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Analytical review of the current state of knowledge of adsorption materials and processes for direct air capture

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ABSTRACT

Significant research interest has been directed towards the deployment of direct air capture (DAC) as a net-negative CO₂ emissions technology to help limit global temperature rise to below 2 °C. The scope of this review is to outline the advancement of adsorption-based DAC technologies, as well as to highlight the still-existing data gaps, for both materials' development and process design in the period 2016 – 2021. On the material side, we highlight the available and missing data on adsorbent properties in relation to what is needed for process modelling and design. We cover material densities, textural properties, thermal properties, adsorption isotherms (i.e. CO₂, N₂, O₂, H₂O), adsorption kinetics, and adsorbent stability towards humidity, oxidation, and cycling. On the process side, we provide a detailed look at key process studies conducted in the same time frame by considering the trade-offs to be expected in the design of the adsorption-based DAC process. We focus on process configuration and contactor design, desorption processes, and the need for systematic reporting of key performance indicators to allow for accurate comparisons and benchmarking. Throughout the review, we identify the lack of synergy between material and process development which must be addressed to advance the field of DAC by adsorption.

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1. Introduction

At the 2015 Conference of Parties (COP21) in Paris, 196 countries signed an agreement to limit global warming to below 2 °C when compared to pre-industrial levels (1850–1900). Since then, anthropogenic carbon dioxide (CO₂) emissions have continued to rise leading to a global mean surface temperature increase of ~1.1 °C (NASA, 2022). Modelling results presented in the recent Intergovernmental Panel on Climate Change (IPCC) report (Assessment Report 6) (Arias et al., 2021) discuss different Shared Socio-economic Pathways (SSPs) that forecast possible trends of greenhouse

gas (GHG) emissions and the subsequent impact on the global mean surface temperature. Two scenarios – SSP1–2.6 and SSP1–1.9 – predict a surface temperature increase lower than 1.5 – 2 °C before 2100 (relative to 1850–1900 levels) by considering the implementation of net-negative CO₂ emissions technologies (NETs). NETs include afforestation, Bioenergy with Carbon Capture and Storage, Soil Carbon Sequestration, and Direct Air Capture with Carbon Sequestration (DACCS). Each technology presents distinct technical, socio-economic, and environmental strengths and challenges, and a mixed technology portfolio is needed to meet the temperature increase target (Minx et al., 2018). Among NETs, DACCS offers long-term carbon storage and allows the amount captured to be accurately measured.

DAC presents a unique challenge when compared to post-combustion carbon capture due to its ultra-dilute nature (419 ppm, 0.042 vol% in air) and the inherent variability of

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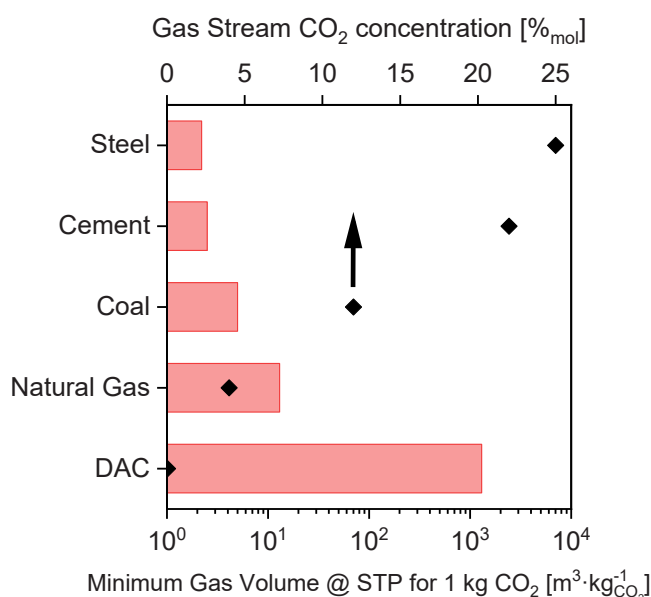


Fig. 1 – The DAC Challenge. Volume of gas (at STP, bar chart) containing 1 kg CO₂ for CCS applications with different inlet process stream compositions (mol%, symbols). Flue gas compositions used in calculations from Bui et al. (2016), Danaci et al. (2020) and Markewitz et al. (2019).

ambient conditions that the process is subject to. To visualise this challenge, we compare in Fig. 1 the volume at standard temperature and pressure (STP) of air that contains 1 kg of CO₂ with its flue gas counterpart originating from different industrial sources. By assuming 100% of CO₂ is captured, 1300 m³ of air would need to be processed as opposed to 13 m³ of gas for a natural gas flue gas stream.

Another challenge for DAC systems is that CO₂ must be selectively isolated from the air in the face of wide variations in key variables such as temperature and relative humidity (RH). As shown in Fig. 2, the conditions at which the DAC unit must operate can vary over a very large range – from 30% to 90% RH, while monthly average temperatures can go below 0 °C and reach almost 30 °C. Within the same geographical location, the average temperature in a year can vary by almost 25 °C. The importance of temperature and humidity conditions is investigated in detail in a review by Kong et al. (2022).

Despite the challenges of DAC, commercial DAC initiatives are being established around the world with the aim of demonstrating the feasibility of processes and business models (Erans et al., 2022). These initiatives are largely limited to a small number of start-ups, with Climeworks, Carbon Engineering, and Global Thermostat presenting the most mature operations (see Table 1). The DAC technologies employed by these emerging companies rely on adsorption or absorption processes. The CO₂ recovered by the DAC plants in Table 1 is either stored or utilised in short term CO₂ removal applications, such as greenhouse fertilisation. Assuming all the operational plants listed in Table 1 are running at their reported annual capacity, the current DAC CO₂ capture capacity amounts to ~17 kt_{metric} year⁻¹. To put this number into perspective, in the IPCC Assessment Report 6, SSP1–1.9 is based on overall net-negative emissions from 2058 reaching 2.5 Gt CO₂ year⁻¹ by 2065 and 14 Gt CO₂ year⁻¹ by 2100. The capacity of operational DAC plants is currently

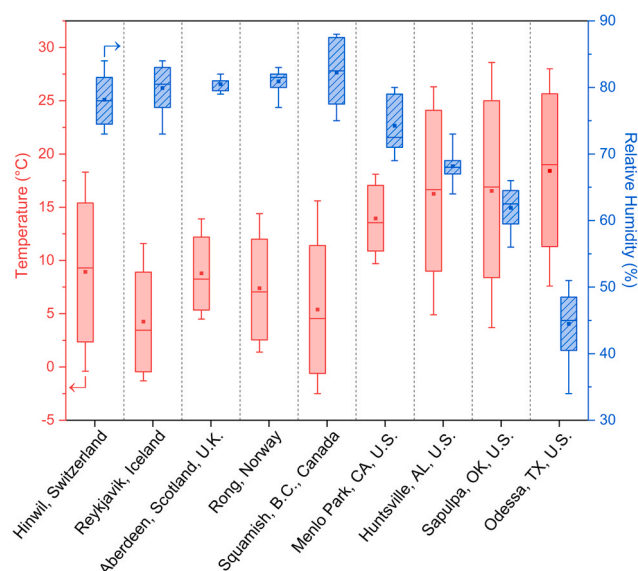


Fig. 2 – Overview of the monthly average temperature and relative humidity distribution of the different DAC project locations listed in Table 1, based on data collected between 1999 and 2019 by the European Centre for Medium-Range Weather Forecasts (ECMWF) (CLIMATE-DATA.ORG). Box edges represent the 25th and 75th percentile, whisker edges represent the minimum and maximum data points, the solid line through the box represents the median, and the filled square symbol represents the mean. Data for Reykjavik, Aberdeen, Rong and Odessa were collected in place of Hellishied, North East Scotland, Kollsnes region, and Permian Basin, respectively.

only 0.0007% of the 2065 removal quantity for SSP1–1.9. Hence, sustained, significant, and consolidated efforts are required for the development and scale up of DAC processes.

Among the current DAC companies, Carbon Engineering utilises absorption and uses an aqueous hydroxide (potassium hydroxide, KOH), which is regenerated in a calciner at 674 °C (Keith et al., 2018). Amine-based absorption processes (e.g., monoethanolamine (MEA) solutions) would offer milder regeneration conditions (~120 °C) (Kiani et al., 2020; Barzagli et al., 2020), however, are not yet commercially established for DAC. Adsorption-based processes also allow milder regeneration conditions (~100 °C) and, unlike absorption processes, do not suffer from water losses (Kiani et al., 2020). Both Climeworks and Global Thermostat use an amine functionalised polymer as an adsorbent, but employ different methods for adsorbent regeneration, i.e. temperature vacuum swing (TVSA) and steam assisted temperature swing (S-TSA), respectively. Overall, in humid environments, MEA-based absorption processes could perform well, but may require excessive water makeup at low relative humidity conditions. Adsorption processes do not face this issue, but they must contend with water co-adsorption in humid environments. Although water co-adsorption can improve CO₂ uptake for amine-based adsorbents (Young et al., 2021), it can also increase the energy required for regeneration (desorption). At this stage, the energy trade-off between aqueous and solid amine-based DAC processes is unclear.

Our review, which encompasses over 110 publications, aims to provide readers with an update on adsorption-based DAC adsorbent materials and processes developed in the

Table 1 – Overview of operating DAC plants and planned projects.

Capture Technology	Company (project name)	CO ₂ Capture Capacity (kt _{metric} year ⁻¹)	CO ₂ Fate	Start Date	Status	Location	Ref
Adsorption Temperature vacuum swing adsorption (TVSA)	Climeworks (Capricorn)	9	Utilisation	2017	Operational	Hinwil, Switzerland	(Beuttlir et al., 2019; Climeworks, 2022a)
	Climeworks (Arctic Fox)	0.05	Storage	2017	Operational	Hellisheidi, Iceland	(Climeworks, 2022b)
	Climeworks, Carbfix, ON power (Orca)	4	Storage + Utilisation	2021	Operational	Hellisheidi, Iceland	(B. P. C.-D. A. C. A. Council, 2021; Climeworks)
Adsorption Steam Temperature Swing Adsorption (S-TSA)	Climeworks + others	1.05 ^a	Utilisation	–	Operational	Italy, Switzerland, Iceland	(B. P. C.-D. A. C. A. Council, 2021; B. Policy, 2021)
	Global Thermostat	0.5	–	2010	Unknown ^b	Menlo Park, California, U.S.	(B. P. C.-D. A. C. A. Council, 2021; Chichilnisky, 2016)
	Global Thermostat	1	–	2013	Unknown ^b	Menlo Park, California, U.S.	(B. P. C.-D. A. C. A. Council, 2021; Chichilnisky, 2016)
Absorption	Global Thermostat	1 ^c	–	2018	Non-Operational	Huntsville, Alabama, U.S.	(Rathi, 2021; Peters, 2019)
	Carbon Engineering	0.219	Utilisation	2015	Operational	Squamish, B.C., Canada	(Viebahn et al., 2019)
	Carbon Engineering Innovation Centre	1.5	Utilisation	2021	Under commission	Squamish, B.C., Canada	(B. P. C.-D. A. C. A. Council, 2021; C. Engineering, 2022a)
	Carbon Engineering, 1PointFive, Oxy Low Carbon Ventures	1000	Storage + Utilisation	2024	Planned	Permian Basin, Texas, U.S.	(C. Engineering, 2022b; Davis, 2021; G. C. Institute)
	Carbon Engineering, Storegga	500–1000	Storage	2026	Planned	North East Scotland, U.K.	(C. Engineering, 2022c)
	Carbon Engineering, Carbon Removal, Oxy Low Carbon Ventures	500–1000	Storage	–	Planned	Kollsnes region, Norway	(C. Engineering, 2022d)

-: indicates information was unavailable

a: calculated by subtracting 900 and 50 from the total capacity of 14 Climeworks plants in 2017, reported as 2000 t

b: Ref (Chichilnisky, 2018) reports that the plants are operational, but ref (B. P. C.-D. A. C. A. Council, 2021) suggests that at least one of the two is no longer operational

c: Original goal by Global Thermostat was 4000 t / year

Table 2 – Summary of adsorbate and adsorbent properties required in the modelling of an adsorption-based DAC process. Other properties will influence the design of the process but do not act as direct value inputs into the process modelling, e.g. textural properties and thermal stability.

Material Property	Process Modelling
Equilibrium isotherms considering co-adsorption for ALL adsorbing components in ambient air at multiple temperatures	Determining total amount adsorbed and desorbed
Overall mass transfer coefficient	Determining the rate of mass transfer and adsorption
Density (skeletal, particle, bed)	Determining mass of solid and volume of process contactor required
Porosity (particle, bed) derived from pore volume estimation	Determining total volume of gas in vessel space and mass of adsorbent
Heat capacity (adsorbent and adsorbed phase)	Determining heat required to perform desorption
Heat of adsorption (of all adsorbing components)	Determining required energy input for desorption and process temperature changes
Overall heat transfer coefficient (related to thermal conductivity of adsorbent)	Determining rate of heat transfer in material

period 2016 – 2021. On the material side, we focus on data availability and data gap of adsorbent properties in relation to what is required for deployment of an adsorption technology. Table 2 highlights such properties and how they inform mass and heat transfer, and ultimately process performance. We include to the best of our abilities all candidate DAC adsorbents developed in the reviewed period, and summarise the material properties and equilibrium adsorption data obtained. On the process side, we focus on adsorber/contactor and process designs. We provide a detailed look at all key process studies conducted in the same time frame and offer suggestions on decision making and trade-offs in adsorption-based processes. Throughout, we highlight the connections and current data gaps between materials development and process studies. Our review complements past and current reports on DAC. In particular, it updates the adsorption component of the 2016 review by Sanz-Pérez et al. (2016) which covers candidate DAC liquid and solid adsorbents. The 2022 perspective by Kong et al. (2022) recommends future research on DAC to focus on material and process development under sub-ambient and humid conditions. We expand on this by also highlighting the need for synergy between material and process development. For a broader view on DAC, we direct readers to the recent article by Erans et al. (2022) which covers the scientific, engineering, economic, and socio-political aspects of DAC and its role compared to other negative emissions technologies.

2. Material properties

Here, we first review the reported material properties of possible DAC adsorbents studied during the period covered. These properties include: density (skeletal, particle, bed), textural properties (surface area, total pore volume, micropore volume), and thermal properties (specific heat capacity, thermal conductivity, thermal stability). As explained in Table 2, these properties are needed to assess the suitability of a material for DAC applications via process modelling. These data are summarised in Fig. 3, where we have classed

the adsorbents being investigated for DAC into six categories: silicas, metal oxides, metal organic frameworks (MOFs), carbons, zeolites, and polymers. These adsorbents can either be functionalised or unfunctionalised. Functionalisation typically ‘converts’ a physisorbent, which binds adsorbates via weak intermolecular forces, into a chemisorbent, which binds adsorbates through covalent or coordination bonds. Amines are the most common chemicals used for functionalisation, e.g. polyamines and aminosilanes. Primary and secondary amines perform better for DAC adsorption compared to tertiary amines, which require the presence of moisture to ensure significant uptake (Sanz-Pérez et al., 2016). Amines can either be physically impregnated (class 1), covalently grafted to the adsorbent’s surface either by silane linkages (class 2) or via in-situ polymerisation (class 3) (Sanz-Pérez et al., 2016). Carbonate functionalisation can also be used for CO₂ capture, although in this case, adsorption occurs only in the presence of moisture (Rodríguez-Mosqueda et al., 2018). For each material property, we first explain how it can be measured and then discuss the data collected in terms of both their availability and the implications of the values reported.

For perspective on the discussion below related to Fig. 3, we highlight two key points. First, there is currently no benchmark DAC sorbent, which leads to an absence of reference DAC sorbent properties. A convenient benchmark could be an adsorbent used in current DAC commercial processes, yet today, their properties remain proprietary. Second, there also do not exist any calculations of theoretical optimal properties of an “ideal” DAC adsorbent. While a priori possible, building such theoretical framework remains complex, owing to the interdependent nature of the various materials properties.

2.1. Density and mechanical properties

2.1.1. Skeletal density

Skeletal density (ρ_{skeletal}) is defined as the mass of a single particle of adsorbent divided by the volume of the particle without including any open pores. The term particle can

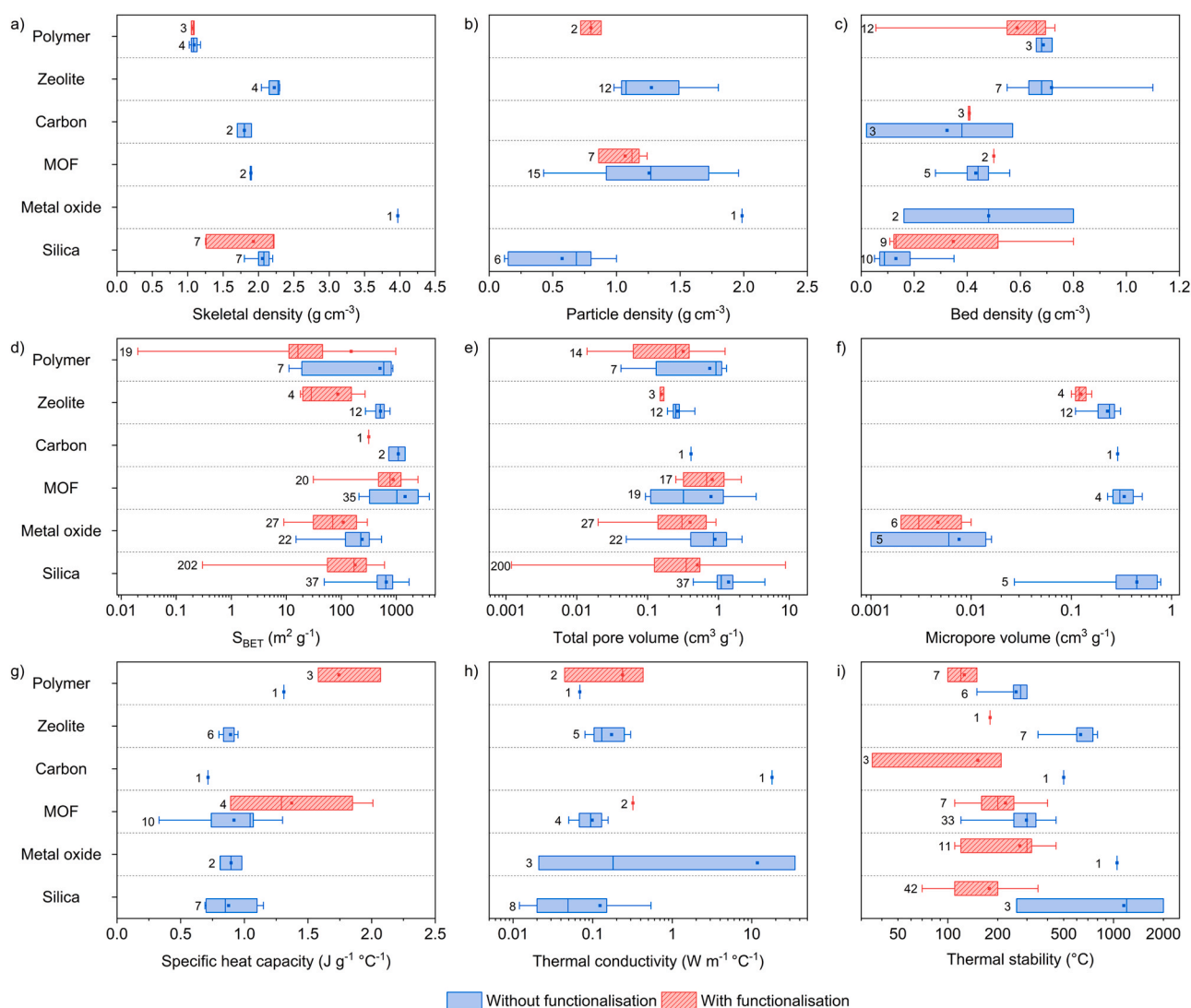


Fig. 3 – Comparison of a) skeletal density, b) particle density, c) bed density, d) BET surface area, e) total pore volume, f) micropore volume, g) specific heat capacity, h) thermal conductivity, and i) thermal stability values between different adsorbent categories, both with and without additional functionalisation. Box edges represent the 25th and 75th percentile, whisker edges represent the minimum and maximum data points, the solid line through the box represents the median, and the filled square symbol represents the mean. Total number of data entries are labelled to the left of each box to better understand the spread of data. All data entries can be found in Tables S1–S6.

refer either to a single powder particle of the adsorbent, or to a single bead or pellet macrostructure. The skeletal density can be measured experimentally using a variety of methods such as helium pycnometry (Nguyen et al., 2019), helium gravimetry (Pini, 2014), or a combination of N_2 adsorption at -196°C and mercury intrusion porosimetry (Azzan et al., 2022). Skeletal density is not always a direct input in process models but is needed to calculate other necessary parameters such as the total adsorbent porosity. While commonly measured for high pressure adsorption experiments, only three DAC specific publications reported skeletal densities and most of the values reported in Fig. 3a were collected from ‘non-DAC’ publications. Overall, the availability of skeletal density is still sparse for adsorbents considered for DAC.

2.1.2. Particle density

Particle density (ρ_{particle}) is defined as the mass of a single particle of adsorbent divided by the envelope volume of the particle, which includes both the open and closed pores. It

can be measured experimentally using mercury intrusion porosimetry (Pini, 2014) or gas pycnometry (Micromeritics, 2001). For unfunctionalised crystalline materials (e.g. MOFs and zeolites), the particle density can be calculated based on the crystalline structure of the materials. For process modelling, the pellet or bead density is needed rather than the density of the powder particle. A higher particle density typically yields a higher bed density, lower porosity, and greater mechanical stability. The particle densities presented in Fig. 3b are mostly for powders except for the polymer materials, which are for a single bead, and some zeolites, which have both powder and pellet densities reported (specified in Tables S1 – S6). Fig. 3b highlights the sparsity of particle density data for most materials except MOFs and zeolites.

2.1.3. Bed density

The bed density (ρ_{bed}) of a porous adsorbent is defined as the mass of the adsorbent divided by the volume of the vessel it occupies. It can be measured by simply filling a container of

known volume with adsorbent and accurately weighing the contents ([Standard Test Methods for Apparent Density, 2017](#)). However, due to the quantity of material needed, typically on the gram scale, this technique is not suited to non-commercial adsorbents. As such, much less data is available compared to other parameters which require less sample mass for measurement, such as the surface area and pore volume. The lower the bed density, the less adsorbent can be placed within the vessel volume, and the lower the volumetric CO₂ adsorption capacity of the bed. However, a higher bed density implies lower adsorbent porosity, which in turn could lead to restricted kinetics. Functionalisation fills the adsorbent pores which thus decreases the adsorbent porosity and increases the bed and particle density. [Fig. 3c](#) shows a rather large span of mean density values, from ~0.10 – 0.70 g cm⁻³. For context, commercial zeolite 13X beads from BASF have a reported bed density of 0.65 – 0.70 g cm⁻³ ([BASF](#)). Approximately half of the bed densities reported in [Fig. 3c](#) are for adsorbents in powder form. However, adsorbents in this form are often impractical to use due to their difficulty to handle at scale and the resulting large pressure drop. Reporting the bed density of shaped adsorbents, such as beads, pellets, fibres, or monoliths, is therefore more useful for process modelling. The choice of the best adsorbent structure depends on the balance of various parameters such as volumetric working capacity, mass transfer, thermal behaviour, and pressure drop. The adsorbent structure selected will also determine the packing porosity in the bed. We direct readers to other sources such as those by [Rezaei and Webley](#) for further information on the pros and cons of different structured adsorbents ([Rezaei and Webley, 2009](#)) and methodologies to compare their performance ([Rezaei and Webley, 2010](#)).

2.1.4. Mechanical stability

Adsorbents with higher mechanical stability can have a longer lifetime, as they are more resistant to vibrational or frictional forces within the bed. The mechanical stability of the adsorbent can be assessed through a variety of mechanical properties, such as the tensile strength, compression strength, or Young's modulus, but can only be done for shaped adsorbents. Although these mechanical properties are not needed for process modelling, they help in appraising the robustness of the material. Assessment of mechanical stability remains rare in the DAC literature as most adsorbents being investigated are in powder form (see [Tables S1–S6](#)). From the remaining studies which involve shaped adsorbents, only four of them report on their mechanical properties. The materials studied were MOF monoliths ([Thakkar et al., 2017](#)), zeolite monoliths ([Thakkar et al., 2016](#)), silica-based fibres ([Sujan et al., 2019](#)), and polymer fibres ([Armstrong et al., 2018](#)).

2.2. Textural properties

2.2.1. Surface area

The surface area of an adsorbent is traditionally obtained by collecting N₂ isotherms at –196 °C and extracting the information using the Brunauer-Emmett-Teller (BET) method

([Brunauer et al., 1938](#)). While this is the most common approach seen in the reviewed DAC literature, we note that this adsorbate does not always provide accurate measurements due to the quadrupole moment of N₂ and possible diffusional limitations in microporous materials at –196 °C. We direct readers to the article by [Thommes et al. \(2015\)](#) for a more detailed explanation. Some publications have also reported the Langmuir surface area as noted in [Tables S1–S6](#), but these were not included in [Fig. 3d](#), where we only report the BET surface areas (S_{BET}). Surface area is a parameter which largely influences the adsorption capacity of a material. Although surface area is not a direct input parameter for process modelling, it remains one of the most commonly reported parameters in materials papers. The larger the surface area, the higher the total gas uptake. This inevitably leads to a reduction in CO₂ selectivity as the uptake of N₂, O₂, H₂O, and all other gases present in the atmosphere increases. Supports with larger surface areas can accommodate higher functionalisation loadings via grafting, which can increase the adsorbent's CO₂ capacity. As seen from [Fig. 3d](#), surface areas span a large range depending on the material and functionalisation typically decreases an adsorbent's surface area, sometimes by over two orders of magnitude.

2.2.2. Pore volume

The total pore volume (V_{tot}) influences many other material characteristics of the adsorbent. The pore volume of adsorbents is often measured using N₂ adsorption at –196 °C, though as stated in the previous section, this may not always be the most appropriate adsorbate to use. The methods employed to extract the pore size information, such as density functional theory (DFT) ([Walton and Quirke, 1989](#); [Lastoskie et al., 2002](#)), Horvath-Kawazoe (HK) ([Horváth and Kawazoe, 1983](#)), or Barrett-Joyner-Halenda (BJH) ([Barrett et al., 2002](#)), are only reliable in the micropore (pore diameter < 2 nm) and/or mesopore (pore diameter 2 – 50 nm) range. For macroporous materials (pore diameter > 50 nm) such as polymeric resins, the use of N₂ – 196 °C adsorption alone would lead to an underestimation of the total pore volume. In these cases, other methods capable of accurate measurements in the macropore region, such as mercury intrusion porosimetry, should be used in conjunction with N₂ – 196 °C adsorption to obtain a complete pore size distribution ([Azzan et al., 2022](#)). The total pore volume of the adsorbent is needed in process modelling to calculate the total adsorbent porosity. A higher pore volume implies a higher porosity, which in turn leads to lower bed and particle density, and potentially lower thermal conductivity ([Taddei and Petit, 2021](#); [Babaei et al., 2017](#)) and higher heat capacity ([Taddei and Petit, 2021](#); [Wieme et al., 2019](#)), the impacts of which are discussed in their respective sections. The higher the total pore volume, the greater the potential for functionalisation loading. For chemisorbents, this will increase the CO₂ saturation capacity of the adsorbent. However, as seen in [Fig. 3e](#), functionalisation can severely reduce the pore volume of an adsorbent. Comparing the data entries in [Fig. 3e](#) vs [Fig. 3f](#), we see that functionalisation often eliminates the presence of micropore volume (V_{micro}) due to pore filling.

This could severely limit gas diffusion within the adsorbent and result in poor kinetics for the adsorption process.

2.3. Thermal properties

2.3.1. Heat capacity

The specific heat capacity (C_p) is the amount of heat needed to produce a unit change of temperature in a unit mass of the adsorbent. This can vary with temperature and gas uptake, and can be measured using differential scanning calorimetry (Mu and Walton, 2011; Standard Test Method for Determining Specific Heat Capacity, 2018). For a temperature swing adsorption process, an adsorbent with a lower C_p will require less energy to be heated to a high temperature for desorption, leading to lower operational costs. Similarly, for the same energy input, an adsorbent with a lower C_p can be heated to a higher desorption temperature, thus increasing the working capacity. However, adsorbents with low C_p may also undergo a larger temperature swing during adsorption due to the released exothermic heat, which would reduce the amount adsorbed at and thus the overall working capacity. Materials with higher porosity tend to have higher heat capacity (Taddei and Petit, 2021; Wieme et al., 2019). Although this parameter is needed for process modelling, it is a massive data gap in the DAC literature, and is rarely reported in materials papers. Of all the DAC papers reviewed in Tables S1–S6, only three reported heat capacity values. All other values shown in Fig. 3g were either found from DAC process papers or other non-DAC articles. To provide perspective on the reported values, the heat capacity of commercial zeolite 13X is $\sim 0.8 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$ (Chan et al., 2015), while that of a 20 wt% MEA-based aqueous solvent is $\sim 3.9 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$ (Weiland et al., 1997). We note that all values reported in Fig. 3g and Tables S1–S6 are for pristine adsorbents, i.e. not loaded with CO_2 and/or other species. The temperature ranges of the reported heat capacities are also indicated in Tables S1–S6 when available.

2.3.2. Thermal conductivity

Thermal conductivity (κ) is a measure of an adsorbent's ability to conduct heat. It can vary with temperature and is often determined theoretically rather than measured experimentally (Taddei and Petit, 2021). A higher thermal conductivity is desirable for adsorption if the system is being operated isothermally, where heat needs to dissipate through the adsorbent and out of the bed. However, for adiabatic operation, lower thermal conductivity would be preferable to minimise the increase in the adsorbent temperature during adsorption, which would decrease the working capacity. For desorption, a higher thermal conductivity is desirable as heat can diffuse faster through the adsorbent when the bed is heated, thus increasing productivity. We note that the contactor/absorber design can compensate to some extent the low thermal conductivity of an adsorbent. Adsorbents with lower porosity tend to have higher thermal conductivity (Babaei et al., 2017). Like heat capacity, this parameter is needed for process modelling but there is limited data available for investigated DAC adsorbents. The data entries in Fig. 3h were found in DAC

process papers or other non-DAC articles. The temperature ranges of the reported thermal conductivities are indicated in Tables S1–S6 when available. As seen in Fig. 3h, unmodified metal oxides such as alumina and semimetals such as activated carbon (in monolith form), respectively, conduct heat well and have high thermal conductivities ($35 \text{ W m}^{-1} \text{ }^\circ\text{C}^{-1}$ (Vasheghani et al., 2011) and $18 \text{ W m}^{-1} \text{ }^\circ\text{C}^{-1}$ (Rodriguez-Mosqueda et al., 2018), respectively), while materials such as silica and MOFs have relatively poor thermal conductivities ($< 0.5 \text{ W m}^{-1} \text{ }^\circ\text{C}^{-1}$).

2.3.3. Thermal stability

The thermal stability of an adsorbent is the maximum temperature the material can withstand before it starts to degrade, for example due to decomposition of the chemical structure or leaching of some functionalisation compounds. This temperature determines the maximum temperature which can be used during the desorption process, and is typically measured using a thermogravimetric analyser (TGA) either in a N_2 or air environment. To be viable for most commercialised DAC processes, adsorbents will need to be thermally stable up to at least $80 \text{ }^\circ\text{C}$ (Fasihi et al., 2019) to withstand the regeneration procedure. For unfunctionalised materials, metal oxides, silicas, zeolites, and carbons have high thermal stability above $500 \text{ }^\circ\text{C}$, while polymers and MOFs exhibit moderate thermal stability between $100 \text{ }^\circ\text{C}$ and $500 \text{ }^\circ\text{C}$. Once adsorbents are functionalised however, the thermal stability depends on the functionalisation compound, and thus functionalisation typically lowers the thermal stability of an adsorbent owing to the organic nature of the compounds that are commonly used for functionalisation. Functionalisation carried out via impregnation leads to less stable materials than grafting due to a lack of chemical bonds. As well, functionalised amines of lower molecular weights tend to be more prone to evaporation or leaching. As seen from Fig. 3i and Tables S1–S6, most functionalised materials being considered for DAC exhibit thermal stabilities above $100 \text{ }^\circ\text{C}$. One exception is a study done by Pang et al. (2017), who investigated SBA-15 adsorbents impregnated with small molecule linear or dendritic PEI or PPI which had maximum regeneration temperatures of $70 \text{ }^\circ\text{C}$. Cuesta and Song (2020) also developed carbon black adsorbents immobilized with bovine carbonic anhydrase enzymes that could be regenerated at $35 \text{ }^\circ\text{C}$, but these needed to be refrigerated or frozen for short or long-term storage, respectively. Overall, thermal stability data is available for most of the investigated DAC adsorbents reviewed here, either from the original study or from other sources.

3. Equilibrium adsorption data

An adsorbent for DAC needs to adsorb a high amount of CO_2 and a low amount of other species. This can be challenging as other species such as N_2 , O_2 , and H_2O are in much higher concentrations in air. The adsorption properties for these species should therefore be investigated and are reviewed in the following sub-sections and in Figs. 4 to 6, following the same adsorbent classification adopted in the previous

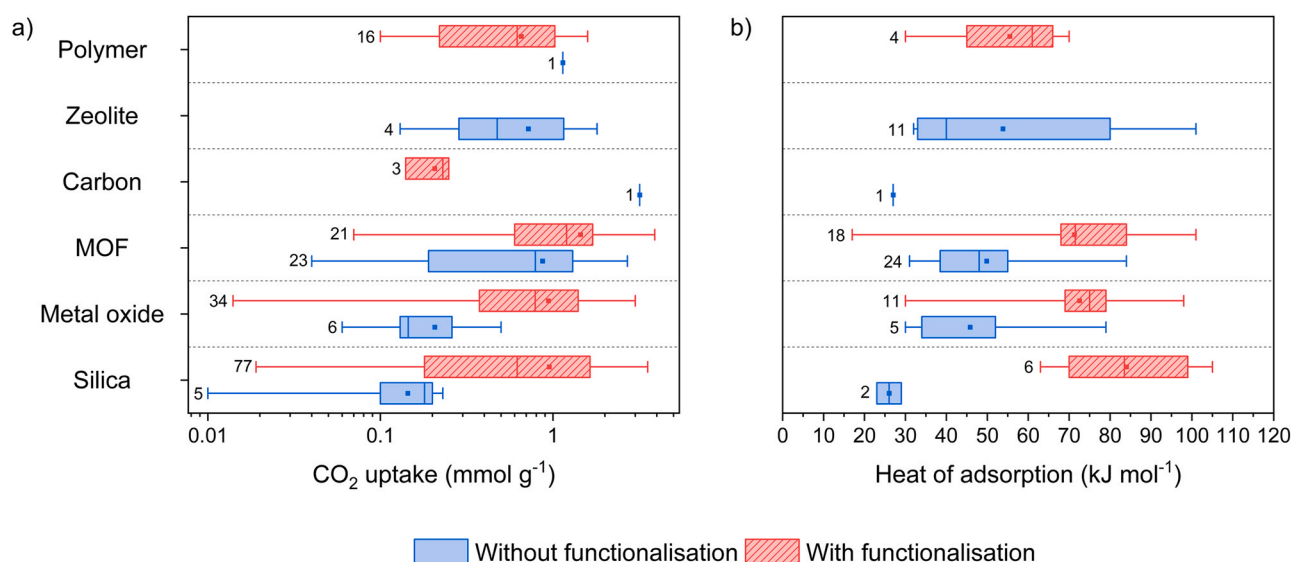


Fig. 4 – Comparison of a) CO₂ uptake values (at concentrations lower than 500 ppm and temperatures between 20 and 30 °C, except for unfunctionalised SBA-15 whose uptake of 0.01 mmol g⁻¹ was measured at 10,000 ppm (entry 4 in Table S7) and b) heat of adsorption values for different adsorbent categories, both with and without additional functionalisation. Box edges represent the 25th and 75th percentile, whisker edges represent the minimum and maximum data points, the solid line through the box represents the median, and the filled square symbol represents the mean. Total number of data entries are labelled to the left of each box. Data entries can be found in Tables S7–S12.

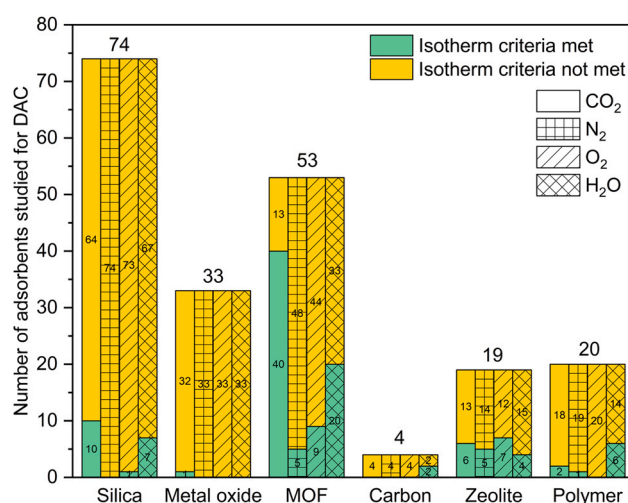


Fig. 5 – Overview of CO₂, N₂, O₂, and H₂O isotherm availability for different classes of adsorbents. For CO₂ and N₂ isotherms, our criterion is met if there are isotherms available at three temperatures and at pressures up to 1 bar. Isotherms that were collected at cryogenic temperatures for CO₂ and N₂ were still included in this count, however we note that these are not suitable for DAC applications and are more useful for porosity characterisation rather than isotherm fittings for process modelling. Indication was made in Tables S7–S12 if this was the case. For O₂ and H₂O isotherms, our criterion is met provided there is an isotherm available, at any temperature and pressure range below 1 bar. An adsorbent was considered to be studied for DAC if a CO₂ uptake between 0.04 vol% and 4 vol% was measured. An adsorbent was not double counted if it was studied by multiple publications, and adsorbents with different loadings of the same functionalisation were counted as just one material. Adsorbents of different structural forms (e.g. powder vs. monolith) were counted as two separate materials. All data entries and their corresponding sources are available in Tables S7–S12. Isotherms were not always found in DAC related publications. Some adsorbents included in the tables which have isotherm data available (e.g. silica gel, γ -alumina, activated carbon) were not considered to be studied for DAC and so were not included in these counts.

section. This analysis focuses almost exclusively on single-component uptake measurements. Multi-component adsorption isotherms are experimentally challenging and time-consuming to measure, and thus are practically non-existent in the DAC literature. The co-adsorption of

multiple gas species can be predicted from the single-component isotherms using approaches such as ideal adsorbed solution theory (IAST) (Walton and Sholl, 2015) or empirically extended binary isotherm equations (Schell et al., 2011).

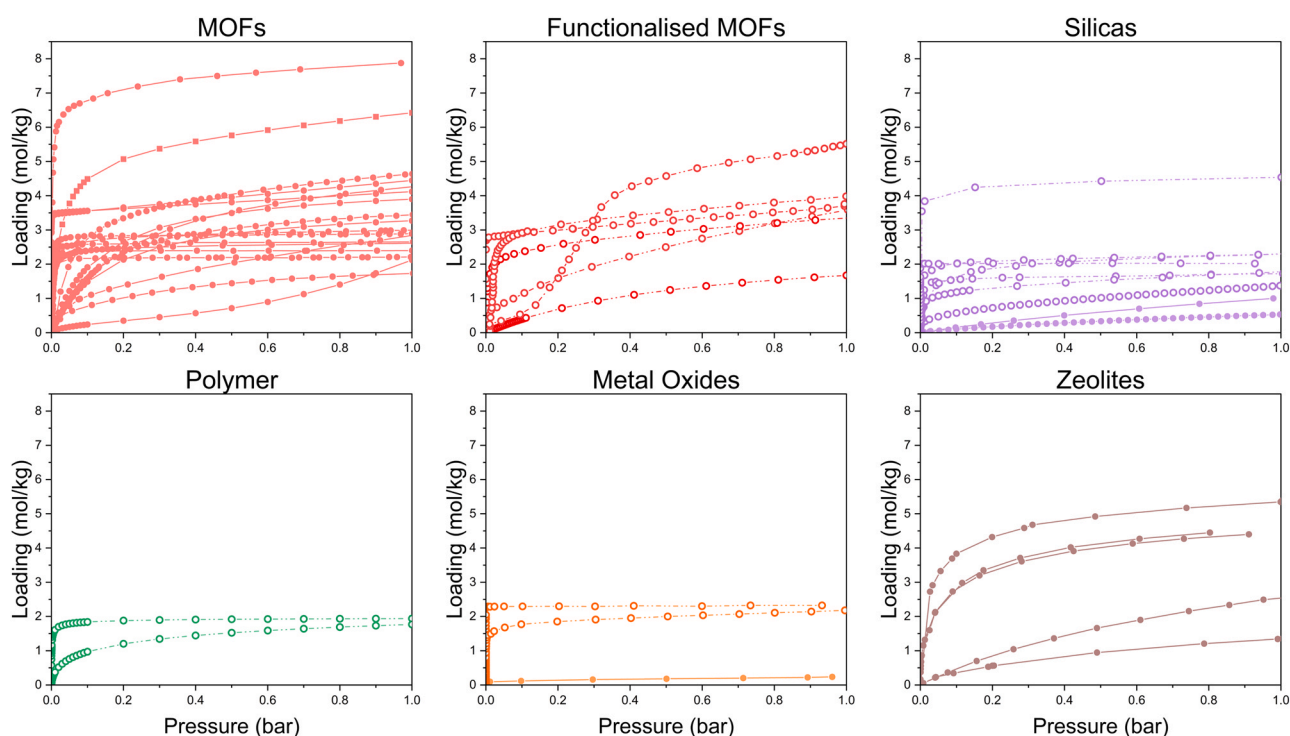


Fig. 6 – CO₂ adsorption isotherms at 25 °C and up to a pressure of 1 bar for materials which have had CO₂ isotherms measured at a minimum of three temperatures as indicated in Tables S7 – S12. Unfunctionalised adsorbents are represented by filled markers / solid lines, and functionalised adsorbents are represented by hollow markers / dashed lines. Data points have either been digitised, plotted using a fitted isotherm model, or plotted from tabulated data.

3.1. CO₂ adsorption

3.1.1. CO₂ uptake at 400 ppm

One of the key requirements for a DAC adsorbent is sufficient CO₂ working capacity, i.e. the difference between the CO₂ uptakes at adsorption and desorption conditions. In this section however, we focus our discussion on CO₂ adsorption uptake, rather than working capacity, to identify trends from available data in materials research. The CO₂ uptake can be measured using volumetric (e.g. commercial volumetric adsorption analyser), gravimetric (e.g. TGA), or dynamic set-ups (e.g. packed bed breakthrough columns) as shown in Tables S7–S12. The data entries shown in Fig. 4a include uptake values up to 500 ppm CO₂ concentrations (see caption for one exception), and between 20 and 30 °C.

As seen in Fig. 4a, the CO₂ uptake by different adsorbents ranges from as low as 0.01 mmol g⁻¹ to over 3.0 mmol g⁻¹. In general, functionalisation of the adsorbent increases its CO₂ uptake compared to its non-functionalised form, and the higher the functionalisation loading, the higher the CO₂ uptake. However, past a certain threshold, pore blockage can occur causing increased diffusion resistance and therefore decreased CO₂ uptake. An example is TEPA-functionalised ZSM-5 and SAPO-34, for which amine functionalisation resulted in blockage of the zeolites' micropores and prevented access to both amine and zeolite binding sites for CO₂ (Thakkar et al., 2017).

It is difficult to distinguish a clear trend in CO₂ uptakes from physisorbents to chemisorbents. For example, some unfunctionalised MOFs have comparable CO₂ uptake to functionalised MOFs. Most of the former are classed as ultramicroporous MOFs, which have pore sizes smaller than 0.8 nm (Kumar et al., 2015). The small pore size and presence of fluorinated ions in MOFs such as TIFSIX-3-Ni (Kumar et al.,

2017), SIFSIX-3-Cu (Shekhah et al., 2014), and NbOFFIVE-1-Ni (Bhatt et al., 2016) yield relatively high CO₂ adsorption uptake (~1.0–1.5 mmol g⁻¹) with the added advantage of lower heats of adsorption compared to the functionalised MOFs. Another example is the Ca²⁺ ion-exchanged 5A type zeolite physisorbent developed by Oda et al. (2021), which shows a high CO₂ uptake of 1.8 mmol g⁻¹ at 400 ppm, attributed to each CO₂ molecule bridging between two Ca²⁺ ions. This uptake is much higher than any of the amine-functionalised zeolites reviewed in Table S11, which were reported for 5000 ppm CO₂ concentrations. Conversely, some functionalised adsorbents have very low CO₂ uptakes (<0.1 mmol g⁻¹) as seen in Fig. 4a. This is often due to insufficient loadings or unsuitable functionalisation. For example, tertiary amines have been shown to have poor CO₂ uptakes in dry conditions, and their uptakes in the presence of humidity may still be lower when compared to primary or secondary amines in dry conditions (Lee et al., 2017). Many of the highest adsorbing materials though are amine-functionalised materials, such as TEPA impregnated SBA-15 (3.4 mmol g⁻¹) (Miao et al., 2021), mmen-grafted Mg₂(dobdc) (3.1 mmol g⁻¹) (Darunte et al., 2018), and hydrazine grafted Mg-MOF-74 (3.9 mmol g⁻¹) (Liao et al., 2016). One exception is the unfunctionalised biochar adsorbent synthesized from sawdust by Kua et al. (2019) which is reported to have a gravimetric CO₂ uptake of 3.2 mmol g⁻¹ at 500 ppm. However, no CO₂ uptake curves were provided nor any material characterisation data.

As mentioned above, we included only CO₂ uptake values up to a concentration of 500 ppm (or 0.05 vol%) in Fig. 4a (see caption for one exception). However, in Tables S7 – S12, we cover publications which report the CO₂ uptake at concentrations up to 4 vol%, which is the threshold for natural gas applications. Although data at these higher concentrations may provide useful insights into the material

performance, effort should be made to conduct experiments at the relevant conditions for DAC as the trends observed may not hold true at 400 ppm CO₂ concentrations.

3.1.2. CO₂ isotherms

A key process model input is the numerical expression of the CO₂ adsorption isotherm, which is obtained by fitting adsorption data collected at constant temperature. The majority of the uncertainty in a process model stems from the parameters of the adsorption isotherm model, but this variability can be reduced by collecting data at several temperatures and over a wide range of temperatures (Ward and Pini, 2022). In Fig. 5, we consider as criterion that at least three temperatures be measured for CO₂ isotherms. Data meeting this requirement remains largely unavailable/unreported for most proposed DAC adsorbents. This data gap is one which requires significant attention. Fig. 6 displays CO₂ isotherms at 25 °C for different materials which have isotherms measured at three or more temperatures and up to 1 bar. We note that materials with the highest CO₂ uptake at 1 bar do not necessarily have the highest uptake at 400 ppm (e.g. zeolites compared to silicas). Rather, materials with steep isotherms in the low-pressure range tend to have high CO₂ uptake at the relevant concentrations for DAC. We also observe that some studies do not collect sufficient isotherm points in the low-pressure range. While gathering this data may be time consuming, it is essential to ensure the isotherm model fitting is accurate in the relevant pressure range. Additionally, even if some publications do collect isotherms at multiple temperatures, they do not always do so up to 1 bar. Although adsorption for DAC occurs at 400 ppm, the adsorption information up to 1 bar becomes relevant for the desorption process, where a CO₂-enriched stream is produced.

3.1.3. Heat of adsorption

The CO₂ heat of adsorption gives an indication of the strength of adsorption between the material and CO₂, and is a necessary input in process models. The higher the value, the more likely the adsorbent will be able to selectively adsorb CO₂ even at dilute concentrations. Yet, a high heat of adsorption also implies higher energy to regenerate the adsorbent and thus higher operating costs. The heat of adsorption is traditionally obtained by measuring three or more CO₂ isotherms spaced 10 °C apart, and by either applying the van't Hoff equation or virial analysis (Rouquerol et al., 1999; Nuhn and Janiak, 2020). For the former, the heat of adsorption at a specific CO₂ loading can be determined from the slope of a plot of $\ln(P)$ vs $1/T$ at a given amount adsorbed, where P is the pressure and T is the temperature. For the latter, the adsorption isotherm data is fitted directly with a virial expansion, generating virial coefficients from which the heat of adsorption can be determined. The isosteric heat of adsorption is the heat of adsorption expressed as a function of the CO₂ loading. At zero loading, one refers to it as the limiting heat of adsorption (ΔH_0). Tables S7 – S12 list the limiting heats of adsorption of candidate DAC adsorbents, along with the heats of adsorption at loadings corresponding to the adsorbents' CO₂ uptake at DAC concentrations if the values greatly differ. All data entries are included in Fig. 4b to show the entire possible range of heat of adsorption values. The general guideline is that materials with heat of adsorption values less than 50 kJ mol⁻¹ are classed as physisorbents and those with higher values are classed as chemisorbents

(Rakić and Damjanović, 2013). As mentioned earlier, unfunctionalised adsorbents are typically physisorbents, and functionalised adsorbents are typically chemisorbents. As seen in Fig. 4b, these classification holds true for most adsorbents. Most amine-functionalised adsorbents exhibit heats of adsorption greater than 70 kJ mol⁻¹, while most unfunctionalised adsorbents exhibit heats of adsorption lower than 50 kJ mol⁻¹.

There remain exceptions to the classification mentioned above. In some cases, unfunctionalised materials are chemisorbents and display high heats of adsorption. Examples include the bare γ -alumina supports, on which CO₂ binds and form bicarbonate and carbonate species on the basic alumina surface (Potter et al., 2017), and the benzotriazolate MOFs with metal hydroxyl sites which allow for CO₂ chemisorption (Bien et al., 2018; Bien et al., 2019; Cai et al., 2020). Some physisorbents, such as the ultramicroporous MOF families of TIFSIX (Kumar et al., 2017), SIFSIX (Shekhah et al., 2014, 2015; Mukherjee et al., 2019), and NbOFFIVE (Bhatt et al., 2016), also exhibit heat of adsorption values bordering either side of 50 kJ mol⁻¹. The alkaline-earth-metal ion-exchanged MFI-type zeolites display even higher heats of adsorption values between 80 and 100 kJ mol⁻¹ due to the strong electrostatic interactions between acidic CO₂ and the M²⁺-O-M²⁺ sites of the adsorbent, where M²⁺ is the alkaline-earth-metal ion (Itadani et al., 2016). Some chemisorbents have uncharacteristically low heats of adsorption. One example is a quaternary ammonium-based polymer adsorbent which features a heat of adsorption of 30 kJ mol⁻¹ due to the presence of moisture to enable CO₂ adsorption (Hou et al., 2021).

General trends are also observed with the heat of adsorption versus CO₂ loading. In most cases, the heat of adsorption is highest at zero loading, and decreases as the loading increases. This pattern implies the presence of heterogeneous CO₂ binding sites, where the stronger sites are filled first. However, some adsorbents maintain a constant heat of adsorption over a wide loading range. This is the case with some members of the SIFSIX family, which according to the authors, suggests the presence of homogenous energetic sites throughout the adsorbent (Shekhah et al., 2015). For other materials, the heat of adsorption increases with loading. An example of this is the diamine-appended Mg₂(dobpdc) MOF developed by McDonald et al., where the increase in heat of adsorption is attributed to cooperative CO₂ adsorption (McDonald et al., 2012, 2015).

Despite the importance of the heat of adsorption, there is still a big data gap in this area, as can be seen in Tables S7–S12, and when comparing Fig. 4a and b. Except for MOFs and zeolites, most adsorbents in all material classes do not have reported heats of adsorption, which corresponds with the data gaps in the CO₂ isotherms.

3.2. N₂ adsorption

N₂ isotherm information should be included in process models for DAC as N₂ accounts for over 78 vol% of the feed gas composition (i.e. atmospheric air). For physisorbents, N₂ is a competitive adsorbate against CO₂ and its uptake will reduce the CO₂ capacity of the adsorbent. For chemisorbents, this is often less of an issue, however some N₂ adsorption can still occur on unfunctionalised surfaces. Even if only a slight amount is adsorbed during the process, performance indicators such as CO₂ working capacity and purity may be impacted. Therefore, like for CO₂, one should collect N₂

sorption isotherms at a minimum of three temperatures to parameterise a suitable adsorption isotherm model and to calculate the N_2 heat of adsorption. Isotherms up to 1 bar should be collected to cover the possible concentration range of N_2 throughout the process. As seen in Fig. 5, it is quite rare to find N_2 isotherms at three temperatures up to 1 bar for DAC adsorbents, even when considering non-DAC related papers. Most commonly, only one isotherm is measured and the impact of N_2 on the process is assumed to be negligible.

3.3. O_2 adsorption

3.3.1. O_2 isotherms

O_2 accounts for over 20 vol% of the gas composition in the atmosphere, and like N_2 , can be a competitive adsorbate particularly for physisorbents. Hence, one should study its adsorption behaviour. If the adsorption is non-negligible, one should collect isotherms at three temperatures up to 1 bar to allow for isotherm fitting and heat of adsorption calculation. In addition, O_2 can react with and damage certain adsorbents (see *Oxidative stability* sub-section below). Assessing the extent of O_2 adsorption is therefore useful to understand how much O_2 can potentially interact with the material. As shown in Fig. 5, there is an obvious lack of data in the O_2 isotherms available for candidate DAC adsorbents, even when considering non-DAC related publications.

3.3.2. Oxidative stability

Oxidative stability is a necessary feature of adsorbents for DAC. Amine-functionalised adsorbents can be susceptible to oxidative degradation particularly at high temperatures (i.e. $>75^\circ\text{C}$) after just one day, resulting in the loss of CO_2 adsorption sites (Heydari-Gorji and Sayari, 2012). This can also occur at lower temperatures over longer periods of time, and under ambient storage conditions (van Paasen et al., 2021). Primary and tertiary amines are known to be more resistant to oxidation compared to secondary amines, which can readily degrade to form imines or amides (Bollini et al., 2011). For aminopolymers, the presence of additional carbons between amine groups (e.g. propylene vs. ethylene linkers) also imparts higher oxidation stability (Pang et al., 2017). Many publications listed in Tables S7–S12 have focused specifically on developing DAC adsorbents with improved oxidative stability, such as those by Pang et al. (2018), Rosu et al. (2020), and Yoo et al. (2019). However, other O_2 stability studies are limited to either measuring one O_2 adsorption isotherm and claiming minimal adsorption, or running their experiments using an ambient air stream. In these cases, further investigation is still needed to look at the impact of O_2 at higher temperatures as well as long-term exposure, as this will be important for the desorption process and shelf-life, respectively.

We have summarised the impact of O_2 on adsorbents in Tables S7–S12 where data is available, although there is clearly a data gap on this topic in the current literature. If the impact of O_2 on the CO_2 uptake was provided, we identify if more than (" $>50\%$ CO_2 ") or less than 50% (" $<50\%$ CO_2 ") of the CO_2 uptake was maintained, and if these studies were conducted at CO_2 concentrations higher than 4 vol%. For papers which looked at the structural integrity of the adsorbent, "N" indicates that either the adsorbent support or functionalisation material degrades in the presence of oxygen, while "Y" indicates that the adsorbent appears to be structurally stable or regenerable. We have also indicated if papers reported a

low O_2 uptake from their measured isotherms. Where possible, we include the % RH and temperature conditions used for these oxidation studies.

3.4. H_2O adsorption

3.4.1. H_2O isotherms

Water is always present in the atmosphere to some degree (see Fig. 2) and can compete with CO_2 , occupying the same binding sites, and reducing the CO_2 saturation capacity. In some cases, H_2O increases the CO_2 capacity of the adsorbent (see *Hydrolytic stability* sub-section below). Regardless of the situation – competitive or synergistic adsorption – a material adsorbing a high amount of H_2O will require higher energy for full desorption/regeneration. Therefore, we recommend for at least one H_2O adsorption isotherm to be measured. As for O_2 , if the H_2O uptake is non-negligible, isotherms at three temperatures up to 1 bar should be measured to obtain the necessary information for process modelling. As seen in Fig. 5, collecting at least one H_2O isotherm is more frequent than for N_2 or O_2 . Yet, there is still a significant lack of data in this area for candidate DAC adsorbents, even when searching in non-DAC related publications. Due to the complex interactions that can occur between CO_2 and H_2O as well as the sorbent, measuring CO_2 - H_2O co-adsorption equilibrium isotherms is critical. Such measurement represents more accurately the impact of H_2O on DAC processes compared to predictions from single-component sorption data. However, this binary sorption isotherms are experimentally challenging to measure and remain largely unavailable in the DAC literature, save for a few studies such as those by Gebald et al. (2014), Elfving and Sainio (2021), and Young et al. (2021). Examples of CO_2 - H_2O co-adsorption models that have been used to model this data include the Guggenheim–Anderson de Boer (GAB) model (Stampi-Bombelli et al., 2020), a kinetic co-adsorption model (Elfving and Sainio, 2021), and a mechanistic co-adsorption model and a weighted average dual site Toth (WADST) co-adsorption model (Young et al., 2021), respectively. These models are discussed in further detail in Section 7.1.

3.4.2. Hydrolytic stability

The presence of humidity can have various impacts on an adsorbent, which we have categorized in Tables S7–S12 where data is available. "N" indicates the worst-case scenario where the structure of the adsorbent itself has deteriorated due to the collapse of the crystal and/or pore structure and is unregenerable. "Y" indicates that the adsorbent structure, including its functionalisation, is unaffected or is regenerable after humidity exposure. Where possible, these are then further classified into "+" or "-" categories, which indicate whether the CO_2 uptake increases or decreases in the presence of humidity, respectively, along with the % RH and temperatures used for these studies. Where data is available, we also identify if the material was stable under steam regeneration ("ss"), which may have benefits from a process standpoint (see Section 7.1). For the purposes of simplicity, we did not consider the effect of humidity on the CO_2 adsorption kinetics in this categorisation. This method of categorisation follows that proposed by Kong et al. in their recent perspective article on DAC (Kong et al., 2022).

In general, the CO_2 uptake for amine-functionalised adsorbents increases in the presence of humidity due to a change in the adsorption mechanism. With water, only one

N atom is theoretically needed to adsorb CO₂ via bicarbonate formation, instead of two N atoms in dry conditions via carbamate formation (Sanz-Pérez et al., 2016). Tertiary amines cannot react to form carbamates, and only show substantial CO₂ adsorption in the presence of water vapour via bicarbonate formation (Sanz-Pérez et al., 2016). Moisture also helps to maintain the long-term stability of amine-functionalised adsorbents by preventing the formation of urea, which would otherwise eliminate CO₂ adsorption sites (Kim et al., 2016). Some adsorbents even require the presence of moisture for CO₂ adsorption to occur. Examples are those functionalised with sodium or potassium carbonate, which react with CO₂ in the presence of moisture to form sodium or potassium bicarbonate (Rodríguez-Mosqueda et al., 2019). For most physisorbents though, e.g. unfunctionalised MOFs, zeolites, and carbons, the presence of humidity reduces their CO₂ uptake due to the competitive adsorption of water on CO₂ adsorption sites (Kolle et al., 2021). Some adsorbents are also simply not structurally stable in the presence of water vapour, such as SIFSIX-3-Cu (Madden et al., 2017), TIFSIX-3-Co (Kumar, 2018), and Mg-MOF-74 (Kumar et al., 2015). Depending on the extent of the impact of moisture on these adsorbents, the removal of water may need to be incorporated into the process which would increase operating costs. For further in-depth explanations of the effect of water on CO₂ adsorption, we direct readers to the recent review by Kolle et al. (2021).

For the chemisorbents and physisorbents reviewed here, the effect of humidity is not always investigated at low CO₂ concentrations relevant to DAC, as indicated in Tables S7–S12. While an adsorbent may maintain high CO₂ capacity in the presence of moisture at high concentrations, the effect of humidity may be more severe when the CO₂ concentration is reduced to 400 ppm. Therefore, one should conduct experiments at the relevant conditions whenever possible.

4. Beyond CO₂ uptake measurements

Determining if an adsorbent is suitable for DAC requires information beyond the measurement of its CO₂ uptake. We have already noted above the importance of considering the impact of other atmospheric gases. Dynamic adsorption studies are needed to determine adsorption kinetics, while cyclic studies are used to estimate the working capacity of the adsorbent and its potential longevity.

4.1. Kinetic studies

In contrast to other separation processes, early breakthrough of CO₂ is not a key concern for DAC as any specification on recovery may be less stringent than with e.g. post-combustion capture (Stampi-Bombelli et al., 2020). Therefore, adsorbents with slower kinetics may still be suitable for a DAC process. Mass transfer coefficients which describe the gas diffusion and the adsorption/desorption kinetics are needed for process modelling. The experiments needed to determine these parameters are not systematically conducted. One reason for this might be that they often require a mathematical model for interpretation. We summarise the presence (“Y”) or absence (“N”) of kinetic studies in the reviewed publications for DAC adsorbents in Tables S7–S12. Over 90% of studies include some form of kinetic study, with packed bed breakthrough studies being the most common set up, followed by TGA. However, not all the kinetic studies are

carried out at DAC conditions as indicated in the tables. Most of the studies measure parameters such as rates of adsorption, or breakthrough, retention, or saturation times. These parameters are dependent on many experimental factors such as gas flow rates, column dimensions, system temperature and pressure, and feed gas concentration. This makes it virtually impossible to compare the kinetic results of different publications. Overall, in-depth kinetic studies are much more common in process-focused papers rather than materials-focused papers.

4.2. Cyclic studies

To be usable at scale, DAC adsorbents must exhibit sufficient structural and chemical longevity upon repeated cyclic exposure to adsorption and desorption conditions, while still maintaining their working capacity throughout their lifetime. The less adsorbent that needs to be replaced throughout the process, the lower the cost. We summarise the presence (“Y”) or absence (“N”) of cyclic studies in the reviewed publications for DAC adsorbents in Tables S7–S12. Overall, over 85% of the studies report some form of cyclic testing, although not all are carried out at DAC conditions as indicated in the tables. Among them, the packed bed breakthrough method prevails, followed by TGA. These methods commonly employ a simple temperature swing adsorption (TSA) process, where CO₂ adsorption occurs at ambient temperature, followed by desorption at elevated temperatures (~70 – 120 °C) using either an inert gas or air stream. These steps are repeated over several cycles, though usually no more than ten. Some publications have also investigated multiple cycles of moisture swing adsorption for adsorbents (Hou et al., 2021; Song et al., 2019; Wang et al., 2020). A recent study has also explored dual functional materials capable of CO₂ adsorption followed by methanation when exposed to H₂, where the process would cycle between the two steps (Veselovskaya et al., 2018; Jeong-Potter and Farrauto, 2021). We discuss other types of desorption processes further in Section 7.1.

5. Synergy between material and process development in DAC

Since ultimately, an adsorbent must be integrated into an adsorption process, material and process development should occur harmoniously. Applying a promising material in a process model or experiment provides understanding of how the material properties can influence the process performance indicators. Between 2016 and 2021, we counted 84 “material studies” focusing on adsorbent development (Fig. 7b) and the number of publications per year roughly doubled within this timeframe, predominantly influenced by an increasing interest in silica, metal oxide, polymer, and MOF adsorbents. On the other hand, “process studies” (Fig. 7a), defined as studies reporting process performance metrics, predominantly use amine functionalised polymers. Many promising MOF- and silica-based adsorbents are not screened/assessed for a given adsorption process, leaving a gap in understanding their suitability for DAC processes.

A common adsorbent applied in process studies is Lewatit® VP 1065, an amine-functionalised polymer. In this case, a temperature-dependent isotherm model and heat of adsorption (Bos et al., 2019; Veneman et al., 2015), a mass transfer coefficient for a kinetic model (Bos et al., 2019), the

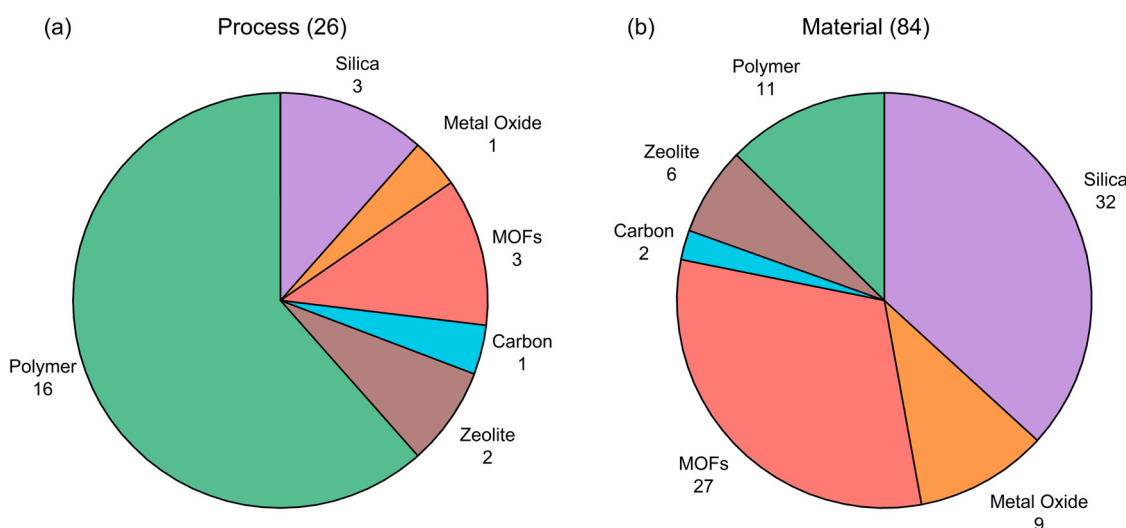


Fig. 7 – Comparison of the number of studies using different material classes in (a) process studies and (b) materials studies. Material studies refer to studies focusing on adsorbent development. Process studies refer to studies reporting process performance metrics or techno-economic assessments. Some materials studies investigated more than one material category (e.g. silica and metal oxide), but these were not double-counted in the final total.

heat capacity (Sonnleitner and Hofbauer, 2018), the heat of adsorption (Veneman et al., 2015), and material pellet and bed density are available in the literature (Young et al., 2021). Even in the case of Lewatit® VP 1065, the mass transfer experiments completed by Bos et al. (2019) are performed at >50 mbar CO₂ where DAC conditions are at 0.4 mbar, therefore the mass transfer coefficient which is commonly applied in the Linear Driving force (LDF) model is not at DAC conditions. An amine-functionalised nanofibrillated cellulose material (APDES-NFC) which is utilised by Climeworks has been applied in fewer process studies as this material is not as readily accessible. The isotherms and heat of adsorption of this material are available in the literature (Gebald et al., 2014). The full extent of material characterisation that is required for application in a process model is rarely completed, where full characterisation of materials is imperative to improve the synergy between material and process

development. For this reason, when materials exhibit promising equilibrium capacity and stability, focus should be on obtaining the complete set of information that is required for process modelling as indicated in our previous sections.

6. Adsorber/contactor design

To achieve the large volumes of air flow required for DAC (see Fig. 1), while maintaining a low process specific energy, an adsorbent-air contactor with low pressure drop, efficient heat and mass transfer, low footprint and low capital cost is essential.

Here, we consider three categories of contactors for adsorption processes (see Fig. 8): fixed bed, moving bed, and fluidised bed. A fixed bed can be described by a vessel with a packing or structured adsorbent material where both the vessel and material are stationary. Fixed beds are operated in

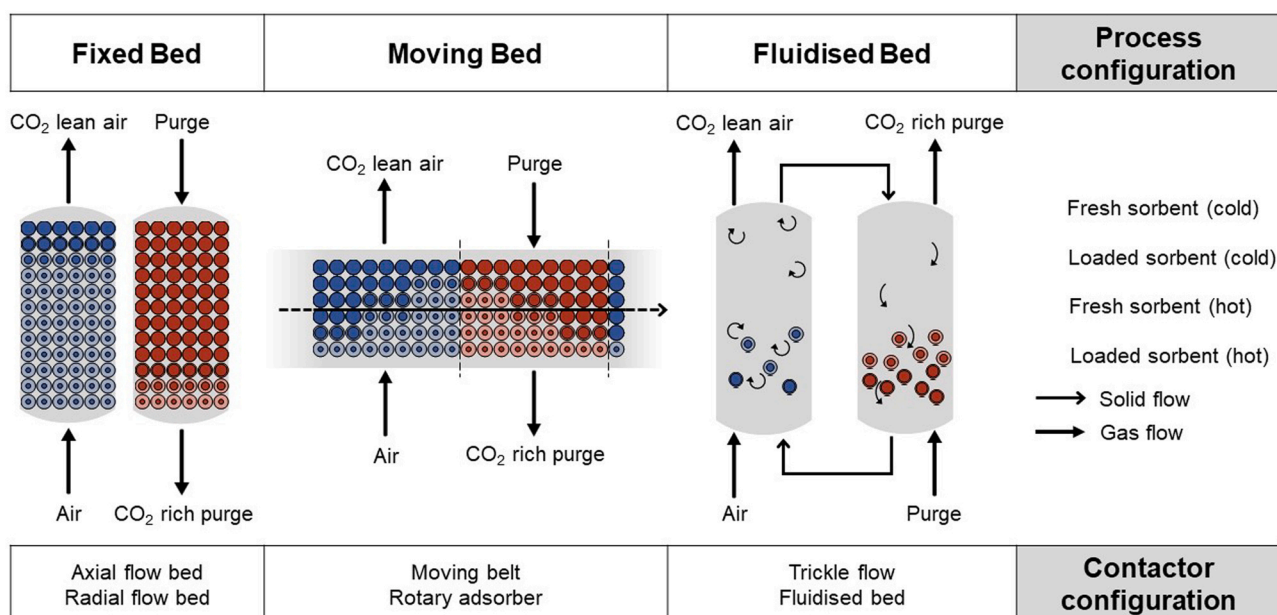


Fig. 8 – Schematic representation of the different process configurations and associated contactor designs for continuous adsorption processes. Contactor configurations are different ways in which these processes can be implemented.

a batch-wise cycle, undergoing adsorption, desorption/heating, and pressurisation/cooling in at least three separate stages. Therefore, multiple vessels are required for continuous operation. In the case of a moving bed, the vessel containing the solid adsorbent and the sorbent move together through adsorption and desorption steps. This allows a continuous process without the requirement of multiple vessels. In the case of a fluidised bed, the pellet, powder, or spherical adsorbent is fluidised and the adsorbent itself moves to different process stages. This is also a continuous process where different physical locations of the process are dedicated to adsorption or desorption.

To understand the requirements of process configuration and contactor design, it is useful to assess the current commercial DAC plant designs. The latter have clearly indicated that contactor optimisation is a key part of the design of the adsorption-based DAC process. The patented Global Thermostat design uses a hybrid moving and fixed bed process (Eisenberger, 2018). The configuration consists of a monolithic structured adsorbent in a fixed bed configuration, where multiple fixed beds are supported on a track. These beds move around the track, albeit not continuously, where one bed is placed in a sealed box for the desorption step once saturated. The design of this system, in terms of number of fixed beds, is dependent on the relative adsorption (time until saturation) and desorption (time until adsorbent regeneration) time of the process. The sequential operation of two of these process configurations allows heat integration of the two regeneration systems where the depressurization and therefore cooling of one system pre-heats the second system.

Climeworks have patented a fixed bed vacuum chamber which is packed with a structured adsorbent (Gebald et al., 2017). The design of the contactor is intended to minimise pressure drop and thermal mass to improve heat transfer. The design has adequate mechanical strength for low vacuum pressures (500 mbar) using ribbing to increase the strength, with an optimised wall thicknesses to reduce thermal mass. Inlet and outlet axial walls with sealing elements are used to allow gas to flow through when open and to provide a seal to allow evacuation to vacuum pressures when closed. A gas tight sealing mechanism is also provided for the adsorbent structure to ensure no air bypasses around the adsorbent. Heat transfer fluids pass through the circumferential walls of the vacuum chamber. Considerations of this design also include optimisation of void volume based on the trade-off between pressure drop, dilution, and pump work (Gebald et al., 2017). Beyond the selection of a process configuration, there remains considerable scope for contactor optimisation.

Although structured adsorbents are used in current commercial DAC process plants, their benefit in the case of DAC remains unclear in the literature. The answer to this question may present itself as more complicated than anticipated. Much of the performance of structured adsorbents, namely laminates, monoliths, and foams, is dependent on adsorbent geometry, adsorbent loading, binder, and thermal properties (Rezaei and Webley, 2009, 2010; Sinha et al., 2017). An optimisation study by Rezaei and Webley (2010) highlights that the enhanced productivity that results from reduced pressure drop in structured adsorbents becomes the over-arching effect at higher superficial velocities. At lower velocities, the smaller mass-transfer zone and low pressure drop suggests that there is little productivity difference

between structured and packed pellet adsorbents. Therefore, the benefit of structured adsorbents in DAC likely depends on material kinetics and controlling mass transfer resistances. Additional sensible heat requirements for structured adsorbents are observed because of the support structure (Sinha et al., 2017), however, heat transfer benefits may be observed from improved uniformity of adsorbent heating and thermal conductivity of the structure. The trade-off between additional sensible heat requirements and improved heat transfer will depend on structure properties, for example thermal conductivity and adsorbent loading (Rezaei and Webley, 2010). Similarly, all improvements in pressure drop, mass transfer, and heat transfer must be evaluated against the often low volumetric adsorbent loading in structured adsorbents (Rezaei and Webley, 2010), which once again highly depends on the structure design. Adsorbent loading is particularly relevant for DAC where it is already very difficult to achieve high adsorbate loadings at the ultra-dilute feed conditions.

Many DAC process studies utilise a fixed bed adsorber for modelling and experimentation. Sinha et al. (2017) and Zhu et al. (2021) performed studies on two MOF adsorbents coated on a monolith structure using amine functionalised MOFs, i.e. MIL-101(Cr)-PEI-800 and mmen-Mg₂(dobpdc). Both studies utilised a steam assisted temperature vacuum swing (S-TVS) process for adsorbent regeneration with the monolith structure in an axial bed. Sinha et al. (2017) reported the monolith wall sensible heat requirement during desorption as 15% of the total process energy requirement, and discussed that reducing the monolith wall thickness could offer significant energy benefits. Schellevis et al. (2021), Stampi-Bombelli et al. (2020), and Young et al. (2021) employed a pancake style packed fixed bed adsorber for process modelling, where the bed diameter is 8–16 times that of the thickness. In similar fixed bed studies for post-combustion carbon capture, this ratio is typically 0.1 or less (Zhao et al., 2019a; Sarkar and Bhattacharyya, 2012; Dantas et al., 2011). A pancake style contactor is particularly appropriate for DAC as the large thin design allows minimal pressure drop for a given amount of adsorbent volume. While a thin process contactor can result in premature breakthrough, uniquely to DAC, one can envisage a process design without specifying a constraint on recovery. A recent study by Yu and Brilman (2020) proposed to use a radial flow contactor, where the adsorbent is packed in an annulus, and the air flows radially through the bed (from the outside to the inside of the annulus). This configuration allows fluid flow to occur across a thin bed, like in the case of a pancake fixed bed, however, also permits a longer column. This design was reported to achieve a pressure drop of 348–681 Pa for an air flow of 180–320 m³h⁻¹ which was compared to 100 Pa for a monolith bed based on a 2012 study by Kulkarni and Sholl (2012).

Fewer studies have focused on moving bed or fluidised bed process configurations. A study by Drechsler and Agar (2019) introducing a moving belt adsorber design using temperature swing adsorption (TSA) presented a highly heat integrated process with Power-to-Gas technology (methanation of CO₂ using the Sabatier reaction). The benefit of this process was observed in its heat integrated and autothermal design. However, the productivity was only 31.2 kg CO₂ per m³ of sorbent per day (kg CO₂ (m³·(day)⁻¹) and the maximum purity was 20 mol% CO₂. Although this design is well adapted to the specific application presented, the moving belt is not suitable for CO₂ storage applications in its current form due

Table 3 – Key desorption methods applied in DAC process studies.

TSA	Temperature swing adsorption
TCSA	Temperature concentration swing adsorption
C-TSA	Closed temperature swing adsorption
S-TSA	Steam-assisted temperature swing adsorption
TVSA	Temperature vacuum swing adsorption
TVCSA	Temperature vacuum concentration swing adsorption
C-TVSA	Closed temperature vacuum swing adsorption
S-TVSA	Steam-assisted temperature vacuum swing adsorption
MSA	Moisture swing adsorption
pHSA	pH swing adsorption

low purity and productivity. Zhang et al. (2014) performed a study on a fluidised bed using PEI-Silica, where the specific energy was reported as $6.6 \text{ MJ (kg CO}_2\text{)}^{-1}$ which is comparable with other studies (see Table 3), and a cost of $\$152 \text{ (t-CO}_2\text{)}^{-1}$ in 2015. The reported productivity was only $7 \text{ kg CO}_2 \text{ (m}^{-3}\text{)}^{-1}\text{(day)}^{-1}$, which can be considered to be relatively low. The pressure drop of the fluidised bed reached 1592 Pa compared to only 348–681 Pa in the case of a radial flow adsorber, indicating a fluidised bed is unlikely to be feasible for a DAC process (Yu and Brilman, 2020; Zhang et al., 2014).

Although pancake-like and radial flow bed designs represent promising options for DAC, there remains significant gaps in assessing process configurations and optimisation of contactor designs. Further research is required to understand the applicability of different moving bed designs to DAC. Moving bed process configurations have the potential to offer improved process cycle time control which may be pertinent in DAC due to fluctuating ambient conditions. Furthermore, a moving bed can bring in further potential for heat integration as discussed in the moving belt design presented by Drechsler and Agar (2019) and the patented Global Thermostat technology (Eisenberger, 2018). Moving bed designs may have potential process intensification benefits, however, the process intensification and capital benefit are dependent on the design of a specific contactor, and data is lacking to allow comparison between fixed and moving beds for DAC. Although a moving bed can offer the benefit of achieving a continuous process with one vessel, continuous operation may not be necessary and is therefore not the sole distinguishing factor between a moving or fixed bed process. Continuous DAC processes may become pertinent if downstream utilisation requires a stable and reliable feed stream. An interesting possibility of a moving bed design is changing the contactor conditions for different cycle steps. For example, in the Global Thermostat design, the contactors are only isolated from air during the desorption step and exposed during the adsorption step (Eisenberger, 2018).

As demonstrated by the Climeworks fixed bed temperature vacuum swing (TVS) contactor design, there is in-depth scope for contactor optimisation within different process configurations (Gebald et al., 2017). The design of compact and efficient contactors is essential in DAC. Compact process designs with efficient heat and mass transfer as well as heat integration will reduce process specific energy, increase productivity, and minimise capital cost. This may be particularly important when considering that DAC processes may become brownfield additions to existing processes where excess waste heat is available, and therefore a compact and modular design will be key for easy installation.

7. Process design

7.1. Desorption method

The desorption method significantly impacts process performance and can make up at least 40–98% of total process energy requirements (Young et al., 2021; Sinha et al., 2017; Zhu et al., 2021; Schellevis et al., 2021; Kulkarni and Sholl, 2012; Wilson and Tezel, 2020), not including subsequent CO₂ compression. Such method should be selected based on the process constraints and location. Specifically, factors that influence the selection include CO₂ product purity and productivity requirements, accessibility to waste heat or low pressure (LP) steam, adsorbent material isotherms and temperature and moisture stability. Several desorption methods have been studied for DAC and are listed in Table 3.

We summarise the main desorption options for DAC processes and their ranked purity and energy use in Fig. 9, and highlight the trade-off between high purity and low specific energy. Climeworks, like most reported DAC studies, employs TVSA to achieve a high purity CO₂ product (Gutknecht et al.). On the other hand, Global Thermostat uses a S-TSA process (Eric Ping et al.). Both desorption methods produce high purity CO₂, with the intention of long-term subsurface storage. Desorption methods and conditions used can have a significant impact on process energy requirements.

Elfving et al. (2021) compared different desorption methods for DAC using an aminoresin in a fixed bed experimental unit. Recognising that not all DAC processes may require high purity CO₂, their study highlights that in low purity applications, TSA and TCSA offer a viable option with lower specific energy requirements than desorption methods that require either vacuum or steam. In this study, introduction of a mild vacuum (500 mbar) to a TCSA process increases the specific energy requirement by 43% but only improves productivity by 14%. When considering desorption, downstream utilisation of CO₂ is key. Purities of 5–20 mol% have been reported using TSA, 95–97 mol% using C/S-TVSA and 95–99.6 mol% in desorption processes with a steam purge (Young et al., 2021; Stampi-Bombelli et al., 2020; Sinha et al., 2017; Zhu et al., 2021; Drechsler and Agar, 2019; Santori et al., 2018; Sinha and Realf, 2019; Brilman et al., 2013). Therefore, the applicability of a TSA process is limited due to a low purity product. Unsurprisingly, desorption processes which use both steam and vacuum conditions tend to result in higher specific energy requirements than TSA processes. TVSA processes can achieve higher productivity when compared to simply TSA based processes due to rapid desorption rates and higher purity, especially when coupled with a purge flow (Elfving et al., 2021; Wijesiri et al., 2019a). Wijesiri et al. (2019a) found through a fixed bed experiment that the desorption rate in a S-TVSA process using a PEI impregnated silica was sixteen times higher than a TVSA process. The experimental study performed by Elfving et al. (2021) also found productivity benefits when coupling TVSA with an air or inert purge.

When considering desorption conditions, a wide range of vacuum pressures has been studied from 20 to 900 mbar (Stampi-Bombelli et al., 2020; Sinha et al., 2017; Zhu et al., 2021; Schellevis et al., 2021; Wilson and Tezel, 2020; Wijesiri et al., 2019a; Wurzbacher et al., 2016; Zhao et al., 2019b; Wurzbacher et al., 2012). The desorption temperature varies between 60 and 120 °C (Stampi-Bombelli et al., 2020; Sinha

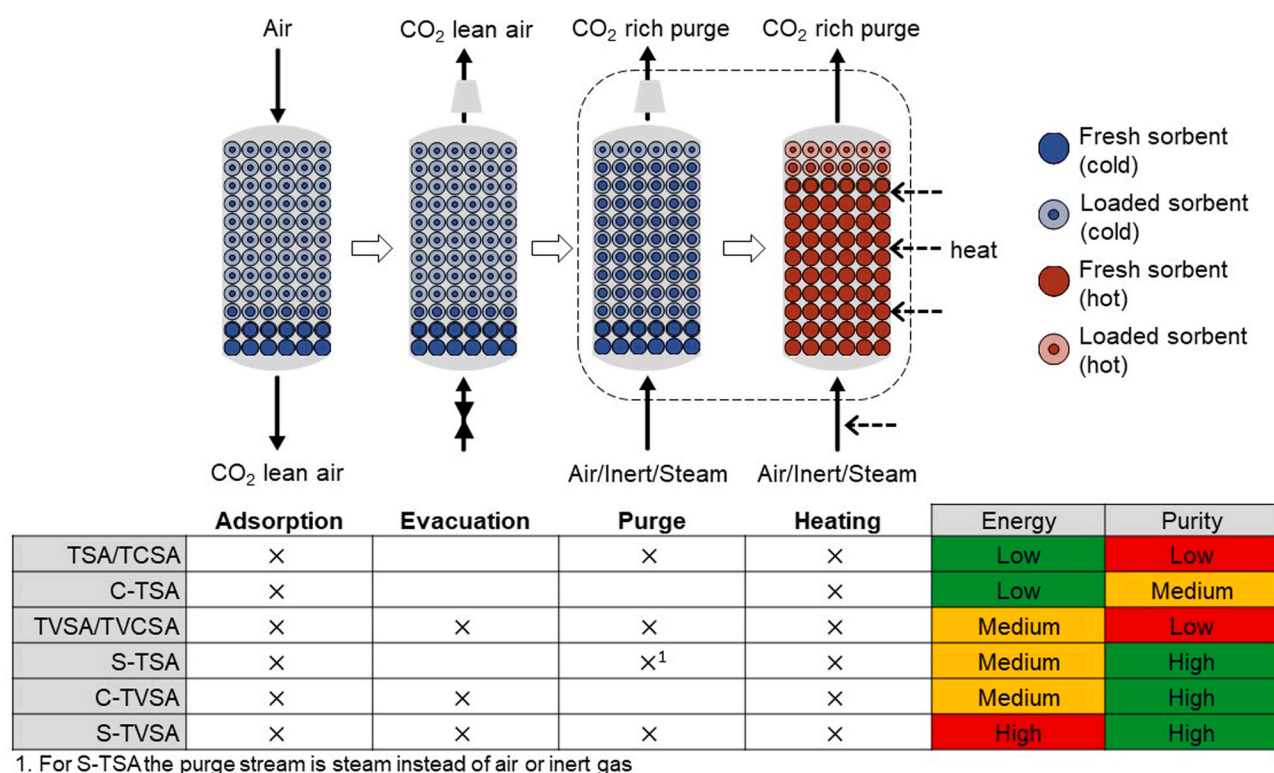


Fig. 9 – Schematic representation of the different process configurations for DAC and qualitative assessment of their energy requirement and achieved purity.

et al., 2017; Zhu et al., 2021; Schellevis et al., 2021; Drechsler and Agar, 2019; Elfving et al., 2021; Wijesiri et al., 2019a; Wurzbacher et al., 2016; Zhao et al., 2019b; Wurzbacher et al., 2012) for amine functionalised sorbents and 95–260 °C for zeolites (Wilson and Tezel, 2020; Santori et al., 2018), this parameter being often governed by material stability (Young et al., 2021; Yu et al., 2017). The selected vacuum conditions represent a trade-off between energy use and the productivity (Schellevis et al., 2021; Elfving et al., 2021). Schellevis et al. (2021) have shown that a higher adsorption temperature (up to the material stability limit) at a constant material working capacity, resulted in lower process energy consumption and higher productivity. When a desorption temperature of 120 °C instead of 60 °C was used the process specific energy reduced by 40% and productivity increased by a factor of at least two. The observations resulted from the energy intensity of vacuum compression and the requirement of harsher vacuum conditions at lower desorption temperatures to achieve a desired working capacity. A similar result was obtained by Elfving et al. (2021) when comparing conditions for a TVSA or TVCSA process, where milder vacuum conditions (500 mbar compared to 25 mbar) resulted in a specific energy ($\text{MJ} (\text{kgCO}_2)^{-1}$) reduction of more than 70%. This effect was accompanied by a small difference in working capacity (1.6% more for TVSA and 6% less for TVCSA), and a reduction in productivity by 10–14%.

A key aspect to consider in optimising desorption conditions, particularly when considering amine-functionalised sorbents, is the co-adsorption of water. Wijesiri et al. (2019a) reported that pre-adsorbed water caused increased consumption of thermal energy due to desorption of water, and also resulted in slower desorption kinetics of CO_2 at the beginning of the desorption step due to the initial temperature drop. Interestingly, mathematical modelling performed by

Zhu et al. (2021) observed the opposite effect when using a higher desorption pressure. The higher desorption pressure resulted in some adsorption (instead of desorption) of water, leading to reduced heating time and improved kinetics. The impact of these effects in process modelling on process performance indicator results has been shown to vary depending on the type of co-adsorption model used (Young et al., 2021). Young et al. (2021) presented two co-adsorption models – the mechanistic co-adsorption model and weighted average dual site Toth (WADST) – and compared this with the Guggenheim–Anderson de Boer (GAB) model used by Stampi-Bombelli et al. (2020). Process key performance indicators (KPI) were similar for the mechanistic and WADST models, however, the GAB model varied significantly to these models (optimum productivity ~25% lower and optimum specific work equivalent was ~44% more). Young et al. (2021) suggested that this is due to the lack of temperature dependence of the GAB model. Elfving and Sainio (2021) proposed a kinetic based model for water co-adsorption based on the rate of reaction of two reactions suspected to occur during chemisorption of CO_2 on a primary amine sorbent. The results of this model agreed well with the measured isotherms. Use of such a model to determine process performance indicators for comparison with other proposed models would be a useful exercise.

Moisture and pH swing adsorption have also been explored for DAC (Cuesta and Song, 2020; Hou et al., 2017), yet not commonly applied in process studies. Vacuum or temperature swing tends to be applicable to a wide range of materials, making them the more common desorption method. Hou et al. (2017) utilised moisture swing adsorption in a greenhouse application, where low purities of approximately 3 mol% were required, making this process at present only applicable for low purity CO_2 requirements. This process

used an ammonium-based anion exchange resin where CO₂ is displaced upon wetting the adsorbent. [Cuesta and Song \(2020\)](#) presented an experimental study utilising pHSA on a functionalised carbon black. In the first cycle phase, CO₂ is captured on the basic sites lowering the pH. A regeneration solution, i.e. ammonium bicarbonate, is subsequently vapourised into the system causing desorption of CO₂ and increasing the pH of the system. The system is then dried and returned to the original state. The benefits of pHSA include: short cycle times, comparable sorbent capacity to TSA and MSA, and low energy requirements. As there is currently only one study discussing a pHSA process, further understanding is required of the potential scalability of this process.

7.2. Performance indicators

Assessment, comparison, and optimisation of DAC processes requires process KPIs (see [Table 4](#)). These KPIs typically include working capacity of the sorbent (WC), productivity of CO₂ for a given quantity of sorbent, purity of the product CO₂ stream, specific energy consumption per unit of CO₂ captured, and cost per unit of CO₂ captured. KPIs provide understanding of how the combination of materials properties (e.g., shape of the equilibrium isotherm, heat of adsorption, material kinetics, porosity, density) influence the process performance. They allow direct comparison between adsorbents for a given adsorption process and comparison of different process configurations and contactors as well as desorption methods for a given adsorbent. The intrinsic properties of materials related to their structure (e.g., porosity) and functional properties (e.g., selectivity) can identify promising materials, however, KPIs are required to provide an informative ranking for the more promising sorbents ([Farmahini et al., 2021; Rajagopalan et al., 2016](#)). Overall, one can use KPIs to understand the best combination of material, process configuration, contactor, and desorption method and to optimise the operating parameters of a process. There are key differences that should be highlighted between assessment of post-combustion carbon capture and DAC processes. Firstly, there is no recovery specification in the case of DAC and optimisation is focused on specific energy and productivity. Secondly, a DAC process may not be constrained by the upstream or downstream process unlike in pre- or post-combustion carbon capture.

[Table 5](#) shows process KPIs reported in key process studies completed since 2016. Many studies are utilising an amine-functionalised polymer adsorbent in a fixed bed configuration, with fewer studies using MOF or silica adsorbents or moving bed configurations. The range of reported values is substantial despite the apparent similarity of some of these

processes. For instance, we observe specific energy values from 0.7 to 57 MJ (kg CO₂)⁻¹. Large differences in performance metrics for seemingly similar processes can be explained either by the process operating parameters, in particular the desorption conditions used, the methods which are used to calculate these metrics, or a combination of the two. For example, [Young et al. \(2021\)](#) and [Schellevis et al. \(2021\)](#) reported a specific energy of 2.5 and 14 MJ (kg CO₂)⁻¹ respectively, both using a pancake fixed bed packed with Lewatit® VP 1065. [Young et al. \(2021\)](#) used a closed instead of open TVSA process, different desorption conditions and a different water co-adsorption model, all of which influence the specific energy estimations. The reported productivities of processes vary less than the specific energy. However, the highest value reported (245.8 kg CO₂ (m)⁻³(day)⁻¹) is seven times that of the lowest reported value of 7.89 kg CO₂ (m)⁻³(day)⁻¹. For working capacity, which has fewer reported values, we note a five-fold variation between highest and lowest values. Purity for a given process is either very high (> 95–99%) or very low (< 20%), where lower purities are typically associated with TSA or alternative desorption methods such as moisture swing. We note that [Table 5](#) includes an experimental study by [Elfving et al. \(2021\)](#) meant to compare different desorption methods for DAC based desorption energy only. It does not present a holistic process design.

Comparison between DAC process studies remains challenging as the assumptions, constraints, and calculation methods vary from study to study. The units of productivity often differ, and the information needed to convert to consistent units is lacking. Productivity has been reported in (kg CO₂ (m³.d)⁻¹), (kg CO₂ (kg_s.d)⁻¹), (kg CO₂ (kg_s.h)⁻¹), (kg CO₂ d⁻¹), and (kg CO₂ h⁻¹), where kg_s refers to mass of adsorbent. The mass or volume of adsorbent being referred to in productivity values is not consistently specified. As mentioned in [Table 4](#), productivity informs the size of a unit to capture a given amount of CO₂ meaning that one should report this KPI either by dry mass of sorbent or total volume of sorbent (incl. bed and sorbent porosity).

The conditions (i.e. RH and temperature) in which processes are explored and possibly compared matter. Focusing first on the importance of RH, so far, process studies consider either a wet feed stream (25–65% RH), or a dry feed stream. Given that it is unlikely that the feed to a DAC process will ever have a RH of 0%, one should rather consider a reasonable baseline RH in the feed stream or include a pre-drying step in process performance calculations. [Wilson and Tezel \(2020\)](#) performed an experimental study on a fixed bed TVSA process using Faujasite zeolites and estimated the energy impact of a pre-drying step. Additional energy requirements

Table 4 – Description of key process performance indicators and their implication on process design.

Performance Indicator	Description	Impact on Process Design	Optimisation
Productivity	Flow of CO ₂ over a given time for a fixed unit of adsorbent.	Impacts size of unit required to capture a given amount of CO ₂	Maximise
Purity	Mole percentage of CO ₂ in the product stream	Impacts opportunities for downstream utilisation of CO ₂	Meet target
Working capacity	Total CO ₂ obtained (amount adsorbed – amount desorbed) for a given amount of adsorbent	Impacts size of unit required to capture a given amount of CO ₂	Maximise
Specific energy	Energy consumption per unit of CO ₂ produced	Impacts operational costs of DAC process and ability to achieve net negative	Minimise
Cost	Cost per unit of CO ₂ produced	Impacts economic feasibility of DAC process	Minimise

Table 5 – Reported key performance indicators in process studies completed since 2016.^{1,2,3}

Desorption Method	Material Class	SE [MJ (kg CO ₂) ⁻¹]	Cost [\$ (t-CO ₂) ⁻¹]	Productivity [kg CO ₂ (m) ⁻³ day ⁻¹]	WC [kg CO ₂ (kg _s) ⁻¹]	Purity [mol%]	Feed Conditions	Ref
Fixed Packed Bed								
TCSA	Polymer	7.1	60	192.9	–	–	Dry, 25 °C	(Yu and Brilman)
C-TVSA	MOF	3.9–5.9	86–221	–	–	95%	Sensitivity on CO ₂ to water ratio (1:2, 1:40)	(Sinha and Reaiff, 2019)
TSA	Polymer	4.5–6.4	–	62.1–65.7	0.019–0.024	–	Dry, 25 °C	(Elfving et al., 2021)
TCSA	Polymer	4.4–6.3	–	54.9–58.5	0.019–0.024	–	Dry, 25 °C	(Elfving et al., 2021)
TVSA	Polymer	6.9–38.4	–	62.6–75.6	0.02–0.025	–	Dry, 25 °C	(Elfving et al., 2021)
TVCSA	Polymer	6.2–41.7	–	66.6–75.6	0.02–0.026	–	Dry, 25 °C	(Elfving et al., 2021)
S-TVSA	Polymer	40.3	–	7.89	–	99.6%	50% RH, 20 °C	(Stampi-Bombelli et al., 2020)
C-TVSA	Polymer	2.5–2.7	–	62.1–78.4	0.040–0.048	> 95%	55% RH, 15 °C	(Young et al., 2021)
TVSA	Polymer	14–57	–	23.2–142.6	0.014–0.045	–	50% RH, 20 °C	(Schellevis et al., 2021)
C-TVSA	Polymer	2.7 – 0.2.1	< 200	94.6–143	–	> 95%	43% RH, 20 °C	(Sabatino et al., 2021)
C-TVSA	Polymer	2.8–3.7	< 200	92.1–109.7	–	> 95%	43% RH, 20 °C	(Sabatino et al., 2021)
C-TVSA	MOF	1.5–2.1	< 200	135.6–245.8	–	> 95%	43% RH, 20 °C	(Sabatino et al., 2021)
C-TVSA	Zeolite	17	–	–	–	95%	0% RH, 23.5 °C	(Wilson and Tezel, 2020)
pHSA	Carbon	–	–	–	0.116	–	60% RH, 35 °C	(Cuesta and Song, 2020)
Fixed Monolith Bed								
S-TVSA	MOF	6.7	–	97.9	–	> 99%	0.78% H ₂ O, 25 °C	(Zhu et al., 2021)
S-TVSA	MOF	3.3	75–140	–	–	95%	25% RH, 25 °C	(Sinha et al., 2017)
S-TVSA	MOF	2.6	60–190	–	–	95%	25% RH, 25 °C	(Sinha et al., 2017)
Fixed Packed Bed in Series								
MSA	Polymer	0.8	35	–	–	3%	Dry, 25 °C	(Hou et al., 2017)
C-TVSA	Zeolite	< 50	–	–	–	> 95	Dry, 20 °C	(Santori et al., 2018)
C-TVSA	Zeolite	50	–	–	–	> 97	Dry, 20 °C	(Santori et al., 2018)
Radial Flow Packed Bed								
TCSA	Polymer	0.7–1.5	–	–	0.066	–	RH 40–65%, 19–22 °C	(Yu and Brilman, 2020)
Moving Belt								
TSA	Polymer	Autothermal	–	31.2	–	20%	Dry, 25 °C	(Drechsler and Agar, 2019)

¹ Several values obtained from these studies have been converted to allow consistent units.

² In the case of productivity, the sorbent bulk density or vessel dimensions were used to determine volume conversions (if not already provided in terms of volume), depending on which information was available.

³ Where productivity was provided in hours, the per day rate was based on an assumed desorption cycle time from the respective study.

from regeneration of the drying bed increased proportionally with RH and exponentially with ambient temperature. Depending on the RH, the additional drying step was estimated to strongly impact energy requirements (~100% increase at 15 °C and 60% RH), making the approach only feasible in cold dry climates. In addition, RH either causes a reduction in CO₂ uptake or improves CO₂ uptake and therefore should be considered in process modelling or experimental work (see discussion in Section 3.4). Water co-adsorption also influences desorption: depending on the operating conditions, during the desorption cycle, additional water could be adsorbed or desorbed resulting in either a cooling or heating effect. Additionally, water has faster desorption kinetics than CO₂. During desorption the rapidly desorbing water provides a purge for impurities, allowing the subsequently desorbed CO₂ to have a higher purity. Pre-adsorbed water can also result in overall higher energy consumption for the process

(Kong et al., 2022; Zhu et al., 2021; Wijesiri et al., 2019a). Turning our attention to the effect of temperature, as highlighted by Table 5, many process studies are performed at room temperature (15 – 25 °C). Kong et al. (2022) discuss the impact of varying ambient conditions on DAC processes, particularly focusing on sub-ambient conditions. Key findings from their work highlight that materials that do not have adequate equilibrium uptake at ambient conditions are discounted, but may offer adequate uptake at sub-ambient temperatures. The authors also discuss the impact of ambient temperature on material kinetics, where lower temperatures often result in slower material kinetics.

Overall, the ambient conditions of both temperature and RH will have notable impact on material selection and cycle design. There is much scope in the field of DAC processes to consider the range of ambient conditions that could be experienced in a single location and how one might implement

a suitable control and optimisation system for that process. Although different ambient conditions must be considered, it can be beneficial to use a baseline ambient and RH humidity value for initial comparison of process configurations and cycles, for example 15 °C, 60% RH based on the mid-range values in Fig. 2.

In this review, we have focused on technical development of DAC materials and processes. Along this angle, one should also explore techno-economic assessments (TEA) to assess feasibility and establish benchmarks. TEA studies for adsorption-based DAC remain scarce and we provide here a few references. Fasihi et al. (2019) compared low temperature adsorption and high temperature absorption processes. Sinha and Realff (2019) studied the impact of adsorbent properties, process conditions and feed streams on the cost of DAC adsorption processes. Wijesiri et al. (2019b) assessed the cost of DAC for a given adsorbent while varying operation process conditions. They identified material kinetics and use of waste heat as the key factors in cost reduction. Sabatino et al. (2021) performed an optimisation and cost assessment on the three key DAC technologies: adsorption, low temperature MEA based absorption, and high temperature alkaline solution absorption. Their works provide comprehensive comparison of the three technologies based on cost, energy, and technical feasibility. Like Wijesiri et al. (2019b), they highlight the importance of sorption kinetics on cost in adsorption-based DAC.

8. Summary and perspectives

Our review highlights the progress made towards the advancement of adsorption-based DAC technologies in the period 2016–2021, for both materials' development and process design. Yet, it also points towards major gaps in data and process analysis that must be addressed to advance the field and reach the CO₂ removal target fixed by the Paris Agreement for NETs. We summarise below what we consider as key findings and trends from our review.

Among promising candidate adsorbents, we highlight amine-containing materials (i.e. polymeric resins as well as functionalised MOFs and oxides) and ultramicroporous MOFs. These materials show high CO₂ uptake at low CO₂ partial pressure (uptake > 1 mmol g⁻¹ at 500 ppm) and their reduced porosity and/or their chemical nature limit N₂ sorption. All materials exhibit a priori sufficient thermal stability for regeneration via a TVSA process, which is the method of choice to reach high CO₂ purity.

Despite the criticality of adsorbent properties on process performance, adsorbent development seldom occurs concurrently with process development. In fact, many process studies do not consider recent and promising DAC adsorbents. The barrier is often the lack of data of material properties that can subsequently be applied to process modelling. To synchronise this work, emphasis should be placed on collecting material properties of candidate adsorbents that are necessary inputs for process modelling, e.g. the heat capacity, thermal conductivity, and bed density. This also implies to evaluate adsorbents in a structured form such as beads, pellets, or monoliths, rather than powders. Equilibrium isotherms must be collected with the intention of using them for process modelling. This means measuring isotherms at a minimum of three different temperatures to achieve reliable parameterisation of the chosen adsorption isotherm model and calculation of the heat of adsorption.

This should be mandatory for CO₂ and N₂, and should also be done for O₂ and H₂O when uptake of these species is high. Finally, material selection must go beyond achieving reasonable equilibrium capacity and consider whether kinetics are favourable at low CO₂ pressures and whether recycling is achievable. Given the number and sometimes complexity of the properties to be evaluated, obtaining them for all adsorbents may be impossible. A screening exercise might be needed based on limited properties with more in-depth characterisation for the most promising adsorbents.

The number of process studies on DAC adsorption has increased over the last five years, with models being established and initial experimental work performed. Significant focus has been on modelling desorption methods. Going forward, these analyses should provide more holistic and consistent process assessments, reporting all relevant KPIs to allow comparison. Although process studies should consider baseline ambient conditions to allow comparison, they should also analyse a range of actual ambient conditions, including the effect of moisture to test the robustness of different processes. Process studies have overall paid little attention to the design of process contactors. The high volumetric flows required by DAC have implications on both the process contactor and material selection. Low pressure drop process contactors are needed to allow large volumetric air flow while minimizing specific energy requirements. The sustainable operation of the DAC unit from an energy perspective is in fact paramount to achieve the climate benefits of DAC.

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Appendix A. Supporting information

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