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Sorption direct air capture with CO_2 utilization

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ABSTRACT

Direct air capture (DAC) is gathering momentum since it has vast potential and high flexibility to collect CO_2 from discrete sources as “synthetic tree” when compared with current CO_2 capture technologies, e.g., amine based post-combustion capture. It is considered as one of the emerging carbon capture technologies in recent decades and remains in a prototype investigation stage with many technical challenges to be overcome. The objective of this paper is to comprehensively discuss the state-of-the-art of DAC and CO_2 utilization, note unresolved technology bottlenecks, and give investigation perspectives for commercial large-scale applications. Firstly, characteristics of physical and chemical sorbents are evaluated. Then, the representative capture processes, e.g., pressure swing adsorption, temperature swing adsorption and other ongoing absorption chemical loops, are described and compared. Methods of CO_2 conversion including synthesis of fuels and chemicals as well as biological utilization are reviewed. Finally, techno-economic analysis and life cycle assessment for DAC application are summarized. Based on research achievements, future challenges of DAC and CO_2 conversion are presented, which include providing synthesis guidelines for obtaining sorbents with the desired characteristics, uncovering the mechanisms for different working processes and establishing evaluation criteria in terms of technical and economic aspects.

1. Introduction

Recent anthropogenic emissions of greenhouse gas (GHG) have unprecedentedly reached the highest level. An increasing concentration of GHG, especially CO_2, is the primary driver for global warming and numerous secondary effects [1]. The total amount of worldwide CO_2 emissions reached 34.17 Gt in 2020, and CO_2 concentration in the atmosphere increased from a pre-industrial value of 250 ppm to more than 410 ppm [2]. The IPCC has pointed out that the global mean surface temperature change in the period of 2016–2035 relative to 1986–2005 would likely be in the range of 0.3–0.7 ℃ [3]. An immediate, rapid and large-scale reduction in CO_2 emissions is necessary, otherwise limiting warming to 1.5 ℃ or even 2 ℃ will be beyond reach [4].

Carbon capture, utilization and storage (CCUS) is considered as an emerging technology to effectively mitigate CO_2 emissions and its concentration in ambient air [5]. Conventional CO_2 capture technologies, i.e., pre-combustion, oxy-fuel and post-combustion carbon capture separate CO_2 from large point sources, such as flue gases from coal-fired power plants [6,7]. Pre-combustion capture implies the removal of CO_2 from fuels prior to combustion processes. Typically, feedstock is first gasified to syngas via partial oxidization or steam reformation. The relatively high CO_2 partial pressure and concentration in the gasifier are suitable for more efficient capture technologies [8]. In an oxy-fuel combustion setup, fossil fuel combustion takes place under nearly pure O_2 atmosphere to reduce the possibility of NO_x generation. Nearly pure CO_2 can be directly subjected to sequestration or used via condensing out water vapour [9]. Post-combustion capture process separates CO_2 from flue gas after fuel combustion in air, which could be widely applied in existing power plants due to the simplicity of retrofitting and availability of mature amine scrubbing technology [10]. There are several common techniques available for post-combustion

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Nomenclature

Abbreviations

AC	Activated carbon
AEM	Anion exchange membrane
ALR	Airlift reactor
APS	American Physical Society
BECCS	Bioenergy with carbon capture and storage
BEIS	Business, energy and industrial strategy
BPMED	Bipolar membrane electrodialysis
CAPEX	Capital expenditure
CCUS	Carbon capture, utilization and storage
CDM	Clean development mechanism
CEM	Cation exchange membrane
CFB	Circulating fluidized bed
CfD	Contract for difference
CI	Carbon intensity
DAC	Direct air capture
DACM	DAC/methanation
DACCS	Direct air carbon capture and storage
DEA	Diethanolamine
DFM	Dual function material
DMC	Dimethyl carbonate
DMFC	Direct methanol fuel cells
DME	Dimethyl ether
DOE	Department of Energy
E-fuels	Electrofuels
ELALR	Airlift reactor with external sparger
EOR	Enhanced oil recovery
ESA	Electric swing adsorption
ETS	European trading system
EWC	Equilibrium working capacity
FT	Fischer-Tropsch
GHG	Greenhouse gas
GWP	Global warming potential
HAS	Hyperbranched aminosilica
HBI	Hybrid biological-inorganic
HOB	H_2-oxidation bacteria
HS	Humid swing
HT	High temperature
ILALR	Airlift reactor with internal sparger
LCA	Life cycle assessment
LSM	Liquefied synthetic methane
LT	Low temperature
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
MeOH	Methanol
MMO	Mixed metal oxides
MOF	Metal organic framework
MPs	Microbial proteins
NETL	National Energy Technology Laboratory
NG	Natural gas
NGCC	Natural gas combined cycle
NMP	N-methylpyrrolidone
OME	Polyoxymethylene dimethyl ethers
OPEX	Operational expenditures
PA	Polyacrylate
PBR	Photobioreactor
PEHA	Pentaethylenehexamine
PEI	Polyethyleneimine
PtG	Power-to-gas
PtL	Power-to-liquid
PTSA	Pressure-temperature swing adsorption
PSA	Pressure swing adsorption
PVSA	Pressure-vacuum swing adsorption
RH	Relative humidity
RWGS	Reverse water gas shift reaction
TEA	Techno-economic analysis
TEPA	Tetraethylenepentamine
TGA	Thermogravimetric analyser
TREN	Tris (2-amino ethyl)
TSA	Temperature swing adsorption
VSA	Vacuum swing adsorption
VTSA	Vacuum-temperature swing adsorption
XPS	X-ray photoelectron spectroscopy

Symbols

n	Total number of moles
q	CO_2 adsorption capacity ($mmol\cdot g^{-1}$)
R	Universal gas constant ($J\cdot K^{-1}\cdot mol^{-1}$)
Re_{CO2}	CO_2 recovery rate
T	Temperature (°C)
W_{min}	Minimum separation work ($kJ\cdot kg^{-1}$)
y	Compositions of various streams

Greek symbols

ΔH	Reaction heat, $kJ\cdot mol^{-1}$
φ_{un}	Efficiency of the reactor

CO_2 separation, i.e., cryogenic distillation, membrane separation, absorption and adsorption [11,12]. Cryogenic distillation could obtain liquid CO_2 which is conducive to transportation and storage though it is highly energy intensive [13,14]. Membrane separation is cost-effective but its main limitation is the requirement of high selectivity to extract a relatively low concentration CO_2 from flue gas [15–18]. Sorption technologies are the mainstream paths for carbon capture. Absorption is currently the most developed technology while adsorption can be used as a viable method with a low energy penalty [19,20].

In comparison with large, concentrated carbon sources related to conventional CO_2 capture technologies [21], roughly half of annual CO_2 emissions are derived from distributed carbon sources in residences, stores and buildings, especially in ambient air [22]. To remove CO_2 already present in the air, bioenergy with carbon capture and storage (BECCS) [23] and direct air carbon capture and storage (DACCS) are regarded as two key technologies [24–26]. For BECCS processes, atmospheric CO_2 is removed by growing plants and trees. Biomass can be burnt to generate heat and electricity. The majority of CO_2 released during combustion are captured and sequestered [27] or utilized to produce fuels [24]. It has great potential to achieve negative GHG emissions and compensate for the existing temperature overshoot [28]. However, land competition for food production, water, and fertilizer requirements as well as CO_2 emissions associated with biomass cultivation, harvesting and processing may come with significant social and environmental impacts [24,28,29].

Direct air capture (DAC) aims to extract CO_2 directly from ambient air. Although DAC has been already adopted in life support systems of spacecraft and submarines [30], it was not proposed for CO_2 extraction from air to mitigate global warming until 1999 [31]. A remarkable fact is that DAC can be used to capture CO_2 emissions unrelated to its source and time, i.e., DAC can potentially be deployed anywhere and operated anytime. Various approaches to technical realization of DAC process have been proposed, amongst which the vast majority of DAC development is based on sorption processes when comprehensively considering their advantages and disadvantages of energy penalty, stability and cost [22,29]. For sorption DAC, ambient air flows over a sorbent that selectively removes CO_2, which is then released as a concentrated stream for further use while sorbents are regenerated and CO_2-lean air is returned to the atmosphere. Thus one main challenge is the deterioration of sorbents due to chemical stability and sorption performance affected after thousands of working cycles when exposed to large amounts of air [32]. Another significant challenge for sorption DAC is the low CO_2 concentration in the atmosphere (~400 ppm), which requires large loading sorbents and high specific energy demand in the regeneration process. It also targets for sorbents with high stability under variable temperature conditions. For sorption DAC, working processes and sorption materials are two key components for high efficiency. The most common methods for gas separation are pressure swing adsorption (PSA) and temperature swing adsorption (TSA). PSA has become the main process for hydrogen purification and air separation, but TSA is of great interest for carbon capture owing to potential availability of low-grade thermal energy for the regeneration process of sorbents [33]. Considering low CO_2 levels, it is critical to determine which process is worthy of additional development to match specific sorbents. Solid sorbents, e.g., zeolites, activated carbon (AC), metal organic framework (MOF), and amine modified materials are investigated to further improve their sorption performance in the atmosphere while chemical sorbents aim to improve their incompatibility with air [34,35]. Subsequent utilization of the captured CO_2 to produce valuable products can help reduce the net cost of DAC process. Moreover, capital and operation costs are equally vital for the evaluation of DAC technology. As the technology is at early stage of development, it is challenging to evolve with high costs, which would not be economically competitive without a technological breakthrough or more incentives [32]. DAC could be predicted to have anticipated needs and opportunities for a large-scale application based on the increasing carbon tax and carbon neutrality target in many countries.

It is evident that review studies of sorption DAC are rarely reported due to its more recent emergence [36–40], and previous literature primarily focuses on various types of sorbents. Instead, this work not only focuses on the latest technological developments of sorption DAC, but also aims to critically assess the benefits and current challenges in combination with CO_2 utilization and its potential future perspective. It provides a holistic context from material evaluation, techno-economic analysis (TEA) to commercial development. First, a state-of-the-art for DAC is presented. Sorption characteristics of physical and chemical sorbents are evaluated in Section 2. Then, representative capture processes, e.g., physical adsorption and absorption chemical loop are compared in Section 3. In Section 4, methods of CO_2 conversion including synthesis of fuels and chemicals as well as biological utilization are discussed with particular emphasis on in-situ CO_2 conversion. Economic and environment analysis are discussed for potential cost reduction and feasibility of sorption DAC in Section 5 which may be reflected to the technical part. Moreover, the commercial development is initially summarized in Section 6. Based on research achievements, future challenges and perspectives of sorption DAC are pointed out. To further clarify the framework of this work, the concerning main components and landscape of sorption DAC with carbon utilization are illustrated in Fig. 1. A bridge of sorption DAC aims to be built from dilute carbon sources i.e., ambient air, to carbon sinks, i.e., pure compressed CO_2 ready for potential utilization. Sorption materials and working processes are the main basis to support DAC application. Life cycle assessment (LCA) and TEA are adopted as the important methods for holistic evaluation, which are expected to achieve reasonable carbon capture costs and economic benefits for potential commercialization.

2. Sorbents for DAC

Since CO_2 concentration in ambient air is low, energy consumption of sorbents is relatively high which is mainly determined by material types, sorption capacities and CO_2 selectivity. Thus, the suitable sorbent selection and development are regarded as key for DAC application. Several sorbents have been widely explored, such as zeolite, AC, MOF, and alkali oxides, etc. In general, sorbents could be classified into physical sorbents and chemical sorbents based on different sorption mechanisms. A detailed analysis of sorbents is conducted in two categories in this section. Composite sorbents are merged into the chemical sorbent category since chemical reactions mainly contribute to their sorption processes.

2.1. Physical sorbents

CO_2 capture using physical sorbents consumes less energy when compared with chemical sorbents. This is mainly because physical sorption relies on typically weaker physical interaction of van der Waals bonds, and no new bond is formed between sorbate and sorbent [12]. Since physical absorbents are rarely reported in DAC applications and often accompanied by chemical absorption processes, physical adsorbents, e.g., zeolite, AC and MOF are mainly illustrated in this section.

Zeolites: Zeolites are three-dimensional (3D) porous crystalline aluminosilicates built of a periodic array of TO_4 tetrahedra (T = Si or Al), which have been widely used in gas separation. Aluminium substitution

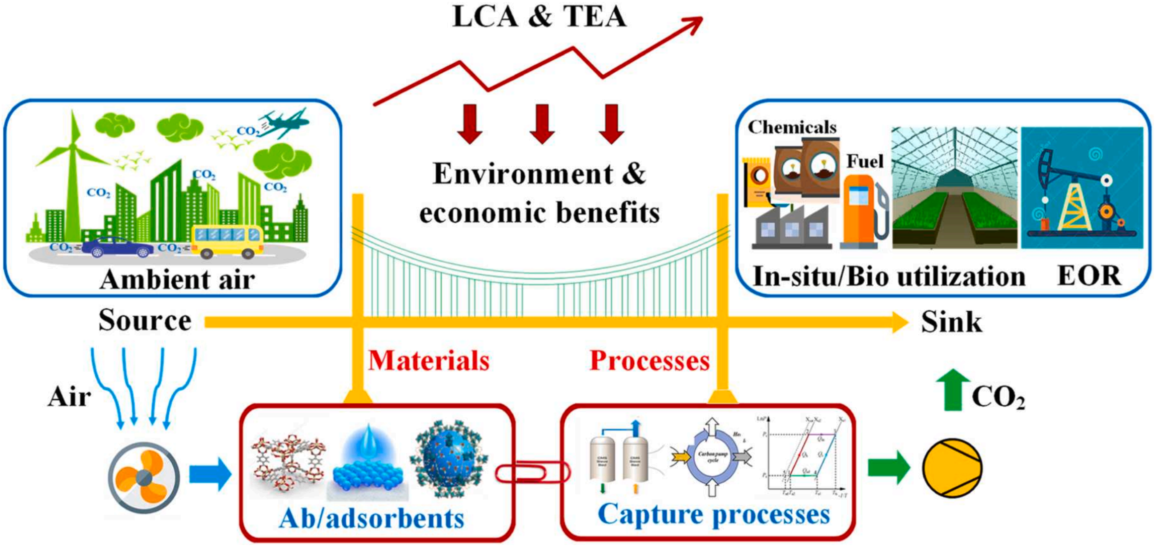


Fig. 1. A schematic summary of the main components in this review.

to silicon in the lattice of zeolite forms isomorphism, resulting in a structure with a net negative charge and a high affinity for quadrupolar molecules, e.g., CO_2 [41]. Na-X, one of low-silica types of zeolite X (LSX), has been applied in air pre-purification processes to reduce CO_2 emissions.

Based on previous research of using NaX at industrial scale, new high micro-porosity LSXs have been investigated under laboratory DAC conditions. An excellent CO_2 adsorption capacity (1.34 $mmol{\cdot}g^{-1}$) was reported for Li-LSX powder in dry air under ambient condition [42]. Bed breakthrough capacities of various LSXs were measured on pellets that contained approximately 15% binder. It is found that Li-LSXs are effective in a fixed bed adsorber and K-LSX has the highest CO_2/N_2 selectivity. This is mainly because the lower specific surface area of these materials could lead to lower capacity at adsorption breakthrough point when compared with pure-component powder. In addition, moisture in the air will lead to a significant decrease of adsorption capacity of zeolite. Besides, faujasite-structured zeolites such as APG-III was also investigated and demonstrated to have a high CO_2 uptake of 0.42 $mmol{\cdot}g^{-1}$ [43]. Except for conventional extrusion process for fabricating zeolite monoliths, 3D techniques were used to fabricate complex geometries [44]. CO_2 adsorption capacities of serval 3D-printed zeolite monoliths were tested under 3000 ppm and 5000 ppm CO_2 in N_2 at room temperature. Zeolites with different mass ratios were compared and the results indicated that increasing zeolite/binder mass ratio led to a higher CO_2 adsorption capacity. Moreover, 3D printed technique could possibly be beneficial to systematically tune the porosity, zeolite loading and mechanical strength of the structures of composite sorbents for DAC.

Although zeolites are mature and economically available, sorption capacity and selectivity of CO_2/N_2 are still two challenges of zeolites for DAC application. Incorporating amine into zeolites to form functionalized zeolites would help to improve sorption capacity, which relies on zeolite types [45]. To overcome the decrease of adsorption capacity under wet conditions, a desiccant bed, e.g., silica gel or potassium substituted zeolite type A (3A) have been used to motivate the pass of CO_2 and capture the moisture from the air [42,43]. Commonly, this solution comes with additional energy input and equipment cost.

Activated carbon: Activated carbon (AC) has a wide range of available sources, which can be produced from coals, industrial by-products and wood or other biomass sources. Higher CO_2 adsorption capacity of AC could be observed at higher pressures [46,47]. AC has also drawn great attention for CO_2 capture because of its low cost, high surface area, insensitiveness to moisture, easily tailorable properties, good stability and low energy requirements for regeneration [48]. High surface area makes it able to adsorb molecules from gas and liquid phases because of its highly developed porosity. Low chemical activity ensures that it does not react with the sorbate and can be easily regenerated. Generally, types and properties of AC depend on preparation methods and raw materials. Pyrolysis, activation temperature and holding time are key factors in the preparation processes [49,50]. Biochar has been widely studied as a useful adsorbent for CO_2 capture in the flue gas, but it is rarely reported for DAC. Fig. 2 compares the average sorption capacity of biochar developed under different pyrolysis temperatures, heating rates and starting concentrations [49]. Biochar produced under control conditions by using thermogravimetric analyser (TGA) has better CO_2 sorption capability (1.16–3.18 $mmol{\cdot}g^{-1}$) than that produced in a furnace (0.15 $mmol{\cdot}g^{-1}$). Pyrolysis temperature is the most important contributing factor, while effects of heating rate and CO_2 starting concentration are insignificant.

Ability to capture CO_2 directly from the atmosphere requires more selective and higher CO_2 binding affinities. Recent studies have reported several effective strategies to improve CO_2 binding affinities for AC: polymers are used as precursors to prepare carbon-based CO_2 adsorbents with desirable properties which have been identified as a useful technique [51]. Phenolic resins are the most used polymer to prepare carbon-based CO_2 adsorbent due to its relatively low costs. It has been demonstrated that under the condition of atmospheric pressure and room temperature, CO_2 capture capacities of the phenolic resins-based AC could reach up to 10.8 wt.%, but they are significantly lower than those at 25 bar and 25 ℃ [52]. Although super-high surface area of AC leads to greater adsorption capacities at high pressure, lower capacities at low pressures and poor selectivity for CO_2 and N_2 makes it not that suitable to be applied for DAC [12].

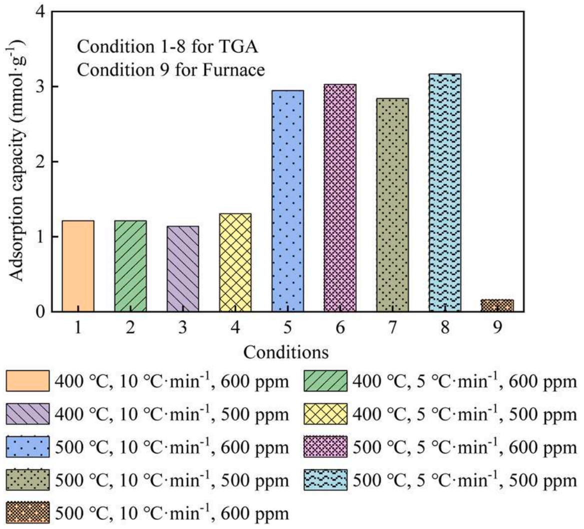


Fig. 2. Comparison of average CO_2 adsorption of biochar using TGA and the furnace (data from [49]).

Metal organic framework (MOF): As a research hotspot in crystalline porous materials, MOFs consist of metal-containing nodes linked by organic ligand bridges and are formed by strong coordination bonds [53]. Compared to zeolites, rigid and divergent character of the added linker makes it easier to tailor apparent surface area and pore volume through control of pore architecture and linker functionalization. Modification of MOFs has been investigated from the replacement of linkers or metal ligands and synthesis methods.

CO_2 adsorption through MOFs is pore size/volume and surface dependant. To enhance CO_2 uptake and selectivity at very low partial pressure relevant to DAC, a 2-D square grid MOF (SIFSIX-3-Cu) with a pyrazine/copper (II) connected by silicon hexafluoride anions was constructed [54]. A large CO_2 uptake is observed when using SIFSIX-3-Cu (1.24 $mmol{\cdot}g^{-1}$) at 298 K adsorption temperature and 0.4 mbar partial pressure. High CO_2 selectivity of this material is a result of tuning pore size and interaction energy to allow physical capture of CO_2 from ultra-dilute CO_2 concentration sources such as air. Thus, a structural analysis of SIFSIX-3-X adsorbents was conducted to pinpoint key structural features responsible for unique CO_2 capture properties [55]. $(NbOF_5)^{2-}$ was proposed to replace original inorganic pillar $(SiF_6)^{2-}$ existing in SIFSIX-3-X. Significantly, the product NbOFFIVE-1-Ni offers an even higher CO_2 uptake at 400 ppm than SIFSIX-3-Cu. The result of changing the pillar from SiF_6^{2-} to TiF_6^{2-} leads to the enhanced CO_2-sorbent interactions and higher selectivity [56]. TIFSIX-3-Ni was found to perform very competitively when compared with the benchmark NbOFFIVE-1-Ni. Five benchmark adsorbents that encompass one chemical sorbent (TEPA-SBA-15), four physical sorbents (zeolite 13X, HKUST-1, Mg-MOF-74 and SIFSIX-3-Ni) were compared and investigated their ability to adsorb CO_2 directly from air [57]. It was demonstrated that SIFSIX-3-Ni has the largest CO_2 uptake (0.182 $mmol{\cdot}g^{-1}$) amongst physical sorbents, while much lower than that of TEPA-SBA-15 (3.591 $mmol{\cdot}g^{-1}$). Fig. 3 shows a good long-time stability of these sorbents when exposed to a controlled humidity chamber. It could be deduced that two kinds of MOFs (HKUST-1 and Mg-MOF-74) are impaired by exposure to humidity. Sorption performance of TEPA-SBA-15, zeolite 13X and SIFSIX-3-Ni are relatively stable after a

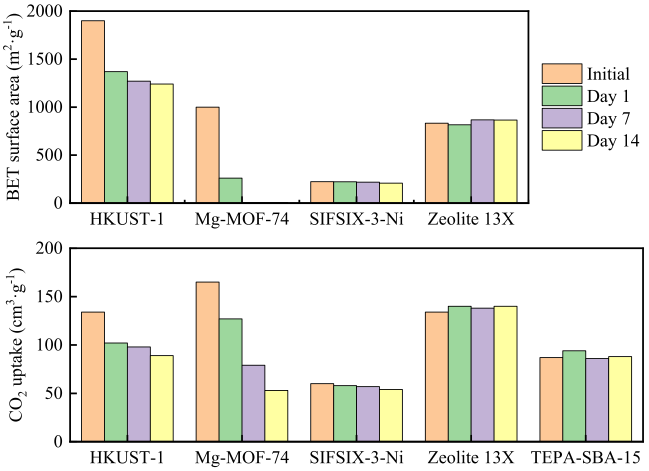


Fig. 3. BET (Brunauer-Emmett-Teller) surface area and CO_2 uptakes at 293 K and 1 bar for each sorbent under initial condition and after 1, 7 and, 14-day exposure in a controlled humidity chamber (data from [57]).

14-day testing. But energetics and recyclability of chemical sorbent TEPA-SBA-15 are not as favourable as those of SIFSIX-3-Ni. Further investigation of SIFSIX-3-Cu at 1 bar and 49% relative humidity (RH) exhibits the highest uptake of CO_2 (0.321 $mmol{\cdot}g^{-1}$), which outperforms CO_2 uptake of Ni analogue since it has an ultra-microporous pore size [58].

A summary of physical adsorbents for DAC is presented in Table 1. Zeolite powder has the higher adsorption capacity than zeolite pellet with binder. Investigation of AC for DAC is rare, because common AC only has a satisfactory capacity at high pressure. It is desirable for AC to have a high sorption capacity and selectivity under the conditions of atmospheric pressure and high humidity. Besides, SiF_6^{2-} (SIFSIX) family exhibits larger adsorption capacity than Mg-MOF-74, which only has the capacity of 0.088 $mmol{\cdot}g^{-1}$ at 0.4 mbar CO_2 partial pressure. When replacing original inorganic pillar SiF_6^{2-} in SIFSIX-3-X with $(NbOF_5)^{2-}$, NbOFFIVE-1-Ni performs better than SIFSIX-3-Cu under the same testing conditions. Although there is a slight difference in the testing temperature, moisture in the air still leads to the decrease of adsorption capacity of SIFSIX-3-Cu. It is indicated that only a few kinds of MOFs have a satisfactory performance under DAC conditions due to the ultra-dilute CO_2 concentration. amongst physical adsorbents, MOFs are the most promising materials due to its high modification flexibility.

Table 1
CO_2 adsorption capacity of physical adsorbents for DAC under different tested conditions.

Types	Adsorption conditions	Capacity ($mmol{\cdot}g^{-1}$)	Ref.
Li-LSX powder	395 ppm CO_2/N_2 at 25 ℃, dry	1.34	[42]
Li-LSX pellets	395 ppm CO_2/N_2 at 25 ℃, dry/wet	0.82/0.01	[42]
K-LSX powder	395 ppm CO_2/N_2 at 25 ℃, dry	0.67	[42]
K-LSX pellets	395 ppm CO_2/N_2 at 25 ℃, dry/wet	0.25/0.03	[42]
NaX powder	395 ppm CO_2/N_2 at 25 ℃, dry	0.41	[42]
NaX pellets	395 ppm CO_2/N_2 at 25 ℃, dry/wet	0.32/0	[42]
NaX	400 ppm CO_2/Air at 20 ℃	0.45	[59]
APG-III	409–441 ppm $CO_2/N_2/O_2/Ar$ at 23.5 ℃	0.42	[43]
Zeolite 13X monoliths	5000 ppm CO_2/N_2 at 25 ℃	1.6	[44]
Activated carbon	500 ppm CO_2/air at 30 ℃ (2 bar)	3.18	[49]
SIFSIX-3-Zn	400 ppm CO_2/N_2 at 24.85 ℃	0.13	[54]
SIFSIX-3-Cu	400 ppm CO_2/N_2 at 24.85 ℃	1.24	[54]
Mg-MOF-74	400 ppm CO_2/N_2 at 24.85 ℃	0.088	[54]
SIFSIX-3-Ni	400 ppm CO_2/air at 23.4 ℃, 49% RH	0.182	[57]
NbOFFIVE-1-Ni	400 ppm CO_2/N_2 at 24.85 ℃	1.3	[55]
NbOFFIVE-1-Ni	400 ppm CO_2/N_2 at 24.85 ℃, 49% RH	0.421	[56]
TIFSIX-3-Ni	400 ppm CO_2/N_2 at 24.85 ℃, 49% RH	0.407	[56]
SIFSIX-3-Cu	400 ppm CO_2/air at 23.4 ℃, 49% RH	0.321	[58]

2.2. *Chemical sorbents*

Compared with physical sorbents, the presence of chemical bonds between sorbents and sorbates results in a strong affinity to capture CO_2, which makes chemical sorbents more attractive for DAC. Solid alkali sorbents, amine-modified solid sorbents and liquid chemical absorbents are three main categories of chemical sorbents [60].

Solid alkali sorbents: Alkali metal oxides react with CO_2 to form carbonate or bicarbonate in the presence of water. Due to commercial availability and low price, CaO-based sorbents have been extensively used for CO_2 separation. The basic carbonation-calcination reversible reaction occurs according to Eq. (1). The carbonation process is operated at 365–400 ℃ while calcination is operated at 800–875 ℃. Steam is added to the carbonation step to enhance its reaction rate through formation of intermediate $Ca(OH)_2$ [61,62]. CaO hydration (Eq. (2)) and overall carbonation reaction of $Ca(OH)_2$ (Eq. (3)) are shown as follows.

$$CaO + CO_2 \rightleftharpoons CaCO_3 \tag{1}$$

$$CaO + H_2O \rightleftharpoons Ca(OH)_2 \tag{2}$$

$$Ca(OH)_2 + CO_2 \rightleftharpoons CaCO_3 + H_2O \tag{3}$$

Carbonation of CaO normally requires high temperature to effectively remove CO_2. To improve CO_2 capture capability of CaO-based materials under ambient conditions, pre-hydrated lime in DAC was explored [63]. It is demonstrated that introducing steam into calcination [64,65] or carbonation [63,66] process has a positive effect on DAC performance. Carbonation conversion ratio is more than 50% after pre-hydration of CaO [67]. Two main phenomena cause faster carbonation of hydrated lime than that of lime at initial stage: more non-bound water contained in the hydrated lime promotes CO_2 dissolution at gas/solid interface; cracks in the sorbents since formation of $Ca(OH)_2$ exposes internal unreacted lime for further carbonation. In the presence of water, $CaCO_3$ formed on the surface of CaO could be converted to $Ca(HCO_3)_2$, which breaks the protection of $CaCO_3$ layer and enhances CO_2 diffusion through bulk of particles [67].

M-based alkali metal oxides/carbonates (M denotes Na or K) can also be applied for CO_2 capture [68,69]. Three independent variables, i.e., temperature, partial pressure of CO_2 and partial pressure of H_2O have influence on the reactions between alkali metals and CO_2. The chemical reactions can be expressed as Eqs. (4)-(5):

$$M_2O + CO_2 \rightleftharpoons M_2CO_3 \tag{4}$$

$$M_2CO_3 + CO_2 + H_2O \rightleftharpoons 2MHCO_3 \tag{5}$$

Alkali carbonates loaded into porous matrices are studied to overcome the problem of low carbonation rates under ultra-dilute CO_2 concentration in the air. K_2CO_3 has been widely introduced to different porous substrates [70–74]. With the presence of CO_2, K_2CO_3 is further transformed into $KHCO_3$ to capture CO_2 as shown in Eq. (6). Under humid conditions, K_2CO_3 undergoes hydration reaction where the unstable product potassium carbonate sesquihydrate ($K_2CO_3{\cdot}1.5H_2O$) is formed as indicated in Eq. (7). Final product $KHCO_3$ is rapidly produced as shown in Eq. (8).

$$K_2CO_3 + CO_2 + H_2O \rightleftharpoons 2KHCO_3 \tag{6}$$

$$K_2CO_3+1.5H_2O \rightleftharpoons K_2CO_3\cdot 1.5H_2O \quad (7)$$

$$K_2CO_3\cdot 1.5H_2O + CO_2 \rightleftharpoons 2KHCO_3+0.5H_2O \quad (8)$$

Composite sorbents $K_2CO_3/\gamma\text{-}Al_2O_3$ absorb CO_2 through the formation of crystalline $KHCO_3$ and nano-dispersed $KAlCO_3(OH)_2$ phase on the surface of $\gamma\text{-}Al_2O_3$ under DAC conditions [70]. $KHCO_3$ phase and intermediate $K_2CO_3\cdot KHCO_3\cdot 1.5H_2O$ phase would convert to K_2CO_3 at a temperature higher than 200 ℃. Potassium dawsonite $KAlCO_3(OH)_2$ is formed as a result of the reaction between K_2CO_3 and Al_2CO_3, and its thermal destruction is not complete until heated up to 300 ℃ [71]. Therefore, a significant heat consumption is required for its regeneration. Based on Y_2O_3 porous matrix, experimental sorption capacity remains relatively stable during the first 20 cycles [73]. A K-Y interaction like K-Al is formed in K_2CO_3/Y_2O_3 composite sorbent. Compared to Al_2O_3 matrix, introduction of ZrO_2 aerogel matrix eliminates negative influence of intermediate $KAlCO_3(OH)_2$, contributing to a higher transformation rate of K_2CO_3 to $KHCO_3$ and higher CO_2 adsorption capacity [74]. Thermal pre-treatments of granular $\gamma\text{-}Al_2O_3$ were conducted to increase the percentage of K_2CO_3 involved in transformation to $KHCO_3$ [72]. When heat treatment temperature increases from 450 to 750 ℃, increasing dynamic sorption capacity may be related to mass transfer enhancement in the larger pore.

Inorganic supported materials, e.g., AC were proposed to avoid formation of by-products when using metal-based matrices [75]. Performance of alkali metal salts is significantly influenced by the moisture in air. K_2CO_3 supported on AC honeycomb will produce $K_2CO_3\cdot 1.5H_2O$ or aqueous solution according to different RHs [75]. Aqueous solution was formed due to deliquescence on the surface of Al_2O_3 when RH is above 43% [76], speeding up the formation of $KAlCO_3(OH)_2$ and reducing CO_2 sorption capacity [72]. Evaporation of the solution generates a local cooling effect which is beneficial to CO_2 adsorption. Adsorption capacities under different experimental conditions using K_2CO_3/AC are compared in Fig. 4. Adsorption capacity decreases with the increase of adsorption temperature and water vapour pressure. It is initially demonstrated that increasing moisture in the gas mixture would be beneficial to the carbonation of $K_2CO_3\cdot 1.5H_2O$. However, it could be inferred from Eq. (8) that increased moisture would make reaction shift to the left and inhibit capture process. Replacing K_2CO_3 with pre-hydrated Na_2CO_3 results in a similar cooling effect [77]. Due to negative effect of reactions between support material and alkali sorbent, their interrelation should be investigated to improve adsorption performance under DAC conditions.

Amine-modified solid sorbents: Amines supported on matrices are popular materials for flue gas carbon capture and are gathering momentum in DAC applications. Compared to solid metal-based sorbents, amine-modified sorbents have quite low regeneration temperature, which results in lower energy and process cost. Features like strong affinity for binding with CO_2, and high tolerance to humidity make amine-sorbents attractive [41].

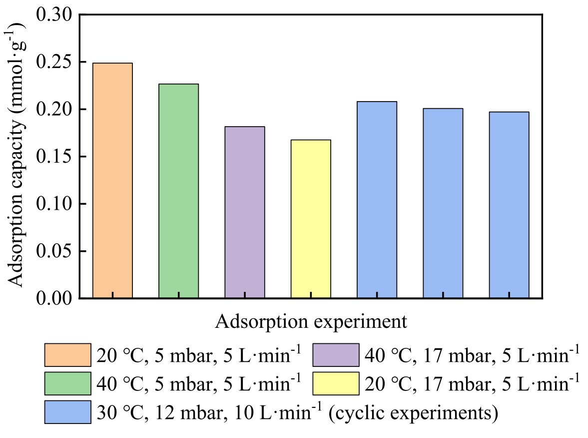


Fig. 4. CO_2 adsorption capacities under different adsorption temperatures, water vapour pressure and volumetric air flow rates (data from [75]).

Mechanisms of amines-modified sorbents for CO_2 capture are based on acid-base reaction: primary and secondary amines react with CO_2 to form carbamate or bicarbonate through a zwitterion mechanism, and tertiary amines react with CO_2 in the presence of water to form bicarbonate [78]. Theoretical amine efficiency is usually defined by molar CO_2/N ratio [37]. Amine-modified sorbents are classified into three classes as shown in Fig. 5 [79]: (1) Class 1, physically loading amines into porous materials; (2) Class 2, amines are covalently bound to the surface of porous materials, e.g., via use of organosilanes; (3) Class 3, prepared by in-situ covalent polymerization of amine on porous materials. Hyperbranched aminosilica (HAS) materials [79] and poly (L-lysine) brush/mesoporous silica hybrid material [80] are promising Class 3 CO_2 adsorbents.

Quite a few studies on DAC using amines based on different supports, e.g., mesoporous silica, alumina, MOFs, have been reported. Silica is the most common support for solid amine sorbents, but suffers from degradation in the presence of steam and poor cyclic stability. Introduction of stable additives on silica composite adsorbent was proposed by Choi et al. [81]. With silane and titanium propoxide additives, modified polyethyleneimine (PEI) samples presented higher decomposition temperatures and enhanced thermal stability over multiple TSA cycles. amongst three types of amines, primary amines show significant performance enhancements by correlated silanes [78]. Efficiencies of primary amines are more than twice of secondary amines at 25 ℃, while tertiary amines have no amine efficiency owing to negligible CO_2 adsorption. For highly loaded primary amines, adsorption efficiencies can reach 0.3, even under dry air capture conditions. Moreover, it is evident that primary amines enhance the hydrophilicity of the adsorbent, whereas secondary or tertiary amines cause the materials more hydrophobic than bare support. Mesoporous silica especially SBA-15 [80,82-84] is feasible as supported materials for DAC because of its structural properties of high pore volume, large pore size and thick walls. Silica gels are also commercially available sorbent with controlled qualities and substantially lowest costs. They can be readily used for amine grafting and fixed-bed adsorption without pre-synthesis to be pellets [85].

It is important to determine locations of amine sites for CO_2 working capacity enhancement based on adsorption mechanisms. Because of moisture in the air, water effect on CO_2 adsorption sites is a key factor that needs to be considered. Pre-humidified adsorbents are available to form bicarbonate, thus increasing amine efficiency, whereas dry sorbents accumulate water over time. Also, polymer network loosened by water allows enhanced CO_2 penetration to some extent [86], and inhibits the formation of stable urea and imidazolidinone species [87]. However, an excess of humidity or extreme hydrophilicity has a negative impact on CO_2 adsorption if water condenses in pores and blocks access of CO_2 to the sites [78]. Capture capacity of PEI/PME(40) (PME = pore-expanded silica MCM-41 with a surface layer of cetyltrimethylammonium cations) is increased by 33.7% from 5.4 to 7.31 mmol·g^{-1} upon humidification of 400 ppm CO_2/N_2 feed gas to 64% RH [87]. Humidity has a predominant effect on adsorption capacity of polymer/silica fibre sorbents, which increases equilibrium CO_2 capacity to 1.6 mmol·g^{-1}, approximately 2.5 times higher than the capacity under dry conditions [88]. Wet-grafted silica gels W-AG-150A shows larger CO_2 uptake (1.97 mmol·g^{-1}) than dry-grafted AG-150A (1.35 mmol·g^{-1}) at 25 ℃ and 1 bar, which proves the superiority of wet grafting synthesis procedure [85].

Alumina supports show more tolerance to steam treatments than silica, which are the preferred supports for practical DAC applications. Mesoporous alumina possesses a large pore volume, 3D connected mesopores and good hydrothermal stability. Alumina surface contains both acidic and basic sites, which are alterable by preparation and post-treatment procedures [89]. Owing to its amphoteric nature, alumina

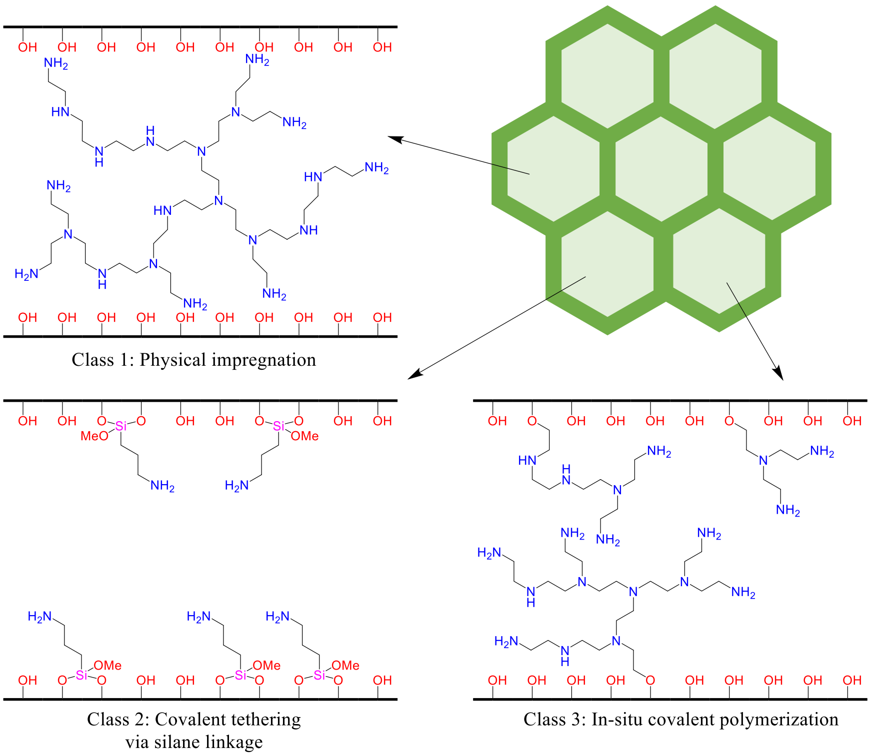


Fig. 5. Schematic diagram of three classes of amine-modified sorbents [79].

supports present more active CO_2 sorption than silica supports, potentially directly participating in the adsorption process [90]. As shown in Fig. 6, when no amine is loaded on bare Al_2O_3 supports (D-Al_2O_3 and O-Al_2O_3), the supports all behave as an initial CO_2 uptake under DAC conditions. The modified amine efficiency (A.E.) considers adsorption sites in Al_2O_3 supports which is compared with the traditional amine efficiency. With a high amine loading, actual amine efficiency might be closer to the traditional amine efficiency, but when amine loading is low, adsorption effect of bare Al_2O_3 support exceeded that of amine. Performance of PEI loaded on monolithic and power alumina were investigated by using TGA [91]. With a low PEI loading, the powder sample has a higher capacity. Comparably, monolithic sample performs better with a high PEI loading. In addition, monoliths show worse kinetics by breakthrough experiments. This may result from the differences in the thickness of PEI layers or due to the fact that monolithic samples have greater characteristic lengths. A novel PEI-functionalized Mg-Al mixed metal oxides (MMO) exhibited higher CO_2-uptake (2.27 mmol·g^{-1}), better kinetics (1.1 mmol·g^{-1}·h^{-1}), and high stability at 25 ℃ under 0.4 mbar CO_2 due to ideal morphologies and nanostructures of their supports [92]. With a high PEI loading ratio, polyamines start to cover MMO frameworks but porous structure is still maintained and amine efficiency is not significantly decreased. Another Mg-Al MMO

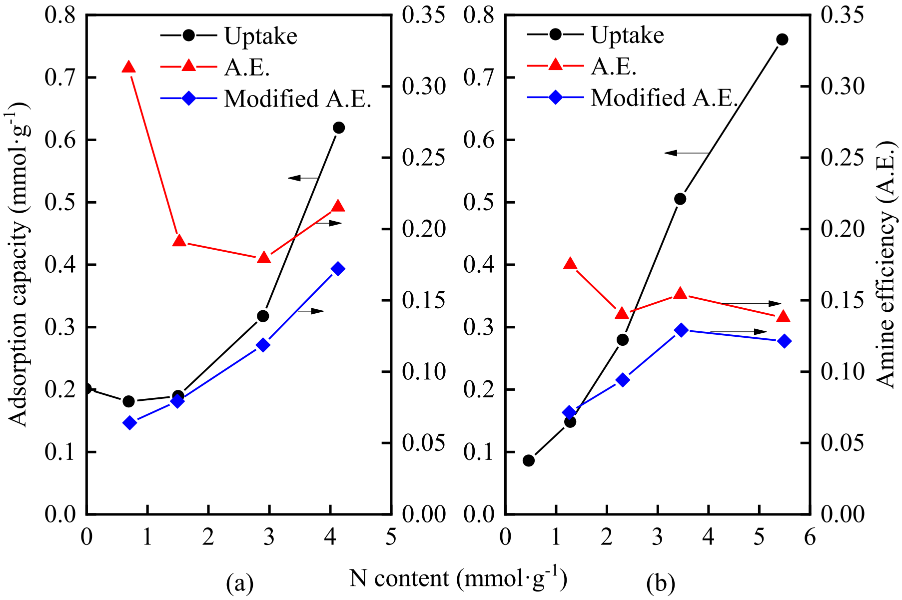


Fig. 6. CO_2 uptake, amine efficiency and modified amine efficiency as a function of amine loading for (a) D-Al_2O_3 and (b) O-Al_2O_3 under the drying conditions of 30 ℃, 400 ppm CO_2 in N_2 (data from [90]).

supported TEPA adsorbent for DAC was recently reported by Zhao et al. [93]. The optimal $Mg_{0.55}$Al-O-TEPA67% demonstrates a high CO_2 uptake of 3.0 mmol·g^{-1} and an excellent regenerability.

MOFs with textural flexibility and high BET surface are desirable as amines supports. However, weak physical interaction between MOFs and CO_2 results in unfavourable adsorption capacities and moderate CO_2/N_2 selectivity. A variety of open metal sites in some families of MOFs, e.g., M_2(dobpdc) (M = Mg, Mn, Zn, Ni, Co, Fe, dobpdc^{4-} = 4,4′-dioxido-3,3′-biphenyldicarboxylate) enable selective post-synthesis modification to enhance the selectivity of gas adsorption [94]. Functionalization of MOFs with amines can improve CO_2 adsorption capacity and cyclic stability. Two representative MOF materials are Mg_2(dobpdc) [95–97] and MIL-101(Cr) [94]. Post-synthesis amine functionalization of modified Mg/DOBDC (DOBDC = 2,5-dioxido-1,4-benzenedicarboxylate) was implemented to create an adsorbent with CO_2 adsorption capacity and improved material stability under DAC operating conditions [95]. Functionalization of the framework was carried out by grafting of ethylenediamine onto dehydrated Mg/DOBDC in anhydrous toluene under reflux for 12 h, which formed amine-modified composite adsorbent ED-Mg/DOBDC. Amine modified ED-Mg/DOBDC indicates the best cyclic adsorption performance amongst common adsorbents. Another amine-functionalized MOF, mmen-Mg_2(dobpbc), possessed a significantly high CO_2 affinity at extraordinarily low pressure [96]. Adsorption capacity of composite is 2.05 mmol·g^{-1} at 25 ℃ and 0.39 mbar CO_2 partial pressure. The easily accessed amine mmen-2 leads to faster adsorption kinetics and enhanced adsorption rates. A new diamine-functionalized MOFs was obtained when using 1-en amine (en = ethylenediamine) [97]. CO_2 capacity of en-Mg_2(dobpdc) at 0.39 mbar is 2.83 mmol·g^{-1}, which is larger than that of mmen-Mg_2(dobpdc) by a factor of 1.4 [96]. For TSA cycle, saturation amount of en-Mg_2(dobpdc) is increased by 1.5 times relative to capacity of mmen-Mg_2(dobpdc). Tris (2-amino ethyl) (TREN) is used as amine component on MIL-101(Cr), and CO_2 uptake of 2.8 mmol·g^{-1} at 0.4 mbar partial pressure could be achieved [94]. However, sorption capacity is significantly decreased in stable cyclic CO_2 adsorption test, which can be attributed to high volatility of TREN. Recently, Guo et al. [98] reported a highly efficient and stable composite of polyacrylate (PA) and NbOFFIVE-1-Ni. CO_2 adsorption capacity of PA/NbOFFIVE-1-Ni is 1.44 mmol·g^{-1} under the condition of 400 ppm of CO_2/N_2 and 298 K, which exceeds the capacity of 1.3 mmol·g^{-1} obtained by NbOFFIVE-1-Ni.

Table 2 summarizes various amine-modified adsorbents based on different matrices. It is demonstrated that PEI is the most common amine used in amine-modified adsorbents for DAC. When compared to physical adsorbents, amine modified materials exhibit excellent performance

Table 2
CO_2 adsorption capacity of amine-modified solid sorbents for DAC based on different matrices.

Amine	Loading*	Matrix	Adsorption conditions	Capacity (mmol·g^{-1})	Ref.
PEI	29.8/37.2/48.1 wt.%	Mesoporous γ-Alumina	400 ppm CO_2/Ar at 25 ℃	1.03/1.33/1.74	[89]
PEI	24.8/39.9 wt.%	SBA-15	400 ppm CO_2/Ar at 25 ℃	0.32/1.05	[89]
PEI	45.1 wt.%	Silica	400 ppm CO_2/Ar at 25 ℃	2.36	[81]
A-PEI	46.0 wt.%	Silica	400 ppm CO_2/Ar at 25 ℃	2.26	[81]
T-PEI	45.0 wt.%	Silica	400 ppm CO_2/Ar at 25 ℃	2.19	[81]
PEI	5/10/30 wt.%	Monolithic alumina	400 ppm CO_2/He at 30 ℃	0.29/0.63/0.75	[91]
PEI	5/10/30 wt.%	Powder alumina	400 ppm CO_2/He at 30 ℃	0.34/0.57/0.71	[91]
PEI	30/40/50 wt.%	SBA-15	400 ppm CO_2/He at 25 ℃	0.65/1.23/0.57	[100]
PEI	27/40/47 wt.%	Pore-expanded MCM-41	400 ppm CO_2/N_2 at 25 ℃	1.63/2.17/2.01	[87]
PEI	35/43 wt.%	Calcined pore-expanded MCM-41	400 ppm CO_2/N_2 at 25 ℃	0.49/0.66	[87]
PEI	55 wt.%	CA-SiO_2 fiber	395 ppm CO_2/He at 35/45/55 ℃	0.62/0.55/0.32[a]	[88]
PEI	55 wt.%	CA-SiO_2 fiber	395 ppm CO_2/He at 35 ℃/ 2–3 mol% H_2O	1.71	[88]
PEI	0.51 g·g^{-1} silica	ePTFE/silica	400 ppm CO_2/He at 35 ℃, 50%RH	1.5	[101]
PEI	50 wt.%	Mg/Al mixed metal oxides	400 ppm CO_2/N_2 at 25 ℃	1.66	[92]
TEPA	67 wt.%	Mg/Al mixed metal oxides	400 ppm CO_2/N_2 at 25 ℃	3.0	[93]
APS	0.69/1.52/2.91/4.13 mmol·g^{-1}	Disordered alumina	400 ppm CO_2/N_2 at 30 ℃	0.18/0.18/0.32/0.61	[90]
APS	0.87/2.01/3.22/5.43 mmol·g^{-1}	Ordered alumina	400 ppm CO_2/N_2 at 30 ℃	0.15/0.29/0.51/0.76	[90]
APS	3.75 mmol N·g^{-1}	Mesoporous silica foam	500 ppm CO_2/He at 25/45/65 ℃	1.38/1.21/0.94	[78]
MAPS	2.41 mmol N·g^{-1}	Mesoporous silica foam	500 ppm CO_2/He at 25/45/65 ℃	0.4/0.2/0.09	[78]
PAA	30/50/70 wt.%	Silica	450–470 ppm CO_2/N_2 at 21 ℃, 60–70% RH	0.287/0.716/4.27[b]	[86]
EDA	Not reported	Porous polymer network	400 ppm CO_2/78.96% N_2/21% O_2 at 21.85 ℃	0.15	[102]
DETA	Not reported	Porous polymer network	400 ppm CO_2/78.96% N_2/21% O_2 at 21.85 ℃	1.04	[102]
DT	6/10/15[c]	SBA-15	400 ppm CO_2/N_2 at 45 ℃	1.86/2.00/1.18	[82]
pH-3-EDA	27/37/43/51 wt.%	SBA-15	400 ppm CO_2/He at 35 ℃	0.42/0.96/1.43/0.9	[83]
pH-3-PD	34/43/53 wt.%	SBA-15	400 ppm CO_2/He at 35 ℃	0.25/0.72/1.23	[83]
pH-6-EDA	32/40/49 wt.%	SBA-15	400 ppm CO_2/He at 35 ℃	0.55/0.87/0.8	[83]
pH-6-PD	30/40/49 wt.%	SBA-15	400 ppm CO_2/He at 35 ℃	0.28/0.46/0.59	[83]
PL	2.76/4.84/5.18 mmol N·g^{-1}	Brush–mesoporous silica	400 ppm CO_2/Ar at 25 ℃	0.19/0.56/0.60	[80]
Aziridine	9.9/42.5 wt.%	SBA-15	400 ppm CO_2/Ar at 25 ℃, humid conditions	0.16/1.72	[79]
ED	5.5 wt.%	Mg/DOBDC	400 ppm CO_2/Ar at 25 ℃	1.55	[95]
mmen	Not reported	Mg_2(dobpdc)	390 ppm CO_2/air at 25 ℃	2.0	[96]
ED	N/Mg = 1.7	Mg_2(dobpdc)	0.39 mbar CO_2/air at 25 ℃	2.83	[97]
TREN	5.67 mmol·g^{-1} MOF	MIL-101(Cr)	400 ppm CO_2/He at 24.85 ℃	2.8	[94]
PEI	0.97/1.32/1.76 mmol·g^{-1} MOF	MIL-101(Cr)	400 ppm CO_2/He at 24.85 ℃	1.15/1.2/1.35[a]	[94]
PA	45.8 wt.%	NbOFFIVE-1-Ni	400 ppm CO_2/N_2 at 24.85 ℃	1.44	[98]

Abbr. : PEI = poly(ethyleneimine); ePTFE = expanded poly(tetrafluoroethylene); TEPA = Tetraethylenepentamine; A-PEI = PEI with (3-aminopropyl) triethoxysilane additive, T-PEI = PEI with tetrapropyl orthotitanate additive; APS = 3-aminopropyl-triethoxysilane, PAA = poly(allylamine), MAPS = (N-methylaminopropyl)-trimethoxysilane; DMAPS = (N,N-dimethylaminopropyl)-trimethoxysilane; EDA = ethylenediamine; DETA = diethylenetriamine; DT = diethylenetriamine alkoxysilane; PL = poly(L-lysine); PD = propylenediamine; ED = ethylene diamine; mmen = N,Nn dimethylethylenediamine; PA = polyacrylates.

[*] Amine loading is mainly represented by mass fraction of amine (wt.%), and tested loading takes precedence over calculated loading. Content of N element (mmol N·g^{-1}) and amine (mmol·g^{-1}) are used when mass fraction of amine is not clear in these references.

[a] : Pseudo-equilibrium capacity;.

[b] : Inlet pressure of 123 kPa at 70 wt.% PAA;.

[c] : Silanol concentration used to calculate the amount of DT loaded, SiOH nm^{-2}.

under DAC conditions. Amines loaded on supports are an effective method to avoid high energy demand of aqueous amine solution. Besides, amines and supports can adsorb CO_2 at the same time, which is subject to adsorption sites on supports. When using physical sorbents like zeolites as support materials, moisture in the air significantly influences the performance of composite sorbents. However, effects of water on CO_2 adsorption using amines still need to be further investigated. The detailed mechanisms are more complex than those of physical sorbents [99]. There are three governing mechanisms: amine efficiency increases from 0.5 to 1 in the presence of water; water influences adsorption heat of amine modified sorbents; adsorbed water molecules block amine sites and hinders CO_2 adsorption. Besides, co-adsorption mechanism of CO_2 on amines and support materials is still not clear.

Liquid chemical absorbent: Amine scrubbing technology is the most mature technology to separate CO_2 from natural gas and flue gas [103]. It is acknowledged that aqueous amines including monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA) are the most widely used amines for CO_2 absorption [104]. Amine solutions have the advantages of high reaction rate, reasonable CO_2 absorption capacity and low cost. Nonetheless, the main disadvantages for amine solutions are its high regeneration heat and oxidative degradation [105]. High regeneration energy consumption mainly comes from sensible heat loss of water. Thus water-lean or water-free chemical absorbent have drawn lots of attentions [106–108]. Potential amine degradation leads to solvent loss, equipment corrosion and generation of volatile degradation compounds, which may be harmful to human health and the environment [10]. To efficiently absorb CO_2 from ultra-dilute ambient air stream, appropriate materials are required to be stable enough and less energy intensive [109]. Aqueous unhindered primary amines were reported as the most suitable sorbents for DAC processes and as efficient as aqueous alkali hydroxides [110]. They are potential energy savings with relatively high efficiency due to lower temperatures for sorbent regeneration. Amine blends have the particularity to combine each advantage and may have better performance under DAC conditions [104]. In addition, ionic liquids [111,112] and phase changing absorbents [113,114] have also been investigated for DAC.

Alkali solutions as solvents are very attractive since the solutions are less expensive and more stable [115]. Moreover, compared to amine solutions, they have relatively low reaction heat, which lead to low regeneration energy cost [116]. Advantages of aqueous hydroxide solutions employed in CCUS include [117]: (1) hydroxides can be easily obtained via electrolysis of aqueous salts; (2) higher efficiency for carbon capture from ambient air; (3) hard to volatilize; (4) low toxicity; (5) easy to regenerate. Similar with CaO-based sorbents, using $Ca(OH)_2$ solution to remove CO_2 from ambient air starts with carbonation, followed by calcination of $CaCO_3$ and regeneration of $Ca(OH)_2$ solution, which can be described as Eqs. (9)-11, respectively [31]:

$$Ca(OH)_2 + CO_2 \rightleftharpoons CaCO_3 + H_2O \tag{9}$$

$$CaCO_3 \rightleftharpoons CaO + CO_2 \tag{10}$$

$$CaO + H_2O \rightleftharpoons Ca(OH)_2 \tag{11}$$

However, low solubility of $Ca(OH)_2$ in water limits hydroxide concentration which is the main factor to bind CO_2. Aqueous solutions using other alkali metals, e.g., potassium hydroxide (KOH) or sodium hydroxide (NaOH) have also been proposed in DAC processes. Their regeneration loops are always accompanied with $Ca(OH)_2$, which are very similar to Kraft caustic recovery cycle that is commonly used in paper mill/pulp industry as shown in Fig. 7 [118]. Four steps of Kraft cycle for DAC are shown as follows:

Step 1: CO_2 sorption via an acid-based reaction to form carbonates (Eq. (12)),

Step 2: $CaCO_3$ precipitation and the regeneration of NaOH (Eq. (13)),

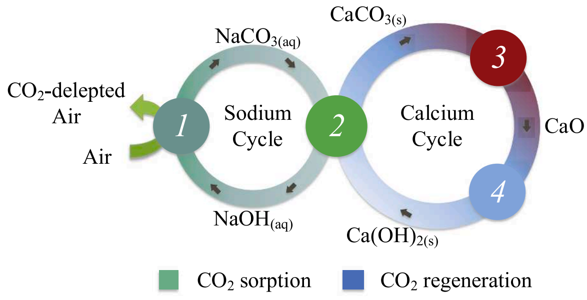


Fig. 7. Schematic diagram of Kraft process for DAC (adapted from [118]).

Step 3: The release of CO_2 from $CaCO_3$ through calcination (600–900 ℃) (Eq. (9)),

Step 4: The regeneration of $Ca(OH)_2$ (Eq. (14)).

$$2NaOH + CO_2 \rightleftharpoons Na_2CO_3 + H_2O \tag{12}$$

$$Na_2CO_3 + Ca(OH)_2 \rightleftharpoons CaCO_3 + 2NaOH \tag{13}$$

$$CaO + H_2O \rightleftharpoons Ca(OH)_2 \tag{14}$$

Enthalpy differences of the four steps are shown in Fig. 8. It is indicated that $CaCO_3$ calcination requires a large amount of energy to break strong calcium carbonate bonds. Energy consumption can be provided by natural gas burnt either in air or gas [119]. High temperature of calcination process would increase temperature gap between burning kiln and the environment, which leads to a large amount of heat loss.

Unlike amines, metal carbonate/bicarbonate can be easily regenerated and release captured CO_2 by an electrolysis process. Therefore, electrochemical regeneration of alkali sorbents has been investigated due to excellent efficiency of electrochemical reaction and environmental-benign characteristic [120]. An electrochemical system was proposed for selective recovery of LiOH from the used CO_2 adsorbents as shown in Fig. 9 [121]. The system is a two-electrode cell separated by a cation exchange membrane (CEM). As the current is applied to the cell, water decomposition reaction takes place and CO_2 is released by the combination of protons with carbonate or bicarbonate. Results indicate that current density and cationic load ratio have an influence on the performance of electrical systems. An equilibrium model also demonstrates the existence of simultaneous solvent regeneration and CO_2 desorption at an identical steady state [122]. Regeneration heat of the system could be achieved as low as 164 $kJ \cdot mol^{-1}$. CEM is not the only option for the electrochemical regeneration of solvents. Bipolar membrane electrodialysis (BPMED) combined with wet scrubbing was applied in a DAC process [123,124]. Energy consumption for K_2CO_3 calculated from BPMED model presents a minimum value when the efficiency and voltage drop achieve a trade-off. Such low energy consumption is in line with other regeneration strategies proposed for DAC, it shows that electrochemical processes could be a competitive alternative amongst all DAC technologies.

Except the above absorption process for DAC, moisture swing was proposed as a new approach to regenerate CO_2 sorbents [125]. It trades heat input in thermal swing, or mechanical energy in a pressure-based swing against water consumption, whose evaporation provides the potential to drive the cycle, while energy consumption by evaporation comes from the low-moisture atmosphere. Later, their team developed an amine-based anion exchange resin in a flat sheet of polypropylene [126]. Quaternary ammonium cations are attached to the polymer structure. Original exchangeable anions on resin are chloride ions, which could be replaced by hydroxide or carbonate ions to absorb CO_2. The resin can absorb CO_2 under dry conditions and release it under wet conditions, which offers an opportunity for regeneration via moisture swing process. Schematic diagram of reaction pathway is shown in

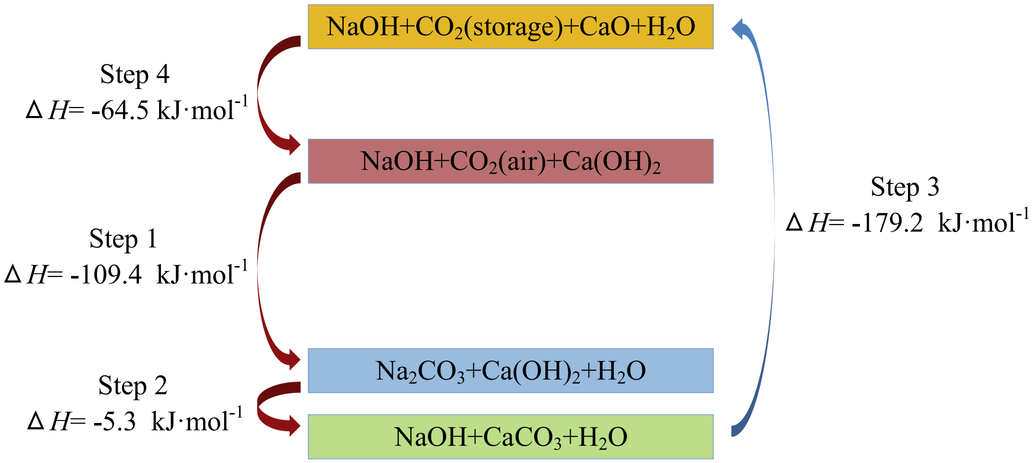


Fig. 8. Enthalpy level diagram for CO_2 sorption and regeneration by NaOH (adapted from [119]).

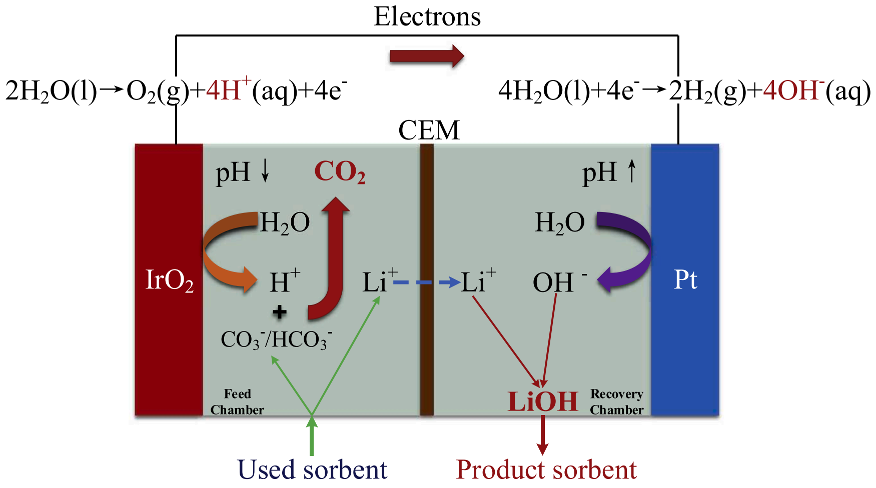


Fig. 9. Schematic diagram of electrochemical system for LiOH recovery from the used CO_2 adsorbents (adapted from [121]).

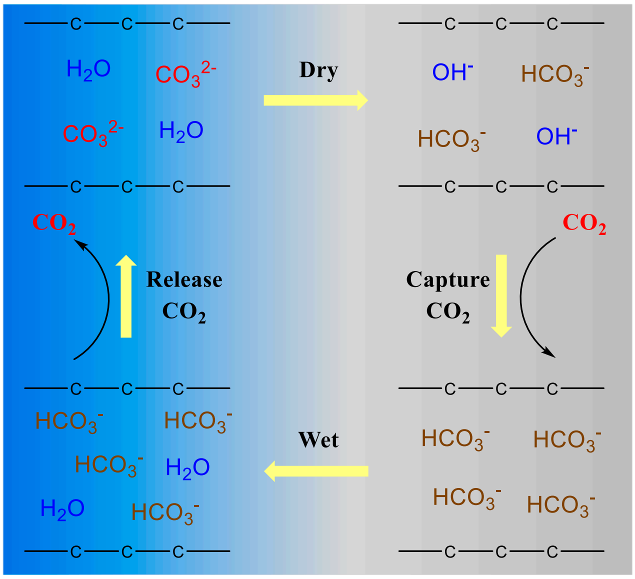


Fig. 10. Schematic diagram of moisture-swing sorbent for CO_2 capture (adapted from [127]).

Fig. 10. Based on quantum mechanics simulation, capture systems energetically prefer bicarbonate and hydroxide ions to carbonate ions when exposed to dry air. Thus, high content of hydroxide ions is more conductive for CO_2 absorption [127]. The resin absorbs CO_2 until all hydroxide is consumed, reaching bicarbonate state [126]. The resin shows a very high saturation rate over 99% for hydroxide and carbonate at 400 ppm CO_2 level and 0.5% water vapour concentration [128]. Wang et al. [129] further developed a modified shrinking core model to evaluate the effects of ambient conditions and sorbents structure on absorption kinetics. Diffusion coefficient and chemical reaction rate reveal significant drop with decreased temperature or increased relative humidity. It is indicated that poor performance of the sorbent in cold and humid weather. To overcome weak tolerance of quaternary ammonium-based sorbents, bamboo fibre was quaternized and compared to the reported moisture-swing absorbents [130]. CO_2 capacity is negligible under dry conditions and is increased with RH to the maximum value of 0.19 mmol·g^{-1}. Results also demonstrate that an extremely low (< 20%) or high (>90%) RH are not favoured for CO_2 capacity. In contrast, moisture swing driven absorbents require less energy to be regenerated, but with lower sorption capacity.

In summary, not all sorbents are suitable for DAC, and several are still facing great challenges with regard to real applications. For physical adsorbents, zeolites, AC and MOFs have their own advantages and disadvantages for DAC application. Activated carbon has lower CO_2 adsorption capacities when compared with zeolites at lower pressure. Zeolites and AC are easily available and well-developed, but poor sorption capacities and selectivity are their weaknesses. MOFs have high flexibility in shape, pore structure, pore size, and surface properties. However, their preparation and modification are troublesome, instable and expensive which also have the issues of toxic raw materials. Generally, the presence of moisture in the air will significantly decrease the amount of CO_2 uptake of physical sorbents and lead to larger energy input for adsorbents regeneration. For some types of physical adsorbents, working capacity could be improved in the presence of less water while more water inhibits its performance. amongst physical adsorbents, zeolites are proposed to be the most appropriate candidate in the near future. The enhanced mechanism of low Si/Al ratios on high CO_2 adsorption capacities under low pressure conditions have been investigated using simulation methods [131,132]. Thus, how to improve the performance of zeolites under low CO_2 partial pressure and humid conditions is the main barrier that restricts their large-scale application. The key is to understand the influence of water on binary sorption of CO_2 and H_2O [133,134]. Comparably, for solid alkali sorption materials, amine modified adsorbents are regarded to be the most suitable materials for DAC applications due to the high working capacity and low regeneration rate. To take advantage of supported amines, future research may focus on co-adsorption mechanism of materials. Liquid chemical absorbents take advantage of high reaction and low cost due to liquid-gas mass transfer process. The disadvantages of high regeneration cost and oxidative degradation should be overcome if it is aimed for large DAC applications. Some absorbents, e.g., ionic liquids, have an improved working capacity in presence of less water and the performance is hindered with more water. Thus water-lean or water-free absorbents are more desirable in the future. Table 3 conducts a general comparison of different sorbents for DAC.

Table 3
Comparison of different sorbents for DAC.

Specifications	Physical sorbents	Chemical adsorbents	Chemical absorbents
Capacity	• Low capacity for most physical adsorbent • High capacity for certain MOFs	• High capacity	• High capacity
Adsorption kinetics	• Relatively low kinetics • Competitive for some MOFs	• Moderate kinetics	• Fast kinetics
Performance under moisture conditions	• Reduced capacity for most physical adsorbents • Improved capacity in presence of less water for several MOFs • Unstable for MOFs	• Improved capacity in presence of less water	• Improved capacity in presence of less water for water-lean or water-free absorbent, e.g., ionic liquid.
Energy for regeneration	• Relatively low	• Moderate	• Significant
Advantages	• Mature, cheap, stable and easily-available for zeolite and AC • High modification flexibility for MOFs	• Great potential to be modified • Lower energy consumption than aqueous solution	• High reaction rate • Reasonable CO_2 capacity • Low cost
Disadvantages	• Poor capacity and selectivity • High cost, instability and toxic raw materials for MOFs • Poor performance under moisture conditions	• High cost • Unstable after thousands of cycles	• High regeneration cost • Oxidative degradation • Solvent loss • Corrosion

3. Capture process for DAC

Based on previous researches in post-combustion carbon capture [11], capture processes for sorption DAC can be also classified according to adsorption or absorption mechanisms. For adsorption processes, common capture processes include TSA, PSA, vacuum swing adsorption (VSA), electric swing adsorption (ESA) and hybrid processes [135]. For absorption, chemical loop is commonly investigated and mainly focuses on different methods of regeneration step.

3.1. Adsorption/desorption process

Pressure swing adsorption (PSA): PSA processes are mainly applied to remove a strongly adsorbed impurity from a gas mixture. In pre-combustion and post-combustion process, CO_2 is a strongly adsorbed component when compared to other major components, e.g., N_2 [136,137]. It is a reliable method for CO_2 separation from flue gas streams with 5–15 vol.% CO_2 [138]. For PSA, CO_2 is adsorbed at high pressure, and desorbed from adsorbent around atmospheric pressure which mainly includes four steps: pressurization, adsorption, depressurization and purge [137,139]. Schematic diagrams of PSA are shown in Fig. 11. Fig. 11a indicates the above working process. The thermal cycle is described as Fig. 11b, where the adsorption isothermal curve reflects CO_2 partial pressure and adsorption capacity. The detailed thermal cycle is illustrated as follows [140]:

Pressurization (1–2, PRE): CO_2 partial pressure is increased from atmospheric pressure P_{int} to P_{ad} by an air compressor. Then compressed air is aerated in the adsorption reactor to generate a high-pressure adsorption atmosphere. Adsorption (2–3, AD): High pressure air enters the reactor, while CO_2 is selectively adsorbed by adsorbent, leaving N_2-rich air to flow out. CO_2 adsorption process and the venting of N_2-rich waste gas are both assumed to be instantaneously completed. Depressurization (3–4–5, DP): The vent valve opens and allows high-pressure air expanding to atmospheric pressure. Desorbed CO_2 and unabsorbed gas in the reactor leave adsorption reactor. Since CO_2 desorption is not completed, a further purge step is needed to obtain additional CO_2 product. Purge (5–1, PUR): CO_2 is desorbed and discharged from the reactor with carrier purge gas at atmospheric pressure. A next adsorption thermal cycle starts until reaching the initial state, i.e., point 1.

Performance of CO_2 separation is typically evaluated by CO_2 purity and recovery, which depends on the amount of desorbed CO_2 and feed CO_2. Due to the limit of external conditions, e.g., structure of adsorption reactor, mass transfer resistance during adsorption and dead volume in the system, efficiency of adsorption reactor (φ_{un}) could be estimated by unused percentage of the reactor [141]. Energy required for a real DAC process should be compared with theoretical minimum separation work ($W_{\min}$) by a completely reversible process under the same working condition. Assuming air as an ideal gas mixture, theoretical minimum work required for capturing per mole of CO_2 could be defined as Eq. (15).

$$W_{\min} = RT\left[\frac{n_2}{n_3}\left(y_{2,CO_2}\ln y_{2,CO_2} + y_{2,N_2}\ln y_{2,N_2} + (y_{3,CO_2}\ln y_{3,CO_2} + y_{3,N_2}\ln y_{3,N_2}\right) - \frac{n_1}{n_3}\left(y_{1,CO_2}\ln y_{1,CO_2} + y_{1,N_2}\ln y_{1,N_2}\right)\right] \tag{15}$$

where n_1, n_2 and n_3 are total number of moles for the supplied ambient air, processed air and product, y_1, y_2 and y_3 are compositions of various streams respectively, R is universal gas constant, and T is temperature.

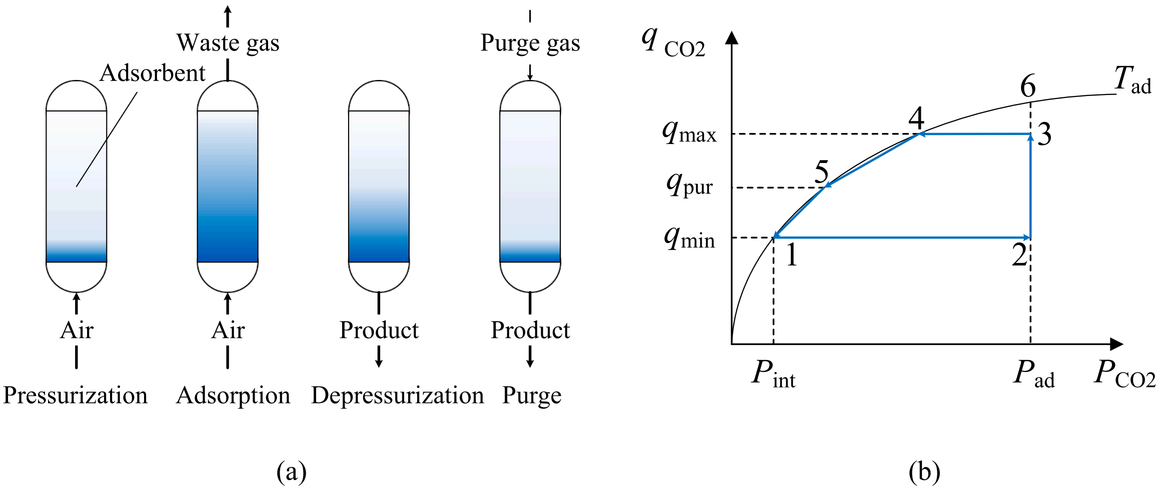


Fig. 11. Schematic diagram of 4-step PSA (a) working process (b) thermal cycle.

According to carbon pump concept [142], the minimum separation work is only related to initial and final state of separation process, which depends on feed gas temperature, CO_2 fraction and recovery rate.

Vacuum swing adsorption (VSA): VSA is a particular case of PSA, of which adsorption takes place at atmospheric pressure, while desorption/regeneration process occurs under vacuum. VSA applications avoid the use of several traditional modules in PSA, e.g., air compressor, process valves, associated dryers and feed air filtering systems. The lower operating pressure reduces water condensation, which allows operation in humid air and provides a superior regeneration of sorbents. Energy consumption for VSA are around 50% of PSA due to the fact that air compressor is not used [11]. At the relatively low gas pressure, VSA is the most economical adsorption technique to handle flue gas with CO_2 concentration from 15% to 55% [143].

Pressure-vacuum swing adsorption (PVSA): PVSA is a combination of PSA and VSA, i.e., its adsorption step occurs at pressures above atmospheric pressure while the desorption process is conducted under vacuum condition [144]. Fig. 12 indicates schematic diagram of PVSA for DAC. As shown in Fig. 12a, the working process consists of pressurization, adsorption, depressurization, evacuation and purge steps [145]. For thermal cycle in Fig. 12b, pressurization (1–2), adsorption (2–3) and depressurization (3–4–5) steps in PVSA are similar to those of PSA. Details of other two steps are illustrated: Evacuation (5–6, EVA): Pressure in reactor is decreased by a vacuum pump and CO_2 is constantly desorbed owing to the reduced partial pressure. Purge step (6–1): This step is conducive to obtain additional CO_2 removal from adsorption reactor by feed gas, in which CO_2 adsorption is assumed not to happen. The next adsorption thermal cycle will start when initial state is reached again.

PSA and VSA experiments have not been widely studied under laboratory DAC conditions. Performance of PSA in DAC conditions has been investigated by temperature-dependant modelling [146]. Equilibrium working capacity (EWC) of polymeric adsorbents was studied under dilute air condition (CO_2 partial pressure up to 5 mbar). Results show that regeneration pressure of 10^{-6} bar is required when producing EWC of 0.49 mmol·g^{-1}. If 1 mbar vacuum is applied and feed gas is pressurized to 12.5 bar (5 mbar CO_2 partial pressure), only 0.23 mmol·g^{-1} EWC is obtained. It is found that PSA may not be viable in DAC, which need further investigation.

Temperature swing adsorption (TSA): CO_2 adsorption and desorption for TSA cyclically take place by controlling operating temperature. Adsorption in DAC process occurs at ambient temperature, while desorption requires a higher temperature which is related to the properties of adsorbents. Schematic diagram of a 4-step TSA in terms of working process and thermal cycle are shown in Fig. 13 [147]. Details of each step are described as follows. Adsorption (1–2): Ambient air flows into adsorption reactor and CO_2 is absorbed. Simultaneously, heat exchange jacket is continuously circulated with cool medium to take away adsorption heat. Preheating (2–3): Adsorption reactor begins to be preheated to a medium temperature. Desorption (3–4): Adsorption reactor continues to be heated to a higher temperature level for desorption process. Desorption occurs when CO_2 adsorption capacity is

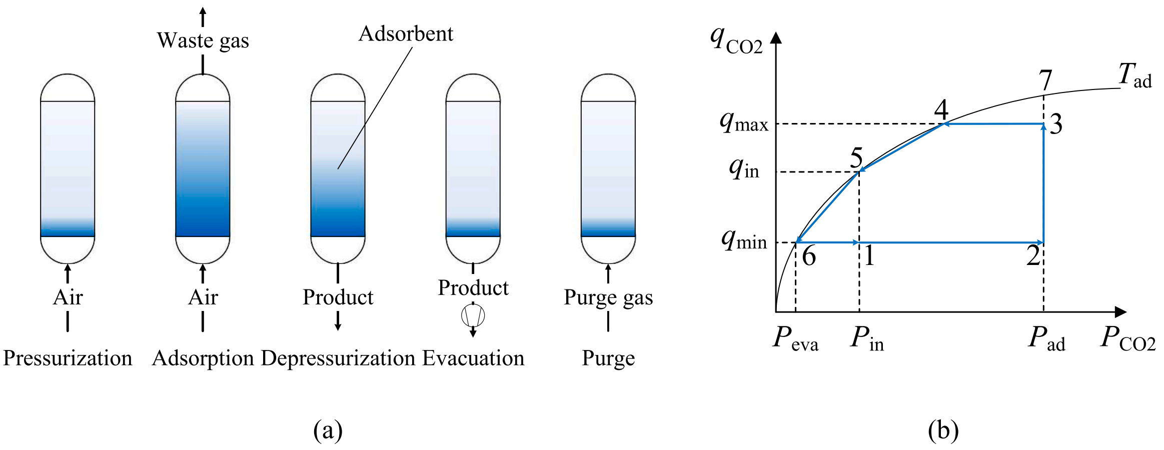
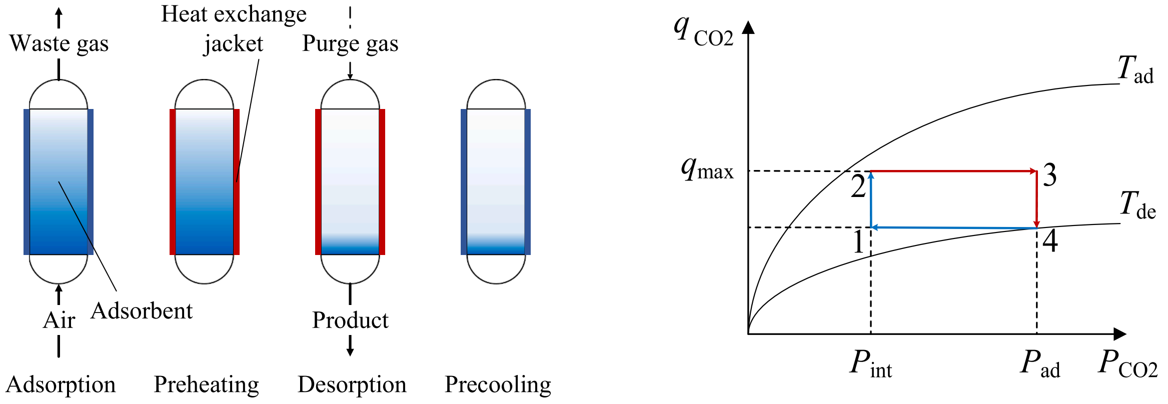


Fig. 12. Schematic diagram of PVSA (a) working process (b) thermal cycle.



(a) (b)

Fig. 13. Schematic diagram for 4-step TSA cycle (a) working process (b) thermal cycle.

higher than the maximum value at a constant pressure when temperature keep increasing [147]. The desorbed CO_2 is concentrated by purge gas and leaves the reactor. Precooling (4–1): When adsorbent is completely regenerated, the heat in adsorption reactor is removed by circulating cooling medium. Both temperature and pressure of the reactor decease to initial state. Then the reactor is ready for next TSA cycle.

A number of DAC studies by using TSA have been investigated based on different adsorbents [74,83,88,94,148,149]. To reduce external energy required for DAC, temperature driving forces sourced from diurnal heating and cooling were introduced to TSA [148]. Compared to pure diurnal temperature swing, low pressure steam could improve TSA performance especially in the location with the lowest average daily temperature. The overall second law efficiency of this process is 7.4%, which is improved by 11% by using a better contactor configuration. Effects of three typical inlet CO_2 concentrations, i.e., atmosphere (400 ppm CO_2), gas turbine exhaust gas (4 vol% CO_2), and solid fuel combustion gas (10 vol% CO_2) were investigated and compared in terms of total energy demand of TSA [149]. Overall energy demand of TSA used for DAC is 10 times higher than that for power station exhaust gases. The relatively low exergy efficiency of a four-step TSA cycle for DAC may be improved by using internal heat recovery and mass recovery [147,150]. TSA is the mainstream working method of adsorption process for DAC.

Electric swing adsorption (ESA): ESA is an extension of TSA and adsorbents are directly heated by electric current [151,152]. To accelerate TSA process, regeneration heat of ESA is electrically produced by an electric current passing through a conductor that can be adsorbents or other ancillary conductors in which Joule effect is adopted. ESA offers some unique advantages including high heating efficiency, fast heat rates, and high system compactness [153]. Its drawback lies in low thermal efficiency which is around 20–25% of TSA and PSA [154]. Only a few ESA researches for carbon capture are found in terms of adsorbents and thermal performance. AC fibre materials were utilized as adsorbents for ESA cycle [155]. This reveals that more attention should be paid to identify the optimal fabrication condition for CO_2 adsorption. A novel composite adsorbent combining AC and zeolite NaUSY was synthesized for ESA application. The optimal ratio of two components was determined as 7:3 [156]. Gas separation process is usually inhibited by the induced adsorptive thermal effects, thus high thermal conductive adsorbents need to be developed [157]. The highest thermal conductivity of a monolithic composite of AC and expanded graphite could reach 30 $W{\cdot}m^{-1}{\cdot}K^{-1}$. Adsorbent has an decisive impact on ESA, mostly related to electrical properties of the material [153]. An et al. [155] and Ribeiro et al. [153] reviewed existent literature of ESA cycle. They pointed that evaluation of energy efficiency for ESA cycle is one of key future research direction.

Hybrid processes: System performance of carbon capture from flue gas can be enhanced by combining various adsorption processes [158]. Analogically, hybrid processes can also improve DAC performance. Hybrid processes aim to simultaneously change temperature and pressure of capture cycle, which are usually described as pressure-temperature swing adsorption (PTSA) and vacuum-temperature swing adsorption (VTSA) [159,160].

Fig. 14 shows a schematic diagram of PTSA and VTSA process for CO_2 capture. For PTSA, the first three steps are the same as those of PSA, which indicates similar adsorption capacities [140]. The rest two stages are replaced by heating and cooling steps from TSA cycle and described as follows. Heating (5–6): CO_2 is desorbed and removed by heating until temperature achieves desorption temperature T_{de}. The amount of desorbed CO_2 can be evaluated as $q_{in} - q_{min}$ according to the increasing temperature. Purge gas could be applied to carry out desorbed CO_2 out of the reactor. Cooling (6–1): The reactor is cooled to ambient temperature by an infinite cold source whose temperature equals to ambient temperature. Because there is no CO_2 flow into the reactor, capture capacity remains as a constant. Thus, point 6 is simplified to point 1 on the isotherm.

It is essential to select an appropriate process that fulfils the excellent performance needed for DAC application [161]. Table 4 compares different adsorption processes and their suitable applications. Hypothetical separation systems using a feed stream with variable concentrations of adsorbate under ambient condition (298 K and 1 bar) were investigated for TSA and PSA [162]. Results indicate that PSA separation efficiency is almost linear with the studied feed concentration and is more efficient for bulk gas separations with 10–20 vol.% CO_2 concentration. TSA system is proposed to be applied in DAC due to the relatively high thermodynamically efficiency under dilute CO_2 concentration. PSA or VSA is beneficial for large-scale flue gas capture which has shorter cycle times than TSA because TSA needs longer heating and cooling times [163]. Compared with TSA, VTSA is more suitable in the applications that require almost pure CO_2, e.g., synthesis processes where raw gas has high purity [146,159,164]. Besides, combination of TSA and VSA reduces regeneration temperature and vacuum pressure. Relatively low regeneration temperature could prevent degradation, reduce energy demand and increase energy efficiency. Standard industrial liquid ring vacuum pump could be used for VSA with moderate vacuum pressure [165].

3.2. Absorption/desorption process

Different from active-surface driven adsorption processes, the absorption capture process removes CO_2 from a gas stream into liquid solvents based on principles of physical dissolution or chemical reaction

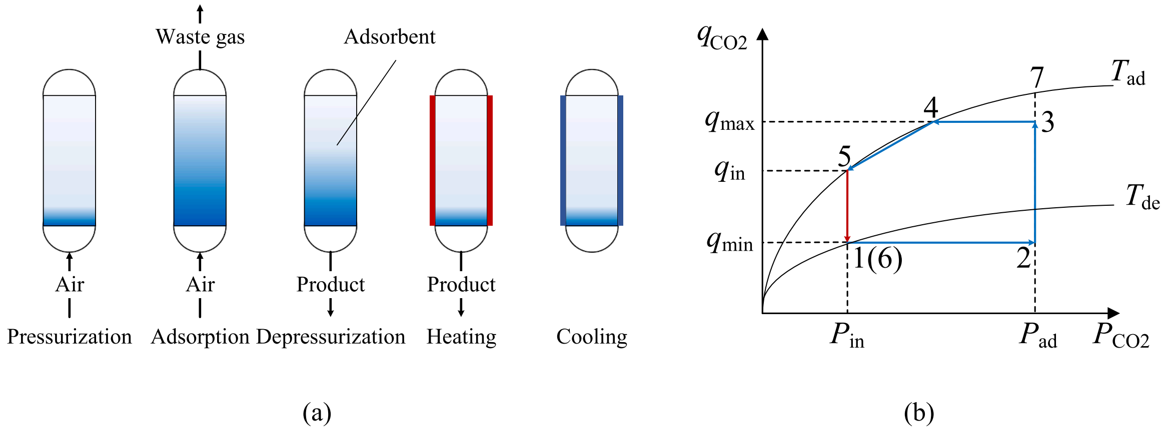


Fig. 14. Schematic diagram for PTSA cycle (a) working process (b) thermal cycle.

Table 4
Comparisons of different adsorption processes for DAC.

Cycles	Advantages	Disadvantages	Recommendation
PSA	• Can be applied at ambient temperature • More efficient with hot feed gas • Short cycle times	• Large energy consumption • Lower efficiency in DAC • Require air compressor • Low product purity	• Pre-combustion • Post-combustion
VSA	• Can be applied at ambient temperature • Simple operation modules • Avoid water condensation • Short cycle times	• Large energy consumption • Require vacuum pump	• Pre-combustion • Post-combustion
TSA	• Low cost • Require low pressure • Multiple temperature driving forces • High product purity • Higher efficiency	• Repeated heating and cooling • High energy consumption • Require adsorbents with high thermal stability	• Pre-combustion • Post-combustion • DAC
ESA	• High heating efficiency • Fast heating rates • High system compactness • Independent control of gas and heat flow rates	• Low thermal efficiency • Need more development	• DAC
TVSA	• Advantages of TSA and VSA • Low regeneration temperature and vacuum pressure • Low energy consumption • High CO_2 purity	• Same as TSA and VSA	• Scenarios with high raw gas purity • DAC
PTSA	• Advantages of PSA and TSA • Higher capacity	• Same as PSA and TSA	Pre-combustion Post-combustion
PVSA	• Advantages of PSA and VSA	• Same as PSA and VSA	Pre-combustion Post-combustion

[11]. But it is not commonly used in DAC since volatility and toxicity of some chemical sorbents are incompatible with large-scale application in open spaces [166,167]. Continuous operation and strong CO_2 binding are two main advantages that promote researches of absorption capture for DAC. Air contactor for chemical absorption loops, can continuously operate and can be built by using a cheap cooling tower, which is unlike DAC adsorption process that needs intervals to switch different steps [168]. In the process of CO_2 captured from air by using sodium hydroxide solutions, CO_2-rich solvent is subsequently regenerated through calcium-based thermochemical cycle [125]. CO_2 absorption by aqueous solvents is a mature technique, resulting in lots of commercially available technologies. Carbon Engineering demonstration pilot plant has been developing an aqueous absorption DAC system since 2009 [169], and their processes comprise two chemical loops like Kraft cycle as shown in Fig. 8. In the first K^+ chemical loop, CO_2 is captured from the atmosphere by using an aqueous solution with a ratio of $OH^-/CO_3^{2-}/K^+$ as 2:1:4. In the second Ca^{2+} loop, $CaCO_3$ precipitates through a combination of CO_3^{2-} and Ca^{2+} and is calcined subsequently to release CO_2 and CaO which is then hydrated to produce $Ca(OH)_2$. They also provide the designs of an air-liquid high surface area contactor as shown in Fig. 15 [170] and outdoor prototype [171] for large-scale DAC. Aqueous systems suffer from complexity of regeneration system and water loss in dry working environments. A thermodynamic loss analysis was presented based on the liquid-sorbent DAC plant, and the results showed that 252 MW are irreversibly lost, which correspond to a second-law efficiency of 7.8% [172].

Several methods are developed for CO_2 regeneration from rich solutions in chemical absorption processes, including conventional heating process, acid addition, addition of stripping carrier and newly membrane technology [173]. BPMED shows great potential due to the utilization of renewable energy [123]. Comparison between Carbon Engineering process and BPMED process are described in Table 5. It is demonstrated that BPMED process can be carried out in a liquid phase, then liquid and solid phases in calcium-based thermochemical cycle will not be separated. Schematic diagram of the wet scrubbing-BPMED process is shown in Fig. 16. An anion exchange membrane (AEM) divides BPMED cell into an acid and a basic compartment. CO_2 is separated from air through wet scrubbing with an aqueous solution of KOH in a cross-flow absorption unit. Rich solution is fed to BPMED which would split water in H^+ and OH^- when an electric current is passed through them. Carbonate ions diffuse through AEM to acid compartment where they combine with H^+ to release CO_2, and KOH is regenerated in the basic compartment.

4. Utilization of CO_2 from DAC

Carbon utilization to create valuable products could result in potential economic benefits to reduce net costs of removing CO_2 from the atmosphere [174]. Conventional industrial pathways for CO_2 utilization mainly include enhanced oil recovery (EOR), CO_2 conversion to fuels, chemicals and food, biological utilization, and mineral carbonation [175–177]. Most of these methods do not distinguish CO_2 sources, e.g., from industries or from air. Also worth noting that the utilization of CO_2

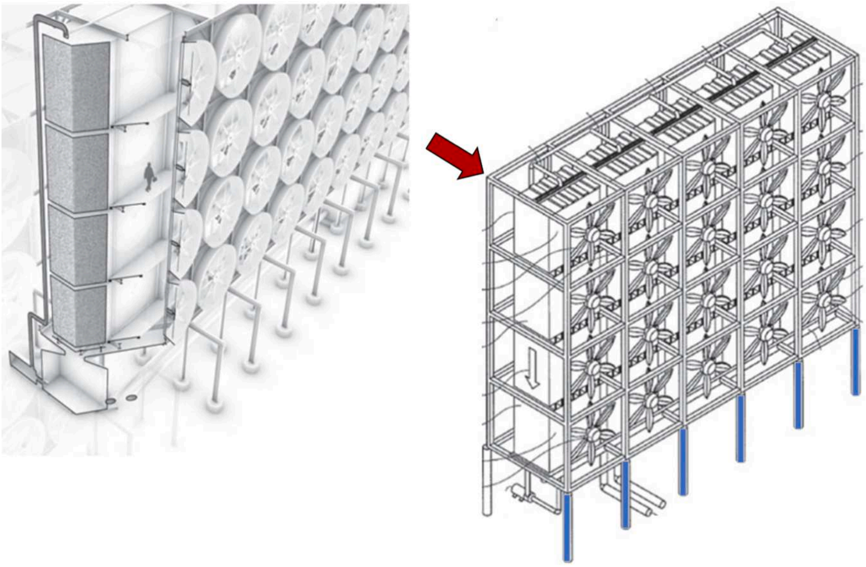


Fig. 15. Carbon Engineering slab air-contactor design [170].

Table 5
Methods of CO_2 regeneration in chemical absorption processes.

Process	Advantages	Disadvantages
Carbon Engineering process	• Continuously operation • Low cost	• Energy-intensive and complex regeneration system • Water loss
BPMED regeneration process	• High energy efficiencies • Good operational flexibility • Simple operation and maintenance	• Capture cost around 3 times higher than that estimated by Carbon Engineering • Laboratory scale

captured from distributed sources is more challenging than that from centralized source like industries. Transportation of CO_2 captured from discrete sources are costly and time-consuming, so it is better to promote *in situ* CO_2 utilization. Therefore, carbon conversion technologies which require feedstocks with relatively low CO_2 concentration are desirable for utilization of CO_2 from DAC. This section mainly focuses on in-situ CO_2 conversion into fuels and chemicals, briefly reviews EOR covered more deeply elsewhere [178–180], as well as biological utilization technologies. The reviewed CO_2 utilization pathways represent the most beneficial near-term applications for the utilization of CO_2 from DAC.

4.1. In-situ CO_2 utilization

4.1.1. Fuels

CO_2 conversion to fuels has been widely investigated in the past decades, in which a liquid can be regarded as more efficient or preferable than a gaseous one in most applications. This option would avoid the transportation of CO_2 and could offer a transition from liquid fossil fuels (gasoline, kerosene, etc.) to a highly desirable energy storage method [181–183]. Energy required for fuel synthesis could come from renewables, meanwhile H_2 can be easily produced through electrolysis of water. Storing renewable energy and H_2 in the form of chemical fuels

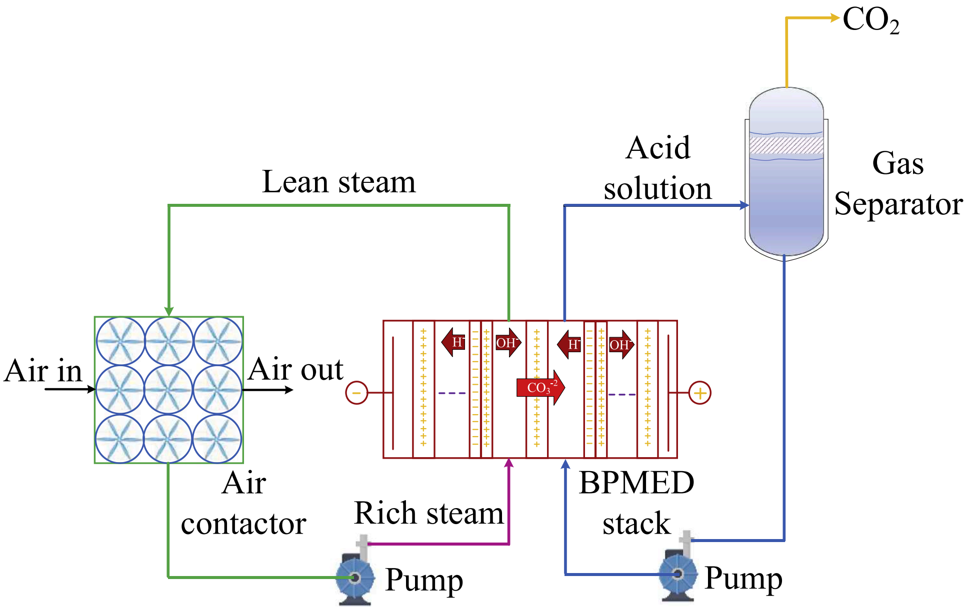


Fig. 16. Schematic representation of the proposed wet scrubbing-BPMED process (adapted from [123]).

by using CO_2 captured from the ambient air is a promising opportunity to mitigate carbon emissions and solve long-term energy storage problems [184]. Recent developments on converting CO_2 into methanol and methane are presented as follows.

Methanol: As a basic chemical product, methanol synthesized from captured CO_2 can substitute conventional fossil fuels in various ways. Methanol can be directly applied as a liquid fuel for internal combustion engines and direct methanol fuel cells (DMFC). Also it can be a hydrogen storage medium and a convenient raw material for various chemicals and products, such as ethylene and propylene [185].

Methanol synthesis can be proceeded via CO_2 hydrogenation in the absence of CO as in Eq. (16) [186]. The main process comprises the formation of CO and water as in Eq. (17) and hydrogenation of CO via reverse water gas shift reaction (RWGS) as in Eq. (18).

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \ \Delta H = -49.4 \text{ kJ·mol}^{-1} \tag{16}$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \ \Delta H = +41.2 \text{ kJ·mol}^{-1} \tag{17}$$

$$CO + 2H_2 \rightleftharpoons CH_3OH \ \Delta H = -90.6 \text{ kJ·mol}^{-1} \tag{18}$$

Methanol was formed for the first time via homogeneous hydrogenation of CO_2 at 240 °C under 80 bar with the catalytic system which consisted of alkaline iodides and triruthenium dodecacarbonyl in N-methylpyrrolidone (NMP) solution [187]. Since then, CO_2 hydrogenation to methanol by various catalysts and approaches have been extensively investigated [188–190]. Currently, commercial low-pressure catalysts generally lie in CuO and ZnO on a carrier of Al_2O_3 with variable stabilizing additives and promotors such as Zr, Cr, Mg, rare earth metals [191,192]. Besides, ruthenium catalyst has been found to be efficient for DAC under laboratory scale conditions.

Fig. 17 shows a schematic diagram of CO_2 capture and in-situ hydrogenation to methanol using an amine solution, in which Fig. 17a indicates the reaction sequence while Fig. 17b presents the overall equation [185]. CO_2 capture from air was performed by blowing synthetic air into an aqueous solution of pentaethylenehexamine (PEHA) at a flow rate of 200 mL·min^{-1} for 64 h at ambient temperature. CH_3OH synthesis was carried out in organic solution formed by 1,4-dioxane/H_2O and triglyme/H_2O mixtures. Metal catalysts for CO_2 hydrogenation to CH_3OH were soluble in organic solvents, and amines were soluble in water, which made easier the separation of the amine and catalyst after hydrogenation process [193]. When the reaction mixture was heated at 155 °C for 40 h with Ru-based catalyst, 2.1 mmol CH_3OH in 1,4 dioxane organic solution was obtained with a yield of 39%. The amount of produced CH_3OH can be increased to 3.3 mmol with 61% yield if the solution is replaced by triglyme [189]. Yield of CH_3OH in triglyme is improved to 79% as the heating time increases to 55 h. Continuous production of CH_3OH is achieved using this method in a dynamic system. CH_3OH is then separated from the mixture through distillation. Schematic diagram of biphasic 2-MTHF/water CO_2 to methanol system is presented in Fig. 17c. After carrying out the conversion process at 145 °C for 72 h and using 2-MTHF as an organic solvent with 50 μmol catalyst loading, the amount of product CH_3OH is as high as 4.8 mmol with 89% yield. For easier separation of the components, amines immobilized onto solid supports was proposed because amines could be easily separated from the solution by filtration [194]. When employing amine-modified sorbents, the catalysts were successfully recycled after several cycles. It was demonstrated that macrostructure of the sorbent changed after two cycles, resulting in decreased amount of captured CO_2 and produced methanol. System optimization could be achieved by enhancing the stability of solid amine and improving methanol yields.

Amine-based systems suffer from oxidative degradation, toxicity issues and volatilization. An alternative approach to avoid these problems is the application of alkali hydroxide solutions [117]. The conventional recycling process of alkali hydroxide leads to high energy penalty. To avoid that, CO_2 hydrogenation with the assistance of alcohols to methanol has been studied [195]. It is indicated that alcohols may trigger hydrogenation pathway from formate salt through the formate ester

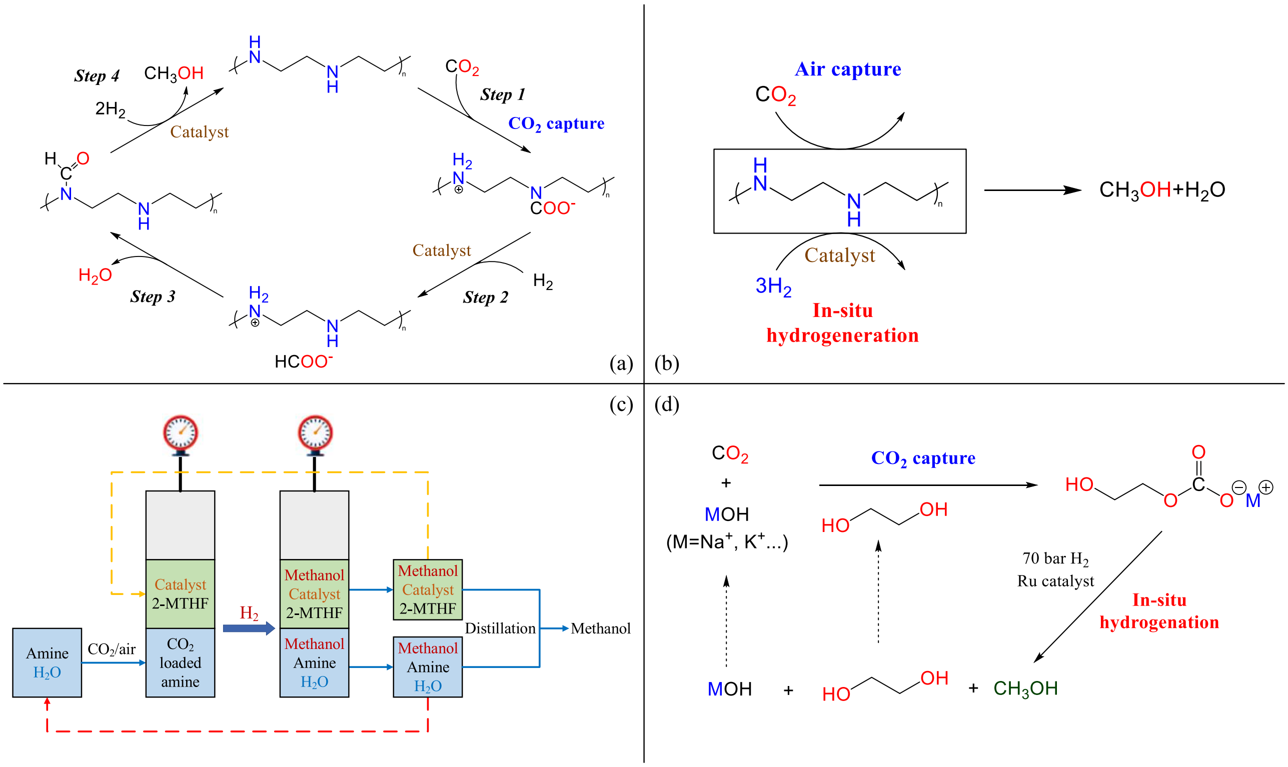


Fig. 17. Schematic diagram of air capture and CO_2 conversion to methanol, (a) reaction sequence using amine solution [185], (b) overall equation using amine solution [185], (c) biphasic system with recyclable catalyst and amine [193], (d) conversion with the assistance of ethylene glycol using alkali solution [195].

intermediate. Ethylene glycol was chosen as the alcohol solvent in the study and schematic diagram of tandem hydrogenation of captured CO_2 in ethylene glycol is shown in Fig. 17d [195]. Hydrogenating captured CO_2 at 140 °C with 0.5 mol% Ru-Macho-BH loading for 10 h achieved 80% CH_3OH yield, while glycol mediated Ru-PNP catalytic system was active for CH_3OH synthesis even at lower temperatures. To test the system for DAC and CO_2 synthesis to CH_3OH, indoor air was bubbled through a solution of 5 mmol KOH in 10 mL ethylene glycol for 48 h and 3.3 mmol CO_2 was captured in the form of carbonate and alkyl carbonates. All CO_2 was converted to CH_3OH when reaction time reached 72 h. Another glycol assisted conversion of CO_2 from air to methanol using Cu-ZnO-Al_2O_3 catalyst was presented [192]. The amount of CO_2 captured from air and CH_3OH yield were 7.0 $mmol\cdot g^{-1}$ and 89% for PEHA solution, and 6.6 $mmol\cdot g^{-1}$ and 97% for KOH solution, respectively. Results show that glycol solvents display a significant increase in CO_2 conversions to methanol.

Methane: Except for conversion to methanol, CO_2 methanation is an another promising process for carbon utilization [196]. Synthetic methane is a readily exportable fuel, which is supported by existing storage, transport and utilization infrastructures. Development of liquefied synthetic methane (LSM) greatly promotes a competition with liquid hydrogen (LH_2) [197]. CO_2 hydrogenation to methane over nickel catalysts was presented more than 100 years ago via Sabatier reaction (Eq. (19)). The reactant H_2 can be generated from water electrolysis using grid electricity or renewable electricity.

$$CO_2+4H_2 \xrightarrow{\text{catalyst}} CH_4+2H_2O \ \Delta H = -165 \ kJ\cdot mol^{-1} \tag{19}$$

Integration of CO_2 capture from ambient air with methane production was subsequently proposed [70]. Composite K_2CO_3/γ-Al_2O_3 was regarded as a promising sorbent for DAC/methanation (DACM) due to its unique thermal stability in high-temperature methanation process. Related experiment was then studied in cyclic mode and its schematic diagram is presented in Fig. 18 [198]. Composite sorbent was placed into a cylindrical fixed-bed adsorber, inside which an electrical heater was located. During adsorption process, indoor air with 380–430 ppm CO_2 was pumped into the adsorber until adsorbent was saturated with atmospheric CO_2. Regeneration process was carried out in hydrogen atmosphere. Then desorbed CO_2 and purge H_2 were directly introduced into the preheated catalytic reactor loaded with nickel catalyst (NKM-2 V) for methane production at 420 °C. At the outlet of the catalytic reactor, only ppm levels of CO_2 concentration were detected and the peak of methane concentration is about 10 vol.%. Results show that CO_2 desorbed from the sorbent is converted to methane thoroughly, with approximately 99% conversion rate. CO_2 conversion to methane is related to H_2/CO_2 ratio. For example, compared to a 82%-conversion rate observed in a mixture of H_2 and CO_2 (3:1) at 420 °C and 1 bar [199], an increased ratio in H_2/CO_2 would make the equilibrium shift towards products and conversion rate would increase to 99%.

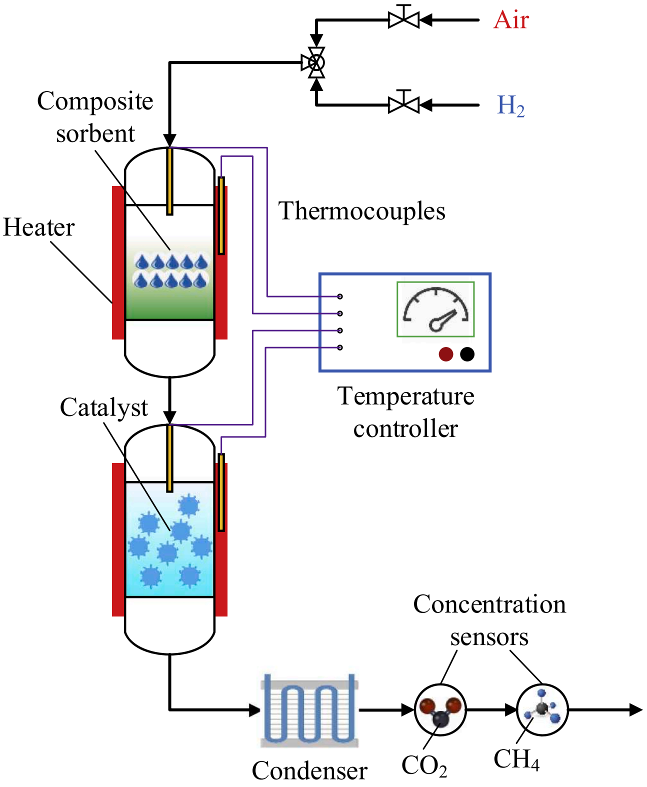


Fig. 18. Schematic diagram of the experimental set-up used for DACM process (adapted from [198]).

Decreasing reaction temperature is obviously conducive to methane synthesis process because thermal energy consumption is decreased. Ru catalyst is chosen to replace previous Ni catalyst because Ru is more active and has mild reduction temperature after oxidation in the air [196]. A process combining CO_2 capture and methanation was presented for DACM. Decreased reaction temperature cannot significantly influence CO_2 desorption amount. Activation of Ru-catalyst in reductive atmosphere and its effect on CO_2 conversion to methane were investigated in continuous DACM cycles [200]. Surface ratio Ru/Al_2O_3 estimated by means of X-ray photoelectron spectroscopy (XPS) revealed that Ru particles were sintered or capsulated/incorporated into the support, leading to decreased activity. Thus, methanation steps of DACM experiment need to prevent metal form of Ru component in hydrogen atmosphere. In addition of catalytic research, thermal modification of Al_2O_3 support was also conducted [72]. Optimization of experimental conditions promoted CO_2 conversion to methane with a yield of 98% at 350 °C and 100 $mL\cdot min^{-1}$ H_2 flow rate. Thermally modified K_2CO_3/Al_2O_3 composite sorbents efficiently reduced regeneration temperature to 200 °C. Lower adsorption temperature and conversion temperature resulted in the decrease of total energy consumption and a higher efficiency.

Requirement of in-situ CO_2 conversion induces a novel dual function material (DFM) that captures CO_2 from industrial flue gas and synthesizes CO_2 under the same conditions [201]. DFM was composed of alkali adsorbent and catalytic metal nanoparticles that were both dispersed on porous carrier with high specific surface area. By eliminating temperature swing process and reducing thermal resistance, CO_2 conversion using DFM can only use renewable energy in the form of hydrogen. The experimental study of DFM in a single reactor at the same adsorption and methanation temperature was then reported [202]. Only 0.5% addition of Ru catalyst has significantly increased CO_2 adsorption capacity by 35–50%. Additionally, it is more efficient than separate desorption and methanation processes using DFM in cyclic mode. For hybrid CO conversion with DAC, Mesters et al. [203] described DAC process with mineralization of magnesium oxide and its direct methanation. Results show that no CO_2 is detected in the presence of excess of Ni catalyst (90 wt.%), which confirms the feasibility of direct carbonate reduction and methane formation. Performance of DFM was significantly improved when ambient air is humidified, and adsorption capacity was 2.36 times greater than in dry conditions, which indicated a larger methane production [204].

Polyoxymethylene dimethyl ethers (OME): OMEs are promising diesel fuels and inhibit the formation of soot during combustion process of internal combustion engine. Producing OME from CO_2 has been analysed based on energy demand and energetic efficiency [205]. Despite multiple CO_2 sources can be supplied as the feedstock of chemical synthesis, applying CO_2 captured from air and indirect synthetic route shows the largest overall energy demand of 78 $MJ\cdot kg^{-1}OME_{3\text{–}5}$. Due to the low CO_2 concentration in air, DAC process led to an increasing total energy demand.

In brief, integrating DAC into fuel synthesis has shown a great potential for a carbon-neutral economy. Synthetic methanol/methane has promising values in global efforts to reduce carbon footprint and establish a sustainable cycle of atmospheric CO_2. Low-carbon fuels and renewables can be applied in those traditional energy consuming scenarios. A well-developed and cost-effective infrastructure based on DAC and fuel synthesis is indispensable for reliable energy supply before complete energy transition from fossil fuels.

4.1.2. Chemicals

Common chemicals synthesized from CO_2 mainly include urea, formic acid, cyclic carbonates, and salicylic acid [175]. However, few studies concern the conversion of CO_2 captured from ambient air to chemicals. This section generally illustrates three representative cases of CO_2 conversion to chemicals, i.e., formate salts [117], dimethyl carbonate (DMC) [206] and polyoxymethylene dimethyl ethers [205].

Formate salt as an intermediate product in the process of CO_2 hydrogenation to methanol has been investigated through direct conversion from captured CO_2 along with H_2 and catalyst [117]. The produced formate salt solutions are further utilized in direct formate fuel cell (DFFC) to generate electricity. This CO_2 conversion is ideal for low concentration CO_2 sources, e.g., atmospheric air, but this method has only been tested under laboratory conditions.

Catalytic performance of $Ce_xZr_{1-x}O_2$ has been successfully evaluated in the synthesis of diethyl carbonate from ethanol and CO_2 [207]. Subsequently, adsorption performance of an inorganic sorbent $Ce_{0.8}Zr_{0.2}O_2$ and its ability to convert CO_2 with methanol to DMC was investigated [206]. Similar as DFM used in CO_2 hydrogenation to methane, $Ce_{0.8}Zr_{0.2}O_2$ can be applied with a role of both adsorbent and catalyst. Schematic diagram of CO_2 adsorption and continuous conversion to DMC is displayed in Fig. 19. It indicates that higher temperature would lead to lower sorption capacities but promote CO_2 conversion to DMC. At 70 ℃, nearly no release of DMC is detected. By increasing temperature to 110 ℃, experiments with the highest quantity of methanol up to 33.4% could yield 26.4 μmol DMC (74.9% yield), which well verifies possibility of CO_2 conversion to DMC.

4.2. Enhanced oil recovery (EOR)

Petroleum field development is usually accompanied by three recovery stages. The tertiary recovery has been widely acknowledged as EOR [178]. In an EOR process, any material that is not naturally present in the reservoir is injected into the oil field to displace the remaining oil. Injection technologies include water injection, chemical injection, gas injection, and thermal injection, etc. [179]. For depleted oil fields, pure CO_2 is injected to increase oil mobility, volume and reservoir pressure. The CO_2 forces the residual oil to be displaced toward production wells [180]. Injected CO_2 is separated from reservoir fluids on the ground, and reinjected into the oil to repeat EOR cycle. [178]. When injected CO_2 has a low purity, e.g., mixed with N_2, gas mixture can accelerate the recovery process, thereby reducing production costs [208]. But the diluted CO_2 can only recover 80–85% of oil when compared with using pure CO_2. Use of N_2-diluted CO_2 could be an alternative way that results in greater viscosity reduction and higher oil swelling under typical injection pressure.

EOR is currently the second largest CO_2 utilisation application with around 80 $Mt_{CO2}\cdot y^{-1}$ used, after the production of urea that uses around 130 $Mt_{CO2}\cdot y^{-1}$ [209]. Thus, EOR is one of the most commercially advanced opportunity for CO_2 utilization. In 2019, Oxy Low Carbon Ventures and Carbon Engineering Ltd. launched the world's largest DAC and sequestration facility located at an occidental oil field in the Permian Basin [210]. The facility is designed to capture and permanently store 500,000 tonnes of CO_2 per year for EOR. It is the first project that combines DAC and geological sequestration on a commercial scale. This plant is larger than any currently operating application of DAC and it is planned to be operational by 2023 to continuously provide sufficient CO_2 for EOR operation of oil field. The final Front-End engineering design is expected to start in 2022 [211].

4.3. Biological utilization

Biological carbon utilization is an indirect carbon sequestration method, which relies on CO_2 conversion into organic carbon through photosynthesis by living organisms using solar energy. It is an environmental pathway for CO_2 conversion by producing useful biofuels and value-added by-products [212]. This section discusses the cultivation of microorganisms, such as microalgae and bacteria, by using captured CO_2 from DAC.

4.3.1. Microalgae-based CO_2 conversion

Compared to terrestrial plants composed of starchy and lignocellulosic materials, microalgae is regarded as promising alternative for biofuel production, which could replace fossil fuels and mitigate GHG emissions [213]. Advantages of microalgae-based CO_2 conversion are summarized as follows [214]: (1) high photosynthetic efficiency; (2) applicable in low concentration CO_2 sequestration; (3) faster sequestration rate; (4) less land use; (5) co-production of food, fuel, fine chemicals, etc. Most microalgae cultivation is based on carbon source from flue gas while growth of microalgae would be inhibited by toxic compounds, e.g., SO_x [215]. CO_2 from DAC as supply for microalgae production can effectively eliminate effects of toxicity in gas and enhance location flexibility. As a result of in-situ CO_2 utilization, complex CO_2 transport pipelines and high cost are avoided. Besides, CO_2 as a feedstock in microalgae cultivation occupies purity in the range of 5–35 vol.%, which is lower than most of CO_2 utilization ways, e.g., EOR, and fuel synthesis [208].

Microalgae is normally cultivated in an open or a closed system. In an open-pond system, carbon sources are supplied through direct CO_2 injection or mixture of CO_2 and air. Distinctive features for open system are simple construction, low cost, and easy operation. However, open ponds need large areas, and often operate under unstable conditions, which are only limited to a few algae strains [214,216]. Microalgae cultivation in closed systems called photobioreactors (PBRs) has many advantages over open-pond systems, e.g., less pollution, less water evaporation, higher cell concentration and better operation control. Different types of photobioreactors used to grow algae include vertical tubular photobioreactor, flat panel photobioreactors, horizontal tubular photobioreactor, helical type photobioreactor, stirred tank photoreactor and hybrid type photobioreactor Singh and Sharma [217]. The simplest photobioreactor may be flasks with continuous air bubbling.

Optimized CO_2 concentration for *Desmodesmus* sp. microalgae strain cultivation was analysed based on the CO_2 from DAC using amine-modified sorbents [218]. Then this concept was compared with CO_2 dosing using fossil fuel derived flue gas. The cultivation was carried out using laboratory glassware bottles with continuous gas bubbling

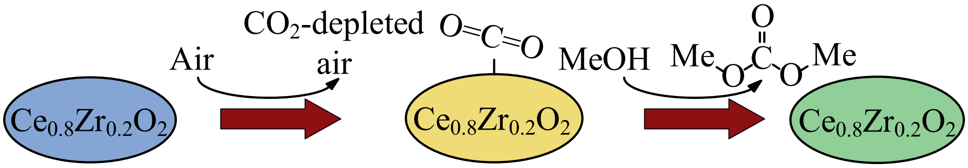


Fig. 19. CO_2 captured from air over $Ce_{0.8}Zr_{0.2}O_2$ and conversion to DMC with methanol (adapted from [206]).

through submerged tube. Regenerated CO_2 can be up to 95% concentration with average sorbent capacity of 2.05 mmol·g^{-1} at a temperature above 120 °C with *Desmodesmus* sp. only requires the purity between 1.5 vol.% and 5 vol.%, it is wasteful using CO_2 in 95% purity. Growth of *Desmodesmus* sp. increases rapidly by adding a slight amount of CO_2 before a decrement of algal concentration is found when 5% CO_2 concentration is used. The highest algae concentration is achieved at 1.5% CO_2 concentration. Furthermore, effects of different CO_2 concentrations on carbon capture and biomass production were accessed for microalgae *Chlorella vulgaris* and *Pseudokirchneriella subcapitata*, cyanobacteria *Synechocystis salina* and *Microcystis aeruginosa* [219]. The cultivation was continuously fed with an air stream containing atmospheric air and CO_2-enriched air. The microalgae growth with ambient air is slower than those under CO_2-rich conditions, indicating the limitation of low CO_2 intake. Increasing CO_2 concentrations to 5% strongly influences the growth of selected microorganisms, which results in the increase of specific growth rates. Mathematical models were then established to explain the influence of CO_2 concentration based on specific growth rates. Optimal concentrations in air streams for four microorganisms are 5.35%, 4.87%, 5.55% and 5.62%, respectively.

The optimal CO_2 concentration for microalgae cultivation in supplied air depends not only on algae species but also on growth conditions and reactor design. amongst various photobioreactors, simple bubble column and airlift reactor (ALR) with internal and external loop should be focused. ALR has better mixing, heat and mass transfer than bubble column owing to the characteristic of draft tube. Except for essential effects of CO_2 and nutrients in algae growth, hydrodynamic of an ALR is also an important factor, which is a function of reactor geometry and operating conditions, e.g., gas and liquid flow rates [220]. An ALR with internal sparger (ILALR) and external sparger (ELALR) were used to investigate the effects of high gas superficial velocity on CO_2 biofixation and microalgae growth using *Chlorella vulgaris* [221,222]. Schematic diagrams of two airlift reactors are shown in Fig. 20. The separator is designed to prevent gas bubbles entering downcomer. At a very low gas superficial velocity, microalgae settling and supply nutrients throughout the cultivation medium are not sufficient, thus poor mass transfer limits microalgae growth. Increasing superficial velocity of input gas increases gas-liquid mass transfer efficiency. Besides, higher gas velocity not only prevents settling of microalgae but also spreads microalgae in all regions of PBRs. Further increasing gas velocity would decrease contact time between CO_2 molecules and microalgae cells, thus reducing growth of microalgae cells. Besides, higher shear stress is harmful to microalgae cells. Similar conclusion could be obtained by subsequent researches on external sparger [221]. To understand the theory of CO_2 fixation in ILALR and optimize the design, a CFD simulation was conducted for the mass transfer and CO_2 fixation using biocatalyst (adsorption with chemical reaction) [223]. CFD results show a great agreement with experimental data with a difference less than 10%. It proves that CFD modelling could be a powerful tool for complex reaction process in ALR.

Cultivators of algal and cyanobacteria typically inject CO_2 to growth systems through sparging or bubbling. However, with only 400 ppm CO_2, such method leads to surplus cost and evaporation. Accordingly, growth media with rich CO_2 could be an alternative resolution. To increase CO_2 solubility in the growth medium, relatively high pH and alkali absorbents are essential to capture and convert CO_2 in the air [224]. Effective CO_2 capture also requires a high concentration difference between the medium and air, thus CO_2 concentration in capture medium needs to be sufficiently low. Reaction of CO_2, H_2O and carbonate results in bicarbonate in the medium. Algae actively transports bicarbonate into cells and releases hydroxide ion, followed by the conversion of hydroxide ion to CO_2. Soda lakes (bicarbonate pool) in which CO_2 was fixed efficiently in the form of high concentration bicarbonate/carbonate was simulated for DAC [225]. The increased bicarbonate and pH in bicarbonate pool are beneficial to microalgae growth. Low CO_2 solubility in water could not supply enough inorganic carbon. When CO_2 is removed from the supplied air, final dry cell weight is significantly reduced, which indicates that part of microalgae biomass growth is supported by CO_2 from air. Moreover, maintaining a stable and appropriate pH by replenishing CO_2 is beneficial for microalgae growth.

Microalgae cultivation systems are currently required to conduct large-scale testing and outdoor studies in bigger units when compared with simulated gas mixture in experiments. The location of process, building integration details and TEA should be taken into consideration [226,227]. End products of this cultivation process are not microalgae cells, but biofuels and bioproducts. An ideal utilization method is to cultivate microalgae at pilot scale to produce a large amount of biomass and then synthesize high-value compounds. Potential utilizations of bioproducts from microalgae cover pharmaceutical industry, cosmetics and personal care, food industry and biofuels [228]. For example, in food industry, pigments and carotenoids from microalgae can be used as food additives as colourings and thickeners or used to improve food quality.

4.3.2. Bacteria-based CO_2 conversion

Autotrophic microbial biomass converted from captured CO_2 can be utilized for human food, protein rich feed for livestock and slow-release

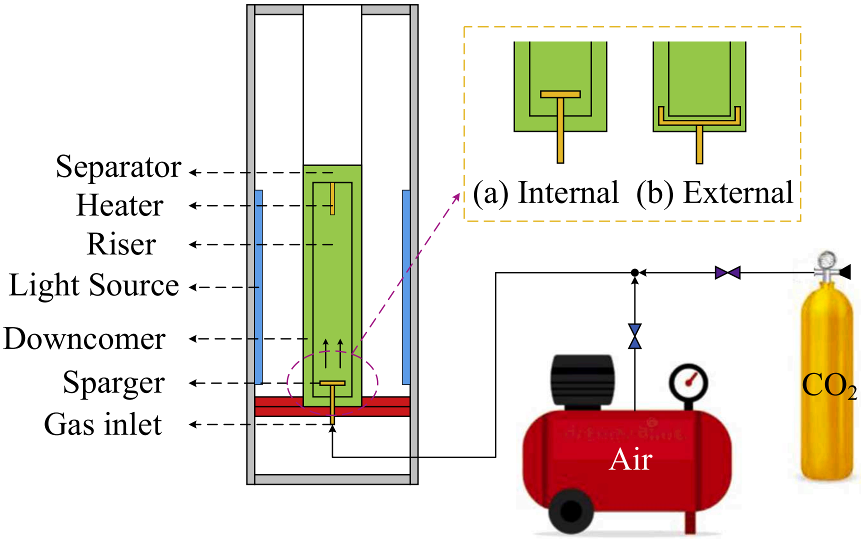


Fig. 20. Schematic diagram of an ALR with (a) internal sparger, (b) external sparger (adapted from [221]).

fertilizer [229]. These are mainly achieved through the assimilation of H_2-oxidation bacteria (HOB) which use hydrogen as energy source and CO_2 as carbon source to produce carbonaceous compounds and energy carriers [230]. The electricity driven CO_2 fixation process that combines in-situ water splitting and specific microorganisms is called hybrid biological-inorganic (HBI) systems. It defines a new class of value-added biosynthetic products and provides novel manufacturing routes for CO_2 utilization [231]. High content of microbial proteins (MPs), valuable amino acid content and availability for proteolytic enzymes in biomass of these bacteria are considered as potential protein source for human and livestock [232]. Sillman et al. [233] evaluated the possibility of bacterial MP production via DAC. It reveals that MPs production using air capture and renewables need less land area and water than those of soybean production. Later, their team presented the integration of DAC with HBI experimental system [234]. The main parts of HBI system are bioreactor tank, DAC unit and water electrolyser as shown in Fig. 21. DAC unit implements VTSA process using amino resin solid adsorbent. Analysis for biomass demonstrated heavy contamination instead of desired HOB biomass, mainly due to inefficient sterilization of the system. However, most of produced hydrogen is consumed inferred from low hydrogen content in the exhaust. It is challenging for system sterilization and the appropriate control of produced hydrogen and oxygen ratio, which may lead to unfavourable growth conditions of MP.

Based on the above illustration, carbon sequestration through CO_2 bioconversion is a natural mechanism for microorganisms, in which microalgae and HOBs are two most widely investigated. Biomass production is still in early R&D stage, but has been proven as a promising method to capture CO_2 and minimize GHG effects. It proves that effective carbon sequestration and bioconversion approaches can be achieved towards environmental sustainability and economic feasibility.

4.4. *Future outlook*

From the perspective of CO_2 utilization, DAC integration with renewable energy sources or low-carbon energy sources is promising to achieve the "closing carbon loop" goal [235,236]. Electricity storage over long periods promotes the conversion of electricity to fuels. Power-to-gas (PtG) and power-to-liquid (PtL) are proposed to be robust means to temporarily store electricity. There should be cases that liquid hydrogen carriers, e.g., methanol, dimethyl ether (DME), would be the preferred solutions to store/transport hydrogen and hence neutral CO_2 will be essential for such projects. In addition, while electrification and hydrogen present a huge potential for GHG emission reduction for road transport, industries such as aviation and shipping will most probably continue to rely on liquid hydrocarbons in the foreseeable future. Therefore, production of CO_2-based hydrocarbons, also known as electrofuels (e-fuels), becomes important as expanded use of biofuels is associated with sustainability concerns and challenges in terms of scalability due to limited feedstock availability in many cases [237–239]. In addition, use of CO_2 captured from the air assures to a great extent carbon-neutrality of e-fuels [240]. Their synthesis comprises various process stages, such as a) energy generation, b) collection and c) conversion of CO_2 to CO (if needed) and dissociation of H_2O, and d) fuel synthesis; each of them can be realized through a variety of technologies, as shown in Fig. 22 [240].

Furthermore, e-fuels production processes can be further integrated, and depending on the DAC technology choice, water and heat integration between the subsystems could create a more synergistic system. As an example, Climeworks claims that their DAC process is capable of producing 1 kg of ambient water for every kg of CO_2 that is captured [241]. For Fischer-Tropsch (FT) fuels and methane production for every mol of CO_2, 4 mol of H_2 are required. By assuming that 1 kg of electrolytic H_2 require approximately 10 kg of water, then roughly 1.83 kg of water is required per 1 kg of CO_2 captured which in turn means that the DAC can provide more than 50% of the required water. Further, the CO_2 based refineries typically produce process water which in theory can be used for electrolysis and further decrease or eliminate the need for fresh water; it should be noted though that the refinery water would require more intensive purification. Therefore, the DAC process can be optimized to achieve adequate working capacities for capturing enough CO_2 and H_2O to meet the electrolyser demands [242]. Fig. 23 describes this concept, as atmospheric H_2O and CO_2 are captured, followed by electrolysis (to generate H_2, or H_2, and CO, depending on the type of electrolyser), and further synthesis gas upgrading, which creates a closed carbon cycle. The studies of Schäppi et al. [243], Bos et al. [242], Marchese [244] and Drechsler et al. [245], for solar fuels, methanol and methane synthesis, respectively, have evaluated this approach from a technical, economic, and/or environmental perspective. Besides, atmospheric CO_2 capture processes in which electrolytic regeneration of absorbent achieves the simultaneous production of H_2 and synthesis gas have been also developed at laboratory scale [246,247]. Similar to water utilization, energy integration could be applied to these systems, as the heat released in the synthesis section could be used to regenerate the sorbent (especially when low temperature DAC technologies are used)

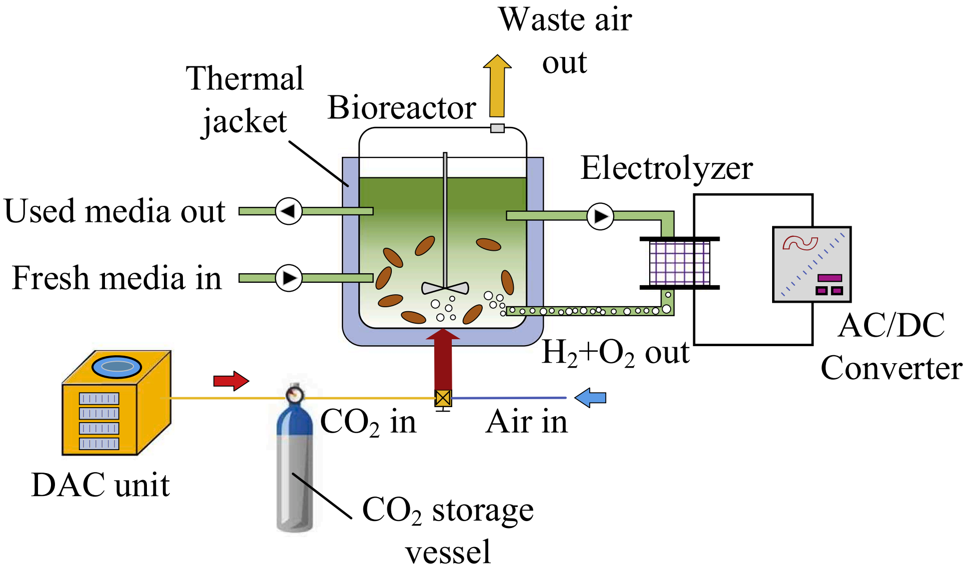


Fig. 21. Schematic diagram of HBI system with in situ water electrolysis and DAC (adapted from [234]).

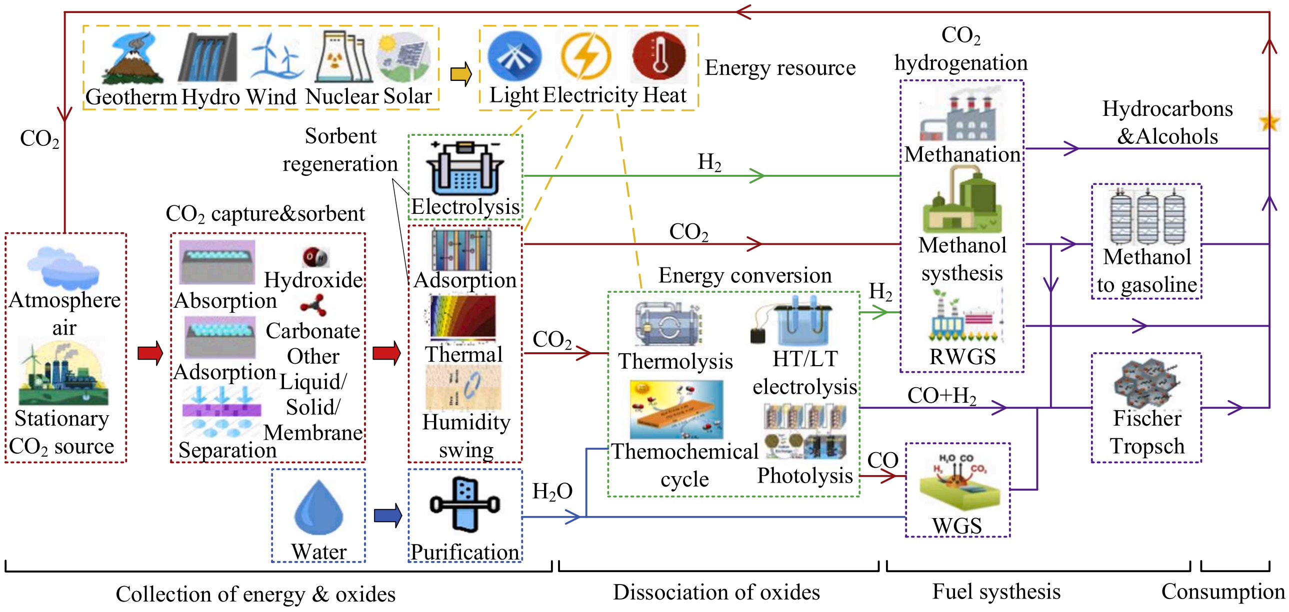


Fig. 22. Possible production pathways of e-fuels including different CO_2 capture technologies, renewable energy sources, electrolysis options and various hydrocarbons production (adapted from [240]).

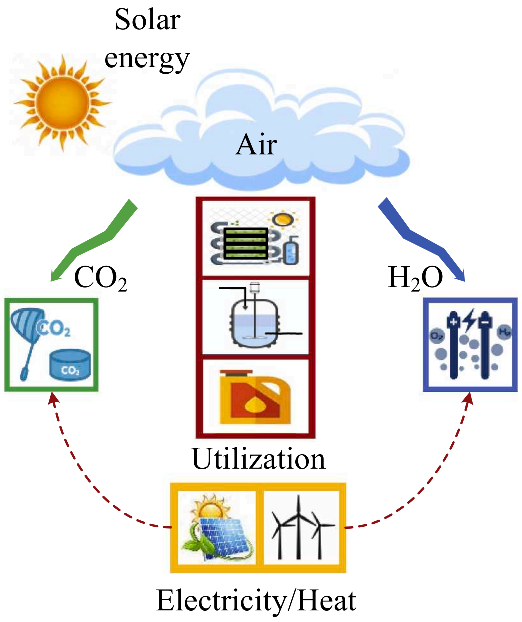


Fig. 23. Schematic diagram of the integrated DAC for carbon utilization with renewable energy systems.

[245].

In summary, fuel synthesis may be the most promising utilization method in the coming decades. The required raw materials can be readily obtained by co-extraction of CO_2 and H_2O from ambient air. Synthesized fuels from CO_2 and renewable energy can utilize existing infrastructure and no new technologies are required. CO_2 emissions from vehicles and airplanes driven by these fuels are further recycled via DAC for continuous production of fuels, thus closing the carbon cycle and reducing the concentration of CO_2 in the air. With appropriate policy support, this carbon-neutral fuels can play an essential role in long-term decarbonization and mitigating global warming.

5. Techno-economic and environmental analyses for DAC

Although DAC removes CO_2 directly from atmospheric air, its benefits to the environment are partly offset by demands to run the process and construction materials [248]. Since DAC is an attractive technology, it is critical to objectively evaluate its technical and economic feasibility [249,250]. DAC requires about twice the theoretical energy input of conventional CO_2 capture from power plants as shown in Fig. 24. Additional energy consumption and cost should be evaluated to decide whether large-scale application of DAC is worth or not.

Generally, costs for DAC are high, which are often 1–2 orders of magnitude higher than CO_2 trading prices. Thus, reducing the cost is of great importance for large-scale applications. The cost to separate a given component from a mixture can be roughly estimated from Sherwood plot [251]. The plot consists of a line in the form as shown in Eq. (20).

$$C = \frac{A}{B} \tag{20}$$

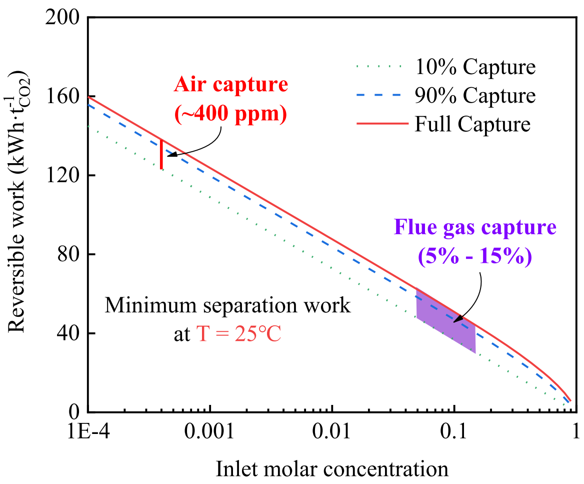


Fig. 24. Theoretical separation work for CO_2 capture from different sources [248].

where C is the price, A is a separation constant, and B is initial concentration of input stream. Dahmus and Gutowski [252] suggested a value of A equalled to 0.001 $\$\cdot kg_i^{-1}$, for the separation of pollutants from a mixture of gases. Using Eq. (20) suggests that the cost for air capture is around 2500 $\$\cdot t_{CO_2}^{-1}$. A Sherwood plot only for mixed acid gas stream separation predicts that the cost is consistently larger than 1100 $\$\cdot t_{CO_2}^{-1}$.

It is obvious that cost estimates using a linear equation is not rigorous enough. Eisaman divided the cost of a DAC plant to three components, which are expressed as Eq. (21) [253] .

$$C = \beta + c_e\left(\frac{\rho g h}{R}\frac{Q}{\eta} + E_{regen}\right) \tag{21}$$

where the first term represents capital expenditures (CAPEX), the second and third terms represent operational expenditures (OPEX). β is the amortized capital cost of captured CO_2. $\rho ghQ/R\eta$ is energy consumption per tonne CO_2 with a capture rate R. ρ is fluid density, h is pressure head, Q is inlet air flow rate, η is the fraction of CO_2 captured and g is gravity acceleration. E_{regen} is regeneration energy, c_e is cost of unit energy consumption.

In early stage of development, it is difficult to accurately estimate the cost of DAC technology. Few studies have attempted to assess the economic performance of DAC systems, yielding a wide range of results that are dependant on the technology under consideration as well as assumptions made. Lackner predicted specific cost of 220 $\$\cdot t_{CO_2}^{-1}$ captured for their first solid sorbent DAC prototype, and could drop down to 30 $\$\cdot t_{CO_2}^{-1}$ after further developments [125]. A report by American Physical Society (APS) estimated the cost for post-combustion capture as 80 $\$\cdot t_{CO_2}^{-1}$ and whilst for liquid sorbent DAC close to 610 $\$\cdot t_{CO_2}^{-1}$ [119]. Based on these findings, it appears that DAC is less cost effective than post-combustion capture of CO_2. However, later, Azarabadi and Lackner [254] found that DAC could be a cheaper solution when natural gas combined cycle (NGCC) units cannot be retrofitted for post-combustion capture, as well as for small natural gas-fired units. DAC can also be used to capture the residual emissions of retrofitted NGCC plants. When compared to post-combustion retrofit, DAC will be competitive to capture one-third and 45% of emissions at prices of 550 $\$\cdot t_{CO_2}^{-1}$, and 100 $\$\cdot t_{CO_2}^{-1}$, respectively.

Regardless of the type of technology chosen, DAC units require thermal and electric energy, which could be a driving vector in the final cost of net CO_2 captured as well as the total carbon footprint of the process. McQueen et al. [255] identified two scenarios to produce compressed CO_2 using DAC technology: waste heat from geothermal-based electric utilities and steam from nuclear-based power plants. The base case comprised utilization of steam from natural gas. Cost of truck transport for captured CO_2 was included to evaluate final net cost, covering all CO_2 emissions involved in the process. It is indicated that the cost for replacement of deactivated sorbent accounts for approximately 80% in CAPEX. At a capture rate of 100 ktonnes CO_2 per year, total cost of capture is 223, 205, and 233 $\$\cdot t_{CO_2}^{-1}$ for base, geothermal and nuclear cases, respectively. Due to incorporation of low-carbon heat, DAC emission footprint was reduced from 0.65 tonne CO_2 emission per tonne of CO_2 captured ($t\cdot t_{CO_2}^{-1}$) for base case to 0.29 $t\cdot t_{CO_2}^{-1}$ for geothermal and nuclear configurations. Simon et al. [256] described a generalized DAC system, and it consisted of air capture, water treatment, carbon sequestration and electricity generation parts. They considered four kinds of electricity generation equipment: wind, enhanced geothermal, NGCC and NGCC with carbon capture. The levelized cost of capture using wind showed the least value of 293.04 $\$\cdot t_{CO_2}^{-1}$, while NGCC system showed the largest cost of 863 $\$\cdot t_{CO_2}^{-1}$. Fasihi conducted TEA on a state-of-art for DAC technologies which are categorized as high temperature aqueous solutions (HT-DAC) and low temperature solid sorbent (LT-DAC) systems [257]. CAPEX of two representative technologies were estimated based on learning curve approach and summarized in Fig. 25. It is concluded that LT-DAC systems are more favourable owing to lower regeneration energy requirement and possible integration with low-grade heat supply. Erans et al. [22]. also summarized TEA of HT-DAC and LT-DAC in more detail. It demonstrates that HT-DAC designs still rely on the use of fossil fuels for the regeneration process. For most of optimal cases, the long-term cost of CO_2 removal ranges 43–95 $\$\cdot t_{CO_2}^{-1}$. But this value could be increased up to 863 $\$\cdot t_{CO_2}^{-1}$ under different scenarios.

While technology developers may have the most up-to-date information, their economic assessments may be overly optimistic. Similarly, the assumptions used in modelling studies could be incorrect. As a result, both approaches may result in underestimation or overestimation of captured CO_2 from the air. In this regard, it is also critical to consider technical experts' opinions on the future costs of DAC. Unlike previous studies, Shayegh et al. [258] collected economic and technical data estimations from a variety of academia, industry, and policy experts in order to gain a better understanding of current or prospective commercial DAC technologies. This assessment concludes that, despite the high degree of uncertainty surrounding current CO_2 removal costs estimates, there was strong agreement amongst experts that, regardless of technology, costs will fall significantly from their current levels (500–600 $\$\cdot t_{CO_2}^{-1}$ removed) but will still be significant (roughly 200 $\$\cdot t_{CO_2}^{-1}$ removed in 2050). The second conclusion emphasises the possibility of deploying DAC systems. Even the most upbeat specialists are hesitant to provide median estimates of annual installed capacity of more than a few Gt CO_2. Furthermore, the main barriers to the implementation of DAC projects are technological and policy-related.

Except for laboratory or real demonstration plants, recently, several models developed for the detailed simulation of DAC are also used to evaluate energy and cost requirements. Sinha et al. [259,260] developed a series of numerical models to simulate DAC process of steam-assisted TVSA cycles, and from their results it could be determined that the choice of solid sorbent as well as the system design impact the economic, and energy performance of the system. Electricity and thermal energy are converted to primary combustion energy by scale-up factors. Results show that the minimum primary combustion energy for MIL-101 (Cr)-PEI-800 and mmen-Mg_2 (dobpdc) are 3.91 $GJ\cdot t_{CO_2}^{-1}$ and 2.95 $GJ\cdot t_{CO_2}^{-1}$, while the concerning costs are 75–140 $\$\cdot t_{CO_2}^{-1}$ and 60–190 $\$\cdot t_{CO_2}^{-1}$, respectively. The lower the contactor to adsorbent ratio is, the lower the thermal and electrical energy requirements become, while the cost initially decreases up to a certain limit, after which it begins to rise. This is mainly due to tradeoff between CO_2 captured amount and adsorbent capital cost. The costs and energy demand are 86–221 $\$\cdot t_{CO_2}^{-1}$, and

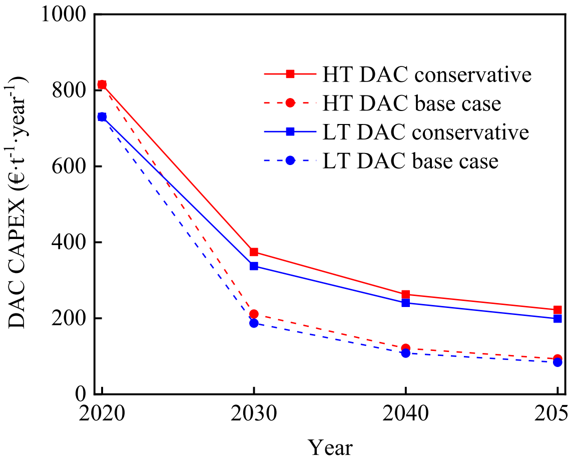


Fig. 25. CO_2 DAC CAPEX development for LT and HT systems based on the learning curve approach and the applied conservative (CS) and base case scenarios (BS) [257].

3.4–4.8 GJ·$t_{CO_2}^{-1}$, respectively if model parameters are in the mid-range. Also, capital cost of adsorbent accounts for most of total cost when using MOFs. Unlike Sinha et al. [259,260], Krekel et al. [261] preferred to estimate DAC energy requirements using a thermodynamic analysis rather than detailed system modelling. They also developed a model for economic analysis of a DAC plant, in which production costs were divided into three categories: investment costs, manufacturing costs and material costs. Investment costs mainly include the component and acquisition costs of adsorber, desorber and other equipment. Total electric energy demand of this system is calculated as 3.65 GJ·$t_{CO_2}^{-1}$, in which two compressors, which compensate pressure losses from air and CO_2, contributed the most. Specific production costs are 792 \$·$t_{CO_2}^{-1}$ when plant productivity is 14,150 t_{CO2}·year^{-1}. A more detailed mathematical model was presented by Sabatino et al. [262], who analysed sorption DAC technologies, such as alkali scrubbing, amine scrubbing and solid sorbents process (VTSA), through modelling by employing advanced rate-based process models and multi-objective process optimization to derive an optimal unit design. Mathematical models for solid sorbents consider co-adsorption of water, an issue that had been disregarded in previous works. It reveals that the most efficient technology is solid sorbents due to their low exergy demand of 1.4–3.7 MJ·$kg_{CO_2}^{-1}$ and high productivity ranging between 3.8 kg_{CO2}·m^{-3}·h^{-1} and 10.6 kg_{CO2}·m^{-3}·h^{-1}, when compared to liquid technologies in which specific exergy consumption is above 6 MJ·$kg_{CO_2}^{-1}$ and for productivities that range between 0.2 kg_{CO2}·m^{-3}·h^{-1} and 1.1 kg_{CO2}·m^{-3}·h^{-1}. The outputs indicate that DAC technology based on solid sorbents is the most promising amongst those analysed, however, its CAPEX has the greatest share in specific CO_2 cost for all technologies that can be operated below 200 \$·$t_{CO_2}^{-1}$. Furthermore, for solid sorbents, the sorbent cost has huge impact in the DAC total cost, and therefore optimization strategies focussed on it could highly help with cost reduction. Due to this reason, the development of new DAC sorbents is a growing area of research aimed at lowering the cost of DAC. Every year, cutting-edge sorbents with enhanced capture and regeneration properties are developed in research facilities but without accurate cost estimates for commercial levels. In this sense, Azarabadi and Lackner [32] developed a generic techno-economic model to value any sorbent based on CO_2 market price and sorbent characteristics: cycle time, loading capacity and degradation rate. The model could estimate the value of a sorbent with known characteristics and could be compared to the production and commercialization of this sorbent. Conversely, it can also estimate the cost of CO_2 capture using this known sorbent price and characteristics. Results indicate that a reasonable budget is achieved only when the sorbent lasts for tens even hundreds of thousands thermal cycles. However, most sorbents usually do not exceed tens of cycles under laboratory conditions. In addition, experimental energy consumption of DAC is barely researched. Bajamundi et al. [263] investigated the energy requirement of a TVSA operation cycle using amine-functionalized sorbent through experimental approaches. After improvement tests, specific energy requirement decreased from 4.68 GJ·$t_{CO_2}^{-1}$ to 3.60 GJ·$t_{CO_2}^{-1}$, which are in the range of those predicted models. Share of thermal energy to total energy improves the performance from 58 to 76%, which allows the utilization of cheap low-grade heat.

New technology costs are subject to uncertainty, and therefore, limited studies have thoroughly assessed the likely CAPEX and OPEX of the different DAC technologies. A comprehensive analysis on design and engineering cost estimation for a complete DAC system was presented by Keith and his team [169]. The baseline scenario research is based on an industrial alkali aqueous absorption DAC system of Carbon Engineering company, as explained in Section 3.2. Several structure and operation optimization of these units were applied to reduce cost. They used cross-flow cooling-tower for gas-exchange process, rather than counterflow vertically orientated tower [170]. Use of cyclic-pulsing solution flow and optimal structure of packing geometry could significantly reduce pressure drop and pumping energy while maintaining good packing wetting and mass transfer performance. Pre-washing and drying of pellets in the reactor avoid vacuum filtration and reduce water carryover, which result in lower energy consumption in the kiln. Moreover, pellets allow the use of a circulating fluidized bed (CFB), which has lower capital cost than a rotary kiln. Calcination of $CaCO_3$ pellets is accomplished in an oxygen-fired CFB, and its conservative heat integration design reduces technical risks instead of design with higher efficiency at the expense of higher capital cost. A CFB design has approximately 78% thermal efficiency, which is higher than the 39% efficiencies of traditional lime mud calciners. Under various plant configurations, levelized cost of CO_2 capture range is 94–232 \$·$t_{CO_2}^{-1}$ and is predicted to drop below 60 \$·$t_{CO_2}^{-1}$ by 2040 [264]. Using data from this literature and Eisaman's model, OPEX for the regeneration is 19.28 \$·$t_{CO_2}^{-1}$, and total cost becomes 29.61–219.61 \$·$t_{CO_2}^{-1}$ compared to Carbon Engineering's conservative levelized cost.

The CAPEX and OPEX of the liquid and solid sorbent technologies were thoroughly evaluated in a National Academies report [265]. Because of the uncertainty surrounding some specific parameters and technological choices, economic and performance results are presented as ranges, spanning from best to worst case scenario. Results were estimated based on 1 Mt_{CO2}·y^{-1} for the different scenarios of both technologies. The calculated carbon capture costs for solid sorbents range from 18 \$·$t_{CO_2}^{-1}$ to 1000 \$·$t_{CO_2}^{-1}$. Because these extreme values correspond to the unrealistic best- and worst-case scenarios, three intermediate scenarios were also assessed, with CO_2 capture costs spanning between 88 \$·$t_{CO_2}^{-1}$ to 228 \$·$t_{CO_2}^{-1}$. However, regardless of the scenario, the CAPEX of the adsorbent dominates the final cost of the solid sorption technology. For the liquid sorbents, the cost of CO_2 capture is equally dominated by the CAPEX and the OPEX, due to the high energy needs. The optimistic and pessimistic scenarios calculated carbon capture prices between 140 \$·$t_{CO_2}^{-1}$ to 254 \$·$t_{CO_2}^{-1}$, and 147 \$·$t_{CO_2}^{-1}$ to 264 \$·$t_{CO_2}^{-1}$, when an oxy-fired calciner fed by coal, or natural gas, is used respectively. When the oxy-fired calciner is substituted by H_2-fired calciner which is fed by electrolysis-derived H_2, the price range increases to between 317 \$·$t_{CO_2}^{-1}$ and 502 \$·$t_{CO_2}^{-1}$. The breakdown of the economic calculations of the described scenarios is presented in Tables 6 and 7.

In addition to energy and cost estimates, a detailed LCA is also necessary for the feasibility evaluation of DAC technologies [266,267]. Although LCA is a key technology to achieve overall environmental target, researches on DAC are rarely reported which is often studied and compared with other related processes, e.g., post-combustion capture and power to gas process.

Giesen et al. [268] was the first to analyse environmental impacts of humid swing DAC (HS-DAC) and results were compared with post-combustion capture. When HS-DAC is sized to achieve the same net life cycle GHG emissions as post-combustion capture, more CO_2 needs to be captured. This is mainly because of the higher electricity demand per amount of CO_2 captured. Moreover, HS-DAC requires fresh water not salty water, and its operation is sensitive to ambient conditions, especially temperature and humidity. De Jonge et al. [269] initially investigated life cycle carbon efficiency of a DAC process based on hydroxide solution as sorbent material. They determined that DAC configurations result in negative emissions. However, negativity of these values is subjected to energy supply, which is the largest contributor to carbon footprint. Besides, Terlouw et al. [270] presented the first comprehensive assessment of life-cycle emissions of solid sorption DAC driven by low-carbon energy sources. The DAC plant is represented based on Climeworks technology (LT-DAC). It concludes that locations with low-carbon grid electricity and with availability of waste heat possess a great potential for providing significant amounts of negative emissions as shown in Fig. 26. Also, it is highlighted the importance of calculating other environmental impacts than Global Warming Potential (GWP) by

Table 6
The estimated CAPEX and OPEX costs for generic liquid solvent DAC systems with a capacity of removal of 1 Mt CO_2 per year [265].

Oxy-fired Calciner			H_2-fired calciner		
CAPEX ($M)	Low	High	CAPEX ($M)	Low	High
Contactor array	210	420	Contactor array	210	420
Slaker, causticizer, clarificator	130	195	Slaker, causticizer, clarificator	130	195
Air separation unit and condenser	65	100	H_2-fired calciner	360	720
Oxy-fired calciner	270	540	Condenser	0.3	0.3
–	–	–	Water	1.1	1.1
–	–	–	electrolyser	260	420
–	–	–	PV+battery	865	1465
–	–	–	Compressor	22	37
–	–	–	Pressurized tank	73	207
Total	675	1255	Total	1921	3045
CAPEX annualized ($M·year^{-1})	81	151	CAPEX annualized ($M·year^{-1})	230	365
OPEX ($M·year^{-1})	Low	High	OPEX ($M·year^{-1})	Low	High
Maintenance	18	33	maintenance	58	91
Labour	6	10	labour	17	27
Makeup and waste removal	5	7	Makeup and waste removal	5	7
Natural Gas (NG)	25	35	PV+battery	7	11
Coal	18	25	–	–	–
Electricity	12	28	–	–	–
OPEX (NG)	66	113	OPEX (NG)	87	136
OPEX (Coal)	59	103	–	–	–
Capture cost (NG) ($·$t^{-1}_{CO_2}$)	147	264	Capture cost ($·$t^{-1}_{CO_2}$)	317	501
Capture cost (Coal) ($·$t^{-1}_{CO_2}$)	140	254	–	–	–

Table 7
The estimated CAPEX and OPEX costs for a solid sorption DAC System with a capacity of removal of 1 Mt CO_2 per year [265].

Parameters	CAPEX ($·$t^{-1}_{CO_2}$)				
	1-Best	2-Low	3-Mid	4-High	5-Worst
Adsorbent	3.6	70	122	186	988
Blower	3.6	2.1	3.7	6.7	13.7
Vacuum pump	4.5	2.6	4.7	8.5	17.4
Condenser	0.03	0.07	0.075	0.1	0.4
Contactor	2.2	1.3	2.3	4.1	8.4
Parameters	OPEX ($·$t^{-1}_{CO_2}$)				
	1-Best	2-Low	3-Mid	4-High	5-Worst
Adsorption	1.3	9	12	19	4.3
Steam	2.5	2.2	2.4	3	43
Vacuum pump	0.3	0.2	0.2	0.24	0.3
Capture cost ($·$t^{-1}_{CO_2}$)	1-Best	2-Low	3-Mid	4-High	5-Worst
	18	87	147	228	1076

demonstrating as an example the trade-off between benefit of achieving negative emissions and the increase of land transformation impact. Deutz and Bardow [248] determined environmental impacts of DAC technologies from four perspectives. Their results show that the construction of DAC plant and adsorbent production reduce carbon capture efficiency by 0.6% and 1.2%, respectively, so carbon capture efficiency would not reach 100% even when applied with carbon-free energy. Synthesis of fuels using CO_2 capture could at best achieve carbon neutrality when using renewable carbon feedstock and low-carbon electricity. However, sensitivity analysis shows large uncertainties for adsorbents, which presents big challenges for researchers' insights. Madhu et al. [271] presented a comparative LCA of two main DAC technologies: DAC using TSA and high-temperature aqueous solution (HT-Aq). It demonstrates that DAC using TSA surpasses HT-Aq DAC by a factor of 1.3–10 in all environmental impact categories. HT-Aq DAC is first designed readily for commercial-scale industries but has higher energy demand requirements.

As previously discussed, the GWP of the energy source has an impact on the carbon footprint of the DAC system. At the same time, the net removed cost is influenced by this parameter, since cost reduction can be achieved through the use of low-carbon energy because of lower carbon emissions through the whole process [255]. This effect is more pronounced for liquid sorption DAC technology due to its higher energy requirements when compared to solid sorbents, according to the findings published in the National Academies report [265]. As shown in Table 8, when fossil fuels are used for any energy source, the capture cost is more inflated in the net removed cost than when renewable energy options are used. As a result, the energy source should be carefully chosen because it not only affects the system's final GWP but also has a significant impact on the capture cost.

The importance of analysing other environmental impacts has been highlighted previously. DAC systems require significantly less land than other carbon removal technologies, while its impacts on biodiversity would be considerably smaller because it does not demand agricultural land. In general, the amount of land required for DAC is determined by several parameters, such as the size of the contactor, the spacing requirements of multiple contactors, and the contactor configuration [265], a comparison between different technologies was presented by Viebahnand is presented in Table 9 [241]. Another important factor to consider is the amount of land required for the energy source. For example, Terlouw et at. [270] thoroughly analysed land transformation for DAC systems with different energy sources. They observed that independent DACCS configurations with solar energy supply perform worse on land transformation than grid-connected layouts.

Water loss from DAC processes has so far received minimal attention in the scientific literature in comparison to other parameters such as energy use [265]. According to Carbon Engineering their KOH solution pilot plant has a net water consumption of 4.7 $m^3 \cdot t^{-1}_{CO_2}$ and this value varies depending on temperature, ambient conditions, and solution concentration [169]. On the other hand, Climeworks claims 1 $m^3 \cdot t^{-1}_{CO_2}$ of water production [272], since it is captured from the air, and this could be further integrated with a CO_2 utilisation process, such as in a water electrolyser. Other environmental impacts have been also referred in few other studies. De Marchin et al. [273] found that lower CO_2 levels reduced the photosystem II (PSII) photochemical efficiency in algae cultures. In which due to concerns of material scarcity, Deutz et al. [248] found out that future deployment of DAC system would not be limited by energy or material requirements.

Another interesting area that requires further investigation is the integration of DAC systems with CO_2 utilisation processes, as demonstrated by Liu et al. [274], and the study presented the first LCA study of DAC-to-fuel process. Two cases are compared in this study: baseline scenario using oxy-fired calciner, and scenario using electric calciner case. A full life cycle emission in the baseline scenario is 0.51 $t \cdot t^{-1}_{CO2}$ captured from air, larger than the 0.16 $t \cdot t^{-1}_{CO2}$ captured for the electric calciner. Using an electric calciner over an oxy-fired calciner avoided further use of fossil fuels and resulted in a lower fuel carbon intensity (CI) per MJ of synthetic fuels combusted. Sensitivity analysis shows that the impact of the electricity CI is larger than variation in any other parameter. The lower the electricity CI is, the lower GHG impact of fuels produced. Kiani et al. [197] conducted a detailed LCA of LSM production from DAC and renewable H_2. The results demonstrate that LSM could compete with liquefied hydrogen (LH_2) and as attractive carbon-neutral method to storage renewable energy.

High demand to mediate global warming causes the government to response for the development and deployment of carbon capture technologies. Thus, quite few TEAs and LCAs are conducted in terms of various DAC technologies. However, DAC technologies are not mature enough to possess standard evaluation models based on reasonable energy and cost demand in large-scale applications. It results in a large deviation for current TES studies when comparing various DAC methods. Similar situation could happen for LCA researches based on

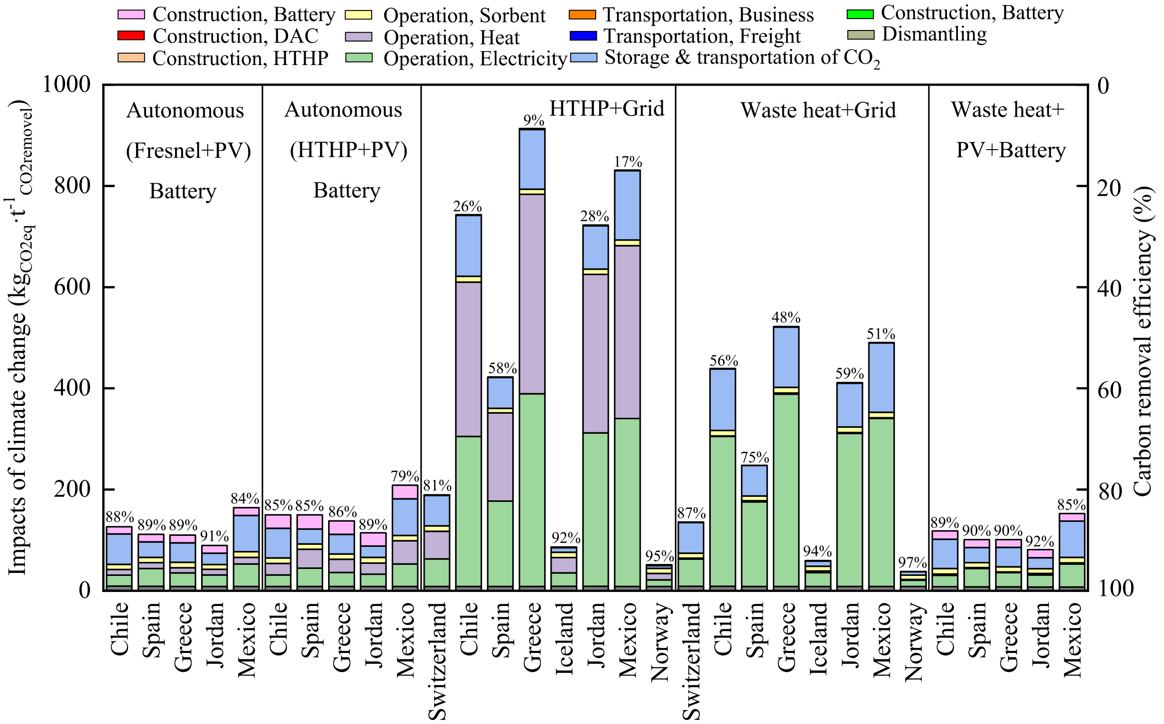


Fig. 26. Carbon removal efficiencies (%) and life-cycle GHG emissions for various DAC systems in different locations (adapted from [270]).

Table 8
Summary of estimated energy, CO_2 footprint and carbon capture for 1 $Mt_{CO2}y^{-1}$ liquid sorption and solid sorption DAC systems [265].

DAC system	Energy source		Energy required (GJ·$t^{-1}_{CO_2}$)		CO_2 generated (Mt_{CO2}·y^{-1})		Net CO_2 avoided (Mt_{CO2}·y^{-1})	Capture cost (\$·$t^{-1}_{CO_2}$)	
	Electric	Thermal	Electric	Thermal	Electric	Thermal		Captured	Net removed
Liquid sorption	NG	NG	0.74–1.7	7.7–10.7	0.11–0.23	0.47–0.66	0.11–0.42	147–264	199–357
	Coal	NG	0.74–1.7	7.7–10.7	0.18–0.38	0.47–0.66	0–0.35	147–264	233–419
	Wind	NG	0.74–1.7	7.7–10.7	0.004–0.009	0.47–0.66	0.34–0.53	141–265	156–293
	Solar	NG	0.74–1.7	7.7–10.7	0.01–0.03	0.47–0.66	0.31–0.52	145–265	165–294
	Nuclear	NG	0.74–1.7	7.7–10.7	0.01–0.02	0.47–0.66	0.32–0.52	154–279	173–310
	Solar	H2	11.6–19.8	7.7–10.7	0.01–0.03	0	0.99	317–501	320–506
Solid sorption	Solar	Solar	0.55–1.1	3.4–4.8	0.0004–0.008	0.008–0.01	0.892–0.992	88–228	89–256
	Nuclear	Nuclear	0.55–1.1	3.4–4.8	0.002–0.004	0.004–0.005	0.91–0.994	88–228	89–250
	Solar	NG	0.55–1.1	3.4–4.8	0.0004–0.008	0.22–0.30	0.70–0.78	88–228	113–326
	Wind	NG	0.55–1.1	3.4–4.8	0.002–0.003	0.22–0.30	0.70–0.78	88–228	113–326
	NG	NG	0.55–1.1	3.4–4.8	0.07–0.14	0.22–0.30	0.56–0.71	88–228	124–407
	Coal	Coal	0.55–1.1	3.4–4.8	0.15–0.3	0.32–0.44	0.26–0.53	88–228	166–877

Table 9
The specific land use of the various types of DAC processes (not including the area set aside for energy generation facilities [241]).

Parameters	DAC liquid solvent		DAC solid sorbent			
	APS	Carbon Engineering[a]	Climeworks	Climeworks	Lackner	Global Thermostat
Land requirement (km^2)	9	>0.0016	9.00E-05	-	3.00E-05	-
DAC capacity (Mt_{CO2}·$year^{-1}$)	6	0.1	9.00E-04	-	3.65E-04	-
Specific land use (km^2·$Mt^{-1}_{CO_2}$·$year^{-1}$)	1.5	>0.016	0.1	2[b]	8.00E-02	0.05–0.002

[a] Only packings.

[b] Including area set aside for heat supply by photovoltaic-powered heat pumps.

different ways to process life cycle inventories. Therefore, in order to get more reliable TEAs and LCAs with results that could approach real operating plants, there is the need for guidance documents, such as a standard, that can limit the variations between assumptions and methodologies used. For example, Sick et al. [275] pointed out the path to harmonized LCAs and TEAs for CCUS. Key requirements and needs for further guidance are identified, especially for assessments of early-stage technologies, reporting details, and guidance for policy makers and nontechnical decision-makers. Also, the Global CO_2 Initiative and the National Energy Technology Laboratory (NETL) have released preliminary TEAs and LCAs guidance documents to help with the implementation of these assessments on CCU projects [276]. Similar efforts are suggested to be implemented in negative emission technologies and particularly in DAC. Moreover, the costly polices are difficult to be imposed on the entrenched interest groups, resulting in a greater need for negative emissions [277]. Cutting down the cost for DAC requires not only the research analysis, but also capital investment by commercial companies as well as long-term policies that will derisk investment ventures.

6. Commercial development

Till now, none of DAC technologies has drawn significant attention in the socio-technical system. This can be solved by either improving the costs of the existing DAC or developing more efficient technologies [278]. Besides, specific policy that promotes either DAC utilization or DACCS is needed. Under this scenario, Caskie et al. [278] selected existing policies that are used to tackle climate change through different DAC initiatives. amongst them, Clean Development Mechanism (CDM), Contract for Differences (CfD), European Trading System (ETS) and the US 45Q legislation are considered. These policies are adjusted to support the development of DACCS projects. It could be classified as a CDM project, but it will compete with other cheaper projects. ETS needs the offsetting of emissions and the creation of a framework that ETS and DACCS can be incorporated. Governments could procure DACCS by entering into multi-year CfDs with private developers. These contracts would set a price for one tonne of CO_2 removal, then pay developers the difference between that price and what they can obtain from the market [279]. The recent Inflation Reduction Act of 2022 has raised the tax credit of the 45Q legislation from 50 $\$\cdot t_{CO_2}^{-1}$ to 85 $\$\cdot t_{CO_2}^{-1}$ for storage and from 35 $\$\cdot t_{CO_2}^{-1}$ to 60 $\$\cdot t_{CO_2}^{-1}$ for utilization [280]. For effective legislation, tax credits have to be increased and DACCS costs will reduce drastically. In the US, the Inflation Reduction Act of 2022 has set a tax credit for DAC of \$180 $\$\cdot t_{CO_2}^{-1}$ for storage and \$130 $\$\cdot t_{CO_2}^{-1}$ for utilization, and reduced the DAC facility capacity required to qualify from 100,000 tons to 1000 tons [281]. In Canada, an investment tax credit rate has been set as 60% for investment on DAC equipment for projects involving CO_2 storage geologically or in concrete [282]. Similarly, Meckling et al. [283] suggested that policy implementation for advanced DAC remained difficult to be achieved due to their high cost and the limited CO_2 market demand. Economic studies of DAC estimate a wide cost range starting at 100 up to 1000 \$ per tonne of carbon removed. Therefore, they suggest that setting such high carbon prices seems to be politically unrealistic [283]. CO_2 demand is nowadays mostly associated with EOR and it is projected to be very limited for CO_2 utilization. A key obstacle for the development and deployment of CO_2 removal, e.g., DAC is that existing carbon pricing mechanisms do not reward negative emissions. In fact, many experts have already highlighted this issue and proposed solutions that assume accounting based on storage, rather than emissions [284, 285]. Necessary incentives for DACCS up-scaling should be realized.

There have been approximately 19 DAC plants all over the world, which can capture CO_2 by more than 0.1 $Mt\cdot year^{-1}$ according to IEA report [286]. In order to promote commercialization of DAC technologies for further development, numerous countries are specifying series of policies. For example, US Department of Energy (DOE) has launched Carbon Negative Shot—its first major effort in CO_2 removal [287]. Carbon Negative Shot is the all-hands-on-deck call for innovation in technologies and approaches that will remove CO_2 directly from the air with durably storage or in products, for less than \$100 per net metric tonne of CO_2-equivalent. UK Department for Business, Energy and Industrial Strategy (BEIS) has announced a competition with 24 projects selected for Phase 1 of DAC and other GHG removal technologies in 2021 [288]. Up to £100 million would be provided to develop technologies that enable the removal of GHG from the atmosphere in the UK, which include DAC technologies. Phase 2 of the competition will take forward the most promising designs from Phase 1. The projects that specifically contains DAC technologies are listed in Table 10. It can be observed that most of these projects implement further conversion of captured CO_2. Additional values of by-products can significantly reduce total cost of DAC industry chains.

Table 10
DAC projects from UK BEIS [288].

Projects	Objectives	Main participants
DAC powered by Nuclear Power Plant	Uses low-temperature steam from the turbine in Sizewell C power plant; Adsorption or absorption; can be scaled up to capture 1.5 million tonnes of CO_2 per year	Sizewell C, University of Nottingham, Strata Technology, Atkins and Doosan Babcock
DRIVE (Direct Removal of CO_2 through Innovative Valorization of Emissions)	A new DAC technology projected by Mission Zero to have 75% lower costs and energy footprints; designed to have 365 tonnes per year with support from Optimus; permanently store CO_2 with building aggregate production from O.C.O. Technology	Mission Zero Technologies, Optimus (Aberdeen) and O.C.O Technology
Project Dreamcatcher	Focuses on the optimization and UK deployment of Carbon Engineering's proven DAC technology; research and develop an alternative to natural gas to power the calciner	Storegga, Carbon Engineering, Petrofac Facilities Management, the Universities of Cambridge and Edinburgh
SMART-DAC (Sustainable membrane absorption & regeneration technology for DAC)	Delivers CO_2 capture significantly cheaper than state-of-the-art; based on membrane and absorption technology; design for a pilot plant with a capacity of 100 $t\cdot year_{CO_2}^{-1}$; can permanently store CO_2 and produce valuable by-products	CO_2CirculAir; OGTC; Heriot-Watt University Research Centre for Carbon Solutions, Process Design center, and Optimus
DAC and mineralization	DAC and conversion into mineral by-products used as construction materials; develop a pilot design, a costed plan and produce a model showing how to capture 50,000 $t\cdot year_{CO_2}^{-1}$.	Cambridge Carbon Capture Ltd (CCC)
Environmental CO_2 Removal	CSIRO have world-leading amine technology commercialized for flue gas capture; deliver a pilot system in the U.K., capable of removing over 100 $t\cdot year_{CO_2}^{-1}$.	Rolls-Royce and The Commonwealth Scientific and Industrial Research Organization (CSIRO)
Modular DAC	Develops a modular DAC design; captured CO_2 will be converted to plastics, building products and carbon-neutral transportation fuels	Carbon Neutral Petrol

In addition to policies from governments, projects proposed by commercial companies are also gathering momentum [289]. According to WRI 2022, currently, DAC technology is still in the large-scale and prototype phase, which means that it is not yet ready for full commercial deployment. However, this also means there is an opportunity to improve the performance by developing novel sorbents to reduce costs, which is the objective of this work to know what we have achieved and what we can do further. Three main DAC companies have pilot plants to process significant amounts of CO_2 from the atmosphere [290–293], i.e., Carbon Engineering from Canada, Climeworks from Switzerland and Global Thermostat from the U.S. An overview of these three companies and their existing and planned DAC plants is summarized in Table 11. DAC technology from Carbon Engineering captures CO_2 from air in a closed chemical loop; K^+ loop and Ca^{2+} loop are both used for the regeneration of $CaCO_3$. The required temperature for calcine step is up

Table 11
Summary of the existing and planned DAC plants [169,290,294-299,301].

Company name	Partners	Plant type	Status	Plant location	Required temperature (°C)	CO_2 Removal Capacity (t CO_2·year^{-1})	CO_2 market application if commercialized	Date of operation
Climeworks	Several	14 Pilot and Commercial Plants	Operational	Across Europe (e.g., Switzerland, Italy, Iceland)	Up to 900	Total of 2000	CDR services; renewable fuels & materials; food, beverage & agriculture	2015–2020
	Carbfix, ON Power	Commercial Plant	Under Construction	Hellisheidi, Iceland		4000	CDR services to corporations (e.g., Microsoft, Shopify, Audi) and individuals (permanent storage via mineralization)	Q2 2021
Carbon Engineering	None	Pilot plant	Operational	Squamish, British Columbia	80–100	350	Not commercial	2015
	None	Innovation Centre	Under Construction	Squamish, British Columbia		1500	Shopify and Virgin will pay CE for CO_2 capture and storage	2021
	1PointFive, Oxy Low, Carbon Ventures	Commercial Plant	Pre-construction	Permian Basin, Texas		1000,000	EOR and geologic storage (planned)	Mid-2020s (goal is 2024)
Global Thermostat	None	Pilot plant (DAC+flue)	Not currently operating	Menlo Park, California	85–100	10,000	Not commercial	2013
	None	Pilot plant	Not currently operating	Huntsville, Alabama		4000	Not commercial	2019
	Large Corporates	Two commercial plants	Under Construction	Sapulpa, Oklahoma		2000 each	CO_2 to fuels; CO_2 as industrial gas	Late 2021

to 900 ℃, which indicates a large amount of thermal energy demand. Details of this technology have been discussed in Section 5. Some of the captured CO_2 will be used for oil production in EOR, or converted to fuels [294]. Nevertheless, the combustion process will inevitably release lots of CO_2 into the atmosphere, which makes this approach not entirely carbon negative [290]. Moreover, Carbon Engineering is proceeding the engineering and design of the world's largest DAC and sequestration facility. Climeworks adopts adsorption technology for DAC using highly selective filter materials [295]. Air flows into the collector and CO_2 is captured on the surface of the adsorbent. Then, the collector is closed and temperature is increased to 80–100 ℃ to release CO_2. Orca plant which is their pilot plant, utilizes the renewable zero-carbon geothermal energy from ON Power's Hellisheiði geothermal power plant in Iceland [296]. The captured CO_2 is injected into the basaltic rock and crystalized into a mineral that permanently holds it. The current cost is as high as up to 1000 $\$\cdot t_{CO_2}^{-1}$ and expected to reduce to 200–300 $\$\cdot t_{CO_2}^{-1}$ in 2030 and 100–200 $\$\cdot t_{CO_2}^{-1}$ in the middle of 2030 [297]. Global Thermostat uses customised equipment and proprietary amine-based chemical sorbents bonded to porous honeycomb ceramic monoliths to selectively remove CO_2 from air [298]. The captured CO_2 is then stripped off and collected using low-temperature steam around 85–100 ℃ at little or no cost. The plants are completely modular, which could capture 50,000 tonnes CO_2 per year. Global Thermostat produces CO_2 at the lowest cost in the industry, using energy provided by residual heat rather than electricity. Global thermostat has already built two pilot facilities, each with the capacity to remove 3000–4000 tnes of CO_2 per year [299]. Also, more start-up companies are developing novel DAC systems. For example, Carbon Collect Ltd has developed a column shaped MechanicalTrees™, 10 m height, to capture CO_2 with sorbent tiles that extend and retract and arranged in clusters of 12 trees expected to capture 1 tonne CO_2 per day [300].

7. Conclusions and perspectives

From this holistic review, recent progress in sorption DAC with CO_2 utilization is closely examined. By using favourable sorbents for DAC that combine working processes, capturing CO_2 directly from air can slow down global warming with a significant amount of CO_2 product to be utilized. Further conversion of captured CO_2, TEA and LCA researches are also summarized. The latest developments and some key remarks are discussed as follows.

1. The choice of sorbents for DAC always focuses on indicators, e.g., adsorption capacity, regeneration energy, working temperature, gas selectivity, cost, thermal and chemical stability, etc. Amongst solid sorbents, zeolites and amine modified materials are currently proposed to be the most appropriate candidates for practical DAC applications. Future research on adsorbents could focus on CO_2 and H_2O co-adsorption mechanism to develop the next generation materials by balancing energy penalty, cyclic performance and cost. For large DAC applications using liquid absorbents, the main barriers of high regeneration energy and oxidative degradation need to be overcome. Further investigation could be focused on water-lean or water-free absorbent for the improved working performance.

2. After selecting sorption materials, it is essential to determine an appropriate working process that fulfils the excellent performance of DAC. Compared with PSA or VSA that is beneficial for flue gas carbon capture, TSA is a good candidate for DAC which can also be integrated with renewable heat source. Moreover, TVSA is currently the most suitable in applications that require almost pure CO_2, e.g., synthesis processes where raw gas has high purity. Besides, TVSA reduces regeneration temperature and vacuum pressure which could prevent degradation, reduce energy demand and increase energy efficiency. For chemical absorption, the BPMED process is recommended which shows great potential of working efficiency by integrating renewable energy.

3. Carbon conversion technologies that require the feedstock with

relatively low CO_2 concentration are desirable for utilization of CO_2 captured from DAC. It mainly includes in-situ CO_2 conversion into fuels and chemicals, the cultivation of microalgae and bacteria. It demonstrates that fuel synthesis may be the most promising utilization method in the coming decades. The required raw materials can be readily obtained by co-extraction of CO_2 and H_2O from ambient air. Synthesized fuels from CO_2 should be integrated with renewable energy for low energy inputs which can utilize existing infrastructure. CO_2 emissions from vehicles and airplanes driven by these fuels are further recycled via DAC for continuous production of fuels, thus a closed carbon cycle is formed to reduce CO_2 concentration in the air.

4. Feasibility of DAC has been verified using quite a few TEA studies. However, DAC technologies are not mature enough to possess standard evaluation model based on reasonable energy and cost demand in large-scale applications which inevitably results in a large deviation. For most of the optimal cases, the long-term cost of CO_2 removal ranges 43–95 $\$\cdot t_{CO_2}^{-1}$. But this value could be increased up to 863 $\$\cdot t_{CO_2}^{-1}$ under different scenarios. Similar situation happens to LCA researches based on different approaches that deal with life cycle inventories and data sources. Current literature on LCA indicates that DAC could achieve lifecycle carbon efficiencies of 85–95% when integrated with renewables which can be improved up to 800% if compared with that using fossil fuel electricity. It is urgent for TEAs and LCAs to set standard guidelines and benchmarks for DAC in the near future.

To conclude, DAC can be a useful tool to mitigate carbon emissions from distributed carbon sources and is expected to reduce atmospheric CO_2 concentration. Future DAC studies should not only focus on capturing CO_2 in the places with low carbon intensity but also with high CO_2 intensity, e.g., office building, hospital, farms in which CO_2 concentration is usually higher than 500 ppm [150,302,303]. Various resources, e.g., solar, geothermal or condensation heat from air conditioner could be integrated for the regeneration process of sorbents [304–306]. This would be attractive to researchers, academics, industry professionals and related manufactures, as well as renewable energy sector. But sorbents, thermal cycles, working processes, carbon utilization and system-scale investigation need to be further explored for its ultimate industrialization. DAC should be treated not only as a stand-alone technology but as a component of a practical large-scale industrial chain. The overall analyses and explorations for DAC are necessary in an industry that is expected to achieve huge potential. To promote commercialization of DAC technologies, government policies prefer to be favourable which could stimulate commercial companies.

Declaration of Competing Interest

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

Data availability

No data was used for the research described in the article.

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