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Review

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**A new relevant membrane application: CO<sub>2</sub> direct air capture (DAC)**

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**Abstract**

Since carbon dioxide (CO<sub>2</sub>) is the primary greenhouse gas emitted due to human activities into the atmosphere, strong research efforts have been developed towards capturing and

decreasing its production. Unfortunately, specific processes and activities make it impossible to avoid CO<sub>2</sub> emissions. Among the different strategies scientists propose for CO<sub>2</sub> reduction, direct CO<sub>2</sub> capture from the atmosphere, also known as direct air capture (DAC), represents a promising alternative in which sorbents have been mainly used. Recently, gas separation membranes have also been speculated to carry out such a separation, thanks to their smaller footprint and simpler setup and operation; however, their application remains a proposition in the field. This paper gives a perspective of the ongoing research and attempts of DAC applications via membrane separation and introduces the main membrane materials and types used for CO<sub>2</sub> separation. Finally, the process considerations for DAC using membranes are stated to guide the new researchers in the field.

**Keywords:** Carbon dioxide; Direct air capture; Gas separation; Membrane; Polymer.

## 1. Introduction

The concept of direct capture of CO<sub>2</sub> from the atmosphere (DAC, direct air capture) was first introduced by Lackner in 1999 [1]. DAC constitutes a new approach to climate change remediation, which would lead to net-negative emissions by decreasing the CO<sub>2</sub> concentration in the air [2]. Extreme reductions in CO<sub>2</sub> emissions are required to meet the 1.5 °C scenario set by the Intergovernmental Panel on Climate Change [3,4]. The amount of CO<sub>2</sub> to be removed from the atmosphere to create a measurable effect would be

significant, and thus the technological challenge is overwhelming. However, the scientific approach to achieve this ambitious target may not be that challenging since the concepts, technologies and materials (mainly adsorbents) for the CO<sub>2</sub> capture already exist, and they (or the separation processes based on them) must just be adapted to the specific conditions of DAC. The conventional processes used for direct air capture are based on sorption technologies. Even though this approach is proven to be very effective, it requires a large amount of energy to desorb CO<sub>2</sub> from the sorbent [5]. Membrane technology is one of the leading approaches for capturing CO<sub>2</sub>, mainly because it offers lower cost, a more straightforward setup and operation, and a smaller footprint. It was pointed out that to make membranes attractive for the DAC, the selective membrane thickness should be reduced to a few nanometers to increase the membrane permeance meaningfully. Such conditions are needed to treat CO<sub>2</sub>, as it is a minor component in the Earth's atmosphere at a concentration of ~415 ppmv (the average value consigned for 2021 is ca. 414 ppmv, see Global Monitoring Laboratory) [6]. As compared to the evidently favorable conditions at point sources CO<sub>2</sub> capture (e.g., from the flue gas generated in energy installations, cement and steel productions), one of the main motivations for DAC comes from the fact that ca. one-third of CO<sub>2</sub> emissions come from billions of non-point-sources, associated with transport vehicles (e.g., several billions of cars and trucks) [7]. Particularly carried out with membranes, DAC would help compensate for these relatively small CO<sub>2</sub> emitters. Nevertheless, large-scale CO<sub>2</sub> separation with membranes is not yet a commercially available technology even though large amounts of funding have been spent worldwide in its R&D, whilst a vast number of reports dealing have been published during the last years. Thus, handling the very low solute concentration arises as a new complication

when the membrane application of CO<sub>2</sub> capture at the easiest conditions still needs additional improvements to become economically feasible. The "easiest conditions" refer to removing CO<sub>2</sub> emissions from combustion flue gases containing 10-15% CO<sub>2</sub> or from cement or steel exhausts with up to 30% CO<sub>2</sub> [8,9], i.e., from point sources. DAC would go beyond these conditions to control the atmospheric CO<sub>2</sub> composition and thus the Earth's average temperature. Besides, the captured CO<sub>2</sub> could become a carbon precursor for synthetic fuels and chemical feedstocks, directly decreasing the use of non-renewable fossil sources [10].

From the thermodynamics point of view [11], the low CO<sub>2</sub> concentration in the feed also makes an important difference. The minimum work ( $W_{\min}$ ) at isothermal conditions can be calculated with equation (1):

$$W_{\min} = RT \cdot \ln\left(\frac{P_p}{P_f}\right) \quad (1)$$

where R is the ideal gas constant, T the temperature in K and  $P_p$  and  $P_f$  are the permeate and feed CO<sub>2</sub> pressures, respectively.  $W_{\min}$  at 298 K needed to concentrate CO<sub>2</sub> to 1 atm increases as the CO<sub>2</sub> concentration in the feed decreases, being 19.3, 5.7 and 3.0 kJ per mol of CO<sub>2</sub> for CO<sub>2</sub> concentrations in the feed to be treated of 415 ppmv (0.04%), 100,000 ppmv (10%) and 300,000 ppmv (30%), respectively. In any event, the highest estimated energy for the most diluted condition is about 20-30 times lower than the actual values needed for the best performing CO<sub>2</sub> capture technologies from air based on amine absorption [11]. CO<sub>2</sub> separation with membranes is more convenient than the typical separation methods that could be used for the same purpose from the point of view of the low energy consumption and cost [12], avoidance of potentially hazardous compounds,

and thus minimization of environmental impacts [13], and modularity for adaptation to several scales of production.

Even if the idea of DAC was proposed at least ca. 20 years ago [14], and considering that the suitability of DAC to decrease CO<sub>2</sub> from the atmosphere has been addressed with some pioneering works based on the use of solid sorbents [15], only recently more detailed general review papers started to appear [1,16], some of them dealing with the so-called passive capture [17] (not the case with membranes where the air has to be forced through the system), as well as just a few specific works dealing with the application of membranes [3]. This is why this work focuses on the membrane application for DAC. This article will pinpoint membrane technology as a potential and attractive approach for DAC. A variety of membrane materials, configurations and processes will be discussed, followed by a commercial comparison of the state-of-the-art and proof of concepts existing both in the market and academia.

## 2. Process considerations

Based on simulation of chemical processes, Fujikawa *et al.* [3] have established the following key conditions for membrane DAC (m-DAC): i) 300 ppm of CO<sub>2</sub> concentration in the retentate; ii) 101.3 kPa (1 atm) feed pressure and vacuum (5 kPa) at the permeate, and iii) multistage separation to achieve a proper CO<sub>2</sub> concentration in permeate (ca. 40% with four consecutive separation stages).

Besides the intrinsic membrane properties (i.e., permeance and selectivity) determining the separation performance, other parameters, such as operation pressures, permeate composition and stage cut (the fraction of the feed gas that passes through the

membrane,  $\phi = F_p / F_f$ ) are key from the point of view of process design. A hypothetical membrane, displaying 100 GPU (1 GPU =  $10^{-6}$  cm<sup>3</sup> (STP)·cm<sup>-2</sup>·s<sup>-1</sup>·cmHg<sup>-1</sup>) of CO<sub>2</sub> permeance and a CO<sub>2</sub>/N<sub>2</sub> separation factor of 35, was used here to estimate the CO<sub>2</sub> molar fraction in the permeate as a function of feed pressure (**Figure 1a**) and the stage cut as a function of permeate pressure (**Figure 1b**) for several values of relative membrane area. Significantly, calculations reported in **Figure 1** are based on considering air as a binary mixture of CO<sub>2</sub> and N<sub>2</sub>. It is well known that the air contains 78% nitrogen, 21% oxygen and 1% of other minor components and water vapor. The CO<sub>2</sub> molar fraction in the permeate was calculated using the following equation (2) [18,19] :

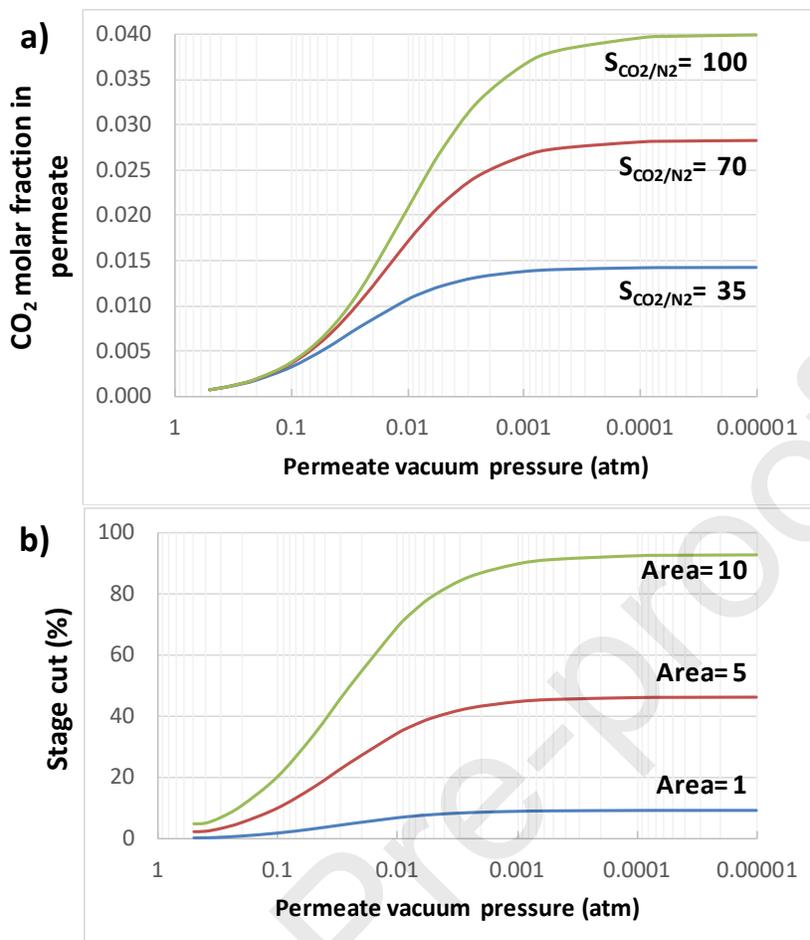
$$(\alpha - 1)y_{\text{CO}_2}^2 + (1 - \alpha - \phi - (\alpha - 1)\phi x_{\text{CO}_2})y_{\text{CO}_2} + \alpha\phi x_{\text{CO}_2} = 0 \quad (2)$$

where  $x_{\text{CO}_2}$  and  $y_{\text{CO}_2}$  are the CO<sub>2</sub> molar fractions in feed and permeate, respectively,  $\alpha$  is the separation factor, and  $\phi$  is the feed/permeate pressure ratio. This is a simplified model that does not reflect the real behavior of a gas separation module but that helps us perceive the difficulties dealing with DAC and suggests further accurate mathematical addressing. Having said that, even though the separation experiments were carried out at 1 atm feed pressure, **Figure 1a** shows that, in the case of CO<sub>2</sub>/N<sub>2</sub> selectivity of 35, there is a significant increase in the CO<sub>2</sub> molar fraction (0.0139) up to approximately 0.001 atm of vacuum in the permeate side, obtaining a moderate improvement of such value (0.0143) at 0.0001 atm. In addition, at the permeate pressure of 0.001 atm, stage cut values are equal to 9%, 44% and 87% for the relative membrane areas of 1, 5 and 10, respectively (**Figure 1b**). This means that, for a given feed flow to be treated, it is possible

to increase the stage cut to the desired value (to be determined from an economic optimization) by modifying the membrane module size (visualized in terms of membrane area). It is worth to mention that, even if **Figure 1** shows a wide pressure range, pressures below ca. 0.01 atm would not be feasible for large scale applications such as DAC. In any event, the low values of CO<sub>2</sub> concentration in permeate require the use of several sequential stages in which the permeate stream would be successively fed in the following membrane stage, as proposed by Fujikawa et al. [3]. The first stages would operate as preconcentration modules to achieve similar CO<sub>2</sub> concentrations as typical CO<sub>2</sub> capture applications. In addition, as **Figure 1a** suggests, the increase in the membrane CO<sub>2</sub> selectivity (e.g. from 35 to 70 and 100) directly impacts the CO<sub>2</sub> concentration in permeate. Therefore, for DAC a high value of membrane selectivity is more important than for traditional CO<sub>2</sub> capture applications in order to decrease the number of sequential membrane stages.

An illustrative example of both the potential and current limitations of DAC is given next. The Global Carbon Budget [20] projected 34.1 Gt of CO<sub>2</sub> emissions for 2020 (due to the COVID-19 pandemic, less than the 36.4 Gt of CO<sub>2</sub> emitted in 2019). Considering the application of m-DAC to remove 10% of this amount (i.e., 3.41 Gt of CO<sub>2</sub> with the atmosphere at 415 ppmv CO<sub>2</sub>) along one year and the use of the ultrathin (34 nm in thickness) PDMS membranes recently claimed to have the highest CO<sub>2</sub> permeance ever reported (40,000 GPU of CO<sub>2</sub> and CO<sub>2</sub>/N<sub>2</sub> selectivity of up to 12) [21]. Equation (2) allows, working at a 0.01 atm vacuum, the rough estimation of the necessity of 10<sup>7</sup> m<sup>2</sup> (i.e., 10 km<sup>2</sup>) of membrane area to obtain a permeate with ca. 0.5% CO<sub>2</sub> with a stage cut of 4.9%. This enormous membrane area is in line with the relatively low driving force close to 1

atm (1 atm in the feed side minus the ca. 0.01 atm vacuum in the permeate side). Besides, this amount of membrane area should be multiplied by ca. 1.2 due to the fact that, as said above, several successive membrane stages would be needed with a stage cut relatively low stage cut to reach the desired concentration of CO<sub>2</sub> in the permeate. If the membrane CO<sub>2</sub>/N<sub>2</sub> selectivity was 200 instead of 12, considering the same membrane area, the permeate would be ca. 2.8% in CO<sub>2</sub>, with the stage cut of 1.7%, alleviating the number of successive stages needed. All these values suggest that for this particular application of m-DAC, beyond the proof of concept in realistic conditions (i.e., treating atmospheric air, including the humidity effect and the fact that CO<sub>2</sub>/O<sub>2</sub> selectivity should be lower than that of CO<sub>2</sub>/N<sub>2</sub> with typical membrane materials), it still needs serious improvements from the point of view of both membrane thickness to extract the maximum permeance of a given material and selectivity [22]. We hope this perspective paper will contribute to guide the research on DAC with membranes in that sense.



**Figure 1.** CO<sub>2</sub> molar fraction in the permeate as a function of permeate vacuum pressure for three different membranes in terms of CO<sub>2</sub>/N<sub>2</sub> selectivity (a); and stage cut as a function of permeate vacuum pressure for three different relative membrane areas, selectivity CO<sub>2</sub>/N<sub>2</sub>= 35 (b).

### 3. Membrane materials for CO<sub>2</sub> capture

#### 3.1. Glassy and rubber polymers

Polymeric membranes, either glassy or rubbery, have been mostly used for selective CO<sub>2</sub> separation. In general, polymeric membranes have been assayed to separate CO<sub>2</sub> from other gases, where the main goal has been to overcome the typical permselectivity trade-

off of existing polymers. For instance, a few glassy polymers (e.g., polysulfone, polyethersulfone, polyetherimide, polyimides) display adequate performance for gas separation applications, as enlisted in **Table 1**. Most polymers have been assayed for CO<sub>2</sub> removal from methane (natural gas upgrading) as the core application of membrane gas separation. However, the interest in membranes towards other applications (e.g., DAC) has promoted the testing of such polymer membranes into CO<sub>2</sub>/N<sub>2</sub> separation as a starting initiative in the framework of CO<sub>2</sub> capture. Besides their high reproducibility and good mechanical properties, glassy polymers have proved interesting CO<sub>2</sub> separation performance depending on their physicochemical features. Glassy polymers are generally highly selective but with low permeability properties related to their structure, along with their physical or chemical attacks resulting in a significant decrease in performance. Moreover, particular polymers observe a reduction in permeability because of physical aging [23]. However, most of them own narrow pores but are opened enough for CO<sub>2</sub> permeation. At the same time, a few of them, such as polyacetylenes, poly(1-trimethylsilyl-1-propyne) (PTMSP) [24], offer high permeability ascribed to their high fractional volume (~20%). It is documented that such large permeability is thanks to the rigid double bonds of the polymer backbone and the bulky side groups, hindering chain segmental motion and concurrently avoiding polymer chains from packing efficiently [25,26].

One of the pioneering attempts at improving the CO<sub>2</sub> separation performance in polymers relies on their blending with other polymers and chemical agents, which can compensate for their weaknesses. As an example, ethylenediamine modified polyvinylamine [27] and poly(ethylene oxide) (PEO)-poly(methacrylic acid) (PMAA) [28] membranes have

demonstrated higher CO<sub>2</sub>/N<sub>2</sub> selectivities (ranged from 106 to 142) than their pristine polymers thanks to the chemical crosslinking protocols, which make a suitable rearrangement at the polymeric chain molecular level [29]. Particularly, ethylenediamine modified polyvinylamine membranes can even display enhanced CO<sub>2</sub> permeance with a value of 607 GPU and guaranteed separation performance over 300 h testing [27]. Interestingly, such membranes did not degrade when exposed to H<sub>2</sub>O-saturated SO<sub>2</sub> at 300,000 ppm. Apart from enhancing the separation performance, an improved CO<sub>2</sub>-induced plasticization resistance, which is a frequent issue in polymer membranes for CO<sub>2</sub> separation under high pressure [30], can also be observed. This was ascribed to the densification of polymer matrix by moderate hydrogen bond crosslinking [27]. Highly permeable membranes deal with the fabrication of hollow fibers such as the ones based on PDMS/PAN composites [31]. These membranes yielded permeance of 3,700 GPU with a CO<sub>2</sub>/N<sub>2</sub> selectivity of 10.

**Table 1.** Gas separation performance of glassy (such as polyimides, PTMSP, PIMs, PSF, PES, among others) and rubber polymers, mixed matrix membranes (MMMs) and inorganic membranes for CO<sub>2</sub> separation. This includes CO<sub>2</sub>/CH<sub>4</sub> separation results to provide potentiality alternative membrane materials to those currently tested for CO<sub>2</sub>/N<sub>2</sub> separation.

<i>Polymer/membrane material</i>	<i>Gas mixture</i>	<i>Operating conditions</i>	<i>CO<sub>2</sub> permeability/permeance</i>	<i>Selectivity/ Separation factor</i>	<i>Reference</i>
<b>Pebax®-MH 1657</b>	CO <sub>2</sub> /N <sub>2</sub>	25 °C, 0.2 MPa	300 GPU	40	[32]
<b>PDMS</b>	CO <sub>2</sub> /N <sub>2</sub>	25 °C, 0.2 MPa	3,395 Barrer	11	[32]
<b>PolyActive™</b>	CO <sub>2</sub> /N <sub>2</sub>	21 °C, 3 bar CO <sub>2</sub> pressure	~1,481 GPU	60	[33]
<b>Pebax®-MH 1657</b>	CO <sub>2</sub> /N <sub>2</sub>	21 °C, 6 bar CO <sub>2</sub> pressure	~740 GPU	50	[33]
<b>Polyimide 6FDA-TMPDA/DAT</b>	CO <sub>2</sub> /CH <sub>4</sub>	35 °C, 2 MPa	187.6 Barrer	33.9	[34]
<b>Polyimide 6FDA-TMPDA/DAT</b>	CO <sub>2</sub> /N <sub>2</sub>	35 °C, 0.2 MPa	187.6 Barrer	22.6	[34]
<b>Polyimide PI-5</b>	CO <sub>2</sub> /CH <sub>4</sub>	30 °C, 1 bar	190 Barrer	34	[35]
<b>Polyimide PI-5</b>	CO <sub>2</sub> /N <sub>2</sub>	30 °C, 1 bar	190 Barrer	26	[35]
<b>Polyimide 6FDA-TMPDA</b>	CO <sub>2</sub> /CH <sub>4</sub>	35 °C, 2 MPa	555.7 Barrer	22.7	[34]
<b>Polyimide 6FDA-TMPDA</b>	CO <sub>2</sub> /N <sub>2</sub>	35 °C, 2 MPa	555.7 Barrer	18.4	[34]
<b>Polyimide 6FDA-durene</b>	CO <sub>2</sub> /CH <sub>4</sub>	35 °C, 10 atm	677.8 Barrer	20.1	[36]
<b>6FDA-based polyimide</b>	CO <sub>2</sub> /CH <sub>4</sub>	30 °C, 1 bar	958 Barrer	24	[37]
<b>PIM-1</b>	CO <sub>2</sub> /N <sub>2</sub>	30 °C, 200 mbar	2,300 Barrer	25	[38]
<b>PTMSP</b>	CO <sub>2</sub> /CH <sub>4</sub>	25 °C	29,000 Barrer	4.46	[39]
<b>PTMSP</b>	CO <sub>2</sub> /N <sub>2</sub>	25 °C	29,000 Barrer	10.7	[39]
<b>PIM-7</b>	CO <sub>2</sub> /N <sub>2</sub>	30 °C, 200 mbar	1,100 Barrer	26.2	[38]
<b>6FDA-DAMA: DABA</b>	CO <sub>2</sub> /CH <sub>4</sub>	35 °C, 10 bar	97.66 Barrer	35.64	[40]
<b>PES</b>	CO <sub>2</sub> /CH <sub>4</sub>	35 °C	2.82 Barrer	28.83	[41]
<b>Blend: PHE + 80 wt. % PES</b>	CO <sub>2</sub> /CH <sub>4</sub>	35 °C	1.29 Barrer	46.08	[41]

<b>Matrimid® 5218</b>	CO <sub>2</sub> /CH <sub>4</sub>	35 °C, 10 bar	7.68 Barrer	34.91	[42]
<b>Blend: Matrimid® 5218+ 5 wt. % PEG 200</b>	CO <sub>2</sub> /CH <sub>4</sub>	35 °C, 10 bar	9.62 Barrer	40.08	[42]
<b>PIM-PI-8</b>	CO <sub>2</sub> /CH <sub>4</sub>	-	8,000 Barrer	20	[43]
<b>6FDA-DMN</b>	CO <sub>2</sub> /CH <sub>4</sub>	-	1,000 Barrer	25	[43]
<b>p-polyetherimide</b>	CO <sub>2</sub> /CH <sub>4</sub>	30 °C, 1 bar	200 Barrer	26.3	[44]
<b>p-polyetherimide</b>	CO <sub>2</sub> /N <sub>2</sub>	30 °C, 1 bar	200 Barrer	24.6	[44]
<b>PIM-1</b>	CO <sub>2</sub> /N <sub>2</sub>	-	1,100 Barrer	26.2	[45]
<b>PSF</b>	CO <sub>2</sub> /CH <sub>4</sub>	25 °C, 2 bar	27 GPU	3	[46]
<b>PES</b>	CO <sub>2</sub> /CH <sub>4</sub>	25 °C, 2 bar	15 GPU	5	[46]
<b>Amine-containing polymer/zeolite Y composite</b>	CO <sub>2</sub> /N <sub>2</sub>	57 °C, 0.1 bar; feed: 20/80% CO <sub>2</sub> /N <sub>2</sub>	1,000 GPU	>200	[47]
<b>Alkyl imidazolium-functionalized cardo-based poly(ether ketone)</b>	CO <sub>2</sub> /N <sub>2</sub>	30 °C, 2 atm	1.19 Barrer	66	[48]
<b>Pebax/PDMS-g-POEM</b>	CO <sub>2</sub> /N <sub>2</sub>	35 °C, 1 atm	442 Barrer	44.2	[49]
<b>Composite polyetheramine–polyhedral oligomeric silsesquioxane (POSS)</b>	CO <sub>2</sub> /N <sub>2</sub>	35 °C, 1 bar	380 Barrer	39.1	[50]
<b>Ultrathin PIM layer on PTMSP</b>	CO <sub>2</sub> /N <sub>2</sub>	35 °C, 3 bar; feed: 10/90% CO <sub>2</sub> /N <sub>2</sub>	>100 GPU	10	[51]
<b>PVAm/ZIF-8/PSf MMMs</b>	CO <sub>2</sub> /N <sub>2</sub>	22 °C, 0.15 MPa; feed: 15:85% CO <sub>2</sub> /N <sub>2</sub>	>1500 GPU	>100	[52]
<b>Poly(ether-block-amide)/attapulgitite MMMs</b>	CO <sub>2</sub> /N <sub>2</sub>	35 °C, 10 bar	104 Barrer	84	[53]
<b>Zeolite filled-carbon molecular sieve</b>	CO <sub>2</sub> /N <sub>2</sub>	35 °C, 1 bar; feed: 21:79 v/v CO <sub>2</sub> /N <sub>2</sub> mixture	2,615 Barrer	31	[54]
<b>Porous covalent triazine piperazine polymer /PEBAX</b>	CO <sub>2</sub> /N <sub>2</sub>	20 °C, 3 bar	73 Barrer	79	[55]
<b>Cu<sub>3</sub>(BTC)<sub>2</sub>/Matrimid MMMs</b>	CO <sub>2</sub> /N <sub>2</sub>	35 °C, 5 bar, feed: 35/65% CO <sub>2</sub> /N <sub>2</sub>	17 GPU	23	[56]

<b>ZIF-8/Matrimid MMMs</b>	CO <sub>2</sub> /N <sub>2</sub>	35 °C, 5 bar, feed: 35:65% CO <sub>2</sub> /N <sub>2</sub>	17 GPU	20	[56]
<b>MIL-53(I)/Matrimid MMMs</b>	CO <sub>2</sub> /N <sub>2</sub>	35 °C, 5 bar, feed: 35/65% CO <sub>2</sub> /N <sub>2</sub>	17 GPU	21	[56]
<b>PDMS/PAN hollow fiber composite</b>	CO <sub>2</sub> /N <sub>2</sub>	25 °C, 2 atm, feed: 35/65% CO <sub>2</sub> /N <sub>2</sub>	3,700 GPU	10	[31]
<b>Interfacially formed poly(N,N-dimethylaminoethyl methacrylate)/PSF</b>	CO <sub>2</sub> /N <sub>2</sub>	23 °C, 0.4 MPa	85 GPU	50	[57]
<b>Poly(N,N-dimethylaminoethyl methacrylate)/PSF</b>	CO <sub>2</sub> /N <sub>2</sub>	23 °C, 0.4 MPa	30 GPU	53	[58]
<b>PIM-1/Matrimid hollow fibers</b>	CO <sub>2</sub> /N <sub>2</sub>	25 °C, 1 atm	217 GPU	27	[59]
<b>Ni<sup>2+</sup>-exchanged zeolite X/polyetherimide MMMs</b>	CO <sub>2</sub> /N <sub>2</sub>	25 °C, 2 bar	1.8 Barrer	34	[60]
<b>Crosslinked PVA/PEG 600</b>	CO <sub>2</sub> /N <sub>2</sub>	25 °C, 1.5 bar	394 Barrer	79	[61]
<b>Sulfonated-PEEK (Na)</b>	CO <sub>2</sub> /N <sub>2</sub>	25 °C, 10 bar	14 Barrer	34	[62]
<b>PDMS/PEI hollow fiber</b>	CO <sub>2</sub> /N <sub>2</sub>	25 °C, 2 bar	59 GPU	21	[63]
<b>NanoFe<sub>2</sub>O<sub>3</sub> – incorporated PEBA</b>	CO <sub>2</sub> /N <sub>2</sub>	14 bar	180 Barrer	100	[64]
<b>Porous reduced graphene oxide/Pebax MMMs</b>	CO <sub>2</sub> /N <sub>2</sub>	30 °C, 0.2 MPa	119 Barrer	104	[65]
<b>UiO-66-NH<sub>2</sub>/PIM-1 MMMs</b>	CO <sub>2</sub> /N <sub>2</sub>	22 °C, feed: 20/20% CO <sub>2</sub> /N <sub>2</sub>	6,000 Barrer	22	[66]
<b>POSS® -PPO/PVA MMMs</b>	CO <sub>2</sub> /N <sub>2</sub>	25 °C, 1.3 bar, feed: 10% CO <sub>2</sub>	~333 GPU	40	[67]
<b>Ethylenediamine modified polyvinylamine</b>	CO <sub>2</sub> /N <sub>2</sub>	22 °C, 0.02 MPa, feed: 20/80% CO <sub>2</sub> /N <sub>2</sub>	607 GPU	106	[27]
<b>Poly(ethylene oxide) (PEO) - poly(methacrylic acid) (PMAA)</b>	CO <sub>2</sub> /N <sub>2</sub>	35 °C, 1 bar	7 Barrer	142	[28]

Polymers of intrinsic microporosity (PIMs) are also an example of highly permeable polymers for CO<sub>2</sub> [45]. The name refers to their high free volume (>20 %), a result of highly inefficient polymer packing due to their non-flexible and contorted macromolecular backbones [43]. In practice, such glassy polymers reveal high CO<sub>2</sub> permeability and good selectivity values towards binary CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> mixtures [68], but unfortunately, the "physical aging" associated with a reversible change in the polymer properties as a function of time constitutes a serious drawback [23]. Physical aging provokes an increase in selectivity but lowers permeation due to increased polymer density and decreased free volume. As a current practice, the embedding of nanomaterials (referred to as nanofillers) into polymer membranes, later termed as mixed matrix membranes (MMMs) [69], has led to not only the suppressing of physical aging in PIMs but also improving the gas separation performance [23]. For example, pristine PIM-1 membranes with CO<sub>2</sub> permeability and CO<sub>2</sub>/N<sub>2</sub> selectivity of 1,100 Barrer and 26 [45], respectively; while its functionalized MOF-embedded counterpart (UiO-66-NH<sub>2</sub>/PIM-1 MMMs), exhibited CO<sub>2</sub> permeability of up to 6,000 Barrer with a slight decrease in selectivity (ca. 22) [66]. Differently from MOFs and PIM matrices, the combination of other inorganic and organic materials has shown more selective properties for CO<sub>2</sub>/N<sub>2</sub> separations, e.g., nano Fe<sub>2</sub>O<sub>3</sub>-incorporated PEBA membranes and porous reduced graphene oxide (GO)/Pebax MMMs exhibited selectivity values of 100 [64] and 104 [65], respectively. Of course, their CO<sub>2</sub> permeability is lower than that of PIM-based MMMs since PIM membrane material itself offers a microporosity within the polymer network, which results in high permeation rates [23,43]. Compared to reduced GO/Pebax MMMs [65], GO/polyetherimide MMMs report

exceptional CO<sub>2</sub> permeance (up to 60,000 GPU) with negligible CO<sub>2</sub>/N<sub>2</sub> selectivity (ca. 1.0) [70]. There is a gap in finding the rational filler loading that may guarantee the membranes' selective properties, which is often detrimental due to the undesirable particle agglomeration.

A typical MMM should join the strengths of polymer and inorganic materials to fabricate superior performance membranes. To date, the application of nanofillers has likely been the most sought strategy at overcoming the performance trade-off. Plenty of nanoparticles has been explored, including metal oxide particles (e.g., MgO, TiO<sub>2</sub>, ZnO), zeolites, carbon molecular sieves, silica, carbon nanotubes, clays, metal-organic frameworks (MOFs), covalent-organic frameworks (COFs) and graphene-based materials, among others, where their influence on gas separation has been reviewed by several authors [69,71–73]. Of course, the performance of a membrane containing any filler will strongly depend on its properties (e.g., size, shape, chemical structure, surface chemistry, etc.), as well as its interaction with the polymer phase. At this point, porous fillers stand out as they can simultaneously improve both permeability and selectivity due to the excellent molecular sieving and precise pore apertures, which usually fall in the microporous range [74,75]. Therefore, a porous filler owning pore sizes around 0.33 nm (the kinetic diameter of CO<sub>2</sub> molecule), such as zeolitic imidazolate frameworks (ZIFs) ZIF-8 [76,77], ZIF-11 [78] and ZIF-94 [79], could be an excellent candidate to sieve CO<sub>2</sub> accordingly to its kinetic diameter. Moreover, other MOF type fillers with larger pores but higher adsorption interaction with CO<sub>2</sub> than ZIFs are also very effective: NH<sub>2</sub>-MIL-53 [80], NH<sub>2</sub>-UiO-66 [81], NH<sub>2</sub>-CAU-1 [82], NH<sub>2</sub>-MIL-101(Al) [83], etc. It is worth mentioning that MMMs or composite membranes have substantially profited from nanofillers to display impressive

gas separation performance towards CO<sub>2</sub>. However, inorganic materials at high loading may present sedimentation/agglomeration in the polymer chain matrix, restricting the implementation of MMMs in large scale gas applications [84,85], but still displaying prominent progress in CO<sub>2</sub> separation.

Thanks to the unprecedented performance for liquid phase and gas separations, inorganic membranes themselves can overcome the Robeson upper bound in different gas pairs separation, including CO<sub>2</sub> [86]. Inorganic membranes become more attractive when separating complex gas mixtures containing various components (H<sub>2</sub>, H<sub>2</sub>S, CO<sub>2</sub> and N<sub>2</sub>) since they present exceptional hydrothermal and mechanical stability [87–89]. Apart from their high fluxes, such membranes can stand high pressures (up to 10 MPa) [84] compared to polymeric ones. Over the last decade, inorganic membranes based on metals (e.g., palladium, nickel and silver) and oxides (e.g., alumina, zirconia, silicon nitride, titania) have been already commercialized for gas separation, as enlisted in **Table 2**. Porous membrane modules have been fabricated in various geometries, such as tubes, disks, monoliths, and plates, of which carbon membranes are produced from the pyrolysis of poly(vinylidene chloride-co-vinyl chloride) (PVDC-PVC) exhibited a CO<sub>2</sub>/N<sub>2</sub> selectivity of 13 [84]. Inorganic membranes are much more expensive than polymeric ones and unlikely to be scaled up for providing the necessary membrane area required for DAC application. However, the main advantage of these membranes comprises the high-pressure operation [90], even though it is not feasible for DAC since the compression of air is energetically impractical for this application [91]. When dealing with process intensification, hollow fiber modules are suitable for industrial applications due to the high permeation rates, which is related to their large effective surface area to volume ratios

[92,93]. Additionally, hollow fibers in cross-flow filtration are less susceptible to membrane fouling compared with tubular and flat sheet membranes since there is shear on the membrane due to bubbling, vibration, or particle scouring [94,95].

**Table 2.** Commercial inorganic membranes for gas separation.[84]

<i>Supplier</i>	<i>Trade name</i>	<i>Material</i>	<i>Pore size</i>	<i>Geometry</i>
<b>TECH-SEP</b>	CARBOSEP®	ZrO <sub>2</sub> /C	10-300 kDa	Tube
<b>Fairey</b>	STRATA-PORE®	Ceramics	1–10 μm	Tube/Plate
<b>USF/SCT</b>	MEMBRALOX®	ZrO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	20–100 nm	Monolith
<b>Whatman</b>	ANOPORE®	Al <sub>2</sub> O <sub>3</sub>	20 nm–0.2 μm	Disk
<b>Osmonics</b>	HYTREX®	Ag	0.2–5 μm	Tube/Plate
<b>Ceramem</b>	-	Ceramics/ Cordierite	0.05–0.5 μm	Honeycomb
<b>Steenacker</b>	-	Al <sub>2</sub> O <sub>3</sub>	0.4 μm	Tube
<b>Fuji Filters</b>	-	Glass	4–90 nm	Tube

At present, even if the inorganic and organic membranes have preliminarily met the current needs for CO<sub>2</sub> separation, new materials are continuously explored with the idea of finding out state-of-the-art membranes. However, if the existing materials could be smartly adapted into new membrane concepts and modules, they could be both more economically attractive and technically efficient. For instance, ultrathin membranes, fabricated as thin-film composite (TFC) membranes, can potentially provide exceptional separation efficiency with high permeation rates considering its very thin selective layer (below ca. 1 μm) [22]. Likewise, the fabrication of ultrathin membranes can lower the membrane cost, in which a small amount of organic (i.e., high-performance polymers)

and inorganic materials (e.g., zeolites, COFs, MOFs, carbon-based materials, among others) can be used. As an example, 1 m<sup>2</sup> of 100 nm layer of ZIF-8 (density 0.95 g cm<sup>-3</sup>), ZSM-5 (density 1.8 g cm<sup>-3</sup>), or graphite (density 2.2 g cm<sup>-3</sup>) would demand approximately 95, 180, and 220 mg of the inorganic material doped onto the porous support. Herein, the right preparation technique and the appropriate membrane structure will determine the thickness of selective layer and desired defect-free morphology [22,96]. According to Fijikawa *et al.* [3], it seems promising that most of the organic and inorganic membranes meet the hypothetically desired CO<sub>2</sub> selectivity (>30) for the 1000-fold preconcentration of the CO<sub>2</sub> from the air, while specific membranes with ultrathin configuration, such as PDMS and GO/polyetherimide (0.5 wt.%) MMMs can reach CO<sub>2</sub> permeances of ca. 10,000-60,000 GPU [22,70]. At the same time, the adaptation of different strategies may also result in highly permeable membranes. For instance, introducing ethylene oxide (PEO) units into the siloxane parts of PDMS as a hybrid PDMS-PEO with a thickness of 100 nm provided exceptional CO<sub>2</sub> adsorption properties, resulting in CO<sub>2</sub> permeance of up to 10,000 GPU [97]. More impressively, thinner PDMS membranes (ca. 34 nm in thickness) can display unprecedented CO<sub>2</sub> permeance (ca. 40,000 GPU) with a CO<sub>2</sub>/N<sub>2</sub> selectivity around 12 [21], in which the high porosity and interconnected structure guaranteed the abundance of gas transport channels. In any event, this high permeable PDMS membrane suggests that membrane DAC would be also possible with low selectivity membranes (just requiring some additional membrane stage), since a high permeance would be a serious factor to reduce the membrane area in line with the process discussion made in section 2.

Finally, often used membrane materials for the m-DAC application and very promising are amino polymers [98]. They are especially attractive since they possess the CO<sub>2</sub> capturing properties of amines (selectively capture CO<sub>2</sub> regardless of the air composition) with the benefits of the polymeric material as a scaffold and/or binding material. A few of the most promising amino polymers are poly(ethylenimine) (PEI), poly(allylamine) (PAA) and poly(propylenimine) (PPI). The following section provides an overview of some amino polymers implemented in membranes for CO<sub>2</sub> separation, along with highly branched, cross-linked poly(ethylene oxide) or poly(dioxolane), and facilitated transport membranes.

### 3.2. *Amino polymers and other promising polymers as membrane materials*

Amino polymers are particularly attractive for practical use due to their commercial availability and good CO<sub>2</sub> capacities and kinetics. Structurally, hindered amines have been effective for energy-efficient CO<sub>2</sub> capture and desorption in aqueous solution due to their weak amine-CO<sub>2</sub> binding and high amine efficiencies [99]. With this in mind, Lee et al. [98] fabricated an amino polymer, such as poly(2,2-dimethylenimine), with large densities of hindered amine moieties, and later incorporated it into mesoporous silica SBA-15. This amino composite presented an amine efficiency, expressed as mol CO<sub>2</sub> adsorbed per mol N, up to 0.22, which was a higher efficiency than that of pristine mesoporous silica SBA-15 (0.05). This improvement in CO<sub>2</sub> adsorption opens a new window for implementing this material in membranes that have not been yet reported. As an interesting development, polyvinylamine was synthesized and used as the fixed-site carrier in amino acid salts for CO<sub>2</sub> facilitated transport. The amine-containing polymer was coated onto a zeolite Y seed layer on top of a PES substrate. The obtained composite

membranes, presenting a selective amine layer thickness of more than 200 nm, displayed a CO<sub>2</sub>/N<sub>2</sub> selectivity of ca. 200 while offering a CO<sub>2</sub> permeance of 1000 GPU [47]. Poly(amidoamine)s incorporated into a cross-linked poly (ethylene glycol) have also promoted CO<sub>2</sub> transport, displaying a CO<sub>2</sub> permeability of 604 Barrer. Interestingly, the permeability increased as the amine content did [100].

Fixed carrier membranes containing tertiary amino groups have been documented by He et al. [101]. Particularly, membranes based on 1,4-bis (3-aminopropyl) piperazin and hexane-soluble trimesoyl chloride (DAPP-TMC) were prepared via interfacial polymerization and subsequently supported on PDMS/PS support. As for CO<sub>2</sub>/N<sub>2</sub> mixture separation, the membranes exhibited a selectivity of ca. 85 with a CO<sub>2</sub> permeance of over 400 GPU. Similar to He's work [101], Salih et al. [102] also reported an interesting CO<sub>2</sub>/N<sub>2</sub> performance with polyether amine membrane with PDMS inter-layer. In this study, the CO<sub>2</sub> permeance was reported as high as 360 GPU together with a CO<sub>2</sub>/N<sub>2</sub> selectivity of 67.2.

Ultimately, interesting polymers have been implemented in membranes for superior CO<sub>2</sub>/N<sub>2</sub> performance. This is the case of highly branched poly(1,3 dioxolane) plasticized by polyethylene glycol [103]. According to the authors, such blending membranes displayed stable mixed-gas CO<sub>2</sub>/N<sub>2</sub> separation performance above the upper bound, e.g., CO<sub>2</sub> permeability of 1540 Barrer and CO<sub>2</sub>/N<sub>2</sub> selectivity of 40 when tested with a model flue gas at 60 °C. Supporting this previous study, polymers with poly(1,3-dioxolane) branches have demonstrated outperforming CO<sub>2</sub>/N<sub>2</sub> separation properties with 4,763 Barrer of CO<sub>2</sub> permeability and CO<sub>2</sub>/N<sub>2</sub> selectivity of 86 [104]. This performance was

ascribed to highly branched amorphous polymers containing poly(1,3-dioxolane) in the branches, which can interact positively with CO<sub>2</sub> but not N<sub>2</sub>.

Thanks to its high CO<sub>2</sub> affinity, poly (ethylene oxide) (PEO) represents an excellent candidate for CO<sub>2</sub> separation. PEO membranes were even improved by using amine-branched poly- (amidoamine) (PAMAM) dendrimers. Such resulting PEO/PAMAM membranes offered 6-fold higher CO<sub>2</sub>/N<sub>2</sub> selectivity than bare PEO membranes [105]. For instance, the PEO/PAMAM membrane containing 2.5 wt. % PAMAM loading exhibited a CO<sub>2</sub> permeability of 32.3 Barrer and a CO<sub>2</sub>/N<sub>2</sub> selectivity of 42; this latter finding claimed to consider these membranes with the best gas separation performance of free-standing high-molecular-weight PEO-based membranes so far. According to a timely review provided by Liu et al. [106], crosslinked PEO membranes tend to offer attractive CO<sub>2</sub>/N<sub>2</sub> selectivities ranging from 17 up to 68 with CO<sub>2</sub> permeabilities from 2.1 to 580 Barrer. To some extent, PEO-based membranes may benefit from a remarkable CO<sub>2</sub> permeability enhancement by tuning their free volume via physical blending with nanomaterials. Interestingly, when the CO<sub>2</sub> plasticization usually represents a serious issue in decreasing the separation performance in glassy polymers [75,107], PEO-containing membranes may offer a better performance when the selective layer is plasticized [108]. This fact has been attributed to the greater polymer chain mobility due to CO<sub>2</sub>-induced plasticization and the enhanced polymer-CO<sub>2</sub> interactions [106].

Other emerging membrane concepts, such as liquid membranes, ion-exchange membranes and fixed carrier membranes, are a current scope of research dealing with facilitated transport membranes for potential CO<sub>2</sub> separation. For instance, potassium bis (trifluoromethanesulfonyl)imide (KTFSI)/Pebax 2533 facilitated transport membrane

exhibited optimized CO<sub>2</sub> permeance of ca. 600 GPU with a CO<sub>2</sub>/N<sub>2</sub> selectivity of approximately 50, as a result of molecular interactions of CO<sub>2</sub> with both K<sup>+</sup> and TFSI species [109]. Compared to the previous study, impressively, a PEIE-HT membrane (copolymerized polyethyleneimine-hydrotalcite complex) yielded a CO<sub>2</sub> permeance as high as 5,693 GPU with a CO<sub>2</sub>/N<sub>2</sub> selectivity of 268 [110]. To date, facilitated transport membranes still remain as early-stage developments and tentatively moving from the laboratory to the scale-up through continuous roll-to-roll fabrication for the preparation of prototype membranes and membrane modules for the feasible technology demonstration, prior to their possible commercialization [111].

#### 4. DAC with membranes

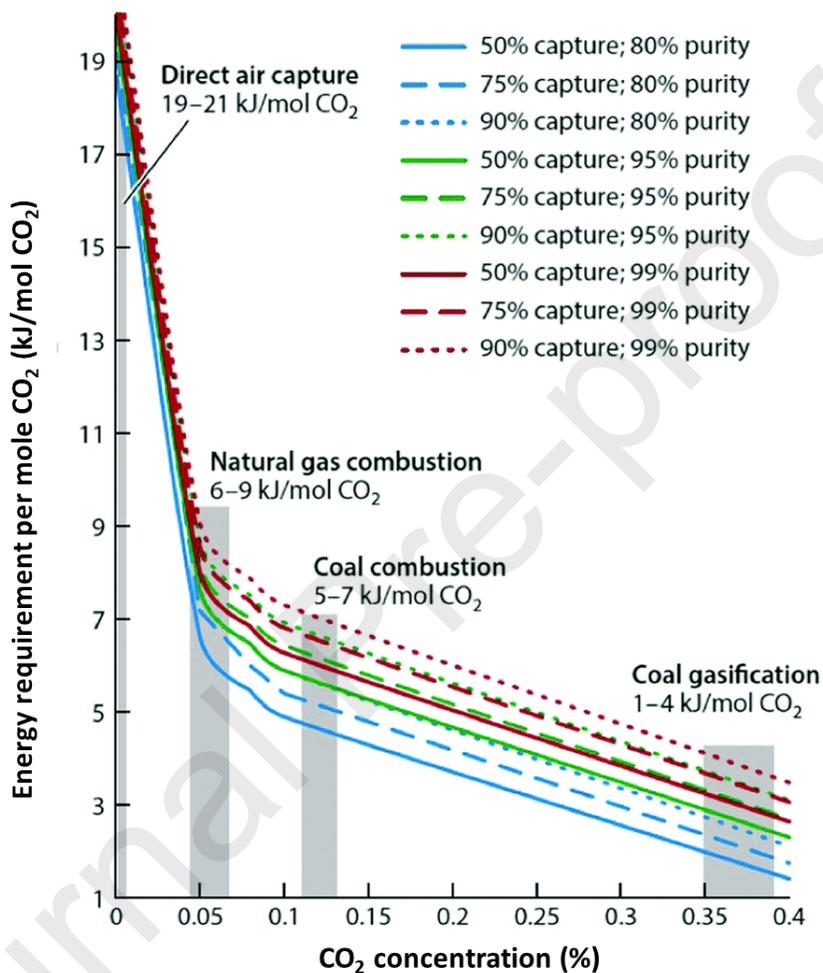
It is widely agreeable by membrane separation scientists that membrane-based direct air capture (m-DAC) could make a significant contribution to reduce the greenhouse gas (GHG) emissions by: (1) acting as a CO<sub>2</sub>-feedstock provider to various processes such as power-to-liquids (i.e., conversion to liquid fuels), power-to-gas (i.e., conversion to gaseous fuels) and power-to-chemicals, and (2) acting as a negative emission technology (NET) [112]. Implementing m-DAC as one of the NETs is also aimed to ultimately achieve the target of reducing the atmospheric temperature by 1.5 °C [112]. The topic of CO<sub>2</sub> capture using m-DAC remains divisive and challenging, generally because of the higher thermodynamic barrier due to the low concentration of CO<sub>2</sub> in the air (~400 ppm, partial pressure of only 40 Pa). Directly, this limitation generates a more significant specific energy requirement (i.e., 19 – 21 kJ·mol<sup>-1</sup> CO<sub>2</sub>, see **Equation 1** and **Figure 2** [113]). Membrane processes are known to have strong parametric sensitivity (i.e., product purity,

energy requirement, and productivity relationship) [114]. Thus, finding the right balance it is essential to compete with other air capture technologies. Recently, two studies presented the generic possibility-and-limitation analysis of an m-DAC and provided the basic feasibility information of the DAC-specific membrane process [3]. Both studies cover only the technical aspects and target performances of an m-DAC process, e.g., purity, recovery, and specific energy requirement without cost performance analysis.

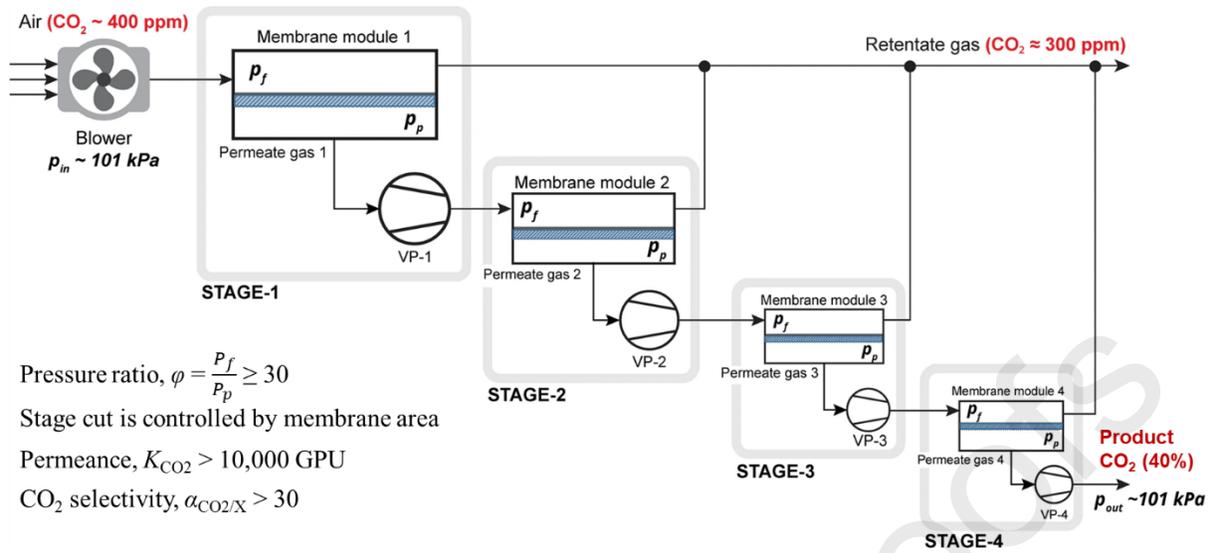
Fujikawa *et al.* [3] evaluated multistage membrane processes consisting of high CO<sub>2</sub> permeance and high CO<sub>2</sub>/N<sub>2</sub> selectivity membranes in a simulation process using software Aspen Plus implemented with Memsic. The preliminary assessment was based on their ultra-thin freestanding siloxane nanomembrane (thickness of 34 nm) with ultra-high CO<sub>2</sub> permeance of 40,000 GPU, which was achieved in their separate study [21]. The CO<sub>2</sub>/N<sub>2</sub> selectivity was set at 70. After the process optimization (CO<sub>2</sub> permeance ( $K_{CO_2}$ ), CO<sub>2</sub> selectivity ( $\alpha_{CO_2/X}$ , X = N<sub>2</sub>, O<sub>2</sub>, Ar), feed to permeate pressure ratio ( $\varphi = P_f/P_p$ ), module stage cut ( $\vartheta = F_p/F_f$ )), the retentate was set at preindustrial atmospheric CO<sub>2</sub> concentration of 300 ppm and CO<sub>2</sub> product concentration at 40% to achieve negative CO<sub>2</sub> emission ( $kgCO_2^{emitted}/kgCO_2^{captured} \leq 1.0$ ). Their findings can be summarized as illustrated in

**Figure 3**, where the relevant permeate CO<sub>2</sub> concentration (>10%) can be achieved by three- and four-stage separations, while single- or two-stage separation remains below 3% CO<sub>2</sub>. Interestingly, their findings indicate that the CO<sub>2</sub> emission related to the energy required for the process is only ~0.6 kg/1 kg-CO<sub>2</sub> captured, leading to negative emission of CO<sub>2</sub>. Additionally, albeit it was set at 40% (400,000 ppmv) in this study, the authors also emphasized no specific concentration requirements for CO<sub>2</sub> utilization (the next step for post CO<sub>2</sub> capture) and thus, the number of separation stages can be amended

accordingly. For example, CO<sub>2</sub> utilization through electrochemical reduction of CO<sub>2</sub> to CO can be achieved efficiently even using low purity CO<sub>2</sub> feedstock, as low as 1,000 ppm CO<sub>2</sub> [115], which can be achieved using only a single-stage m-DAC (CO<sub>2</sub> concentration in permeate of 0.7%  $\approx$  7,000 ppm) [3].



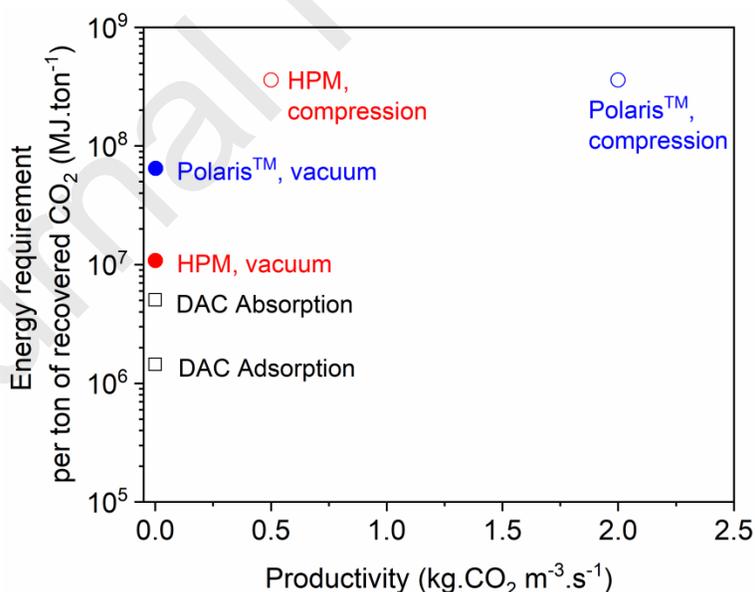
**Figure 2.** Minimum work required for CO<sub>2</sub> capture based upon initial CO<sub>2</sub> concentration, capture rate, and final CO<sub>2</sub> purity. Reproduced from Wilcox *et al.* [113].



**Figure 3.** Simplified scheme of the four-stage membrane separation model, optimized using Aspen Plus (process constraints: retentate  $\text{CO}_2 = 300$  ppm at every separation stage, feed pressure  $P_f \sim 101$  kPa, permeate pressure  $P_p = 5$  kPa, pressure ratio,  $\varphi \geq 30$ ; membrane  $\text{CO}_2/\text{X}$  selectivity  $\geq 30$ , where X identifies as the other air components, i.e.,  $\text{N}_2$ ,  $\text{O}_2$ , Ar).  $P_{\text{in}} = P_{\text{out}} \sim 101$  kPa, and VP-1 to VP-4 are vacuum pumps. Image adapted with permission from Springer Nature 2021 [3].

In another study, Castel *et al.* [116] simulated a single-stage m-DAC using commercially available Polaris™ (extrapolated values of  $K_{\text{CO}_2} = 2,000$  GPU,  $\alpha_{\text{CO}_2/\text{N}_2} = 30$ ) and a most promising high performance ultrathin graphene oxide (GO) membrane, referred to as HPM ( $K_{\text{CO}_2} = 2,500$  GPU,  $\alpha_{\text{CO}_2/\text{N}_2} = 680$ ) [117]. When relating the specific productivity of an m-DAC as a function of  $\text{CO}_2$  purity, as expected, increasing selectivity indeed systematically induces a larger membrane surface area requirement. This is due to the faster decrease in the driving force as the permeating purity increases. The energy requirement results are presented against productivity in their simulated single-stage m-DAC (target  $\text{CO}_2$  purity was set at  $0.2 - 0.25\% \approx 2,000 - 2,500$  ppm) in **Figure 4**, in

comparison with non-membrane based DAC processes (absorption and adsorption) [118,119]. Interestingly, both Polaris™ and HPM showed much higher process capacity with  $0.002 \text{ kg CO}_2 \cdot \text{m}^{-3} \cdot \text{s}^{-1}$  and  $0.0005 \text{ kg CO}_2 \cdot \text{m}^{-3} \cdot \text{s}^{-1}$ , respectively, with vacuum pumping, and even higher with compression (Polaris™ =  $2.0 \text{ kg CO}_2 \cdot \text{m}^{-3} \cdot \text{s}^{-1}$ ; HPM =  $0.5 \text{ kg CO}_2 \cdot \text{m}^{-3} \cdot \text{s}^{-1}$ ). Whereas the absorption and adsorption processes (limited to the feed stage and do not include the regeneration/purge unit) only showed  $0.00001 - 0.0002 \text{ kg CO}_2 \cdot \text{m}^{-3} \cdot \text{s}^{-1}$  and  $0.00031 \text{ kg CO}_2 \cdot \text{m}^{-3} \cdot \text{s}^{-1}$ , respectively. In their specific test conditions of m-DAC simulation (with a very low stage-cut,  $\phi = F_p/F_f$  of around 0.01), it is important to note that the feed compression and vacuum pumping energy requirement curves are similar but resulted in different permeate concentrations (i.e.,  $\text{CO}_2$  productivity). The result demonstrates the direct influence of the pressure ratio ( $\phi = P_f/P_p$ ) since a very low vacuum level (1 – 10 mbar) is difficult to be achieved at an industrial scale. In fact, Fujikawa *et al.* proposed 50 mbar as work vacuum pressure [3].



**Figure 4.** Mapping of energy requirement per ton of recovered  $\text{CO}_2$  versus productivity of the simulated m-DAC performances using Polaris™ and advanced HPM membranes,

evaluated by Castel *et al.* [116], in comparison to absorption and adsorption DAC processes presented by Kiani *et al.* [118] and Kulkarni and Sholl [119].

Castel *et al.* [116] also simulated the separation of an m-DAC consisting of Polyactive™ membrane ( $K_{\text{CO}_2} = 1,100$  GPU,  $\alpha_{\text{CO}_2/\text{N}_2} = 46$ ,  $\alpha_{\text{CO}_2/\text{O}_2} = 17$ ,  $\alpha_{\text{CO}_2/\text{H}_2\text{O}} = 0.1$ ) [33] using a multicomponent feed steam corresponding to air ( $\text{N}_2$  79%,  $\text{O}_2$  21%,  $\text{CO}_2$  400 ppm, dry basis), saturated in humidity at 25 °C. Because this polymeric membrane showed very high water permeance and larger  $\text{O}_2$  permeance than  $\text{N}_2$  permeance, the permeate was enriched with oxygen and collected almost integrally the water feed flux. This finding further emphasizes that membrane materials selection is crucial as the permeate product composition is essential to determine the target captured- $\text{CO}_2$  application, i.e., catalytic conversion processes can be, in some cases, sensitive to oxygen or wet  $\text{CO}_2$  feed [116].

Assuming the fixed  $\text{CO}_2$  feed and retentate concentration (at ~400 and ~300 ppm, respectively) and fixed feed-permeate pressure difference for either vacuum or compression dependent m-DAC system (at ~100 kPa), the determining factors to establish a practical m-DAC system would be:

*i. Membrane permeance (K);*

Many researchers have presented and validated that increasing  $\text{CO}_2$  permeance mainly reduces the membrane area required [120,121]. This aspect is the most crucial component in strategizing the minimization of membrane area and energy consumption in an m-DAC system, and with the currently available advanced methods fabricating very thin selective layer membranes (membrane thickness ( $l$ ) of < 200 nm) are achievable, as demonstrated with

several high-performing ultra-thin composite membranes [122,123] for gas separation application.

Nonetheless, high permeating membranes usually have lower selectivity values, in line with the well-known permeability-selectivity trade-off [124]. Therefore, applying a low selectivity membrane in a single-stage m-DAC is unsuitable due to low CO<sub>2</sub> product purity ( $y_{CO_2}$ ), and m-DAC may require multiple stages to achieve high separation efficiency.

ii. *Membrane selectivity ( $\alpha$ );*

With a fixed retentate CO<sub>2</sub> concentration, a higher membrane selectivity ( $\alpha_{CO_2/X}$ , X = N<sub>2</sub>, O<sub>2</sub>, Ar) leads to a higher permeate gas CO<sub>2</sub> concentration ( $y_{CO_2}$ ) and its partial pressure in permeate ( $P_p \cdot y_{CO_2}$ ), owing to the low permeance of the less permeable components (N<sub>2</sub>, O<sub>2</sub> and Ar). Following that, the permeate gas flow rate ( $G_p$ ) decreases (see Eq. 3), influenced by the decreasing driving force for CO<sub>2</sub> to permeate steadily. Considering the apparent decrease of CO<sub>2</sub> flow rate, it can be concluded that an increase in membrane selectivity leads to a lower permeate gas flow rate at each differential area. In consequence, a larger membrane area is needed, which directly influences the membrane module and power consumption costs.

More detailed membrane performance and process specification analyses applicable to m-DAC were presented on membrane-based post-combustion CO<sub>2</sub> capture systems [125,126].

$$G_p = F_f \left( \frac{x_{f,CO_2} - x_{0,CO_2}}{y_{p,CO_2} - x_{0,CO_2}} \right) \quad (3)$$

iii. *Practical permeance-selectivity balance for each membrane in a multistage process*

As discussed above, applying a low selectivity membrane with high permeance in the first stage will require high selectivity membranes in the following stages. For example, in a two-stage m-DAC system, the high CO<sub>2</sub> permeance will effectively reduce the total membrane area in the first stage but increase the energy consumption due to the low accompanied selectivity. To achieve the lowest possible CO<sub>2</sub> capture cost, the second stage would require a higher selectivity membrane with moderate CO<sub>2</sub> permeance.

Xu *et al.* [126] comprehensively evaluated the optimal membrane permeance and selectivity in their techno-economic study of a membrane process for post-combustion CO<sub>2</sub> capture. The authors emphasized that when the second-stage CO<sub>2</sub> permeance was fixed at 519 GPU, the first-stage CO<sub>2</sub> permeance increased to 2,916 GPU (from 1,453 GPU) with a total membrane area of  $9.7 \times 10^5 \text{ m}^2$  to be economically feasible. When the first stage CO<sub>2</sub> permeance was further increased to 7,314 GPU, the total membrane area also decreased to  $4.0 \times 10^5 \text{ m}^2$ . They also recommended that the first stage CO<sub>2</sub> permeance be kept at 3,000 GPU to have a total membrane area below  $9.0 \times 10^5 \text{ m}^2$  and the CO<sub>2</sub> capture cost below USD 27.5 ton<sup>-1</sup> CO<sub>2</sub>. From this techno-economic analysis and considering the current membrane availability, it is safe to suggest that the first stage membrane could be the commercially available Generation-2 Polaris™ spiral-wound membrane ( $K_{\text{CO}_2} = 2,000 \text{ GPU}$ ,  $\alpha_{\text{CO}_2/\text{N}_2} = 49$ )[127] and an advanced thin-film PVAm/PG-containing membrane ( $K_{\text{CO}_2} = 700 \text{ GPU}$ ,

$\alpha_{\text{CO}_2/\text{N}_2} = 140$ ) [128], which is produced at pilot scale by Ohio State University [129]. The same group is also working on a pilot-scale  $\text{CO}_2$  capture from less than 1%  $\text{CO}_2$  sources, using their improved cost-effective nanoporous polymer support and a top layer coating of thin, highly-selective, permeable, amine-containing polymer membrane ( $K_{\text{CO}_2} = 1,800$  GPU,  $\alpha_{\text{CO}_2/\text{N}_2} = 140$ ) [130].

As highlighted by Xu *et al.* [126] and several other techno-economic evaluations [125,131], an important balance between membrane module and power costs needs to be achieved, and it is highly dependent on whether compression or vacuum is applied. Descriptively, when a low feed pressure provides the minimum energy consumption, it also gives lower separation productivity and thus larger membrane area is required. Equally, increasing feed pressure at a higher energy requirement reduces the membrane area required.

To bring the m-DAC technology forward, we (researchers) will need to provide extensive techno-economic assessment studies, evaluating future technical development needs such as the energy (compression and vacuum) requirements, the efficiency and process specifications, combining with economic calculations (such as the potential cost of captured  $\text{CO}_2$ ). It is also advisable to assess the m-DAC potential as integrated capture-and-utilization models, combining several  $\text{CO}_2$  utilization techniques such as electro-reduction processes. We will also need commercial organizations to participate in the large-scale pilot testing. One of the few excellent examples is Carbon Engineering (<https://carbonengineering.com/>), where the company aimed to capture  $\text{CO}_2$  with air-liquid contactor technology at a megaton-scale globally. The company has demonstrated the effectiveness of their DAC and AIR TO FUELS™ technologies, and has captured  $\text{CO}_2$

directly from the air since 2015 and has produced synthetic fuel since 2017. Another interesting approach for DAC is the combination of membranes and moisture swing phenomena, as described by Lackner et al. [132] The method constitutes a low humidity atmosphere on the membrane feed side and a high humidity atmosphere on the membrane permeate side. The  $\text{CO}_2$  permeates through, for example ion exchange membrane, and binds to water creating a bicarbonate brine. The membrane permeate side is heated up to separate water and  $\text{CO}_2$ . In this process, water acts as an energy source, i.e., the free energy is released by the water evaporation and it is consumed in the concentration of  $\text{CO}_2$ . In this case the membrane works as a membrane contactor, combining the benefits of the membrane material and the liquids that are in close contact with the membrane. In any event, some of these potential membrane technologies for DAC would have to be submitted to an economic analysis to objectify their feasibility.

##### **5. Advantages of membranes over other potential DAC technologies**

As mentioned in previous sections, there is a clear need for technologies for  $\text{CO}_2$  capture and separation. Over the years, different methods were examined. For example, calcium hydroxide solutions were commonly used in the 90s; however, the drying and calcination of calcium carbonate, formed after binding to carbon dioxide, to release  $\text{CO}_2$  require energy and thus results in the most significant component of the energy penalty for calcium hydroxide systems [1]. Sorption (e.g., using microporous materials and liquid amines) and membrane operations are the most common technologies to separate  $\text{CO}_2$ . As for solid amine sorbent-based adsorption, porous oxide (most common is porous alumina) is often used as a support. On the other hand, liquid absorbents always show

challenges in terms of the risk of leaking, equipment corrosion, liquid degradation, and release of volatile organic compounds [133]. Moreover, current liquid-scrubbing technologies require large footprints and the installation sites are limited.

All the drawbacks of conventional methods turned the attention to membrane engineering. Besides all the advantages of membrane-based CO<sub>2</sub> capture methods, one of the major advantages is that, unlike in conventional sorbent-based DAC processes, there is no need to apply high energy to separate CO<sub>2</sub> from the sorbent [1]. Moreover, the technology has high scalability and installation possibilities in various locations (e.g., looking for low energy cost) [3], and it can be operated continuously and require less energy for separation or purification [134]. The comparison of the most common carbon capture technologies can be seen in Table 3, including energy costs in terms of MJ/kgCO<sub>2</sub>, taking into account that these correspond to situations where the CO<sub>2</sub> concentration is much higher than in DAC.

**Table 3.** Comparison of carbon capture technologies [135–139].

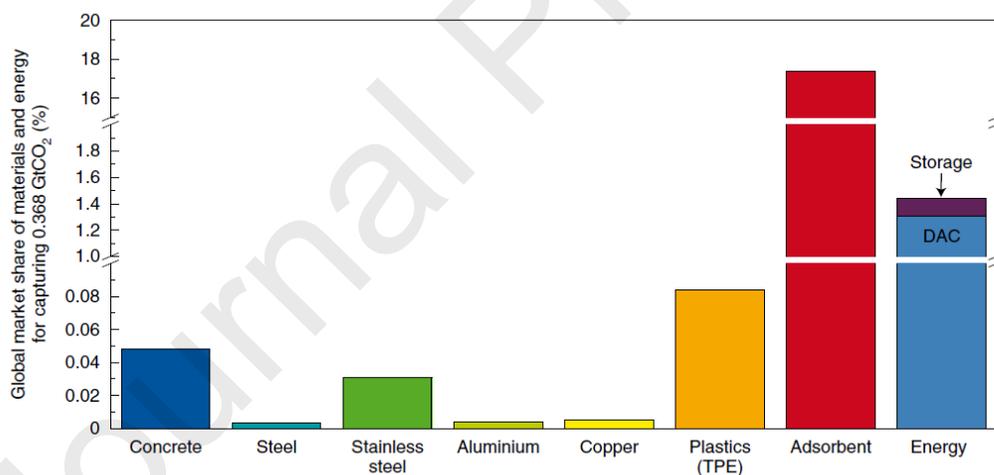
	<b>Absorption</b>	<b>Adsorption</b>	<b>Cryogenic distillation</b>	<b>Membrane</b>
<b>Operating flexibility</b>	High	Moderate	Low	High
<b>Control requirement</b>	High	High	High	Low
<b>Toxicity</b>	Emission of corrosive and harmful solvent	N/A	No solvent need	Clean
<b>Response to variation</b>	Rapid (5-15 min)	N/A	Slow	Instantaneous

<b>CO<sub>2</sub> recovery efficiency</b>	90-98%	80-95%	>95%	80-90%
<b>Energy requirement</b>	4-6 MJ/kgCO <sub>2</sub>	2-3 MJ/kgCO <sub>2</sub>	6-10 MJ/kgCO <sub>2</sub>	0.5-6 MJ/kgCO <sub>2</sub>

Another advantage is that the membrane properties (thickness, porosity and configuration) are, in principle, relatively easy to tune into specific applications. It is also possible to enhance their performance by incorporating a filler as MMMs, immobilizing a chosen compound, fixing a gas carrier (facilitated transport membranes, or designing and fabricating composite structures.

The membrane throughput can be increased by changing membrane configuration from flat-sheet thin films into hollow fiber structures. Hollow fibers are characterized by a high surface-to-volume ratio and can be utilized as a medium for the immobilization of other phases, as it was presented by Xu *et al.* [134], where PVDF hollow fiber membranes contained sodium carbonate solution and immobilized carbonic anhydrase enzyme to facilitate CO<sub>2</sub> transport and separate it from the air. In another CO<sub>2</sub> recovery study [140], hydrophobic microporous hollow fiber membranes were used with the help of electrolysis. A K<sub>2</sub>CO<sub>3</sub> solution formed by carbon dioxide absorption in KOH was fed to a membrane electrolyzer, where acid (CO<sub>2</sub>) and base (KOH) were regenerated by electrolysis. Hollow fibers offered a way of creating a large, fixed contact area in an adsorber that could then be optimized considering pressure loss of the media to be contacted. The liquid was placed on the lumen side of the hollow fiber, and the mass transfer occurred via gas phase diffusion through gas-filled pores to the liquid.

Moreover, there are a number of commercial companies that try to implement different technologies to be used for DAC. Climeworks, a spinoff company from the ETH Zurich in Switzerland, uses amine-based nano-fibrillated cellulose as adsorbents for CO<sub>2</sub> capture [141]. The company built a DAC and storage plant in Iceland, collaborating with Carbfix using geothermal energy for underground storage. The authors claim that the new plant will capture 4000 tons of CO<sub>2</sub> per year – making it the world's most extensive climate-positive facility to date [141]. Recently, Deutz and Bardow [142] analyzed the carbon footprint of Climeworks' DAC plant construction, considering the materials used, the energy required, the use of sorbents etc., to capture 1% of the global CO<sub>2</sub> emissions (see **Figure 5**). It is clear that this approach requires a high amount of adsorbent and energy. Such a high demand (materials and energy) could be reduced by using membranes as the direct air capture technology.



**Figure 5.** Material and energy requirements to capture 1% of the global annual CO<sub>2</sub> emissions, based on Climeworks' DAC plant. Reprinted with the permission from Nature Publishing 2021 [142].

Other interested companies are Global Thermostat, which develops a technology based on porous amine sorbents supported on a monolithic contactor [1,143], and Inphitree, which uses an ion exchange sorbent material to concentrate the atmospheric CO<sub>2</sub>. Inphitree then discharges the CO<sub>2</sub> when desired by a humidity swing method within greenhouse environments, enhancing photosynthesis rates and increasing yields of indoor plants' growth [144]. As mentioned, the US-based Carbon Engineering has been developing an air-liquid contactor for DAC since 2009, using potassium hydroxide to bind the CO<sub>2</sub> molecules and trapping them in the liquid solution as a carbonate salt. CO<sub>2</sub> is then released through a pellet reactor and a calciner where high temperature is involved [145,146]. Even though the mentioned companies make a great effort in direct air capture, they all have to deal with some serious limitations connected with liquid adsorbers and the need for high energy needed to desorb/separate CO<sub>2</sub>. Best to our knowledge, there is only one company that uses m-DAC to date. A Dutch company, Carbyon, designed the m-DAC system using a thin membrane film, initially developed for solar PV applications. The film is a porous structure with a large interior surface coated with a solid-state sorbent for CO<sub>2</sub>. The large interior surface was obtained, thanks to nano-imprinting fabrication method (pitch and height of the master were 1 μm and 350 nm, respectively). The company claims that the thermal budget to regenerate the active medium is much smaller compared to conventional approaches, as a result, Carbyon drastically reduces the energy required to extract CO<sub>2</sub> from ambient air [147,148].

As can be seen, several companies are already adapting their processes to decrease the energy demand. The most efficient way is to use renewable energy sources and reduce the overall energy requirement for the DAC process. Not to forget, there is a need to

optimize the CO<sub>2</sub> capture and the membrane/sorbent regeneration from the energetic point of view. In this sense, moisture driven CO<sub>2</sub> membrane-based capture is a promising alternative since it utilizes the free energy released by water evaporation. In this way, the use of heat for sorbent regeneration can be avoided. The water consumption in the moisture-driven cycle was estimated to be 13 to 37 mole of water per mole of CO<sub>2</sub> [132].

## **6. Conclusions, perspectives and recommendations for new scientists in the field**

DAC process, mainly developed using sorbents, has been pointed out as a feasible alternative to process a large amount of air. In a first approach, the idea of using gas separation membranes would seem to be infeasible, but the great advances in membranes and membrane processes could change the outlook in the near future. The DAC process can benefit from membrane separation since the membrane is adequate to transport CO<sub>2</sub> selectively, hindering other gas molecules. Of course, the main challenge is concentrating CO<sub>2</sub> from its depleted form in the air; here, once the high CO<sub>2</sub> concentration (proportionally to its component's driving force) is achieved, CO<sub>2</sub> capture via membranes could be more efficiently performed, otherwise the first membrane stage, in a multistage configuration, would have a preconcentrator role.

Additionally, several membranes, either based on organic, inorganic and their combination, have been outlined in this review as potential CO<sub>2</sub> separation interfaces. Initial attempts towards m-DAC have been evaluated in the ability to separate CO<sub>2</sub> and N<sub>2</sub> containing mixtures to preliminarily select the membrane materials with compelling CO<sub>2</sub>/N<sub>2</sub> separation efficiency. This timely report overviews several candidates for DAC application; however, since most research has experimented with different gas separation

conditions for fair performance comparison, selecting the best membrane is challenging. As a recommendation for future scientists in the field, it is suggested to report their gas separation data in terms of permeance (e.g., GPU), especially in case of supported thin membranes, and membrane selectivity [149]. To date, most of the organic, inorganic and hybrid materials adapted in membranes meet the suggested CO<sub>2</sub> selectivity for DAC, whilst the requirement for ultra-high CO<sub>2</sub> permeable membranes [22] can be achieved such as with the highly promising ultrathin PDMS membranes [21,97]. In the future, the suitable membranes may be ready when DAC needs them, and the potential implementation is closer than it looks since most governments are more aware of the high greenhouse gases emissions and their effects on our planet [150]. This awareness has led to the establishment of meaningful regulations, policies and protocols (e.g., Kyoto protocol, <https://unfccc.int/>). The effort of companies, such as Carbon Engineering, Climeworks, and Global Thermostat [151], on increasing the capacity and lower the costs of atmospheric CO<sub>2</sub> extraction systems will open the possibility to membranes in DAC applications. In addition to the CO<sub>2</sub> reduction, the idea also addresses the utilization of such carbon sources.

Finally, even if DAC with membranes may seem like an entelechy, the researchers still need to prove the other membrane values, among others: (i) cheaper and affordable membrane materials, (ii) optimum specific permeance and selectivity parameters obtained from mixture separation (ideal selectivities from single gas permeation measurements would not clarify the assessment of membranes for DAC), (iii) effectiveness in removing other harmful greenhouse gasses, (iv) process and application durability of the membrane system against the typical, high TRL (Technology Readiness

Level) separation operations such as adsorption, absorption and cryogenic distillation, v) process cost analysis since DAC conditions are different for those operating in typical CO<sub>2</sub> capture, and (vi) process cost reduction to make the process viable.

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### Note

The authors declare no conflict of interest.

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Among the different strategies proposed by scientists for CO<sub>2</sub> reduction, direct CO<sub>2</sub> capture from the air (DAC) represents a promising alternative in which sorbents have been mainly used. Very recently, gas separation membranes have been also speculated to carry out such a separation thanks to their smaller footprint and simpler setup and operation; however, their application still remain as a proposition in the field. This paper gives an overview of the ongoing research and attempts of DAC applications via membrane separation, along with the introduction of the main membrane materials and types used for CO<sub>2</sub> separation. Finally, the process considerations for DAC using membranes are stated to guide the new researchers in the field.

## Highlights

- Membranes as a promising tool for CO<sub>2</sub> capture.
- A perspective on direct air capture (DAC) from atmosphere is given.
- Process considerations to make DAC feasible are addressed.
- Advantages and drawbacks of membranes over other DAC technologies are provided.
- An outlook of DAC using membranes is elucidated.

