerating ammonia by their thermal degradation. In post-combustion applications, prior to scrubbing, the flue gas undergoes pre-treatment in order to fully oxidize the nitrogen and sulphur oxides impurities to $NO_2$ and $SO_3$, which then lead to the by-production of ammonium sulphate ($(NH_4)_2SO_4$) and nitrate ($(NH_4NO_3)$), valuable chemicals usable as fertilizers (76).

Some systems are also based on a "dual alkali approach", similar to the Solvay process, for sodium bicarbonate production, in which ammonia is used as primary alkali to catalyse the $CO_2$ reaction with sodium chloride to form the sodium bicarbonate precipitate, eventually collected, and then heated to produce sodium carbonate ($Na_2CO_3$), while lime is subsequently added, in the desorption tower, as secondary alkali to recover ammonia by ammonium chloride (77), following the reactions (5), (6).

(5) $$NH_3 + CO_2 + NaCl + H_2O \rightarrow NH_4Cl + NaHCO_3 \downarrow$$

(6) $$2\, NH_4Cl + Ca(OH)_2 \rightarrow 2\, NH_3 + CaCl_2 \downarrow + 2\, H_2O$$

However, lime is produced from limestone by the calcination reaction (8) followed by hydration (9), reported below, thus the overall reaction involves that for every two moles of $CO_2$ removed from the flue stream, one mole of $CO_2$ is released back to the atmosphere. Moreover, the heat requirement for calcination, still maintains energy intensive regeneration step for this process and, similar to amines, ammonia-based $CO_2$ capture also keeps drawbacks which have to do with the upstream production of ammonia, via the Haber-Bosch process, and its impacts.

### *3.1.1.3 Causticization processes*

Causticization processes are based on the use of aqueous solutions of alkali or alkali-earth metal hydroxides, that chemically react and remove $CO_2$, and have been historically employed as part of the life support systems in confined environments, such as submarines and space crafts, where the resulting precipitates of insoluble carbonates are filtered and removed from the solution (66). Because of the ultra-dilute nature of $CO_2$ in the atmosphere, these chemical sorbents with strong $CO_2$-binding affinities are typically employed in DAC applications, while result less suitable for carbon capture from point sources, due to higher regeneration energy requirements than many other sorbents. Another concern on many of these processes is given by the water losses in spray towers, such as in other utilities, due to water evaporation during contact with air, that could be reduced increasing the solution concentration.

The initial DAC "strawman", involves the use of calcium hydroxide, following reactions (7), (8), (9); pools of hydroxide solution, either passive or agitated, provide one of the simplest concepts in which $CO_2$ from air can be captured with calcium carbonate precipitating and accumulating. Calcium carbonate is separated and dried before a calcination step, above 700 °C, to release the captured $CO_2$ as a concentrated stream, forming calcium oxide; calcium hydroxide is finally regenerated by a slaking process, via hydration of calcium oxide (78).

(7) $$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \downarrow + H_2O$$

(8) $$CaCO_3 \rightarrow CaO + CO_2$$

(9) $$CaO + H_2O \rightarrow Ca(OH)_2$$

Although calcium hydroxide systems result efficient in capturing $CO_2$, drying and calcination steps both require energy and provide the largest component of the energy penalty; indeed, the calcination requires 179 kJ/mol of $CO_2$, while the thermodynamic minimum required energy for inverting reaction (7) is only 109.4 kJ/mol. Moreover, the kiln should use pure oxygen instead of air to avoid the further separation of desorbed $CO_2$ from nitrogen which, as discussed below, results particularly difficult due to selectivity issues (79).

The issue of low calcium hydroxide solubility in water, which limits the maximum hydroxide concentration practically achievable to bind $CO_2$, could be addressed using sodium hydroxide solutions, still offering sufficiently strong binding of $CO_2$ with the added benefit of higher water solubility of the formed carbonate. NaOH is regenerated through a causticization process, borrowed from the paper industry Kraft process, in which this compound is used to extract cellulose from wood, which involves the exchange of carbonate ions from sodium to calcium by reaction (10), with a theoretical efficiency of 96% (80). Despite its solubility NaOH concentration is limited to 1 mol/L, as the use of calcium could even result in the unwanted precipitation of calcium hydroxide. Another alternative is represented by KOH, which forms a more soluble carbonate, but is, on the other side, more expensive than NaOH; however, this compound could result more useful in processes aimed at avoiding calcination step, where calcium is not used and is possible to increase the absorption solution concentration. For example, $CO_2$ can be released through acidification with sulfuric acid, following reaction (11), while KOH and $H_2SO_4$ are subsequently recovered by electrodialysis (81).

(20) $Na_2CO_3 + Ca(OH)_2 \rightleftarrows CaCO_3 \downarrow + 2\,NaOH$

(31) $K_2CO_3 + H_2SO_4 \rightleftarrows K_2SO_4 + H_2O + CO_2 \uparrow$

Still borrowing from the pulp industry, an alternative method to solve the issues connected to the use of calcium and the need of carbonate calcination is autocausticization, where the reaction product is water-soluble and is maintained as a caustic solution throughout the entire cycle. Sodium metaborate ($NaBO_2$) can react with sodium carbonate, resulting from the absorption, to directly release $CO_2$ by reaction (12) and subsequently soda is regenerated through reaction (13) with water; anyway, this step keeps high energy requirements, involving temperatures above 800 °C.

(42) $NaBO_2 + Na_2CO_3 \rightarrow Na_3BO_3 + CO_2$

(53) $Na_3BO_3 + H_2O \rightarrow 2NaOH + NaBO_2$

Direct causticization of sodium carbonate using titanium dioxide, indeed, involves the separation from the solution of the formed insoluble carbonate, that reacts with the decarbonizing agent after further drying and dehydration; depending on reaction conditions, a variety of sodium titanates would form. The main reaction (14) is that between $Na_2CO_3$ and $Na_2O \cdot 3TiO_2$; the overall decarbonization enthalpy is equal to 90 kJ/mol and much lower than for calcination, whether the process occurs above or below the melting point of $Na_2CO_3$, however at temperatures between 800 and 900 °C. Sodium trititanate and NaOH can be then regenerated and recycled by hydrolysis at temperatures near 100 °C, through reaction (15).

(14) $7Na_2CO_3 + 5(Na_2O \cdot 3TiO_2) \rightarrow 3(4Na_2O \cdot 5TiO_2) + 7CO_2$

(15) $3(4Na_2O \cdot 5TiO_2) + 7H_2O \rightarrow 5(Na_2O \cdot 3TiO_2) + 14NaOH$

#### *3.1.1.4 Carbonates aqueous solutions*

Due to their non-volatility, low corrosivity, and non-toxicity, sodium or potassium carbonate-bicarbonate slurries, could be also applied for $CO_2$ capture by reaction (16), inverted at higher temperature, borrowing the absorption utility design from the $CO_2$ extraction for methanol synthesis. Anyway, they exhibit low absorption rates compared to many of the amine-based and inorganic caustic solutions, that involve the use of higher absorption towers and make their application less favourable (58).

(16) $Na_2CO_3 + CO_2 + H_2O \rightleftarrows 2\,NaHCO_3$

As the rate of absorption of $CO_2$ in carbonate solutions is limited by physical mass transfer, it could be improved by creating smaller and uniform bubbles, which lead to increase the interfacial area between gas and liquid and consequently the mass transfer rate. Surfactants known as frothers, having a polar hydrocarbon group and a non-polar group reduce the surface tension and prevent bubble coalescence, thereby producing tiny and uniform bubbles. While most of the available additives, like piperazine (PZ) and MEA, negatively affect the desorption energy requirements and the solution corrosive properties, recently, the addition of a frother showing none of these effects, at 5-20 ppm, allowed even dilute sodium carbonate solutions to achieve 99.9% $CO_2$ capture, almost doubling its efficiency, so these compounds would attract great interest in further studies (82).

### 3.1.2 Physical absorption

Some processes are based on physical absorption of $CO_2$, which would require lower energy intensity for the desorption step, relying only on its solubility behaviour in the solvent, governed by Henry's law at the interface; where $p_i$ is the solute partial pressure in the gas phase, proportionally linked to its concentration in the liquid solvent $C_i$ by the mixture specific Henry's constant, depending on temperature.

$$p_i = H_i(T) \cdot C_i$$

It is clear that the capacity of the solvent is limited by the $CO_2$ partial pressure, affected by each the pressure and the $CO_2$ fraction of the feed stream, making this method more suitable for the treatment of gases from pre-combustion or oxy-combustion. As the solubility of gasses in liquids usually decreases with increasing temperature, the absorption step involves operation at reduced temperatures and high pressures, in order to dissolve the maximum quantity of $CO_2$, which is then released, acting on temperature, pressure or both. In this way, however, $CO_2$ remains partly dissolved in the liquid and the effectiveness of the process results to mainly depend on the difference between absorption and desorption conditions.

Several commercial processes based on physical absorption are available for industrial scale separation and capture of $CO_2$, but they are often aimed at the concurrent removal of other impurities, like $H_2S$, for the purification of industrial flue streams, rather than the capture of a component. Besides these processes can offer several advantages including low vapor pressure, low toxicity and low corrosion activity, they are severely limited by uptake capacity and their and still energy intensive due to the operating temperature regime thermal requirements. There is need for developing better and more stable solvents with higher solubility for $CO_2$ at higher temperatures than those available today (69).

#### 3.1.2.1 Perfluorinated compounds (PFCs)

Perfluorinated compounds (PFCs), due to the strong C-F bonds in their molecular structure and negligibly small dipole moments, offer high stability and low molecular interactions; this implies a good solubility for $CO_2$ during absorption, as well as a low energy barrier to its release during desorption step. In particular, the properties of different compounds, including perfluoroperhydrofluorene ($C_{14}F_{24}$), perfluoroperhydrophenanthrene ($C_{17}F_{30}$), and perfluorocyclomethyldecalin ($C_{13}F_{22}$), known respectively as PP10, PP11, and PP25, have been evaluated for the removal of $CO_2$ by wet scrubbing of flue gasses. In these solvents $CO_2$ is up to 7 times more soluble than $N_2$ and they resulted to be stable and reliable at process temperatures up to 227 °C and pressures up to 3 Mpa, but reduced solvent loss by evaporation would involve an increase in viscosity, which poses limitations to the mass transfer coefficients and the contact area technically achievable (83).

#### 3.1.2.2 Ionic liquids (ILs)

Similar technical advantages and drawbacks for $CO_2$ absorption are offered by ionic liquids (ILs), an extremely rich class of high molecular weight organic salts, most of which have melting points near room temperature, formed by an organic cation, and either an inorganic or an organic anion. These materials are able to offer exceptional chemical and thermal stability, negligibly low vapor pressure, non-flammability, recyclability and low toxicity, but are also characterized by high viscosity, even increased by the formation of gel-like structures due to high polarity, rising the same issues highlighted for PFCs.

The main advantage of ILs is that their properties could be easy tuneable through an appropriate selection of anions and cations, relying on a good stock of commonly employed ions, which already offers a quite large number of possible compositions. However, the preparation and purification are usually difficult and costly and, by the moment, the obtained $CO_2$ uptake capacities make their use as liquid physical adsorbents less favourable than other capture solutions. The possibility to introduce task-specific functional groups (TSFGs) allow to increase $CO_2$ capture by chemical reaction, commonly adding amine derivatives groups; however, this kind of compounds seems to be more promising in supported forms, on solid sorbents or membranes, which are resumed later, to circumvent the difficulties typical of liquid absorption systems (84).

#### 3.1.2.3 Nanoparticle organic hybrid materials (NOHMs)

Liquid-like nanoparticle organic hybrid materials (NOHMs) have been investigated as they have features similar to bulk ILs but can address their viscosity related issues. Liquid-like NOHMs are constituted by a silica core, having a size of about 10 nm, covered by the polymeric material through ionic or covalent interaction; like for ILs compounds, this material could either contain or not TSFGs. NOHMs firstly prepared using polymers that do not contain functional groups with strong chemical affinity toward $CO_2$ can contribute to $CO_2$ capture via Lewis acid-base interactions, although this effect is insignificant compared to the effect of TSFGs such as amine. In all cases, multicyclic $CO_2$ capture tests confirmed superior recyclability of NOHMs, which also show a high selectivity toward $CO_2$ (85).

## 3.2 Cryogenic distillation

Cryogenic distillation is very energy intensive and generally considered impractical for large scale $CO_2$ separation, as it requires cooling of the flue gas down to below the $CO_2$ sublimation temperature of -100 to -135 °C and from 10 to 20 MPa pressure, in order to solidify the $CO_2$ in the flue gas mixture, by external refrigeration and Joule-Thompson effect. After the removal of water, which tend to freeze and block the heat exchangers, the gasses are separated with respect to their boiling points, and up to 90% to 95% of the $CO_2$ in the feed flue stream is captured. Recovery of $CO_2$ by cold liquefaction has the advantage of enabling the direct production of very pure liquid $CO_2$, which can be readily transported but, the amount of energy required in refrigeration, particularly in dilute gas streams, limits its application to preferred concentrations higher than 90 vol%, like those available in precombustion and oxyfuel combustion processes (68).

## 3.3 Membrane technologies

Membranes are aimed at the separation of one or more components from a stream through selective permeation; these are an attractive technical solution, (9–16) not requiring a separating agent, and its cyclic regeneration, or any phase change, that involve small footprints and low maintenance compared to other processes. In addition, membrane systems compactness and modular aspect allow easy positioning, useful in particular for retrofitting applications, multi-stage operation and fast scale up to larger units, with a linear increase in costs.

Each membrane offers different selectivity and permeability properties towards any compound, which in turn determine the separation factor and the permeate flow, by the equation below; where $x$ represent the molar fraction of the compounds to be separated in the feed and in the permeate, respectively, $P_m$ is the overall membrane permeability and $TMP$ is the trans-membrane pressure, given by the difference at each side.

$$S.F. = \frac{x_{i,p}/x_{j,p}}{x_{i,f}/x_{j,f}}$$

$$j_p = TMP \cdot P_m$$

It results clear that the performances achievable in terms of capture capacity are proportional to the adopted TMP, given by the difference between the pressure applied at each side of the membrane, but strongly depend on the features of the stream to be treated and of the membrane material, with desirable high selectivity and permeability difficult to achieve together. Tuning and modification of materials properties by doping, pore size and porosity control, and process engineering, as well as surface treatment and functionalization may help achieve more favourable membrane properties, while, as the driving force for transport is the TMP and the resistance is proportional to the membrane thickness, keeping an adequate mechanical integrity is required.

However, membranes are an appealing option for $CO_2$ separation, offering good permeating properties by itself; indeed, this species is a very small gas molecule, only larger than He and $H_2$ among permanent gases, respectively having a kinetic radius of 3.3 Å, 2.59 Å and 2.89 Å. Moreover, $CO_2$ molecular structure enables it to naturally adsorb more strongly to or dissolve at much higher concentrations in many membrane materials compared to other gas species and so a high selectivity can be achieved too (68). Anyway, for their layout, membrane technologies are more suited for relatively high concentrations of $CO_2$ such as those encountered in some natural gas deposits or for pre-combustion separation in fossil fuel burning power plants, while they may not be the best choice for post-combustion $CO_2$ capture or from other more dilute sources which would involve great recirculation duties.

#### *3.3.1.1 Polymeric membranes*

Among the different membranes available for industrial purposes, polymeric membranes mainly act by preferential solution of gaseous species within void spaces in the polymer matrix and diffusion through the open channels among the polymer chains. Further development of $CO_2$-selective polymeric membranes should focus on the polymer matrix features control; careful design and fabrication of polymers with appropriate void spaces or channels, having a certain size, side groups, structure, and chain conformation, may improve both selectivity and permeability. Mixed-matrix membranes, made by grafting or blending different polymers or by blending inorganic adsorbents into polymer matrices, may also be a good improvement. However, absolute selectivity is almost impossible to achieve with polymeric membranes, especially for $CO_2/N_2$ mixtures, and they also offer poor mechanical and thermal stability, requiring to cool down flue gas streams to less than 100 °C, so their application to post-combustion and other dilute sources capture is quite impractical, while major benefits could be obtained using them as an auxiliary technology for other capture processes (86).

#### *3.3.1.2 Microporous inorganic membranes*

Inorganic membranes are grouped in the two broad categories of porous membranes, and dense membranes, on the basis of their void fraction; among these, the former offer practical relevance to $CO_2$ separation. Gas transport mechanisms across microporous inorganic membranes are generally Knudsen diffusion, when pore size and the molecular diameter of the species are comparable, surface diffusion, when the species have appreciable difference between surface diffusion coefficients, capillary condensation within the pores of the membrane, and molecular sieving by size exclusion principle, as schematically illustrated in Figure 7. Separation by inorganic microporous membranes is often regulated by the membrane adsorption properties, which could be enhanced acting on porosity and tortuosity of the membrane, thickness of the active membrane layer, operating temperature, and specific surface area, by micro- and nano-structuring. Surface engineering and functionalization, commonly by amine groups, further improves the $CO_2$ adsorption capacity and surface diffusion, but a too strong adsorption would involve a reduction in the maximum permeation flux. (87)

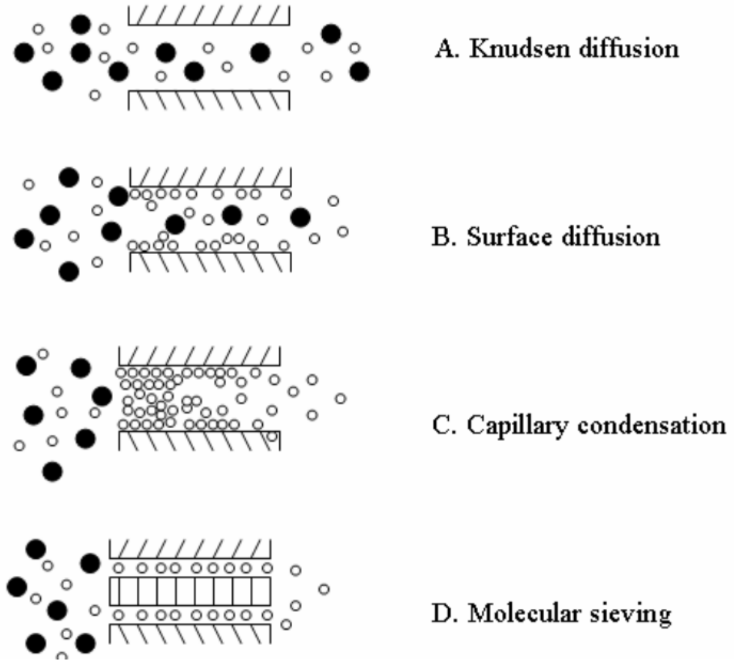

*Figure 7: Main gas transport mechanisms across microporous inorganic membranes. (87)*

Microporous inorganic membranes can be self-standing or be deposited as thin layers or dispersions on inert or active substrates, that provide mechanical support and robustness and may be made of porous ceramics, such as silica, alumina, titania and zirconia, porous glasses or porous metals, such as stainless steel. The inherent chemical and thermal stability of inorganic materials make them attractive for $CO_2$ capture from power plant flue streams, having a wide operating temperature regime and good resilience against contaminants typical of coal. However, selectivity of most inorganic membranes is seriously affected by operating temperature above 200°C and by the presence of humidity in the feed gas, even affecting permeability (87).

Carbonaceous adsorbents in various nanostructures, such as single-wall and multi-wall carbon nanotubes, carbon molecular sieves, carbon hollow fibres, and graphene, offer the advantages of abundance, wide availability, thermal stability, low cost, and low sensitivity to moisture, which could anyway compete with $CO_2$, due to the weakness of adsorption for both, especially operating at high temperatures. The carbon microstructures can be often supported on porous inert substrates including alumina, zirconia, titania, or polymers for improved mechanical integrity (88).

Alumina, indeed, has poor selectivity for $CO_2$ and, as it is possible to make mesoporous structure membranes, it is employed more often as a support material rather than the active membrane, relying on its high chemical, thermal and hydrothermal stability, which are desirable especially for high temperature applications. Porous silica, in the same way, is often employed not as the active membrane but as the inert or less active support material for the more active and $CO_2$ selective membrane or sorption material. Accordingly, most of the silica-based mesoporous membranes used for active separation have either undergone amine surface functionalization, or impregnation into the pores in order to improve their $CO_2$ adsorption and separation properties, however this affects permeability by itself and in concurrence with the presence of moisture (89).

Zeolite-based membranes, indeed, are usually fabricated on a porous substrate by hydrothermal synthesis as an active phase, relying on preferential adsorption and size and shape selective properties of zeolites, which regulate their action by a molecular sieving mechanism. High separation factors have been reported for FAU (faujasite) and T-type (Linde type T) zeolites, respectively equal to 70 and 200, on a 50:50 mixture of $CO_2$ and $N_2$ at room temperature; anyway, this kind of materials still poses the issues of $CO_2$ selectivity and permeability weakening due to high temperatures and moisture presence conditions. Moreover, also chemical and structural modification of the zeolite cages, with appropriate cations or amine-functionalization, to achieve preferential adsorption involves the drawbacks highlighted above (87). Some other membranes could be made on the principle of a supported active phase, such as MOF, which may allow a detailed tuning of poses size and surface structure to regulate and achieve the best adsorption properties. However, for some features of the two processes, and of the possible CO2 capture sources, the application of many active materials would result more effective for adsorption processes, which are discussed below.

## 3.4 Adsorption on solids

Compatibility between the high exit temperatures of flue gasses and operational parameters of the $CO_2$ capture process is highly desirable for effective thermal management and increased process efficiency in CCS applications to power plants. While $CO_2$ capture by absorption in liquid solvents often requires cooling of the gas to temperatures that are compatible with the used solvent, and membranes have technical limitations on temperature too, solid sorbents are usually tolerant to high temperatures of flue gasses emitted from industrial processes, more stable and generally less expensive than liquid solvents.

Moreover, as discussed before, liquid systems usually involve large sizing of the absorption unit to achieve sufficient gas/liquid contact area and mass transfer rates and use of solid sorbents can also overcome this limitation. Indeed, solids with large surface areas can be fabricated to maximize the gas/solid contact area for adsorption and, much higher diffusion coefficients in gasses than in liquids, being of the order of $10^{-5}$ $m^2/s$ and $10^{-9}$ $m^2/s$, render gas / solid interfacial processes to occur inherently faster, allowing ready replenishment of adsorption sites by $CO_2$. These features make solid sorbents a promising solution in particular for $CO_2$ capture from more diluted sources, such as in post-combustion capture and direct air capture (DAC) applications.

Adsorption-based $CO_2$ separation and capture technologies refer to thermal and pressure swing regeneration processes technologies (TSA and PSA), even under vacuum (VSA), well known and widely diffused for industrial gas separation and purification. Each PSA cycle includes pressurization, high pressure feed, co-current depressurization, counter-current depressurization, counter-current purge and several equalization between two beds; while in a TSA mode, the adsorbent bed is usually regenerated by using a hot purge gas, that does not adsorb appreciably, to effect desorption of $CO_2$. The key factors to successful deployment of this technology for $CO_2$ capture are performance, cost, and reliability of the available adsorbents and matching them with adequate cycle configurations, which is critical in both PSA and TSA processes (68).

A wide variety of solid sorbents including zeolites, carbon- and calcium-based sorbents, organic-inorganic composites, and metal-organic framework structures are attracting interest for their $CO_2$ sorptive properties (90), in general, as already outlined, $CO_2$ may be selectively adsorbed mainly by physical interactions or chemical reactions on the solid surface and diffusion into the pores of the solid, even controlled by size and shape selection rules. Sorbent materials research is focused on $CO_2$ selectivity and sorption capacity, regeneration energy requirement and recycling stability, which are strongly conditioned by the adsorption and desorption kinetics; also, chemical and thermal stability, in particular for flue gasses treatment, have to be kept in account. The main issues for active materials, still connected to sorption kinetics, are the interference effects of water vapor, and even of other molecules at high temperature; moreover, large improvements are necessary for solid sorbents to compete with more consolidated absorption processes average $CO_2$ uptake capacities, ranging from 3 to 4 mol$CO_2$/kg of sorbent (91).

### 3.4.1 Physical adsorption and molecular sieving

Physical adsorption happens through the general equilibrium reaction (17), which involves the formation of weak bonds among $CO_2$ molecules and the solid surface; the access to adsorption sites could even be regulated by molecular sieving, using materials with defined pores structures.

$$(17) \qquad CO_2 + Surface \rightleftarrows (CO_2 \cdot Surface)_{ads}$$

Many of these solid sorbents are the same applicable for membrane technologies but, in this solution, they are dispersed on solid supports crossed by the gas flow to capture CO2, instead of allowing its selective permeation, so the desired bonds strength may be different and maximum uptake capacity becomes a relevant feature.

Among carbon-based adsorbents, activated carbons (ACs) are low cost with fast adsorption kinetics and require low regeneration energy, exhibiting a low heat of adsorption, of about -30 kJ/mol, for $CO_2$. However, this also determines lower adsorption capacity, in example of 2.27 mmol/g, and selectivity than other materials, of which the former decreases as temperature increases and both are negatively affected by the competition with water vapor. Attempts to use carbon molecular sieves (CMSs), which are prepared to obtain a microporous structure with unique textural characteristics, revealed an almost deniable difference to common ACs; instead, micropore diffusion may be the rate-limiting step in adsorption dynamics (92).

#### *3.4.1.1 Carbon-based sorbents*

The use of new generation materials, such as carbon nanotubes (CNTs) and graphene, has also become an active area of research, also thanks to the possibility of getting considerable information through theoretical modelling and simulation, to identify the most suitable solutions, before targeted experimental studies. While the equilibrium $CO_2$ adsorption capacity of raw CNTs may be relatively lower than that of granular ACs, purified single-walled carbon nanotubes (SWCNTs) could offer an adsorption capacity, which is an increasing function of the diameter, even twice that of ACs, as reported in Figure 8. Moreover, transport diffusivities for $CO_2$ in nanotubes with diameters ranging from about 1 nm to 5 nm are roughly independent of pressure, at room temperature, and CNTs exhibit higher selectivity of $CO_2$ over $N_2$ than many other sorbents (93).

#### *3.4.1.2 Zeolites*

Synthetic and natural zeolites, widely used for gas separation and purification, are based on silicate frameworks in which substitution of some of the Si with Al, or other metals, leads to a negative charge on the framework, balanced by exchangeable cations within the pore structure, such as Na or other alkaline or alkaline-earth metals, which determine the adsorption properties. Introducing hydrogen as cation provide instead these materials of strong acidic catalysis sites; molecular sieving effect, which regulates the molecules access to pores is due to the defined microporous crystalline structures obtainable, having uniform pore sizes in the interval of 0.5 nm to 1.2 nm. Separation of gases by the zeolite adsorbents depends on these features and on size, shape and polarity of the target molecules; therefore, the $CO_2$ adsorption capacities could be improved by considering and optimizing different factors, such as basicity, pore size of zeolites and electric field strength caused by the exchangeable cations (94).

Chabazite and 13X, resulted to be better adsorbents for $CO_2$ separation from $N_2$ among various natural and synthetic zeolites, respectively; the highest adsorption rates and capacities are achieved in highly charged frameworks, having a low Si/Al ratio, and through the introduction of small and strongly electropositive cations, such as Li. In general, the heat of adsorption of $CO_2$ on zeolites is comparatively large, having a value of -36 kJ/mol for 13X and even higher for other structures, so equilibrium capacity could be achieved within a few minutes; however, lower adsorption for increasing temperature and competition of $CO_2$ with water vapor still pose issues on the gas stream conditions, which may involve some pre-treatments requirement. Moreover, the use of zeolites in fluidized beds poses a technical concern, as they often exhibit a much higher attrition than that of AC and activated alumina, that would possibly cause high maintenance costs and problems in the operation (90).

#### 3.4.1.3 *Metal-organic frameworks (MOFs)*

Metal-organic framework (MOF) structures are another class of promising materials, with highly tuneable molecular sieve effect, for potential applications in hydrogen and methane storage, $CO_2$ capture and separation, as pointed out above, and even catalysis, such as zeolites; they also show similar heat of adsorption values to more common sorbents, however, they are yet to be demonstrated for $CO_2$ capture at pilot scale. MOFs are three-dimensional organic-inorganic hybrid networks formed via multiple links between transition metal, such as Cu and Zn, ions or clusters and organic ligands, including a variety of carboxylates, azolates and phosphonates, that connect them. (95, 96).

Flexibility in changing these building units allows modification and tuning of the structural and functional properties of MOFs; in example, the length of the organic ligand increases the accessible adsorption sites and improves adsorption capacity, but long ligands would result in more fragile structures. More than 20000 MOFs have been studied, varying structures, functional groups and pore sizes, with a typical porosity of more than 50 % of the crystal volume and surface area values ranging from 1000 to 10000 $m^2$/g. The synthesis and characterization of MOFs is one of the most rapidly developing areas of chemical science; identification and description of the nets that describe the underlying topology of these structures led to advances in methods of computer simulation, in particular for the adsorption isotherms calculation, which makes the computer pre-screening of potential materials an attractive procedure. Moreover, the ability to vary the size and nature of MOF structures without changing their underlying topology gave rise to the isoreticular principle and its application in making MOFs with the largest pore aperture, of 98 Å, and lowest density, of 0.13 g/$cm^3$ (95).

The $CO_2$ absorption capacity of many MOFs is much higher than that of other physical sorbents, showing maximum uptake values even beyond 15 mmol/g, but however requiring a higher pressure, as shown in Figure 8. Despite such high $CO_2$ capacities, thermal compatibility with flue gas streams is still a concern for post-combustion $CO_2$ capture and the impact of moisture and other contaminants on the sorbent stability requires more investigation and improvement. The adsorption capacity of MOFs, especially at low $CO_2$ pressures, could be further increased by tethering reactant groups on their pores surfaces to achieve stronger chemical adsorption; however, the features of these materials make them a promising solution for DAC technologies, in particular adopting this option, which is discussed below (96).

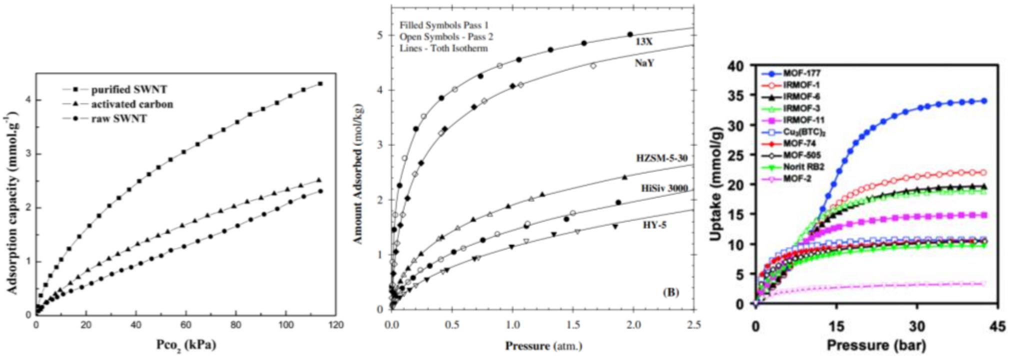

*Figure 8:* Adsorption isotherms for different carbonaceous materials at 35 °C, zeolites at 22 °C and MOFs at 25 °C. (*93*, *94*, *96*)

As the most common and suitable application for solid sorbents is in PSA processes, the selected materials are often firstly characterized through the determination of adsorption isotherms at different temperatures, which give useful information on the maximum achievable $CO_2$ uptake capacities and on the best conditions to adopt for the capture and regeneration cycle; in example, adsorption isotherms for some materials of the described classes are shown in Figure 8, above.

### 3.4.2 Chemical adsorption

Most of the conventional physisorbents described above suffer from low adsorption capacities and selectivity toward $CO_2$, especially at increasing temperature and low partial pressures. To solve these issues, modifications in the surface chemistry of the porous materials by incorporating basic sites capable of interacting strongly with acidic $CO_2$ are considered very promising. The common modifying functional groups are alkaline carbonates and various amine groups, which follow reactions similar to those involved in chemical absorption systems; the stronger binding achievable through chemical reactions, instead of only physical interactions, makes TSA more adequate than PSA, and allow to attempt other designs, such as temperature-vacuum swing adsorption processes (TVSA). This kind of sorbents results adequate for the capture from more diluted sources, such as post-combustion flue gasses, however, strong $CO_2$ binding affinities and limitations on thermal conditions could make some of them more effective for $CO_2$ direct air capture (DAC).

### 3.4.3 Solid oxides, hydroxides and carbonates

The use of solid inorganic bases, rather than their solutions, for ultradilute $CO_2$ removal provides a conceptually straightforward path to $CO_2$ capture from air and can offer effective sorbents for power plants flue gasses treatment; the reactions for different metals cycles are the same involved in water solution processes but, in these cases, take place on the solid surface, commonly in presence of moisture.

Direct carbonation of quicklime (CaO) could be achieved at temperatures between 300 and 450 °C while higher temperatures, often near to 900 °C, are involved in desorption, as thermodynamically favour the formed limestone ($CaCO_3$) decomposition. Despite being not necessary, the presence of water vapor, increases the extent and the rate of carbonation, due to the formation of a film on the solid surface and the adsorption of $CO_2$ by $OH^-$ groups. The use of $Ca(OH)_2$, as expected, offers a faster carbonation reaction with a higher degree of conversion, even without the presence of moisture; for this reason, the carbonation step can be carried out at slightly lower temperatures, ranging from 200 to 425 °C, but the sorbent regeneration still relies on a calcination step (97).

The main drawbacks of these solutions are that the $CO_2$ solid bulk diffusion from the surface result to be strongly limiting the practical achievement of maximum uptake capacity, which also suffers from a marked reduction by subsequent cycles, and its, and gas/solid contact enhancement would emphasise material attrition issues. Moreover, high temperatures are involved both in the desorption, to reverse the strong binding of $CO_2$ commonly achieved through calcination, as in the adsorption step, to assure effective reaction rates. Anyway, the low cost of the limestone sorbent, its reactivity toward both $CO_2$ and $SO_2$ and its resistance to high temperatures, indeed required for the process, make it particularly suitable for post-combustion capture, as neither cooling nor desulfurization pre-treatment would be needed.

Despite Na-based thermochemical cycles are favourable processes in solution and can offer energy benefits also in solid systems, the significantly slow reaction rates during carbonation and subsequent large mass flow rates render the associated processes inefficient respect to those applying Ca-based cycles. Indeed, during carbonation at 25 °C, NaOH was found to reach only 9% conversion after 4 h, while $Na_2CO_3$ in water-saturated air achieved only 3.5% conversion after 2 h. The closing of the cycles could be carried out easier, starting from $NaHCO_3$ as well as $Na_2CO_3$, that reached completion after heating at 90−200 °C for 3 min, and at 1000−1400 °C for 15 min, respectively (98).

Similar thermochemical cycles based on lithium can be also exploited, using its zirconates ($Li_2ZrO_3$) and silicates ($Li_4SiO_4$), that absorb $CO_2$ through the reactions (18), (19), involving the formation of a lithium carbonate solid phase.

(18) $Li_2ZrO_3 + CO_2 \rightleftarrows Li_2CO_3 + ZrO_2$

(19) $Li_4SiO_4 + CO_2 \rightleftarrows Li_2SiO_3 + Li_2CO_3$

Lithium zirconate offers reaction reversibility within the temperature range of 450 to 590 °C, allowing improved thermal management by swinging the temperature in a narrow window for adsorption and regeneration cycles; moreover, the addition of other alkali metal oxides or carbonates, such as $K_2CO_3$, forms binary or ternary eutectic compositions, which improve $CO_2$ adsorption by a molten carbonate film on the surface of the zirconate particles (99).

Lithium silicate exhibits higher $CO_2$ capacity than its zirconate, up to 10 times with respect to other oxides values, and could offer great advantages in post-combustion capture, as an alternative carbonation process to Ca cycles, like shown in Figure 9. Indeed, it offers rapid adsorption kinetics, stability and operation at elevated temperatures below 720 °C; in addition, reaction reversibility at temperatures slightly above, allows to achieve great thermal efficiency. However, the overall rate of $CO_2$ uptake, which exhibits first order kinetics with respect to $CO_2$ partial pressure, seems to be controlled by a highly activated and sluggish surface reaction, so the introduction of lattice defects doping the adsorbents with many different hetero metal atoms, including Al, Ti, V, Fe, Ge, Mg and Nd, is a promising solution for promoting the adsorption capacity of $Li_4SiO_4$ (100).

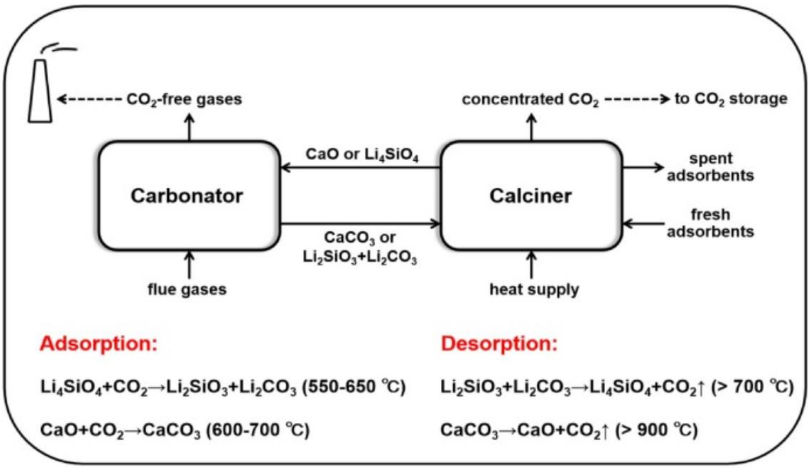

*Figure 9:Comparison of Ca-based and Li-based cycles for CO2 capture from flue gases. (100)*

Chemical adsorption of $CO_2$ with a dry regenerable alkali-metal (Li, Na, K) carbonate-based solid sorbent exploits reaction (16), listed above for sodium, to absorb $CO_2$, with moisture, through bicarbonate formation at 60 to 110 °C and extract it heating the bicarbonate at 100 to 200 °C. Among different alkali metal, $K_2CO_3$ performs the best out of the three carbonates, showing a wide carbonation temperature range where the sorbent efficiency is 100%, while $NaCO_3$ could be even used as it offers better economics. Due to solid mass transfer limitations these sorbents should be often dispersed on different, active or less, supports; despite $CO_2$ uptake capacity of the sorbent is higher as the higher is the carbonate loading, above an optimum value, excess carbonate would block the support micropores, restricting $CO_2$ supply at the active reaction sites, with a reduction of adsorption kinetics (101).

Support materials could be both hydrophilic, like silica gel, alumina and vermiculite, and hydrophobic, such as different kinds of ACs; as discussed above, the porous support matrix is often a sorbent by itself, and can show different synergic, as well as undesired, effects when combined with an active phase. Porous alumina support, impregnated with the active phase, offers the highest dynamic capacity, which however decreases heavily after the first cycle, while AC-impregnated sorbent systems allow a completely reversible adsorption and regeneration. The main cause of $CO_2$ uptake capacity loss in carbonates supported on alumina or other metal oxides, such as MgO, is attributed to the formation of $KAl(CO_3)_2(OH)_2$, $K_2Mg(CO_3)_2$, and K2Mg(CO3)2 3 4($H_2O$) phases during carbonation, which are not converted to the original $K_2CO_3$ phase after regeneration (102).

In summary, the high $CO_2$ capture capacity and the favourable process temperatures could make supported carbonates a better solution than metal oxides and hydroxides, also cheaper than many other sorbents, for post-combustion $CO_2$ capture as for DAC. Anyway, to be commercially viable, the long-term stability and persistence performance of these sorbents under real operating conditions have yet to be established.

### 3.4.4 Organic-inorganic hybrid adsorbents

Organic-inorganic hybrid sorbents are mainly based on the introduction of various amine groups on the surface of different kinds of support materials, relying on their analogous chemical reactivity to the typical aqueous amine absorbents, which leads to the formation of carbamates and carbonates or bicarbonates by reactions (2), (3), (4), listed above. In this way, amine-based adsorbents offer the same $CO_2$ strong binding and capture even at low concentrations, while exhibiting the advantage of low regeneration heat requirements due to the low heat capacity of solid supports. Their low $CO_2$ maximum uptake capacity and high cost, however, are the major challenges to commercialization and deployment of these sorbents, that could be addressed mainly through the preparation of supports with high amine loading, the use of amine with high nitrogen content and the development of effective methods for amine introduction. Indeed, the $CO_2$ uptake capacity results proportional to the quantity of reactant groups, by the adsorption reactions stoichiometry and, in particular, by the typical $CO_2$/N ratio, equal to 0.5 for dry carbamate formation and increased to 1 for carbonates formation, in presence of moisture (89, 90).

The heat of adsorption and the selectivity toward $CO_2$ obtainable through amines functionalization are higher than for physical sorbents, but issues on thermal stability during regeneration could rise, as for alkanolamines solutions. For these reasons, physical sorbents still remain a more affordable solution for post-combustion capture technologies, while organic−inorganic hybrid materials based on amines could result highly suitable for direct air capture and, maybe, are currently the most promising option at this aim, due to some technical and economic advantages of solid (LT-DAC) on liquid (HT-DAC) systems (103).

As already pointed out, most commonly, temperature swing (TSA) and, to a much lesser extent, pressure swing (PSA) processes have been applied to $CO_2$ capture with amine sorbents, however, a diluted $CO_2$ stream is obtained after desorption when conventional inert gas stripping is applied. Thus, to instead obtain a concentrated $CO_2$ stream, a temperature-vacuum swing adsorption (TVSA) process, as well as steam stripping could be applied for $CO_2$ desorption. For these cycles, $CO_2$ capacities are typically lower, but this disadvantage can be offset by the much higher $CO_2$ purities obtained and the possibility of achieving good capture rates by fast cycling. Indeed, the recoverable capacity is linked to the desorption temperature, but its excessive increase would lead to a faster irreversible degradation of the sorbent, probably due to the formation of stable products, such as urea, by the secondary reaction (20) between $CO_2$ and amines above 135 °C. As that reaction involves dehydration, the use of steam as a stripping agent instead of vacuum, substantially consisting in $CO_2$, would be a better alternative (104).

(20) $2\, R_1R_2NH + CO_2 \rightleftarrows (R_1R_2N)_2CO + H_2O$

#### 3.4.4.1 Hybrid sorbents classification and make-up

Regarding to the technical method adopted for the insertion of reactant groups, amine-containing sorbents have been divided into class 1, prepared by impregnating amines into the pores of a support, class 2, consisting of amines covalently bonded to the walls of porous materials, and class 3, where amine monomers have been polymerized in situ, resulting in polyamine structures tethered to the walls; in Figure 10 a schematic example is reported for any of these three classes and in Figure 11 some of the most used compounds for DAC sorbents are shown. Recently, several combinations of class 1−class 2 sorbents have been also proposed to form a new class 4, with amines grafted to the surface and an additional impregnated, as a way to improve the properties of amine-based $CO_2$ sorbents (103, 104, 105).

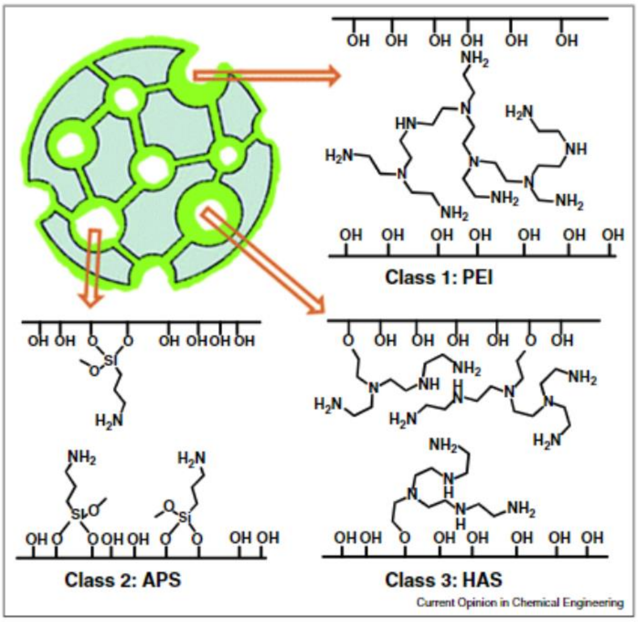

*Figure 10: Amine-functionalized materials classification on their manufacturing method. (104)*

For the make-up of class 1 hybrid sorbents, organic amine species are loaded into pores and on the surface of the mesoporous support material by wet impregnation and, after drying, a flowing powder is commonly obtained. This relatively simple method can introduce a large amount of amine species, and thus a high amine-based loading can be achieved. However, weak physical bonding to the support would allow amines evaporation and high molecular weight compounds should be used to contain losses. Among different types of amines that can be selected to prepare the adsorbent, polyethylenimine (PEI) and TEPA (tetraethylenepentamine) are the most widely used amine species due to high stability and nitrogen content (105).

The amount of amine loaded into the porous material is determined by the total pore volume of the porous material and the amine density; if exceeding this theoretical limit, the overloaded amines will be attached to the outer surface of the support and determine the adhesion of fine porous material particles to form larger agglomerated powders, and even a slurry mixture, with obvious reduction in reaction sites affordability. Therefore, the adsorption performance of the material is mainly determined by the loading amount and distribution of the amine group, which are in turn strongly affected by the pore structure properties of the carrier. Anyway, the transfer of carbon dioxide within the adsorbent is limited and the amine utilisation is not complete because it occupies a large part of the internal pores. While impregnation method generally adopt an organic solvent, such as ethanol or methanol, subsequently removed by heat drying, the preparation of the adsorbent by a freeze-drying process, using water as a solvent, can overcome the disadvantages of energy consumption, amine loss and collapse of the pore structure due to heating; in addition, new voids in the loaded organic amine layer are formed as a feature of water removal mechanism (106).

Class 2 hybrid sorbents are prepared by reacting an aminosilane with the surface hydroxyl functional group of the support material; this grafting process offer high amine efficiency and cycle stability because of the chemical bond between the amine group and the carrier. Therefore, the amount of amine species introduced is closely related to the amount of hydroxyl functional groups on the surface of the support. Anyway, the number of amine groups capable of grafting is limited and leads to low CO2 uptake capacity while higher diffusion rates than class 1 materials are achieved, due to lower pore structure changes and occupation after the introduction of aminosilane (107). The grafting method is generally applicable to a carrier material rich in hydroxyl groups, such as mesoporous silica, and MOFs materials.

The direct synthesis method for class 3 adsorbents, still relying on chemical bonding of the active phase, involves the in-situ polymerization of amine monomers in the porous support material, during its preparation. The one pot synthesis method offers the advantages of reduced operation process and more uniform distribution of the adsorption sites (108). At present, the direct synthesis method of the carrier material generally uses silicon-based molecular sieves and MOFs. As pointed out, a new kind of sorbents assignable to class 4 can be produced through grafting and subsequent impregnation with amines; more active sites are exposed for $CO_2$ capture as the impregnated compound can be better dispersed in the pores of the material due to the steric hindrance effect of grafted aminosilane. In this way the two methods advantages are combined, increasing both gas diffusion rate, amine efficiency and $CO_2$ uptake capacity (109).

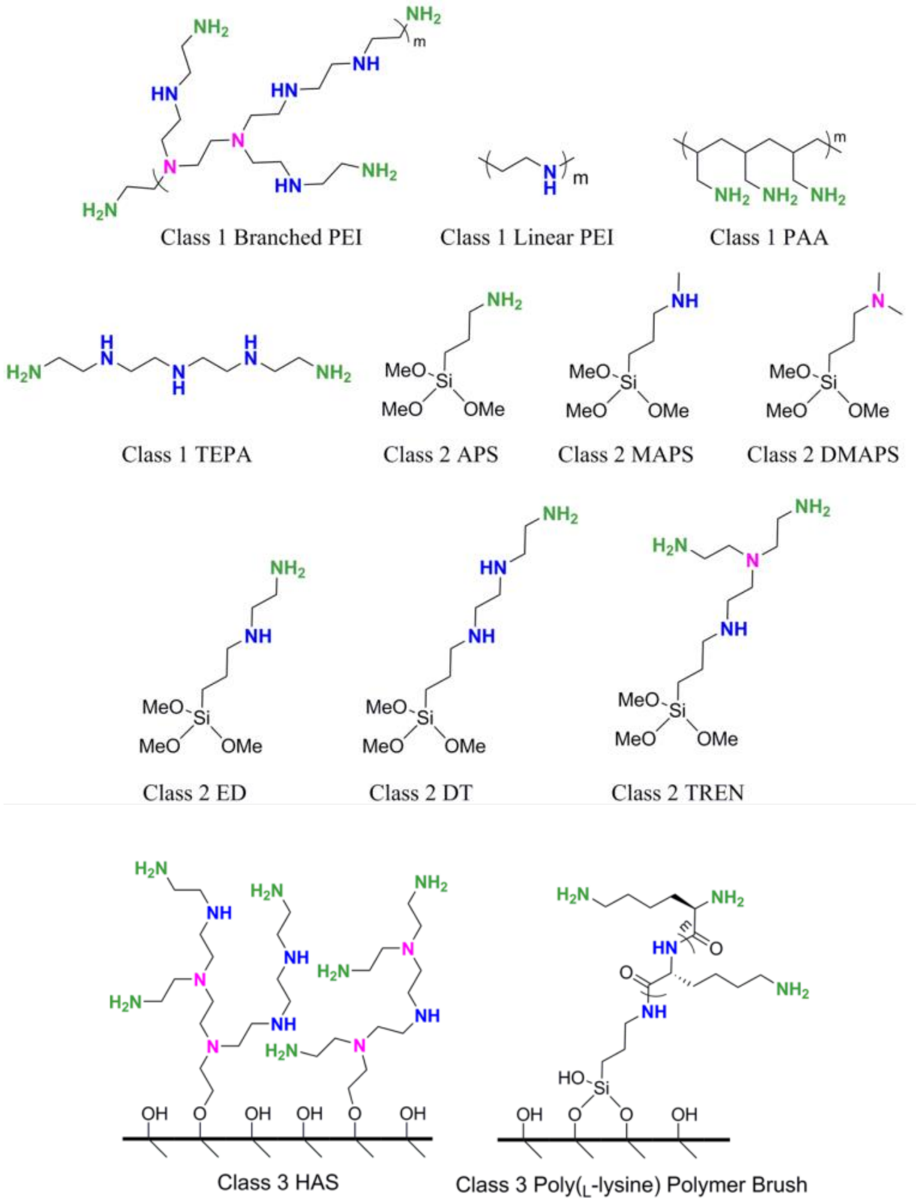

*Figure 11: Most adopted compounds for amine-functionalization of each hybrid sorbent materials class.* (105)

#### *3.4.4.2 Amines physically adsorbed on oxide supports*

Among class 1 materials, mesoporous silica impregnated with low molecular weight, branched polyethylenimine (PEI), or other linear amines such as tetraethylenepentamine (TEPA), have been the primary adopted solution to develop effective $CO_2$ hybrid sorbents for flue gasses capture and also for first DAC applications. Because of large density of amine groups and good stability under thermal swing desorption, good cyclic regeneration capacities could be achieved, in example of about 2 mmol/g using pure $CO_2$ (104, 110).

While the utility of smaller amines, such as those used in absorption processes, is limited by their low boiling points, inadequate for the process temperature swing, in a similar way, the tuning of adsorption features, based on decreasing heats of adsorption from primary to ternary amines, have been attempted preparing a linear, low molecular weight polyallylamine (PAA), containing only primary amines. PAA achieved $CO_2$ uptakes and amine efficiencies similar to those of linear PEI, where all amines are secondary, showing a fair cyclic stability and a $CO_2$ uptake up to 0.86 mmol/g; however, branched PEI, with an high content of tertiary amines, useless for $CO_2$ capture in the absence of moisture showed the better performance. These results, ascribed to the higher accessibility of primary amines, located at the ends of the PEI branches. suggest that structurally tuned polymers such as PAA might offer advantages, related to functional groups accessibility, especially in developing class 2 and 3 sorbents. Fumed silica loaded with 33 and 50% PEI showed $CO_2$ uptakes of 1.18 and 1.71 mmol/g from atmospheric air at 25 °C, respectively; the negligible $CO_2$ uptake of the bare support, which often shows to specific gas−solid interaction sunder higher concentrations, highlighted the importance of amines for $CO_2$ capture under ultra-dilute conditions using silica-based materials (110).

As polyethylene glycol (PEG) is known to enhance their $CO_2$ sorption by mixing with amines, it could be coadded to PEI and other amine compounds during impregnation of solid supports to improve the arrangement of the active phase, resulting in scattered aggregates rather than a compact layer. This allows for high amine efficiencies, even in highly amine-loaded materials; indeed, while PEI−SBA-15 can achieve a net uptake of 0.63 mmol of $CO_2$/g, with an amine efficiency of 0.10 mol of $CO_2$/mol of N, in PEG−PEI−SBA-15 sorbents, the addition of PEG200 and PEG1000, with different molecular weights, yielded $CO_2$ uptakes of 0.79 and 0.71 mmol of $CO_2$/g, with amine efficiencies being 0.14 and 0.13 mol of $CO_2$/mol of N (111).

Porous supports have also been subject to modification to produce adsorbents with better performance; as PEI-SBA-15 incorporating different amounts of aluminium, titanium, zirconium, and cerium showed a higher $CO_2$ uptake from air for all of them, this is mainly due to the change in textural and morphological properties derived from the metal incorporation rather than its presence, similar results can be achieved just modifying SBA-15 silica with higher pore volume, larger mesopores, and less microporosity (112).

Alumina is an alternative support to the most common silica materials which offers higher resistance to structural changes and degradation in adsorption capacities under steam-stripping regeneration conditions, due to its crystallinity and lower hydrophilicity. Mesoporous γ-alumina impregnated with PEI exhibits higher stability to steam stripping respect to PEI-SBA-15 and strongly reduced losses of $CO_2$ adsorption capacities after cycling, also offering comparable or even higher initial values, up to 2.7 mmol/g, especially for DAC conditions (113).

The best the optimum $CO_2$ uptake for class 1 sorbents often occurs at somewhat elevated temperatures, due to the competition of thermodynamic and kinetic factors; while adsorption is favoured at low temperature, better diffusion of $CO_2$ through the amines layers and higher reaction rates are achieved at elevated temperature. The optimal balance between these effects is obtained at temperatures quite above 25 °C, resulting in a narrow temperature swing cycle, of less than 60 °C, as effective desorption can be carried out at about 85 °C. The presence of humidity could show opposite effects on impregnated amines absorption properties, which seem to be related to different loadings and consequent interparticle arrangement of these compounds. Indeed, it has positive effects on well-dispersed active phases while in highly loaded materials water could block the access to the amine groups via oversaturation, hindering the diffusion of $CO_2$ and decreasing the uptake efficiency. However, despite moisture presence resulted favourable in flue gas capture, more studies are needed in direct air capture applications, as, due to $CO_2$ high dilution, competition issues would become relevant (110).

Impregnation with amines can be also applied to zeolites to improve their properties; in particular, $CO_2$ adsorption capacity could reach values near to 2 mmol/g at temperatures above 100 °C and a higher selectivity towards $H_2O$ is achieved. To successfully introduce amines on the support large pore volumes are necessary, so mesoporous zeolite 13X offers better results than traditional zeolite 13X materials, featured by high microporosity, and ZSM-5 materials with larger mesoporous structure are preferred. Indeed, they can be loaded with more amine and the presence of large pore volume and mesopores, eventually promoted by starch addition during the make-up, allowed to obtain a $CO_2$ capture capacity of 6.13 mmol/g at 75 °C with 30% $CO_2$, for synthesized ZSM-5 functionalized with ethylendiamine (ED) (114). Recently, zeolites coated with a mesoporous silica shell, such as 5A@MSA, attracted interest for exploiting abundant hierarchical pore structure of zeolites, which can provide better structure conditions for amine loading and gas transport, while softening the influence of water on their $CO_2$ adsorption capacity. Anyway, all these solutions are mainly aimed at the improvement of zeolite sorbents for post-combustion capture rather than at finding the best material to support amine active phases for $CO_2$ DAC (115).

#### *3.4.4.3 Amines covalently tethered to oxide supports*

As discussed above, amines covalently tethered to the support material surface could belong to class 2 or class 3 materials; for their main features and the abundance of reactive hydroxyl functions, oxide supports are commonly constituted by silicon materials. The by far most used compounds to be introduced via grafting, for applications in $CO_2$ capture, are aminopropyl (APS) and diethylenetriamine (DT) silanes. In example, pore-expanded MCM-41 silica (PE-MCM-41) functionalized with DT achieved a $CO_2$ uptake of 0.98 mmol/g at 25 °C and a relative pressure corresponding to 400 ppm of $CO_2$, also keeping a very high selectivity to $CO_2$ over $N_2$ and $O_2$, which make this kind of solutions very promising for air capture purposes. Class 2 materials can be also made by post-grafting amination of alkyl halide organosilanes, subsequently converted to primary amines with ammonia; this method could offer a better spacing among active functions, which is potentially favourable for $CO_2$ adsorption in highly loaded materials but can instead inhibit the amine-amine pairing needed to bind $CO_2$ under dry conditions (116).

The effect of amine groups spacing over the sorbent surface have also been highlighted by using linkers with 1 to 5 carbon atoms; indeed, respect to APS

(C3), shorter chains showed low flexibility, limiting the interaction of two neighbouring amines and affecting dramatically the $CO_2$ uptake, while the longer did not yield significant improvements. For these large aminosilanes, high amine efficiency can be achieved adopting supports with large channel size, such as modified SBA-15, showing the maximum enhancement of surface amine density due to a decrease of the space hindrance in the support. Therefore, in developing amine grafted adsorbents with high capture properties, an accurate selection of the molecular weight of aminosilane and the pore size of carrier would be crucial (117, 118).

Because of the presence of both primary and secondary amines in many active phases, the role of different amine types in $CO_2$ capture have been evaluated in detail, testing class 2 materials grafted by organosilanes containing only primary or secondary amine functions. At DAC conditions, primary amines show higher efficiency values than the secondary amines; however, this is not an enthalpic effect, ascribed to different heats of adsorption, but rather an entropic effect, as the experimentally measured heats of adsorption for the primary and secondary amines were found to be similar at low coverage, and the behaviour differences seem to be mainly related to $CO_2$ dilution and its diffusion mechanism through the pores. Moreover, the amine rank has also an effect on the adsorbent hydrophobicity and the more hydrophilic primary amines may be preferred for $CO_2$ adsorption when moisture is present (119).

Class 2 sorbents show lower maximum $CO_2$ uptakes compared the class 1, due to a lower achievable active phase loading, but the higher accessibility of reaction sites could make them more effective for $CO_2$ capture from ultra-dilute streams and allow to carry out the adsorption step at even lower temperatures. However, while higher desorption temperatures would be applied without significant amine losses, real conditions applications show a dramatic effect on the adsorption capacity, which becomes negligible only after few cycles, potentially driven by amine oxidation processes, occurring in presence of oxygen and even other pollutants (120).

Class 3 materials are sorbents with amine monomers polymerized off the support surface in situ, yielding polyamine structures covalently bound to the walls; these materials couple a thermal resistance similar to that of class 2, due to strong bonding, with nitrogen loadings even higher than in class 1. Indeed, hyperbranched aminosilica (HAS), obtained by aziridine in situ polymerisation, can offer a nitrogen loading up to 9.9 mmol of N/g and a $CO_2$ uptake of 1.72 mmol/g under air capture conditions at 25 °C. Polymers attached to the support surface can be also obtained by one pot synthesis, through their addition to the make-up solution for silica powders manufacturing, offering a cheap production process and good active phase dispersion (121).

Another approach could involve the polymerization of aminoacids, such as L-lysine and L-alanine, by chain reaction of their derivatives, starting from compounds previously grafted on the silica surface, such as the aminosilanes used for class 2 sorbents. While resulting highly expensive, this method allowed to produce a high density of a grafted linear PEI-like polymer composed of secondary amines with terminal primary amines, which offers an impressive adsorption capacity of 11.8 mmol/g under flue gas conditions at 25 °C, attractive also for improvements aimed at DAC (122).

As mentioned above, the coupling of class 1 and 2 main advantages can be also attempted through their combination in novel class 4 materials; the “double functionalization” process involves a further physical impregnation of an aminosilane class 2 sorbent. Different supports, including pore-expanded SBA-15, MCM-41 and the zeolite composite ZSM-5/KIT-6, can be grafted with APS or its analogues, such as TMPED and TMPTA, showing an ethylendiamine or diethylenetriamine group instead of the terminal amine function, and then impregnated commonly with TEPA or PEI. All the combinations of these materials generally rise much higher $CO_2$ uptake capacities than other classes sorbents, even up to 6.28 mmol/g, due to the highest amine loadings achievable (109).

#### *3.4.4.4 Amines supported on solid organic materials*

Amine-functionalized hybrid sorbents can be realised using some other supports as an alternative to the most common silica materials; carbonaceous materials, as discussed above, would offer the advantages of wide availability and good mechanical, chemical and thermal stability. Moreover, the adoptable manufacturing processes allow to obtain various forms, such as biochar, ACs molecular sieves, CNTs and graphene, showing different microstructures. These materials are often functionalized through impregnation, as the large pore volumes achievable allow an increased loading of the active phase, as already pointed out for other materials. However, in a similar way to zeolites, these methods are mainly aimed at improving the sorption properties of already structured materials, showing features more useful for flue gas capture rather than for DAC technologies (123). Instead, carbon structures used as a support to obtain DAC active materials are more often aimed at the realisation of class 3 sorbents, by grafting an atom transfer radical polymerization (ATRP) initiator on their surface, which could be carried out relying on nitrene chemistry, acid oxidation, or Pschorr-type arylation (124).

Active reaction sites can be also located on porous polymeric networks (PPNs), thanks to the wide availability of various monomers and of many different synthesis approaches, such as inverse templating and high internal phase emulsions (HIPEs). PPNs functionalization could be achieved by both impregnation, grafting and co-polymerization with amine compounds; anyway DAC $CO_2$ uptakes remain modestly below those obtained using other sorbents and the manufacturing processes could pose techno-economic issues (125).

Many co-polymerized PPNs contain quaternary ammonium hydroxide active groups, derived by chlorine groups after polymerization, which are also functional groups responsible for $CO_2$ adsorption in anion exchange resins. These materials are particularly attractive as could allow the development of a novel humidity swing process, which could compete with other sorption solutions due to lower desorption energy requirements, as it is achieved mainly by increasing moisture presence; moreover, the dispersion of the resin in a thin polymeric film allows to achieve high adsorption rates, despite the limited maximum uptake (126, 127).

#### 3.4.4.5 Amines tethered to metal-organic frameworks

Metal-organic frameworks (MOFs) are an emerging class of porous materials characterised by unique features, promising for many industrial purposes including $CO_2$ selective capture from gas streams, as highlighted above. Recent continuous acknowledgement on MOFs preparation methods and on the deriving features suggest that high tunability of the pore geometries can be achieved varying organic linkers and metal atoms. In this way, MOFs could offer great physical adsorption properties by themselves; anyway, they are still under development and the widely adopted amine-functionalization can be also attempted to improve their $CO_2$ adsorption properties (105).

Use of amine-functionalized ligands is an approach to decorate MOF pores with amines by one-pot synthesis; moreover, use of amine linkers coupled with another pillaring ligand could enhance both $CO_2$ adsorption, as well as $CO_2$ selectivity over nitrogen, through narrow pore-induced diffusion resistance. Various ligands, often containing both amine and adeninate groups, allow to reach $CO_2$ uptake capacities up to 3 mmol/g; however, the obtained materials show lower heats of adsorption, ranging around -40 kJ/mol, than other chemical sorbents and would result more suitable for improving post-combustion capture efficiency (128).

Post-synthetic modification of MOF frameworks with alkyl amines, instead, is another approach, which offers stronger adsorption features, aimed at improving $CO_2$ capture at low partial pressures. This method commonly involves the functionalization at open metal sites of the material, provided by the thermal or under vacuum removal of appropriate attached solvents after the MOF build-up. Open metal sites can then be bonded with one amine group of small amines, such as ethylene diamine (EN) and dimethyl ethylene diamine (MMEN), or larger polyamines, such as PEI. Functionalization of open-metal sites of Mg-MOF-74 (Mg2-DOBDC), already showing an uptake capacity of 6.1 mmol/g under flue gas conditions, with ED provided a regenerative functional sorbent having an adsorption capacity of 1.51 mmol/g at 400 ppm of $CO_2$, which would be increased introducing a higher number of amine available sites. Moreover, this solution can be useful to make MOFs more stable and practical materials as it also resulted in improved stability under practical operating conditions respect to the bare support, indeed the open metal sites result protected by the linked amines, with regard to oxidative reactions and moisture presence, which may otherwise affect the MOF crystallinity (129).

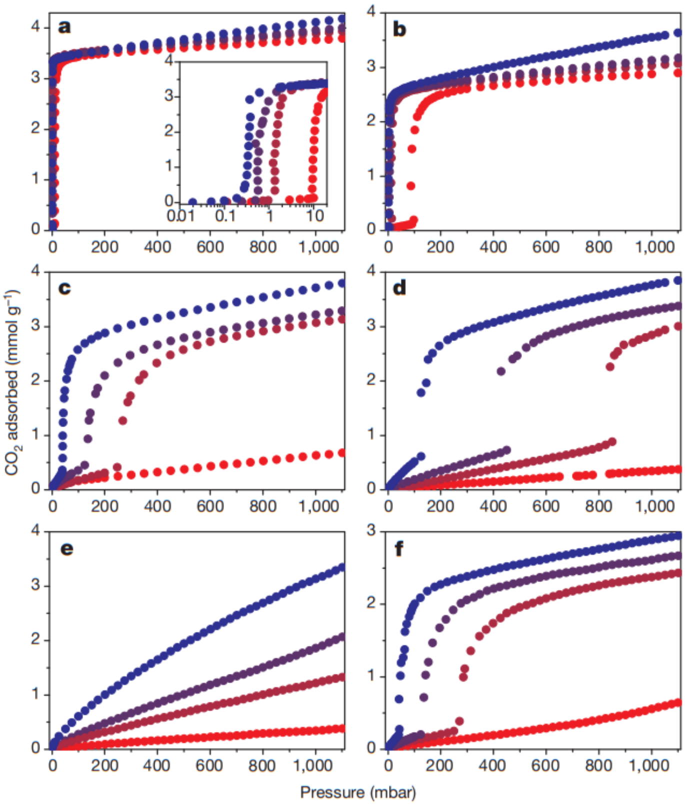

*Figure 12: Adsorption isotherms at 25 °C, 40 °C, 50 °C and 75 °C for MMEN-$M_2$-DOBPDC functionalised MOFs, respectively containing Mg, Mn, Fe, Co, Ni, Zn (130)*

To improve amine diffusion, an expanded analogue of MOF-74 was synthesized, using M-4,4′-dioxido-3,3′-biphenyldicarboxylate, an increased size biphenyl variant of the original linker; the obtainable $M_2$-DOBPDC MOFs, where M could be Mg, Mn, Fe, Zn, Co, and Ni tethered with N,N′-dimethyl ethylene diamine (MMEN), both offering high theoretical $CO_2$ uptake capacities. However, except for Ni, all showed steep steps in the adsorption isotherms, reported in Figure 12, that shifted at higher temperatures. As these steps occur at increasing $CO_2$ pressures for the listed metals, Mg and Mn MOFs result more suitable for a TSA process, at even low temperatures and exhibit high uptake capacities at DAC conditions, equal to 2.2 mmol/g for $Mg_2$DOBPDC, anyway lower than theoretical 3.4 mmol/g calculated based on the amount of amine inserted. The use of EN instead of MMEN for the functionalization of this Mg-MOF increased the $CO_2$ uptake capacity to the highest values of 4.57 mmol/g and 2.83 mmol/g at 25 °C and 1 bar or 0.39 mbar atmospheric level, respectively, for EN-$Mg_2$-DOBPDC (130).

## 3.5 Electrochemical applications

Electrochemical technologies are currently at an earlier stage of development compared with other $CO_2$ capture and separation methods; however, this kind of approach is attracting interest, as great energy efficiency could be achieved. The main concept is based on the electrochemical transport of the carbonate ions, formed by $CO_2$ adsorption on the cathode, to the anode, where $CO_2$ is desorpted, by applying a potential difference, which involves electric energy consumption.

(21) $$CO_2 + {}^{1}\!/_{2}\, O_2 + 2\, e^- \rightleftarrows CO_3^{2-}$$

Molten carbonates fuel cells (MCFCs) would represent a promising option for flue gas capture as they are already designed for operating at temperatures above 500 °C and involve the use of binary or ternary eutectic mixtures of alkali metal carbonates, as an electrolyte. However, turning their regime to that of an electrolyser, to supply the energy needed for $CO_2$ adsorption, through reaction (21), $CO_3^{2-}$ transport and $CO_2$ desorption, by inverting the reaction, would also lead to the evolution of oxygen at the anode. As the presence of $O_2$ in the $CO_2$ concentrated stream makes necessary an undesirable further separation step, the option of keeping a fuel cell regime, where hydrogen is fed to the anode, should result favourable. Indeed, hydrogen oxidation is exploited to produce electric energy, with a penalty due to concurrent $CO_2$ capture, forming $H_2O$ with the carried oxygen, which is easier separated by the $CO_2$ stream. Anyway, while offering large potential energy savings, most of these solutions needs further studies and development to become actually feasible and the direct conversion of the $CO_2$ to value-added products, rather than just its capture, would result a more advantageous option (131).

### 3.5.1 Liquid absorbents regeneration

Electrochemical processes in liquid phase, commonly using aqueous solutions, are not actually a $CO_2$ capture technology by themselves, but rather a regeneration method for absorbents, alternative or supplementary to thermal desorption. Indeed, while the classical desorption processes require elevated temperatures, with the already discussed drawbacks, electrochemical processes can be carried out at almost room temperature and would by far overcome the energy efficiency of thermal processes (75, 132).

As chemical absorption reactions are based on the acid character of $CO_2$, various electrochemical regeneration methods are based on a pH-swing approach; bipolar membrane electrodialysis could be applied to continuously enrich the solution under desorption with carbonate ions, forcing their migration from the absorption solution, which is in turn regenerated, while direct hydrolysis allow to swing the pH through the migration of hydroxide and hydrogen ions to opposite electrodes. Anyway, for both these methods applying high voltages would involve in the evolution of $O_2$ at the anode, rising the same issue pointed out for MCFCs. In a similar way, $H_2$ could be fed at the anode to be oxidized instead of oxygen and supply the energy for the process (133)

Alternatively, pH-swing could be achieved by proton-coupled electron transfer (PCED), using proton carriers undergoing redox reaction, such as biomimetic compounds like phenazine derivatives or proton intercalating metal oxides like $MnO_2$. These method could be applied in continuous processes, where the solution contacts the cathode and the anode before adsorption and desorption of $CO_2$, respectively, or in swing processes, where the contact with each electrode is kept along alternate adsorption and desorption cycles (134).

Other electrochemically mediated $CO_2$ separation processes from liquid absorbents include the use of $CO_2$ carrier compounds, such as quinone materials and benzyldisulfide, which uptake $CO_2$ by reduction at the cathode and then release it when re-oxidized at the anode; anyway, the low hydrophilic features of these compounds limit their application in water solutions, while make them more suitable for ionic liquids (ILs) absorbents (135). However, $CO_2$ capture and release happen on the electrodes and counter-diffusion issues would rise due to pumping $CO_2$ against concentration gradient, thus, a potential swing approach could be preferred. In this way the active compound is deposed on a porous electrode, where the feed gas passes through for adsorption; desorption is then achieved switching the electrode potential to reverse the reaction and release $CO_2$ under adequate conditions (136).

A further promising approach is based on the competition among $CO_2$ and cupric ions to form complexes with amine compounds, through equilibrium reaction (22), and can be applied to design smart energy management layouts for traditional alkanolamines absorption processes. The electrochemically mediated amine regeneration (EMAR) uses ethylene diamine (ED) and forces the $CO_2$ equilibrium reactions by regulating the cupric ions concentration, which is increased at the anode, before desorption, and reduced at the cathode, on which Cu is plated out, to get free amines for absorption, through reaction (23).

This regeneration method currently implies energy requirements similar to those of steam stripping; however, while energy efficiency could be further improved by process development, a great advantage is already given by the fact that the EMAR system only needs electrical energy, without the need of steam generation, and shows a “plug-and-play” nature. These features expand the range of application of the process and would make it particularly suitable for $CO_2$ capture technologies coupled with renewable energy (137).

$$(22) \qquad Cu^{2+} + n\ R_1R_2NH \rightleftarrows\ [Cu(R_1R_2NH)_n]^{2+}$$

$$(23) \qquad Cu \rightleftarrows\ Cu^{2+} + 2\ e^-$$

Anyway, as widely discussed, $CO_2$ absorption is an exothermic reaction, but thermal recovery and management result difficult in absorption columns due to the even lower temperatures than desorption. Recently, a process based on the same concepts applied in EMAR, was designed to electrochemically recycle the absorption energy to the desorber; in the $CO_2$-regenerative amine-based battery

(CRAB), indeed, cupric amine complexes equilibrium reaction (22), is exploited to carry absorption energy release and turn it in electrical power. This process reverses the layout of EMAR, as shown in Figure 13; in this way, $CO_2$ adsorption and desorption are the driver of cupric ions release and uptake by the amine, respectively, and this would make the electrochemical system as a galvanic cell. As expectable, this solution feasibility strongly depends on the absorption and desorption conditions and would be mainly appliable to flue gas capture, rather than to DAC, as an energy efficiency enhancer but not as an actual power generation unit (138).

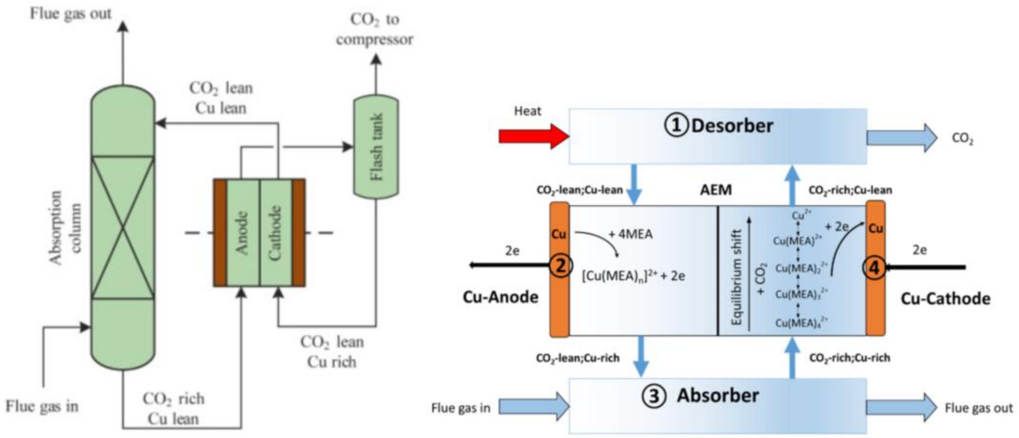

*Figure 13: Illustration of electrochemical $CO_2$ capture by EMAR and CRAB processes. (137, 138)*

# 4 $CO_2$ DIRECT AIR CAPTURE (DAC)

The need of a large-scale deployment of NETs in the future, to meet an adequate decarbonization pathway and keep the global temperature increase at least under 2°C, have been already elucidated; among the potential solutions, with different features, $CO_2$ direct air capture (DAC) technologies would offer several advantages. Indeed, many approaches rely on natural processes, often occurring at slow rates, that, regardless of the amount potentially stocked, would take long time to actually subtract $CO_2$ from the atmosphere, and would also require large land resources. Instead, DAC is carried out in fully industrial plants, and, despite this involves higher technical costs, the effect on atmospheric $CO_2$ is achieved instantaneously and results proportional to the operation activity. Anyway, to concretise the results, downstream processing is necessary to store (CCS) or re-use (CCU) the $CO_2$.

BECCS, which is regarded with interest, could be even considered a technical approach, but the upstream supply of biomass involves the management of natural processes on wide land areas, further complicating the fossil power CCS basis technology. As mitigation strategies based on fossil power CCS and bioenergy (BE) alone have both still to be deployed on large-scale, DAC results a more versatile non-competing technology, particularly suitable for the exploitation of floating RES other than biomass, such as photo-voltaic (PV) and wind power. Moreover, while both fossil and biomass power plants produce a large amount of $CO_2$, which necessarily needs to be stored, the development of effective utilisation pathways would avoid the need of a storage facility for DAC. Indeed, this technology could result useful to supply $CO_2$ for some industrial purposes and the deployment of integrated DAC-CCU systems, such as $CO_2$-to fuels plants, would allow to make-up an effective RES-fed recycling process for carbon.

In addition, by the moment only a small fraction of the global $CO_2$ is captured and, anyway, CCS results appliable only to large industrial and power generation plants, which account for less more than a half of the total, while the rest is emitted from distributed sources, including transport sector, which accounts for about a quarter, as depicted in Figure 14. These distributed sources, for which upstream decarbonising is inapplicable, or even requires huge structural changes, represent the main driver of DAC technologies deployment.

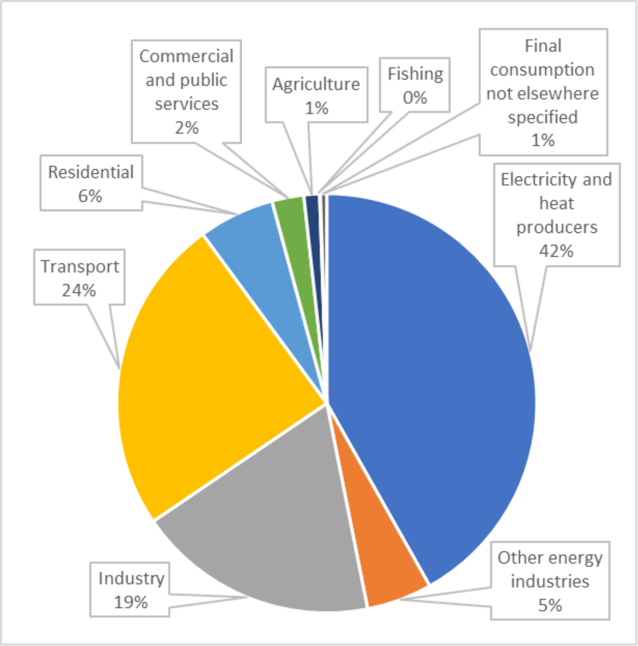

*Figure 14: $CO_2$ global emissions distribution, by sector, in 2019. (6)*

Like other capture technologies, DAC is not new as a technical solution, but innovative in the intention; thus, some drawbacks, deniable for other applications, would result crucial in its deployment as a NET. Indeed, for life support systems in confined environments, compactness could be a much more relevant feature than the requirements for regeneration, which could be even avoided using disposable sorbent materials (66). For DAC of atmospheric $CO_2$, instead, the design of a process layout aimed at the maximum efficiency is the main goal, as the desired effect is an environmental benefit, which otherwise would be seriously affected; so, durability of the materials, desorption energy requirements and recovery efficiency result the most important issues.

As already mentioned, operation units and materials adoptable for DAC are often modifications of those applied in post-combustion capture; however, while similarities on physiochemical mechanisms of $CO_2$ capture could allow their first development on a common knowledge basis several substantial differences have to be kept in account for the detailed design, both of materials and process operations. Indeed, DAC operates on ambient air, which is always available, with the aim of capturing the largest amount of $CO_2$ with the lowest energy requirement, in absolute terms, while post-combustion capture treats a fixed quantity of fossil power flue gas and must get the best balance among technical effort and $CO_2$ capture yield.

Ambient air has the disadvantages of an extremely low $CO_2$ concentration, near to 400 ppm, and of wide variability of temperature and humidity conditions, both in time and in space, while flue gas offer higher $CO_2$ tenor, often around 15%, and stable conditions, but involves the presence of contaminants, having some poisoning effect on sorbents, and high contact temperatures, leading to potential thermal losses. These features make chemisorbent materials, with strong binding affinities towards $CO_2$, more suitable for DAC, while physisorbents with high uptake capacities and low energy requirements for regeneration would be preferred for post-combustion capture. Moreover, the difference among pollutants content in the captured $CO_2$ remarks the convenience of applying CCS to flue gas while implementing CCU on DAC technologies, able to deliver high purity $CO_2$ (105, 139).

The most consolidated concepts for DAC are based on high temperature (HT) and low temperature (LT) processes, referring to the temperature at which $CO_2$ desorption is carried out. The former involves the use of liquid absorbents, mostly represented by alkali hydroxides or carbonates, while the latter is based on adsorption on solids, including various kinds of functionalised materials. Due to the possibility of exploiting low-value waste heat, LT-DAC is considered to be more favourable on energetic point of view; however, HT-DAC has a more consolidated process layout, which offers technical simplifications in achieving high efficiencies to balance the higher energy requirements (67).

## 4.1 HT-DAC

$CO_2$ HT-DAC technologies are commonly designed relying on causticization processes, which involve the absorption in inorganic alkali solutions and the regeneration of the formed carbonates through a calcination step, involving high temperatures, as exemplified in Figure 15.

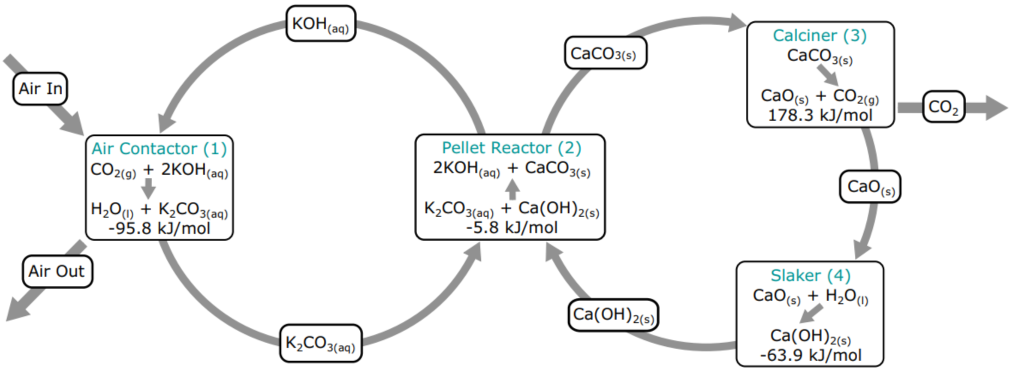

*Figure 15: Scheme of the "dual-alkali" thermochemical K-Ca-cycle, adopted by the Carbon Engineering commercial HT-DAC technology.* (150)

Aqueous sorbents offer the advantage that the contactor can operate continuously, can be built using cheap cooling-tower hardware, and the liquid surface is continuously renewed allowing very long contactor lifetimes despite dust and atmospheric contaminants. Due to the ultra-dilute nature of $CO_2$, absorption contactors represent the most critical component of these systems and are designed in a different way from those applied for point source capture. Indeed, as the reaction occurs at a fast rate and the initial concentration is just low, relatively short columns are used, while very large cross sections allow to satisfy the need to limit pressure drop for the processing of large volumes of air. To provide a large surface area for air / liquid contact and to maintain a low pressure drop, absorption could be also realised in spray towers rather than in packed towers; in this way the cost of large packed columns can be avoided, but in return, creation of the spray incurs its own energy losses and issues. Droplet coalescence is a major factor affecting the $CO_2$ capture rate; to reduce coalescence flow rates must be decreased and, like for packed towers, the height of the contactor must be limited, to allow a fast renewing of the absorbent and keep high efficiency. After $CO_2$ capture, carbonate enriched solution can be easily pumped to a central regeneration facility, allowing economies of scale and avoiding the need to cycle conditions in the inherently large air contactor (140).

Main disadvantages of HT-DAC are related to absorbent water losses in dry environments, due to evaporation in the large amount of contacted atmospheric air, and the cost and complexity of the regeneration systems, necessary to achieve a satisfying efficiency. In fact, regeneration of the sorbent, through calcination, is energy intensive and many approaches are aimed at overcoming this issue by the adoption of innovative energy supply and recycling methods; as DAC should be supplied by RES, main attempts are to optimise the integration of their extraction and accumulation, commonly as electric power. Among these, processes fed by concentrated solar power (CSP) for $CaCO_3$ calcination in a fluidized bed reactor offer an interesting perspective and can even carry out a high temperature adsorption on solid CaO from moistened air, operating in a temperature swing mode on parallel reactors. (141).

## 4.2 LT-DAC

$CO_2$ LT-DAC technologies are based on the use of solid sorbents, mainly represented by supported active amines, operating under various adsorption-desorption cycles, involving temperature, pressure or humidity swings, even combined.

As already discussed, solid sorbents would offer energy efficiency advantages respect to strong alkali solutions, as the required regeneration temperatures are even much lower and, appropriately selecting both active compounds and the supports, it is possible to regulate the interaction mechanisms and the strength of binding towards $CO_2$, aiming at the maximum adsorption uptake with the minimum desorption heat duty. Still considering, that these solutions should be preferentially fed by RES, the low regeneration temperatures are also suitable for the use of waste heat, if otherwise it is lost, and this would be relevant in realising autothermal processes integrating DAC and CCU. As air passes on a solid support, water evaporative losses are avoided but, on the other hand, attrition in the gas-solid contactors could be a concern, especially for moving bed configurations (142, 143).

The main issues of solid adsorption processes are given by the even limited $CO_2$ uptake capacity of sorbents, which involves the need of a swing process, carrying out the adsorption and desorption steps in the same utility. In addition, the sorbent material could be subject to cycling properties losses, mainly due to irreversible reactions of the active phase or pore structure variations.

Considering the main goal of capturing $CO_2$ using the minimum energy and the unlimited availability of feed gas, swing cycles can be designed to work under the best process conditions, in particular limiting desorption temperature, not necessary effecting a complete charge and discharge of the sorbent.

Anyway, PSA processes allow to avoid heating for desorption, but require a partial pressure difference which, as feed $CO_2$ concentration is around 400 ppm, would involve a compression stage for a huge volume of air or the application of an extremely high degree of vacuum for desorption. TSA modes, instead, result optimal at dilute feed conditions, and become more thermodynamically efficient with increasing adsorption affinity. Indeed, the desorption energy is almost independent of the adsorbate loading in nearly saturated materials and the work is applied to the concentrated product rather than the dilute feed, making a strong adsorption to the maximum $CO_2$ uptake favourable; in addition, direct heating of the sorbent material is useful to achieve a high energy efficiency (144, 145).

However, as high temperatures could lead to irreversible reactions on the active sites and variations in the support pore structure, affecting sorbent lifetime, temperature swings are often combined with a diffusive driving force, by applying vacuum (TVSA) or an inert gas (TCSA), acting on concentration. While the latter has fast desorption kinetics and would be even suitable for post-combustion capture, the former is more cost-effective and is preferred for DAC applications. The option of directly supplying heat by steam, acting both as energy carrier and inert stripping gas in steam assisted temperature and concentration swing adsorption (S-TCSA), offers several technical improvements. Steam avoids harmful dehydration reactions of amines and compete with $CO_2$ adsorbing on them, thus favouring its release, also offering facile downstream separation from $CO_2$ by condensing water. Moreover, the increased energy requirements for moisture desorption are overcame, as part of $H_2O$ is still adsorbed after stripping and avoids further uptake from the air, also resulting in a lower sensitivity to air humidity conditions. In the same way, steam stripping can be combined with a low degree vacuum (S-TVSA), showing a synergic effect, that would offer DAC processes with operating costs ranging from 60 to 190 $/t. Indeed, steam purge can be supplied to S-TVSA at temperatures below 100 °C, using a low exergy source and preserving sorbent properties towards cycling, and enhanced desorption rates of about 3.75 mmol/(g h) are achieved, at 0.12 bar and 100 °C (146, 147).

On a similar interaction principle, polymers and anionic resins can be used in a moisture swing process (MSA), where desorption is driven only by $H_2O$ competitive adsorption and is carried out suppling a moistened strip gas or directly by water washing. However, this would imply a strict drying pre-treatment on the inlet air and the slow sorption kinetics, even of water desorption after $CO_2$ discharge, could be limiting (126, 127).

## 4.3 DAC companies and working plants

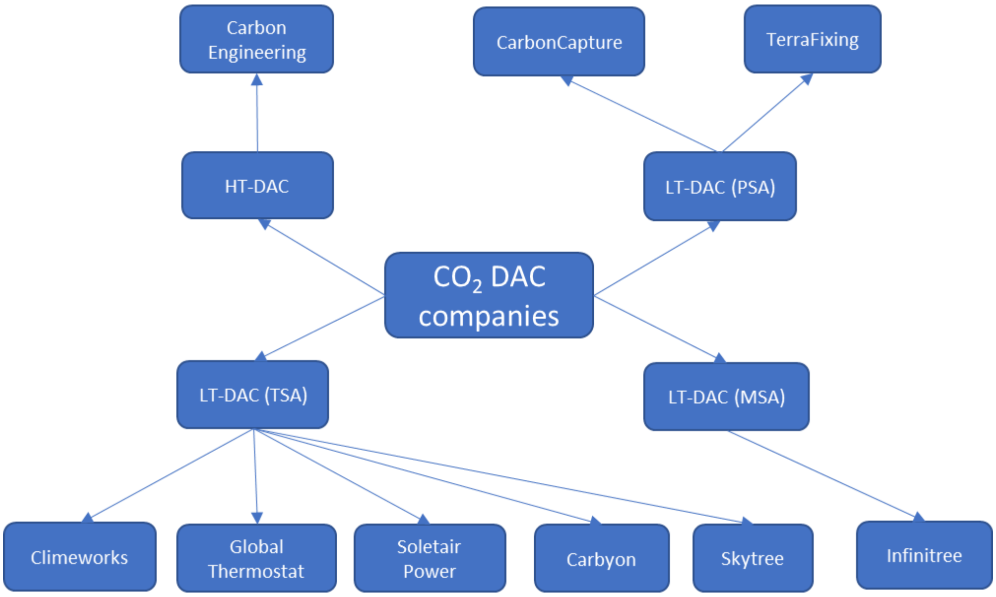

*Figure 16: Active $CO_2$ companies across the world in 2022.*

However, currently only 19 DAC plants are operating worldwide at demonstration scale and capture about 0.01 Mt $CO_2$/year. The expected level of deployment will require several large-scale demonstrations, to refine the technology and reduce capture costs, adopting a “design one, build many” approach; the first plant of this kind is in advanced development in the United States and should come online by 2024 to capture 1Mt $CO_2$/year. This will hugely increase the current global $CO_2$ capture capacity, which would be doubled by the deployment of smaller early development plants by 2025, preceding the scale-up, achieved by 2030, as shown in Figure 17 (7, 9, 148).

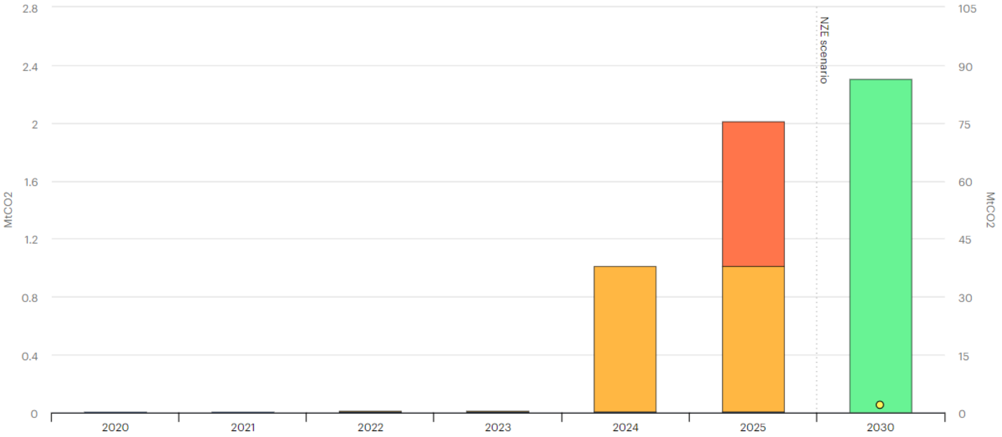

*Figure 17: Current and expected $CO_2$ annual removal capacity of DAC plants operating across the world; the technology scale-up should be achieved by 2030. (148)*

Currently there are 19 $CO_2$ direct air capture (DAC) plants operating worldwide, deployed by Carbon Engineering, Climeworks and Global Thermostat, based both HT-DAC and LT-DAC systems, and several other new companies are establishing in this field, also offering innovative moisture swing adsorption (MSA) processes, as highlighted in Figure 16. Moreover, many joint projects are rising, remarking the multi-task approach needed to adequately integrate DAC with other technologies, even for $CO_2$ storage or utilisation (CCSU), and the opportunity to get economic benefits from both the applications.

### 4.3.1 Carbon Engineering

Carbon Engineering (CE), established in 2009 by David Keith in Calgary, Canada, is the only company active in high temperature (HT) aqueous solution-based DAC. CE has fast developed its technology on an absorption process, innovating and integrating well-known pieces of equipment, widely used in large-scale industries to deliver a scaled-up technology, achieving megatons, for early deployment, in particular aiming at the direct production of synthetic fuels. The $CO_2$ is absorbed by a non-toxic KOH solution, pulling air through a fan into a large structure modelled off industrial cooling towers, filled of a plastic material packing. The absorbent is then regenerated in a pellet reactor, adapted from water treatment technology, by exchanging carbonate ions in a K-Ca cycle. The $CO_2$ is released as pure gas through $CaCO_3$ pellets calcination, at about 900°C, and the resulting CaO pellets are hydrated in a slaker and recycled to the causticizer, as depicted in Figure 18 and Figure 15 above (149, 150). CE's technology is designed to be fed by a mixture of renewable electric energy and natural gas; while the company underlines the possibility of also avoiding hydrocarbons supply using only electricity from RES, gas feed makes the process versatile and reliable, and offers technical advantages on the high temperature heat supply for calcination.

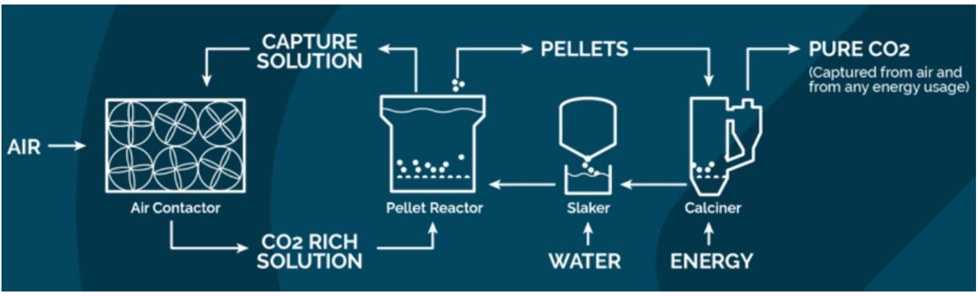

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*Figure 18: Simplified process flow diagram (PFD) of the Carbon Engineering CO2 HT-DAC commercial technology. (149)*

The features of this absorption process result particularly adequate to constantly assure high production volumes for large scale synthetic fuels production, as the additional $CO_2$ emissions can be avoided recycling products from the coupled P2X system, and even capturing the fossil $CO_2$ in the short term. The process design has been improved on a demonstration scale facility, operating since 2015 in Squamish, British Columbia, Canada, to capture 1 $tonCO_2$/day, which also incorporated fuel synthesis, by 2017, to offer an industrial, easy scalable AIR TO FUELS™ process. The technology itself is ready for deployment and the company is now starting to cooperate with plant developers to deploy large-scale, commercial DAC plants globally.

The first project of this kind will the largest DAC plant in the world, operating by 2024, and is at advanced development in the Permian Basin, US, in partnership with 1PointFive, a company formed by Oxy Low Carbon Ventures. This facility is expected to capture 1 $MtCO_2$/year from the air to permanently stored it into deep underground geological formations. Together with a similar project, in partnership with Storegga, targeted for North-East Scotland to permanently remove between 500 kt and 1 Mt of $CO_2$ from the atmosphere annually, the Permian Basin facility would allow the company to get a complete process knowledge packet for the design of efficient large-scale HT-DAC plants, aimed both at CCS as at CCU (151).

Recently, the Norwegian company Carbon Removal, Carbon Engineering and Oxy Low Carbon Ventures, joined another partnership for deploying large-scale DAC and $CO_2$ storage commercial projects in Norway, starting by a facility targeted for the Kollsnes area, to permanently store $CO_2$ up to 1 $MtCO_2$/year deep below the seabed in an offshore geological storage site. Moreover, the collaboration with BeZero Carbon, a London-based Climate Asset and Liability Management solutions provider, allow new retail offering for $CO_2$ negative emissions customers through an integrated hub of data, products, and services for the entire climate economy, to incentivise the rising of new projects (152).

Many commercial partnerships are also establishing in the air-to fuels sector, especially for aviation, which among transports is the most critical to directly decarbonise and is also beginning to be subject to environmental policies (65). In 2021, CE and the biotechnology company LanzaTech UK have partnered the first-of-a-kind project AtmosFUEL, that will investigate the feasibility of a large-scale, commercial air-to-jet facility in the UK, to produce more than 100 million litres of sustainable aviation fuel (SAF) each year, to supply the companies British Airways and Virgin Atlantic. The project will be also funded by the UK Department for Transport’s Green Fuels Green Skies Competition, to support plant development, and the proposed facility is targeted to be operational until 2030, to deliver significant aviation emission reductions, while cascading socio-economic benefits. The CE’s DAC technology will supply the CO2 to be fed into LanzaTech’s Gas Fermentation process to produce low carbon ethanol, then converted into SAF using the LanzaJet™ Alcohol-To-Jet technology, developed by LanzaTech and Pacific Northwest National Laboratory. The fuel will undergo certification by the Roundtable on Sustainable Biomaterials (RSB), globally recognised as the most robust approach to sustainability for the bio-based and circular economy and the deployment of other plants is expected to meet the UK’s 10% SAF by 2030 and up to 75% SAF by 2050 proposals (153, 154).

Moreover, the aviation company Air Canada, which already reports its carbon footprint, targets and climate protection strategy, as part of its climate targets to reach a goal of net-zero greenhouse gas emissions by 2050, has committed to invest in a variety of alternative fuel and carbon reduction solutions. This company plans to cooperate with CE to explore the potential opportunities in how DAC technology can advance aviation decarbonization, by permanent CO2 removal and/or by purchasing SAF through the innovation of CE’s AIR TO FUELS™ process. In 2021 also the Canadian company Huron Clean Energy announced the preliminary engineering and design on a large-scale, commercial facility in British Columbia, based on CE’s AIR TO FUELS™ to deliver up to 100 million litres of ultra-low carbon fuel each year, in a partnership including The Upper Nicola Band and Oxy Low Carbon Ventures. The B.C. Government’s Innovative Clean Energy Fund is also funding the initial design work, as the project is also the largest green hydrogen project in the country and is expected to deliver wide economic benefits. Construction is expected to begin in 2023, on one of Upper Nicola Band’s eight reserves with operations, powered by clean hydroelectricity, targeted to commence approximately three years after that (155).

### 4.3.2 Climeworks

Climeworks, founded by Christoph Gebald and Jan Wurzbacher in 2009 in Zurich, Switzerland, is the leader company in the development of LT-DAC processes. This company developed a demonstration prototype in 2011 and delivered a commercial-scale process by 2017, with the deployment of the first DAC facility in the world, delivering 900 $tCO_2$/year to a next-door greenhouse in Hinwil, Switzerland. In 2019 Climeworks acquired the relevant assets of Antecy, a Netherlands company founded in 2010 by Paul O'Connor and active on the same kind of technology, to join forces and fully merge teams, technology development, brands and business activities (156, 157).

Climeworks has developed modular $CO_2$ collectors, with a simple design that can be stacked to build machines of any size, fitting 6 of them in a standard 40 ft ship container (about 12 m), as shown in Figure 19. During adsorption the air is pulled through the sorbent filter by a fan; $CO_2$ is then released by sealing the unit and heating at 80 to 100 °C temperature and collected at high purity. These operations are powered solely by renewable energy or energy-from-waste and the grey emissions of the process, evaluated by LCA, result to be less than 10% (158).

*Figure 19: Climeworks $CO_2$ LT-DAC modular units installed around Carbfix central storage facility at Orca plant.* (158)

Climeworks DAC technology would result particularly suitable for DACCS applications as it requires relatively low temperature heat and can operate in a "plug and play" mode, allowing the most efficient use of RES without the need of large accumulation or integration by other sources. At this aim, in 2017, the company started a partnership with Carbfix, which is one of the world's experts in rapid underground mineralization of $CO_2$, deploying the first pilot plant, Artic Fox, to capture and store $CO_2$ in Hellisheiði, Iceland. The process has then been scaled up to the company flagship facility, Orca, which started operation in 2021 as the world's largest direct air capture and storage plant by the moment, able to remove 4 kt$CO_2$/year by 8 container units. The plant is fully supplied by a geothermal power plant and its successful operation will lead to the deployment of many other similar units, as an actual NET, funded by customers who need to mitigate their unavoidable $CO_2$ emissions. From 2019, the company is also offering a suitable $CO_2$ removal service to the global community, posing the attention on the urgent need of repairing to the past uncontrolled emissions (158).

Anyway, even if it does not fit the main goal of achieving positive environmental impacts the company, $CO_2$ recycling processes (CCU) also offer climate benefits, and Climeworks is involved in several projects and partnerships within this field. Among these, Kopernikus Power-to-X P2X, is the world's first integrated plant into operation to produce fuel from air and renewably generated electricity; the small size about of an industrial container produces approximately ten litres of fuel daily but the model is scheduled to be scaled up by twenty times, by 2022. Climeworks is also involved in the EU's STORE&GO project, aimed at the production of synthetic natural gas (SNG) by green hydrogen and renewable energy, involved the deployment of three facilities, in Germany, Switzerland and Italy, to evaluate compatibility of the solutions towards the current grid. The Italian plant, in Troia, a rural Mediterranean region with high PV potential, relies on LT-DAC modules to get the needed $CO_2$ from air and produce renewable LNG in a small facility. Moreover, large partnerships are establishing in the aviation sector, such as with Norsk e-Fuel, Sunfire, Valinor, and Paul Wurth, to develop an integrated process from power, $CO_2$, and water to fuel via the Fischer-Tropsch pathway. Climeworks, Sunfire and Norsk e-Fuel will respectively supply $CO_2$ DAC, $H_2O$ electrolysis and reverse water gas shift (r-WGS) technologies, to come onto operation by 2024 and double the production through an alternative pathway line by 2026, to reach 25 million litres output and compare the two processes features (159).

### 4.3.3 Global Thermostat

Global Thermostat, formed in 2010 by Graciela Chichilnisky and Peter Eisenberger in New York, USA, is the other most advanced LT-DAC company; the unit layout is like the Climateworks one, anyway, the contactor is a honeycomb monolith charged with a proprietary amine-functionalised material, regenerated by steam injection at 105 to 120 °C, utilising waste heat (160).

Global Thermostat has already built two pilot and commercial demonstration plants operating since 2010 at SRI International in Menlo Park, California, and

Huntsville, Alabama, each with the capacity to remove 3 to 4 kt$CO_2$/year. ExxonMobil started a cooperation with the company, aiming to help the deployment of a large number, around 20000, of bigger facilities, until they're removing a gigaton of $CO_2$ every year. Global Thermostat will also supply its DAC equipment to HIF, building a synthetic gasoline pilot plant in Magallanes, Chile, to convert up to 250 kg/h of $CO_2$ from the air. The plant will use wind power to produce hydrogen, combined with $CO_2$ to produce gasoline through the methanol route and HIF would move forward with the construction of its first commercial scale facility in 2022, to achieve the production of the equivalent of Chile's national gasoline consumption by 2030 (161).

### 4.3.4 Hydrocell - Soletair Power

Hydrocell is a Finnish company, active from 1993, in the fuel cells sector, which developed a $CO_2$ DAC unit combining high performance brush-type heat exchanger and regenerative $CO_2$ scrubber technologies. This unit was supplied to VTT Technical Research Center of Finland for Soletair project, in 2017, to produce fuel by air and $H_2$, using LUT solar power plant energy. is supplied by Hydrocell (162).

Currently, Soletair Power has grown as a company and offers innovative solutions suited for application in buildings; while a simple device is designed to remove and release ambient air $CO_2$ in adequate moments, aiming at keeping an healthy indoor environment, $CO_2$ actual subtraction from the atmosphere could be achieved as a further benefit by simple integrating a DAC utility on the building ventilation system. The concept of this solution is based on the demonstration P2X unit synthetising methane, presented at the Expo 2020 in Dubai, and would couple the quality improvement of indoor air with the production of low-carbon footprint fuel, making buildings $CO_2$ sinks. Soletair Power, anyway, also delivers outdoor applications for industrial purpose, with a typical container design which, in this case, includes the hole equipment to supply pure compressed $CO_2$; for these processes, the company has developed an anion resin adsorbent and a temperature-vacuum swing process requiring temperatures below 90°C (163).

### 4.3.5 Skytree

Skytree, founded by Max Beaumont and located in Amsterdam, Netherlands, spun out from the European Space Agency (ESA) in 2012, after two years incubation, and commercialises a $CO_2$ capture technology based on sorbents tested for its removal on space shuttles. This adsorbs $CO_2$ and $H_2O$ from air and release them in a concentrated stream by heating the sorbent material; while capturing $CO_2$, Skytree solution is mostly focused on small use applications, rather than on multi-purpose scalable plants, and is not developed to supply a pure $CO_2$ product but would offer energetic improvements in some cases (164).

Indeed, the possible applications of this technology are designed to offer "$CO_2$ as a service" which would result the most suitable way to immediately start mitigation efforts gaining additional benefits. In example, $CO_2$ for direct use in greenhouses, which is currently a widely adopted practice, can be supplied from the air directly in the greenhouse atmosphere, offering costs savings and so favouring a larger deployment of this utilisation pathway. Another solution could result an innovative vehicle air conditioning system to assure a healthy environment removing moisture and $CO_2$ with large energy savings, anyway this may achieve environmental benefits but does not act as a NET (165).

### 4.3.6 Infinitree

Infinitree, founded in 2014 and located in Huntington, New York, is another company offering specific solutions for enclosed agricultural applications, to be widely deployed in the short term thanks to their economic convenience; indeed, the current practice involves the transport of captured $CO_2$ or even its on-site production by fossil fuels combustion. The process adopted utilises an ion exchange material in a moisture swing adsorption cycle, resulting particularly convenient as the $CO_2$ is captured by dry air and released in presence of moisture at adequate concentrations for greenhouse farming, with low energy requirements; moreover, the utility is scalable to cover each size application in this sector (166).

### 4.3.7 CarbonCapture

CarbonCapture is a start-up, recently founded by Bill Gross in Los Angeles, California, which removes $CO_2$ by adsorption on a zeolite molecular sieve material. The company deals with the competition among $CO_2$ and $H_2O$ carrying out an upstream drying treatment and offering applications to be coupled with deionised water consumption industries, such as cosmetics and beverages, or even with mineralization storage, at a large scale. The scale-up of this technology would result more affordable, due to the cheaper sorbent material adopted, however the energy requirements for drying could become relevant and need to be evaluated, also keeping in account the facility location. To supply the electric energy necessary to the process, the company started a partnership with Heliogen, which is developing a concentrated solar power technology (167).

### 4.3.8 TerraFixing

TerraFixing, founded by Sean Wilson in Ottawa, Canada, is a company offering know-how in the $CO_2$ LT-DAC, which claims to have developed a process based on pressure swing adsorption on zeolites, only requiring electricity and suitable for cold climates, anyway no active projects are currently reported (168).

### 4.3.9 Carbyon

Carbyon has been recently established by Hans De Neve in Eindhoven, Netherlands, and uses a different process design approach compared to other companies. Indeed, a fast temperature swing process is carried out by means of a rotating drum, which is the key component for lowering the energy consumption as well as the machine cost; the sorbent is constituted by thin membranes, which would assure a low pressure drop, manufactured borrowing knowledge from the industry of semi-conductors (169).

# 5 CONCLUSIONS

## 5.1 $CO_2$ DAC further acknowledgements

$CO_2$ DAC technologies are currently at the commercial demonstration step of their development; both for HT and LT technologies a good knowledge on the available materials and their features have been achieved and the realisation of large-scale pilot plants will offer data on real operating conditions, useful for process optimisation. Indeed, the performance of these technologies, by the moment, have been estimated through laboratory tests, modelling simulations and bench-scale pilot plants, but some issues and opportunities would be determined by the specific deployment layout and framework, and the available data need to be improved and validated.

For what concerns HT-DAC processes, major efforts should be aimed at reducing additional energy requirements for support instrumentation through the design of short, large absorbers, to maximise gas/liquid contact and keep low pressure drops, and of heat recovery systems, both from the absorber as from the calciner. Moreover, the configuration of calcination process could be tuned to suite many different absorption towers and have strong influence on the downstream $CO_2$ purification and compression treatments, even required. Main improvements to existing facilities of this kind could be only achieved by adding unit operations, modifying the absorption tower packing or varying flow rates, so a preliminary detailed design is essential.

The modular aspect of LT-DAC facilities, instead, would allow a gradual, data-assisted deployment and the layout of each module makes them highly flexible in the application, as adsorption and desorption cycles can be easily managed by the control system and solid sorbents can be substituted. This kind of technology offers a great potential for further improvement; indeed, better performances of the sorbents can be achieved by tuning the process cycle and new sorbents would even be developed. On these aspects, the overall evaluation of the processes would keep in account the durability of adsorbents, which are often amine functionalised materials, involving the upstream production of ammonia by the energy intensive Haber-Bosch process. By extensive life cycle assessment analyses (LCA), some kinds of materials with lower adsorption properties than others would even result more efficient in actually subtracting $CO_2$ to the atmosphere. Moreover, regeneration cycles, under mild conditions, involving only a partial discharge of the sorbent could even offer a better performance due to process rates and reduced thermal degradation of the sorbent.

## 5.2 $CO_2$ DAC role in the short-term emissions mitigation strategy

Anthropogenic $CO_2$ emissions-driving climate change evidence and its deriving harmful effects, both on the environment and on human health, makes today its mitigation, by tackling the amount of $CO_2$ released in atmosphere by human activities, one of the most challenging issues to be overcome for sustainable development. The Paris Agreement posed an ambitious target of keeping the global average temperature increase below 1,5 °C respect the preindustrial levels; however, even to keep it at least under 2 °C, the $CO_2$ level in the atmosphere, currently at 420 ppm, would not be increased as far and, to avoid dramatic consequences of the required strong cut in emissions, an economy decarbonisation pathway allowing further emissions, to be subsequently remediated by NETs, have been adopted.

Anyway, while this involves the attracting opportunity of keep exploiting fossil fuels to feed the economy activity, there is not much consciousness on the magnitude of NETs deployment and their role is not even well defined in any concrete scenario. As already highlighted, several proposed NETs based on natural process approaches could offer great cost-effective atmospheric $CO_2$ removal potentials, but pose increasing concerns, both on the feasibility, the safety and the effectiveness, and, for this reason, it is not advisable to rely on their wide deployment. However, some of these solutions could offer many additional benefits or integrate other NETs, and so further studies aimed at identifying the best deployment way would result useful.

In particular, soil carbon sequestration (SCS) techniques are also regarded as innovative agricultural practices, improving water retention properties and allowing a reduction in fertilizers use. While soil amendment with organic matter needs to be assessed with its competing use as a feedstock for bioenergy (BE) and could fast bring to sink saturation, biochar is much less sensitive to this issue and would even raise synergies in the BE sector. As it is obtained as a by-product of the modern, low-$CO_2$ emission pyrolysis processes applied to biomass, in this way, it is possible to design an alternative approach to BECCS, which could offer better overall performances. Indeed, BECCS technology does not show much difference to fossil power plants equipped with CCS units in the $CO_2$ storage step, while its actual removal from the atmosphere is strongly determined by the biomass source growth, making biochar a less effective but potentially much more easily deployable carbon sequestration solution; these features also reveal the deep interconnection among BECCS and afforestation and reforestation (AR) practices, which cannot be taken in exam separately. As the current $CO_2$ emissions are still determined by untreated fossil fuels use, there is much room for BE even as mitigation technologies and, by the moment, much more attention should be given at the most efficient use of renewable sources, rather than at capturing a $CO_2$ emission which is integrated in a natural cycle by itself. Under this perspective, AR activities should be designed as low-impact feedstock production methods, adopting logging and forest management integrated approaches and locating BE plants as near as possible to the extraction site, without much regard to the affordability of a storage facility.

Anyway, the deployment of NETs is only reasonable if major part of $CO_2$ emissions from point-sources is before denied by the application of CCS technologies, which are already at a good level of development but still not widely deployed. Doing this, keeping in account that capture treatments are almost the same for BECCS, would allow an easier further implementation of this technology; indeed, process simplifications to post-combustion capture, developed on current plants layout, can be obtained adopting oxy-combustion and pre-combustion configurations for new plants, offering higher concentrated $CO_2$ streams to be captured. The latter would result particularly versatile as it relies on an upstream gasification process to produce syngas, particularly suited for coal and even adaptable to woody biomass feedstocks; moreover, the adoption of pyrolysis treatments allow to by-produce a tuneable amount of char, consequently reducing $CO_2$ amount, and would result the most effective way to exploit coal in the short term, even before equipping it with CCS, with an easy conversion to biomass feedstocks, once available. In addition, the deployment of new plants and storage facilities should keep in account the proximity among feedstocks extraction and $CO_2$ storage sites, which are by chance often matching.

Under these assumptions, $CO_2$ direct air capture (DAC) represent the most promising, and almost the only deployable, solution in the short term, also offering great potential improvements in the long term. Except from some BECCS demonstration facilities, which are necessary to consolidate and scale-up the technology, DAC plants are currently the only NET under deployment, which allow to actually determine the removal of $CO_2$ from the atmosphere. $CO_2$ direct air capture processes are completely carried out in relatively small industrial facilities, which can be located almost everywhere $CO_2$ is required for some purpose, including underground storage, relying on the unlimited availability of the air feedstock. Indeed, $CO_2$ has even to be captured in some way and the additional efforts needed using air as a source would be overcome by the benefits of avoiding its transport; moreover, the low land requirements of the plants by themselves allow to place DAC facilities also on offshore platforms. The availability of well-developed industrial operation units and consolidated thermochemical absorption cycles has allowed the deployment of HT-DAC large plants at contained costs, while extensive research on materials properties and great advances in manufacturing methods already allowed to develop some LT-DAC commercial processes and still offer good further improvement perspectives on the energy requirements.

The modular aspect, typical of LT-DAC technologies, which allow to deploy plants of small size, gradually scalable, and the possibility of supplying only energy from RES, also operating in a discontinuous mode, make them particularly adequate for storage purpose near the injection site. Indeed, the deployment of such small facilities would allow to get acknowledgements on the overall performances of the DACCS system and to keep its size following the available RES extraction capacity. Some LT-DAC utilities, such as those based on moisture swing adsorption (MSA), are also designed on specific applications, like greenhouse farming, to satisfy the $CO_2$ supply conditions with extreme energy efficiency capturing it from the air. This can be considered maybe the most affordable utilisation pathway by the moment, as the adopted alternatives involve the capture, compression and transport of $CO_2$, which also poses purity concerns if from fossil sources, or even its on-site production through fossil fuel combustion. Another already consolidated direct use of $CO_2$, that could get great advantage of LT-DAC technology, thanks to their simple layout which allow the transport of almost complete plants as container blocks, is in enhanced oil recovery (EOR), which is often carried out on offshore reservoirs and otherwise would require to transport by ship the injected $CO_2$.

HT-DAC technologies, instead, are designed for continuous operation and result more convenient to be applied as part of industrial utilisation pathways, where $CO_2$ has to be supplied as a feedstock. Among these, the production of synthetic fuels certainly represents the highest potential solution to be scaled-up in the long-term for substituting fossil resources in activities difficult to directly decarbonise and would also offer early economic benefits in low-fossil resources countries. Anyway, the production of polymers and the $CO_2$ addition to building materials offer an “almost-storage” solution, useful especially in the short term, to make these processes work as a NET, or at least to take time on the challenge.

## 5.3 $CO_2$ DAC-P2X systems for carbon circular economy in the long term

On the long term, large cuts of the $CO_2$ emissions would be achieved by a massive deployment of RES extraction technologies, and even of CCS to fossil power plants, but a large excess of $CO_2$, emitted in the past and in the oncoming years, would still be removed to restore the climate balance. On this purpose, BECCS would become relevant as a NET and start to substitute the residual fossil power, borrowing the storage facilities. Anyway, also considering a full RES scenario to avoid $CO_2$ emissions, some considerable issues would be solved; indeed, most of RES are characterized by volatile availability and the energy produced has to be stored and delivered to fit the network consumption profile, in time. Currently the only developed and regarded solutions are green hydrogen production, through water hydrolysis, and electric power accumulation in batteries; however, batteries show self-discharge and pose concerns on their durability and life cycle, while hydrogen accumulation require stringent conditions to keep it in liquid form, at about -253 °C (20 K), and even large volumes, storing it as a highly compressed gas. Moreover, both the methods involve the delivery of only electric power, and even some hydrogen to the grid, which in turn require radical modifications of many energy use activities, some of which are particularly difficult to decarbonise. Indeed, while electric energy is suitable for many residential and industrial purposes, some energy intensive processes, agricultural and transport sector would lead to a huge overall inefficiency, or even to unfeasibility in some cases.

In particular, railway is a low impact mean of land transport already under deployment and electric automotive is fast developing, offering great advantages, especially in urban areas, while road transport, shipping and aviation, mainly involved in goods circulation, require to be fed by some kind of hydrocarbons, due to strong limitations on the batteries weight. Moreover, also tractors and machines utilised for many agricultural practices, which are even at the base of BE and NETs, such as AR and SCS, are commonly powered by diesel engines. The difficult in decarbonising these applications could be overcome by biofuels production, mainly by ethanol route, anyway it would be still affected by biomass growth rates and management operations impacts. On these assumptions, industrial processes aiming at the synthesis of low-carbon fuels by $CO_2$ and $H_2O$ would be the best solution to achieve a technically improvable production, able to supply each hydrocarbon use, if involving a higher overall efficiency. It is clear that this kind of processes should be mainly powered by RES and supplying the $CO_2$ close to the site of extraction, and even $H_2$ production, would offer several advantages. Moreover, while the first re-use cycle can be carried out downstream the capture stage of a fossil power plant, instead of supplying the $CO_2$ to a storage facility, in this way the $CO_2$ emission in atmosphere is only delayed; so, DAC technologies will be definitely the only solution to close the techno-sphere carbon cycle, that is by the moment a linear process involving anthropogenic $CO_2$ emissions.

On this purpose, $CO_2$ HT-DAC technologies could result convenient, even in the long term, for the realisation of industrial hubs around RES extraction plants, including H2 production, $CO_2$ DAC and P2X utilities, to deploy massive recycling processes for carbon. Indeed, the integration of many operations would allow to develop continuous autothermal systems, recycling part of the products, with high overall efficiencies, and $CO_2$ absorption technologies processes also offer lower materials costs and a more advanced state of the scale-up. Anyway, LT-DAC technologies can be as well applied, particularly to small facilities aimed at distributed production, which could be installed, in example, in airports to supply aviation or in rural areas for agricultural activities.

In addition to substituting fossil resources, synthetic fuels would also allow to overcome main drawbacks of hydrogen use as an energy carrier. Indeed, this is much more challenging to transport than and poses serious concerns on steel cracking, while hydrocarbons, both gaseous and liquids, would offer great advantages by the possibility of sharing existing infrastructures, such as pipelines, without substantial modifications. In a similar way, this approach could be an effective solution for reinforcing the sustainability of hydrocarbons-based activities, allowing further use and development of already consolidated technologies coupled with carbon recycling processes instead of designing new concepts, currently unaffordable. Moreover, synthetic fuels CCU pathways show a much higher safety and social acceptability than underground storage of fossil $CO_2$ emissions and could be a helpful way to solve the huge social issues connected to fuel resources supplying, making them available even where fossil reservoirs are not present, and would also result in an economic driver for many regions with large amounts of unproductive land.

As an example, a DAC $CO_2$-supplied power-to-gas pilot plant, fed by renewable power, have been operating in southern Italy, having good potential for photovoltaic and wind technologies. Here, and in similar areas, carbon recycling processes could be view as an economic solution to the already occurring climate change damages, mainly due to reduced water availability and spring temperature drops, affecting agriculture. In such environments, LT-DAC technologies deployment, with a smart management of the desorpted moisture and by-product streams, would even be suitable to support enhanced greenhouse farming practices, restoring agriculture sector.

If a high carbon-recycling scenario is achieved, and CCS is deployed as expected, the role of DACCS would become marginal in the long-term; anyway, as this technology would be even relevant in the short-term strategy, with already operating and under development plants, it could be adopted as the most effective, already deployed NET. Moreover, even if fossil fuel displacement and storage capacity lead to a decrease in the amount of $CO_2$ to be removed from the atmosphere, DACCS facilities would be easily converted to supply CCU pathways or to work on both purposes.

Overall, considering that are involved both in promising CCS applications as in main CCU and recycling pathways, $CO_2$ DAC technologies would be the key to meet climate neutrality and net-zero emissions targets. Indeed, the ease of deployment of DACCS respect to point-source CCS could partly overcome it and integrated DAC with P2X could offer several advantages respect to other RES stocking solutions. Thus, $CO_2$ DAC results the core technology in decarbonised energy systems, where its stage of development would set the targets for many other technologies involved both in the short and the long term.

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