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Hoseinpoori, S., Pallarès, D., Johnsson, F. et al (2023). A comparative exergy-based assessment of direct air capture technologies. Mitigation and Adaptation Strategies for Global Change, 28(7). http://dx.doi.org/10.1007/s11027-023-10076-3

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ORIGINAL ARTICLE



A comparative exergy-based assessment of direct air capture technologies

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Received: 29 September 2022 / Accepted: 24 July 2023 © The Author(s) 2023

Abstract

The 6th Assessment of the IPCC underlined the need for urgent measures for carbon dioxide removal from the atmosphere, so as to meet the 1.5 °C goal by the end of this century. One option to achieve this is direct air capture (DAC) technologies. This work assesses the thermodynamic performances of different categories of DAC technologies, i.e., adsorption-based, absorption-based, ion exchange, and electrochemical. An exergy analysis is performed on the DAC processes in each category to identify hotspots for efficiency loss within the system. The results show that the consumption of materials is responsible for 5-40% of the exergy consumption of the most-developed DAC processes. Despite their greater use of materials compared to absorption-based processes, adsorption-based processes, together with ion exchange technologies, have the highest exergy efficiencies of the DAC technologies investigated. Moreover, the results highlight the importance of limiting material consumption and electrifying large-scale DAC plants, which cannot run exclusively on waste heat from industrial processes.

Keywords Direct air capture · Exergy analysis · Adsorption · Absorption

1 Introduction

1.1 Aim and background

In the Paris Agreement of 2015, the international community pledged to restrict global warming to well below 2 °C, and to strive for 1.5 °C, as compared to preindustrial levels. Most of the mitigation scenarios in IPCC's 5th Assessment report, which limit warming in line with the Paris Agreement, include carbon dioxide removal (CDR) technologies applied at a large scale to account for the overshoot in CO_2 emissions from hard-to-abate sources (Edenhofer et al. 2014). The IPCC's 6th Assessment scenario estimates that negative emissions of 300–350 GtCO₂ will be needed for the 1.5 °C scenario and 400–500 GtCO₂ for the 2 °C scenario. Thus, there is an immediate need for actions to expand CDR deployment

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(IPCC 2022). Direct air capture (DAC) is a CDR technology that removes CO_2 directly from the air. The underlying concept was first introduced by Klaus Lackner in 1995 (Lackner et al. 1995). Since then, extensive research has been dedicated to understanding the feasibility and the potential global role of DAC, since DAC is able to decouple CO_2 removal from the emission source. Therefore, the location of DAC is deemed arbitrary. While it is theoretically possible to locate DAC at an arbitrary location, localization of a DAC system is strongly dictated by factors such as local weather conditions, access to resources (such as water, sorbent, heat, and electricity), and access to CO_2 transport and storage infrastructure.

Direct air carbon capture and storage (DACCS) processes comprise the following five main steps (Pritchard et al. 2015):

- 1. Circulation of air through a sorbent for the removal of CO_2
- 2. Regeneration of the sorbent
- 3. CO₂ conditioning (e.g., liquefaction for transport)
- 4. Transport of CO_2 to the sequestration location
- 5. Sequestration

Circulating air through the DAC system accounts for a large share of the electricity consumption, owing to the large volumes of air processed (Mazzotti et al. 2013; Socolow et al. 2011), while sorbent regeneration consumes most of the heat (Keith et al. 2018a, 2018b; Wurzbacher 2015). DAC developers try to reduce the energy consumption of the process by removing one step completely or by reducing its energy consumption. For example, natural drafts or winds are being studied as options for circulating the air through the system (Zeman 2007, 2014) or cooling the CO_2 so as to generate dry ice, which is then allowed to melt under ambient condition as a means of compression (Goldberg et al. 2013b).

Steps 3–5 are part of CO_2 capture technologies in general and are not exclusive to DAC. Furthermore, any technological development in these steps will apply to all processes and benefit them essentially to the same extent. Therefore, in this work, each technology is investigated within the scope of the first two steps listed above. Note that the output pressure of the system evaluated is the sorbent regeneration pressure, which differs from process to process. In the analysis, to ensure a fair comparison between technologies, an output pressure of 1 bar is assigned to all the CO_2 leaving the evaluated system, e.g., if the process studied contains a compression train, the compression work is reduced from the exergy requirements. Thereafter, in step 3, the pressure will be increased¹ to the level required for transport.

Lifecycle assessments of DAC have shown that it can deliver negative emissions along its entire value chain (de Jonge et al. 2019; Deutz and Bardow 2021). Therefore, DAC can contribute to offsetting residual emissions from hard-to-abate sectors such as aviation and agriculture, so as to reach the year 2050 net-zero target and compensate for historical emissions. In the longer term, DAC can contribute to establishing net-negative emissions.

Recent research on DAC has focused on developing novel processes that will minimize the use of energy and provide cost estimates for more developed processes (Fasihi et al. 2019; María Erans et al. 2022). However, the estimates and simulation results provided by the previous studies cover a wide range of energy requirements for the DAC process, i.e., 200–3000 kWh/tCO₂ captured, for different operating conditions and assumptions.

¹ In principle, temperature may instead be lowered for cryogenic transport (Goldberg et al. 2013b).

Moreover, most of the energy assessments have failed to consider the material consumption levels of the DAC systems. Furthermore, most of the assessments have focused on the techno-economic characteristics of DAC but have not included the thermodynamic efficiency of the system. House et al. (1998) have conducted an empirical analysis on second law efficiencies of the DAC systems based on CO_2 concentrations, while Danaci et al. (2021) have proposed a second law perspective to assess the performances of DAC systems. However, both of these works neglect the thermodynamic value of the sorbent makeup as part of the assessment. The present work considers solid adsorption (Azarabadi and Lackner 2019; Deutz and Bardow 2021) and liquid absorption (Baciocchi et al. 2006; Keith et al. 2018a, 2018b; Socolow 2011) DAC processes, which use significant makeup flows of sorbent material.

The aim of the present study is to assess the thermodynamic performance of the different DAC processes from exergy point of view and also to quantify the role of material consumption on the thermodynamic performance of the DAC system. This is achieved by applying the definition of exergy as the maximum theoretical extractable work (Bejan et al. 1996) to all heat, work, and material flows, for the different technologies. We also use different scenarios based on material stability to examine process hotspots for efficiency losses. Finally, a qualitative discussion of the results of the thermodynamic assessment is provided.

1.2 DAC processes and materials

DAC systems can be divided into four categories based on the core technology used to remove CO_2 from the air:

- Absorption
- Adsorption
- Ion exchange
- Electrochemical

The processes built around these core technologies are summarized below.

1.2.1 Absorption processes

Absorption processes have been researched for a long time as they are used in the pulp and paper industry (Goeppert et al. 2012). Therefore, the processes are considered to have reached maturity. In general, an absorption process consists of four main components (as indicated in Fig. 1): air contactor, causticizer, calciner, and slaker (Baciocchi et al. 2006).

In the air contactor, the air passes through structured packings that are wetted with sorbent (Socolow et al. 2011). The sorbent material is normally an alkali material hydroxide (Goeppert et al. 2012) (commonly sodium (Baciocchi et al. 2006) or potassium (Keith et al. 2018a, 2018b), with the latter used as the example hereinafter). During the contact, CO_2 is removed from the air to produce carbonates according to Reaction 1 (Keith et al. 2018a, 2018b).

$$2\text{KOH}_{(aa)} + \text{CO}_{2(a)} \rightarrow \text{K}_2\text{CO}_{3(aa)} + \text{H}_2O_{(1)} \qquad \Delta H = -95.8 \text{ kJ/mol}$$
(1)

The second phenomenon that occurs during contacting is the evaporation of water. Air contactor is the main cause of water loss in the absorption process. Moreover, the water



Fig. 1 Carbon-engineering absorption process adopted from the International Energy Agency (2022)

loss also accounts for the major share of the chemical exergy consumption of the absorption technology, which is in turn dependent upon the relative humidity of the air. Water loss is reduced in line with the relative humidity of the input air (Keith et al. 2018a, 2018b; Socolow 2011; Zeman 2007). Therefore, from the exergy point of view, it is preferable to site the absorption DAC systems in locations with high levels of humidity. Since the generated sodium and potassium carbonates are highly soluble, it is difficult to remove them from the solution. Therefore, the carbonate solution is moved to the causticizer where it reacts with calcium hydroxide (Keith et al. 2018a, 2018b). Reaction 2 results in the regeneration of the hydroxide solution and the production of solid carbonates. Traditionally, this step was carried out using a series that involves a precipitator, clarification unit, thickener, and mechanical filtration (Baciocchi et al. 2006). More recently, a pellet reactor has been introduced as part of a single-unit method for removing precipitates from the solution.

$$K_2CO_{3(aq)} + Ca(OH)_{2(s)} \rightarrow CaCO_{3(s)} + 2KOH_{(aq)} \qquad \Delta H = -5.8 \text{ kJ/mol}$$
 (2)

The solid calcium carbonate is then dried using a preheater and sent to a calciner, where it is heated to 900 °C. The calcium carbonate decomposes into calcium oxide and CO_2 , which can then be separated and compressed for sequestration. The heat required for sustaining calcination is typically provided by combustion. This represents the main drawback of the absorption process since it in addition to producing CO_2 emissions also increases the capital costs. Calcium makeup enters the system in the form of calcium carbonate and is converted to calcium hydroxide onsite. This is the procedure followed because calcium carbonate can be directly mined from nature, whereas calcium hydroxide needs to be artificially produced, which results in a higher cost.

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)} \qquad \Delta H = 178.3 \text{ kJ/mol}$$
(3)

Calcium oxide is sent to the slaker, where it is steamed for the regeneration of calcium hydroxide, thus closing the process cycle.

$$CaO_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_{2(s)} \qquad \Delta H = -63.9 \text{ kJ/mol}$$
(4)

1.2.2 Adsorption processes

Adsorption processes are based on the affinities that a solid surface has for certain gas species under different conditions.



Fig.2 Climeworks temperature vacuum swing (TVS) process. Adopted from the International Energy Agency (2022)

Unlike absorption processes in which each process step occurs in a dedicated component, in most of the adsorption processes, one component/module hosts the entire process (as indicated in Fig. 2). Each of these modules follows a batch operation of a two-step (adsorption-desorption) cycle:

In the case of adsorption, the air entering the system has to be in contact with the sorbent. Since the conveying of large air flows entails significant energy consumption, the contactor design is a key aspect in which the aim is to maximize the gas-solid surface contact, while minimizing the pressure drop. This step represents the first characteristic of the adsorption process. Regarding the contacting technologies, fluidized beds are recognized as the best option for high gas-solid heat and mass transfers, although they imply substantial pressure drops (Krekel et al. 2018; Zhang et al. 2014). Some existing processes (Wurzbacher 2015; Wurzbacher et al. 2011, 2012) instead use several shallow packed beds in a zigzag formation (Christoph Gebald 2014). Packed beds result in a trade-off that involves choosing the particle size, since smaller particles provide a larger surface area but result in a greater pressure drop. Monoliths have been proposed as a suitable contactor option due to their large surface areas (Ping 2018), although they are associated with significant parasitic heat losses that can reach up to 40% of the total heat requirement of the system (Ping 2018; Sinha et al. 2017).

Once adsorption is completed, the CO_2 -lean air is evacuated, and sorbent regeneration (desorption) starts. The method for regenerating the sorbent represents the second characteristic of the adsorption processes. Since adsorption-desorption rates and equilibria are functions of temperature, pressure, and gas composition (Do 1998); a sufficiently large change in one of these parameters is required for regeneration of the sorbent (Cavalcante 2000). The most commonly used strategy to achieve regeneration is to increase the temperature of the sorbent, which is referred to as "temperature-swing adsorption" (TSA). While regular TSA does not result in full capacity use of the sorbent, complementary measures can be taken in order to enhance its performance. One way is to use steam as the gas, which in the case of cooperative adsorption reduces the partial pressure of the CO_2 in the chamber to zero as well as increasing the sorbent temperature, therefore resulting in the desorption of CO_2 . In the case of competitive adsorption between water and CO_2 , water will replace the CO2 molecules on the surface due higher affinity of most sorbents towards water. The stream is purified during subsequent water condensation (it should be noted that steam acts both as a regenerating and carrier agent) (Krekel et al. 2018). This would comprise the adsorption process's water requirement. However, this water can be regenerated later on in the condenser alongside the moisture adsorbed from the air. Climeworks has reported 0.8-2 tH₂O/tCO₂ as a result of co-adsorption of water and CO₂ on their sorbent. This would allow the process to be located in a wider range of locations. Moreover,

the produced water can be used as input to the electrolyzer for the production of hydrogen (International Energy Agency 2022). An alternative way is to desorb CO_2 under sub-atmospheric conditions using a vacuum pump, the so-called "temperature vacuum swing" (TVS). After sorbent regeneration, the process cycle starts again. Since desorption part of the process occurs at temperatures 80–120°C, the system can operate on waste heat from industrial processes. While this is possible at smaller scales, for a large-scale deployment (millions of tons of CO_2 captured), no process will have sufficient waste heat to allow the running of a DAC system (although it could cover a significant share of the heat requirement).

The third characteristic of the adsorption processes is the choice of sorbent material (Sanz-Pérez et al. 2016). Ideally, the sorbent material should have a large surface area and high affinity for CO_2 (Do 1998). Furthermore, the high affinity towards CO_2 translates to higher heats of adsorption/desorption.

The most common sorbents for DAC purposes are amine-based materials, since amine groups have a high affinity for CO_2 adsorption in comparison to other sorbents (Belmabkhout et al. 2010; Gebald et al. 2011, 2014; Kothandaraman et al. 2016; Stuckert and Yang 2011). Amine groups are usually grafted onto a solid structure such as silica (Belmabkhout et al. 2010; Serna-Guerrero et al. 2008; Serna-Guerrero and Sayari 2010; Stuckert and Yang 2011; Zhang et al. 2014), aluminum (Ping 2018), or cellulose(Gebald et al. 2011, 2014). Amine-based materials have high capacities for CO_2 , and, unlike zeolites, their capacities are enhanced in the presence of moisture (Gebald et al. 2014; Goeppert et al. 2012). However, in a situation of highly humid weather, the capacities of amine-based materials dwindle (Wurzbacher et al. 2011, 2012), albeit only marginally (International Energy Agency 2022). Recently, metal organic frameworks (MOFs) have been receiving much attention due to their large surface area, large pore volume, and cyclic stability (Sinha et al. 2017). Due to its high capacity, potassium carbonate has also been used as a sorbent for removing CO_2 from the atmosphere (Roestenberg 2014).

1.2.3 Ion exchange process

The ion exchange (also called "moisture swing") process, was introduced by Klaus Lackner in 2009 (Lackner 2009). This process removes CO_2 through bringing atmospheric air (typically by means of natural wind, although this is not an inherent or exclusive concept to this process) into contact with a membrane. The membrane is composed of a 1:1 mixture of quaternary anionic exchange resin and polypropylene. The material contains chloride ions, which are replaced by hydroxide and carbonate ions when the material is washed in solutions that contain these ions. These ions bind to CO_2 in the bicarbonate state according to Eq. 5:

$$\mathrm{CO}_{3}^{2-}(R^{+})_{2}.x\mathrm{H}_{2}O + \mathrm{CO}_{2(g)} \leftrightarrow 2[\mathrm{HCO}_{3}^{-}\mathrm{R}^{+}. \ \mathrm{yH}_{2}O] + (x - 2y - 1)H_{2}O_{(g)}$$
(5)

In order to release the CO_2 , the equilibrium can be pushed backwards by exposing the saturated material to water vapor (in primary prototypes, this is done in a chamber of steam or water). Thereafter, the material is placed back in contact with ambient air for natural drying (which requires dry and not-extremely-cold weather conditions for good performance of the technology). It should be noted that this method of desorption would impose high water requirements for the process.

The sorbent will cycle between the carbonate and bicarbonate forms. Since each bicarbonate needs one positive charge and each carbonate needs two positive charges, the maximum loading of the material is equal to half of the positive charge concentration. Therefore, in contrast to adsorption where the effective working capacity is dependent upon the adsorption and desorption conditions, here, it only depends on the adsorption condition.

1.2.4 Electrochemical process

With the growing interest in electrifying DAC systems (María Erans et al. 2022), electrochemical processes have come into focus.

Electrodialysis is one of the main electrochemical DAC systems (Eisaman et al. 2009). In this process, hydrogen is sent to an anode to produce ionic hydrogen, while air is sent to a cathode to generate hydroxide. The CO_2 is absorbed by the hydroxide at the cathode, yielding carbonate or bicarbonate, which react with hydrogen at the anode to release CO_2 . Bipolar membrane electrodialysis is another electrodialysis process presented (Sabatino et al. 2020) for direct air capture where CO_2 is removed from the air via KOH scrubbing, and the rich solvent is regenerated via a bipolar membrane. At the bipolar membrane, potassium ions react with hydroxide to regenerate KOH, and CO_2 -carrying ions pass through the anion exchange membrane to react with hydrogen ions and produce water and CO_2 .

In electro-swing adsorption, the air passes through a quinone-based polycarbon nanotube (Voskian and Hatton 2019a) in which the quinone affinity towards CO_2 has been increased by positively charging the material. When the material is saturated, the process is reversed by changing the polarization to release CO_2 . During experiments, this process exhibited an electricity consumption level of 100 kJ/mol_{CO2} (630 kWh/tCO₂) (Voskian and Hatton 2019b).

Research has also been conducted on dissolving calcium carbonate in water to create calcium ions and then electrolyzing the water to create hydroxide; the reaction of calcium ions with hydroxide ions results in calcium hydroxide formation. The calcium hydroxide, in turn, captures CO_2 and is regenerated to calcium carbonate (Zhou et al. 2021).

The main advantage of electrochemical processes is that there is no need for many auxiliary components, such as heat exchangers. Furthermore, it removes the need to heat up large volumes of materials, thereby increasing the thermodynamic efficiency of the system. Moreover, in the electrochemical process, unlike adsorption processes, the CO_2 is directly targeted and removed. This removes the need for any heating fluid (María Erans et al. 2022). Electrochemical processes for DAC are still in the early stages of development and the stabilities of the sorbent materials remain to be proven. Therefore, they are not considered in this assessment.

2 Methodology

A review was made of the DAC technologies that have emerged in the past 20 years. Thereafter, an exergy analysis was carried out on these technologies. Exergy can be divided to physical and chemical exergy. Physical exergy consists of thermal, work, kinetic, and potential exergy, but the latter two are neglected. With this, the physical exergy results in the maximum attainable work for bringing the system from an initial state (pressure and temperature) to the reference environment state. The chemical exergy is defined as the maximum attainable work for bringing the system from the reference environment temperature and pressure to the so-called "dead state" (where chemical composition is also in equilibrium with the reference environment). Therefore, if a system consists of a single component available in the reference environment, the chemical exergy would be reduced to the reversible work for expanding the system until the partial pressure of the reference environment.

The exergy of electricity is equivalent to its work (Szargut 2005):

$$\mathbf{E}\mathbf{x}_{\mathrm{el}} = W_{\mathrm{el}} \tag{6}$$

The exergy content of heat is calculated according to Eq. (7) by assuming an ambient temperature of 25 $^{\circ}$ C.

$$Ex_{th} = Q * \left(1 - \frac{T_{env}}{T_{bf}}\right)$$
(7)

The chemical exergy used by the sorbent materials is either taken from literature for the case of solvents (Szargut 1989) or estimated from the respective lower heating value (LHV), or the case of solid sorbents (Szargut 2005) as follows:

$$Ex_{ch} = \beta * LHV$$
(8)

where the coefficient β (ratio between chemical exergy and LHV) is calculated as for solid fuels:

$$\beta = 1.0347 + 0.0140 \frac{\text{H}}{\text{C}} + 0.0968 \frac{\text{O}}{\text{C}} + 0.0493 \frac{\text{N}}{\text{C}}; \frac{\text{O}}{\text{C}} < 0.5$$
(9)

$$\beta = \frac{1.044 + 0.016(\text{H/C}) - 0.3493(\text{O/C}) \left[1 + 0.053(\text{H/C})\right] + 0.0493(\text{N/C})}{1 - 0.4124(\text{O/C})}; \frac{\text{O}}{\text{C}} < 2$$
(10)

The LHVs of the sorbents are calculated from their elemental compositions with the Boie equation (Marlair et al. 1999) as follows:

$$LHV = 35.160C + 116.25H - 11.090O + 6.28N + 10.465S \quad (MJ/kg)$$
(11)

The oxidation heat of minor elements that may be present within the material, such as silicon, chromium, and magnesium, is neglected. Moreover, the chemical exergy of the inert parts of the sorbents is neglected since it is not experiencing any significant changes between input and output. The active material accounts for around 50% of the sorbent mass (Madhu et al. 2021; Zhang et al. 2014). This is assumed to be the general composition for all the sorbents assessed in this work.

The net exergy destruction of the system is the exergy lost due to irreversibility and is calculated as follows:

$$Ex_{Destruction} = Ex_{el} + Ex_{th} + m_{in}ex_{ch,in} - m_{out}ex_{ch,out}$$
(12)

The destruction of chemical exergy related to sorbent consumption is dependent upon four main parameters: (i) the chemical exergy of the sorbent; (ii) the cyclic capacity of the sorbent, i.e., the difference in sorbent saturation capacity between adsorption and desorption conditions (this should not be confused with the normal adsorption capacity of the sorbent); (iii) the minimum viable capacity, i.e., the capacity at which used sorbent material is replaced with fresh sorbent (set at 60% in this work); and (iv) the stability of the sorbent, expressed as the sorbent capacity loss per cycle. The data for the consumption levels of heat and electricity have been retrieved from previous publications. The material flows are either taken from the literature or calculated based on system parameters.

For solid adsorption systems, the level of material consumption is calculated based on the maximum capacity of the sorbent and the sorbent capacity loss per cycle. Assuming that the sorbent is replaced when its capacity is reduced to a certain level, the maximum number of cycles of a sorbent and the material consumption per tCO_2 captured can be determined.

For absorption-based technologies, the material consumption accounts for both the amount of sorbent (hydroxide solution) and the amount of calcium carbonate required per unit of CO_2 captured. The chemical exergy is determined according to the number of cycles (calculated based on the recovery factor of the causticizer) and the stoichiometry of the DAC process (Madhu et al. 2021). Values for calcium carbonate consumption are taken from estimates and simulations in the literature (Baciocchi et al. 2006; Keith et al. 2018a, 2018b; National Academies of Sciences 2018; Socolow 2011).

The efficiency of the DAC system has been assessed from three perspectives. The firstlaw efficiency (I) represents the system ability to quantitatively convert energy to a product and is written as follows:

$$\eta_I = \frac{W_{\min,CO2}}{\mathrm{EL}_{\mathrm{in}} + Q_{\mathrm{in}}} \tag{13}$$

The second law efficiency (II) is also known as rational exergy efficiency, which compares the system with an ideal reversible system considering both quantity and quality of the energy input (see Eq. 14). However, commonly, the thermodynamic value of the input materials, except fuel, is neglected in the calculation of second law efficiency and can then be written as follows:

$$\eta_{II} = \frac{W_{\min,CO2}}{\mathrm{EL}_{\mathrm{in}} + Q_{\mathrm{in}} * \left(1 - \frac{T_{\mathrm{env}}}{T_{\mathrm{bf}}}\right)} \tag{14}$$

Finally, the functional exergy efficiency evaluates the system performance with respect to how close it is to an ideal reversible system and takes into account the function of the system, i.e., the allocated roles for all the output streams are as follows: product (in this work, removed CO_2), by-product (in this work, water), and loss. Thus, in the current study, any product streams other than CO_2 are considered as a by-product ($Ex_{ch, byproducts}$) and therefore reduced from the exergy cost of the product.

$$\eta_{\rm ex} = \frac{{\rm Ex}_{\rm ch,CO_2}}{\sum {\rm Ex}_{\rm ch,in} - \sum {\rm Ex}_{\rm ch,byproducts}}$$
(15)

The chemical exergy of CO_2 is calculated as the minimum work that is thermodynamically required to remove CO_2 from the air under ambient conditions (Brandani 2012; Lackner 2013):

$$Ex_{ch,CO_2} = W_{min,CO2} = RTln \frac{p_{env}}{p_{CO_2}}$$
(16)

Since most of the energy (electrical, thermal, and chemical) requirement data in the literature are provided in the form of ranges, the assessment of each technology is calculated for the best-case and worst-case scenarios, using the minimum and maximum values of each energy input, respectively. Note that in those cases for which the literature provides a single value (rather than a range) for any energy requirement/s, the use of a single value for any of the inputs will yield a narrower range for the resulting overall exergy consumption of the system. Furthermore, when a range of desorption temperatures is given in the literature, the minimum thermal exergy is calculated with the minimum desorption temperature as $T_{\rm bf}$ in the Carnot factor and vice versa. Moreover, the effect of sorbent material degradation is accounted for through provided inputs over a certain range. For the adsorption processes, the material stability is considered to lie in the range of 50–200% of the literature values. For the absorption processes, which uses more mature sorbents thanks to the experience gained from other applications, the recovery factor is varied between the highest value found in the DAC literature (National Academies of Sciences 2018) and the value averaged from experiences with mature industrial processes employing a similar sorbent (provided by Honghi Tran 2008). This facilitates the inclusion of the different values provided by the literature and alleviates in part the uncertainties related to system operations.

3 Results and discussion

In order to carry out a fair comparison of the DAC processes, it is important to compare quantitative operational properties as well as qualitative ones. The operational parameters of the different DAC systems considered have been taken from the literature and are presented in Table 1. The material consumption levels of the DAC systems have been calculated as explained in Section 2. Sensitivity analyses carried out to account for uncertainties in the system yield a range of values for DAC performance indicators, rather than a single value.

Figure 3 shows the ranges of exergy efficiency and exergy destruction values obtained for the processes considered. In general, the highest exergy efficiency values are seen for ion exchange process, due to the use of natural air drafts instead of fans and the ability to regenerate the sorbent with low-temperature steam that is generated internally using the heat from sequestration compressors.

The energy and exergy requirements of the DAC systems are listed in Table 2. Adsorption-based DAC processes have high levels of energy consumption, mainly due to the need for regeneration heat. However, from the second law perspective, the heat does not account for as large a share of the efficiency losses, as compared to the first-law perspective, due to the relatively low temperature of the heat. This is confirmed by comparing the physical exergy consumption levels of the absorption and adsorption technologies. Table 2 highlights the importance of electrification: there are three KOH absorption cases in which the system operates with only electricity, only fuel, and a mixture of both. In terms of exergy, the electrified process provides a much higher level of performance. There are few options to achieve the high-temperature heat provision by means of electrification. It can be directly (through, e.g., plasma burners or indirectly (through, e.g., electrolysis followed by oxyfuel combustion of the output streams). The latter presents an opportunity to substitute the air separation unit in the process. A similar observation applies to adsorption processes: from an exergy point of view, they perform much better when electrified, albeit with the difference that, here, the heat can be produced by a heat pump.

In order to adapt to future energy systems, it is important to consider the operation of DAC processes that are powered with low-carbon energy inputs. In this context, the

Table 1 Operatio	nal parameters of DAC pro	ocesses given in literature				
Technology	Material	Desorption temperature (°C)	Desorption pressure (bar)	Capacity loss/recovery (%/cycle)	Material consumption (kg/t _{CO2})	Water consumption (t/ t _{CO2})
Adsorption TVS	Amine functionalized (Deutz and Bardow 2021; Gebald et al. 2011)	80–120 (Beuttler et al. 2019)	0.2 (Gebald et al. 2011)	0.05 (Azarabadi and Lackner 2019; Gebald et al. 2013)	13.87	Produces 0.8–2 (Fasihi et al. 2019)
Adsorption TVS	MOF (Cr) (Sinha et al. 2017)	100	-	1.5 (Azarabadi and Lackner 2019)	531.51	
Adsorption TVS	MOF(Mg) (Sinha et al. 2017)	100	-	0.005 (Azarabadi and Lackner 2019)	0.73	
Adsorption TVS	PEI on alumina (Ping 2018)	85–95	0.5–0.9	0.05 (Azarabadi and Lackner 2019)	7.39	
Adsorption TVS	K2CO3/AL2O3 (Ves- elovskaya et al. 2013)	150-300	1	0.21 (Veselovskaya et al. 2013)	75.26	
Adsorption TVS	Hydrated K2CO3 on support (Roestenberg 2014)	80-100	∼ 1	0.05	88.77	
Adsorption TSA	TRI-PE-MCM-41 (Kulkarni and Sholl 2012)	110	1.4	6.25 (Azarabadi and Lackner 2019)	3435	
Adsorption TSA	PEI on silica (Zhang et al. 2014)	130	1	0.05 (Azarabadi and Lackner 2019)	7.39	0.23
Absorption	KOH (Carbon Engineering Direct Air Capture of CO2 Home 2022; Keith et al. 2018a, 2018b)	006	_	_	25.45 KOH, 30.86 CaCO ₃	4.7–9 (Keith et al. 2018a, 2018b)
Absorption	NaOH (Baciocchi et al. 2006)	006	-	-	18.18 NaOH, 228 CaCO3 (Baciocchi et al. 2006; Madhu et al. 2021)	1.27–46 (Fasihi et al. 2019)

Table 1 (continu	led)					
Technology	Material	Desorption temperature (°C)	Desorption pressure (bar)	Capacity loss/recovery (%/cycle)	Material consumption (kg/t _{CO2})	Water consumption (t/ t _{CO2})
Absorption	NaOH (Socolow et al. 2011)	006	T	I	 18.18 NaOH, 3.5 CaCO₃ (Baciocchi et al. 2006; Board 2019; Madhu et al. 2021) 	0-46 (Fasihi et al. 2019)
Ion exchange	Anionic exchange resin (Goldberg et al. 2013a; Lackner 2009; Wang et al. 2011)	45 (Goldberg et al. 2013b)	1	Maximum of 100,000 cycles (van der Giesen et al. 2017)	1.515-2.02 (van der Giesen et al. 2017)	4.9–15.2 (van der Giesen et al. 2017)

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TSA temperature-swing adsorption, TVS temperature vacuum swing



Fig.3 Exergy efficiency and exergy destruction levels of the DAC systems assessed in this work. The green bars represent the ranges for exergy efficiency and the red bars indicate the ranges for exergy destruction

possibility to employ electrification plays an important role. Currently, three of the four categories of DAC can be electrified. Electrochemical and ion exchange processes are already electrified. Most of the adsorption processes can be electrified using heat pumps. However, as discussed above, the absorption processes still need some innovation for electrification (International Energy Agency 2022), even though the high-temperature heat required for calcination can be provided by renewable fuels (biogas, biomass, or hydrogen from renewable sources) or concentrated solar power (Nikulshina and Steinfeld 2009). It should be noted that there is also a negative aspect to the electrification of DAC systems, in that the electricity demand should be met by low-carbon electricity generation technologies (renewables or nuclear), which in the case of renewables will increase the land usage of the system (Madhu et al. 2021).

Table 2 reveals the relevance of the sorbent flows used, as the related chemical exergy consumption accounts for a large share of the total exergy destruction. Figure 4 compares the values of the first-law, second-law, and exergy efficiencies for the different DAC systems. The interval bars illustrate the range of possible values for first-law and second-law efficiencies for cases having different values available from literature. The first-law efficiencies are much lower than the second-law efficiencies for adsorption processes owing to the large amounts of heat required at low temperatures, mainly attributed to parasitic losses of the sorbent material and the module's construction material (Kulkarni and Sholl 2012). In general, absorption processes have lower second-law efficiencies due to their heavy demands for high-temperature heat. In this case, the drying of the calcium carbonate contributes significantly to the level of heat consumption (Zeman 2007). House et al. (1998) calculated the second law efficiency of the DAC systems in two ways: (i) through empirical analysis based on the concentration of CO2, yielding values below 5%, and (ii) from literature data on detailed DAC processes design, yielding values up to 13.5% for absorption

Table 2 Energy and exergy	requirements of the DAC systen	ns investigated in this work				
Material	Heat (kWh/tCO ₂)	Electricity, W _{el} (kWh/tCO ₂)	Physical exergy, $Ex_{ph}(kWh/tonCO_2)$	Chemical exergy, Ex _{ch} (kWh/tCO ₂)	Total exergy input (kWh/ tCO ₂)	Exergy destruc- tion (kWh/ tCO ₂)
Amine-functionalized sorbent	1,500–3305 (Deutz and Bardow 2021)	500–700 (Deutz and Bar- dow 2021)	733.71–1364	277.7–347-13	777.6-1145	643.5-1294.5
MOF(Cr)	2688 (Sinha et al. 2017)	220 (Sinha et al. 2017)	761	857.3-1069.3	1618.8-1830.8	1495.9–2209
MOF(Mg)	1319 (Sinha et al. 2017)	201 (Sinha et al. 2017)	467	1.4–1.75	468.58-468.93	344-346
TRI-PE-MCM-41	1,656 (Kulkarni and Sholl 2012)	218 (Kulkarni and Sholl 2012)	470	10,848–13,435	11,319–13,905	11,196–19,998
PEI on silica	889 (Zhang et al. 2014)	945 (Zhang et al. 2014)	1176	33.31-41.64	1210-1218	1087-1115
PEI on alumina	1170-1410 (Ping 2018)	150-260 (Ping 2018)	360-542	33.31-41.64	379.4–569.8	256.4-466.5
K_2CO_3/Al_2O_3	2102 (Veselovskaya et al. 2013)	76 (Veselovskaya et al. 2013)	697–1084	5.12-6.4	702.2-1091.2	579.3–971.3
Hydrated K ₂ CO ₃ on a support	2083 (Roestenberg 2014)	694 (Roestenberg 2014)	1018-1112	6.04-7.55	1024.5-1120.4	901.6–1001
KOH (NG + grid)	1458. (Keith et al. 2018a, 2018b)	366.00 (Keith et al. 2018a, 2018b)	1453	65.64–167.07	1519–1620	1396–1497
KOH (NG only)	2450. (Keith et al. 2018a, 2018b)	0 (Keith et al. 2018a, 2018b)	1727	65.64–167.07	1793–1894	1670–1771
KOH (grid only)	0 (Keith et al. 2018a, 2018b)	1500 (Keith et al. 2018a, 2018b)	1500 (Fasihi et al. 2019)	65.64–167.07	1567–1667	
NaOH (Baciocchi et al. 2006)	1678 (Baciocchi et al. 2006)	440 (Baciocchi et al. 2006)	1591	28.09–678	1,619–2270	1496–2147
(Socolow et al. 2011) Anionic exchange resin	2250 (Socolow et al. 2011) 0 (Lackner 2009)	494 (Socolow et al. 2011) 378 (Lackner 2009)	2172 195	0.366–668 85.74–228.8	2172–2841 281–424	2049–2718 158–301



Fig.4 Comparison of the average efficiency values (first-law, second-law, and exergy) for different DAC systems. The black bars show the possible range of first-law and second-law efficiencies based on available literature data. In case of data unavailability for the best case and worst case, a single value is presented

processes and 50% for moisture swing adsorption. Sabatino et al. (2021) also calculated the second-law efficiency for absorption (13.1-37.7%) and adsorption (7.6-7.9%) processes based on a process model which, i.e., they obtained values that differ somewhat from those of House et al. The values obtained in the current work are in agreement with results of Sabatino et al. Thus, we obtained 7.1-8.5% for the absorption process, 15-35% for the adsorption process, and 62.6% for the moisture swing adsorption process. The main reason for the difference between the current results (and those of Sabatino et al.) and the results of House et al. is that in this work the dependency on temperature of the conversion from heat to work is accounted for. However, both works indicate very low values of the second-law efficiency for the majority of the DAC processes and a relatively high value for the moisture swing process.

Finally, the exergy efficiency is lower than the second-law efficiency because it takes into consideration the loss of chemical exergy linked to the consumption of the material, which affects the different cases to different extents.

Figure 5 gives the shares of heat, electricity, and chemical exergy for the exergy consumption of the DAC in the best-case and worst-case scenarios. For each case, the left bar represents the best case, the right bar represents the worst case. It should be noted that the values are relative. Therefore, for few cases, although the absolute value of chemical exergy consumption increases, the share of chemical exergy in the worst case is lower than the best case due to larger changes in thermal and electrical exergy. The interval bars illustrate the range of possible values for first-law and second-law efficiencies for cases having different values available from literature. Generally, the largest shares of exergy consumption are dedicated to heat and electricity. However, the effect of material stability on exergy becomes clear for the case of TRI-PE-MCM-41 and MOF(Cr). Since they have very low stability, this material



Fig. 5 Exergy consumption profiles for the best-case and worst-case scenarios

needs to be replaced at a relatively high rate and, therefore, has a high chemical exergy consumption. The opposite is seen for MOF(Mg), which has a low chemical exergy consumption due to its high stability and high cyclic capacity. Another important conclusion is that, in terms of exergy, adsorption-based technologies are more chemical exergy consuming than other technologies. The main reasons for such a difference are the low specific chemical exergy of hydroxides and carbonates and very high reported recovery rates (between 97 and 99.84%) for hydroxides. Furthermore, the large share of the chemical exergy consumption in absorption-based processes is dedicated to water consumption.

4 Conclusions

A thermodynamic assessment of DAC systems that accounts for the makeup material flows has been carried out to evaluate the first-law, second-law, and exergy efficiencies of the most developed DAC processes in the literature. The results show that the chemical exergies of the sorbents used represent up to 60% of the overall exergy consumption. A sensitivity analysis designed to evaluate the dependence of exergy efficiency on the material stability and capacity reveals a deviation in exergy efficiency of up to 30% compared to the reference case. This underlines the importance of including the chemical exergy of the material flows in the performance indicators of process optimization for DAC systems. In detail, the exergy efficiency of adsorption processes is found to be more heavily dependent upon the sorbent material than that of absorption processes, which highlights the importance of developing more stable sorbent materials with higher capacities for the adsorption processes. For absorption processes, water is the main contributor to the chemical exergy consumption of the system, despite the high sorbent flows. This is a consequence of the very low chemical exergies of potassium carbonate and calcium carbonate.

The results also show that although adsorption processes have higher levels of energy consumption, the use of stable, high-capacity sorbents results in a lower exergy consumption than the case for absorption technologies, due to the lower temperature of the required heat. Thus, for absorption processes, the development should focus more on the areas that have stronger potentials for technical development, such as electrifying the calcination step, rather than on new sorbents.

Abbreviations

CDR: carbon dioxide removal; *DAC*: direct air capture; *DACCS*: direct air carbon capture and storage; *IPCC*: Intergovernmental Panel on Climate Change; *LHV*: lower heating value; *TSA*: temperature swing adsorption; *TVS*: temperature vacuum swing adsorption

Symbols

ex_{ch}: specific chemical exergy; *Ex_{el}*: exergy equivalent of electricity; *Ex_{th}*: thermal exergy; *T_{bj}*: bulk flow temperature; *T_{env}*: environmental temperature; *W_{el}*: work equivalent of electricity; *EL_{in}*: input electricity; *Ex_{ch,CO2}*: chemical exergy of CO₂; *Ex_{ch, byproducts}*: chemical exergy of by-products; *Ex_{ch, in}*: input chemical exergy; *Q_{in}*: input heat; *W_{min,CO2}*: thermodynamic minimum work of separation; *m_{in}*: input mass; *m_{out}*: output mass; *p_{CO2}*: partial pressure of CO₂ in environment; *p_{env}*: environmental pressure; *η_l*: first-law efficiency; *q_{ux}*: exergy efficiency; *Ex_{Destruction}*: exergy destruction; *Q*: heat; *R*: universal gas constant; *T*: temperature; *ex_{ch, in}*: specific chemical exergy of input; *ex_{ch, out}*: specific chemical exergy of output; *β*: ratio between specific chemical exergy and lower heating value

Funding Open access funding provided by Chalmers University of Technology. The authors acknowledge financial support from the Swedish Energy Agency and project partners within the project "Negative emissions with Direct Air Capture for Sweden" (P 2020-008294).

Data availability Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Declarations

Competing interests The authors declare no competing interests.

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