## **Membrane-Based Direct Air Capture Application**

Subjects: Polymer Science

Contributor: Pavlo Ignatusha, Haiqing Lin, Noe Kapuscinsky, Ludmila Scoles, Weiguo Ma, Bussaraporn Patarachao, Naiying Du

Direct air capture (DAC) is an emerging negative  $CO_2$  emission technology that aims to introduce a feasible method for  $CO_2$  capture from the atmosphere. Unlike carbon capture from point sources, which deals with flue gas at high  $CO_2$  concentrations, carbon capture directly from the atmosphere has proved difficult due to the low  $CO_2$  concentration in ambient air. Current DAC technologies mainly consider sorbent-based systems; however, membrane technology can be considered a promising DAC approach since it provides several advantages, e.g., lower energy and operational costs, less environmental footprint, and more potential for small-scale ubiquitous installations. Several recent advancements in validating the feasibility of highly permeable gas separation membrane fabrication and system design show that membrane-based direct air capture (m-DAC) could be a complementary approach to sorbent-based DAC, e.g., as part of a hybrid system design that incorporates other DAC technologies (e.g., solvent or sorbent-based DAC).

Keywords: direct air capture ; membrane

## 1. Introduction

The terms climate change and climate action have been on the tip of everyone's tongues for the last few years. Although carbon capture is a promising start, with the carbon budget clock ticking away, it is clear that simply lowering emissions, e.g., capturing  $CO_2$  from point sources, will not make enough of an impact. It is not long until the carbon budget is depleted, and every additional ton of CO<sub>2</sub> will need to be managed by the use of negative emission technologies  $\frac{|1|2|}{2}$ . In fact, in order to meet the Paris Climate Agreement goals of preventing a 1.5-2 °C temperature increase over preindustrial levels, 10 GtCO<sub>2</sub>/yr will need to be removed from the atmosphere by the midcentury, increasing to 20 GtCO<sub>2</sub>/yr by the end of the century <sup>[3]</sup>. Failing to prevent the increase in temperature has a very real social cost. For example, wheat, rice, maize, and soybean represent over 67% of human caloric intake; only a 1 °C increase in temperature will reduce the global production of wheat by 6%, rice by 3%, maize by 7.4%, and soybean by 3.1%<sup>[4]</sup>. Additionally, changes in weather patterns, acidification of oceans, and melting of polar ice caps place much of the planet's biodiversity at risk. Therefore, the development of cost-effective negative emission technologies becomes essential to remediate climate change. As one of the negative emission technologies, direct air capture (DAC) describes a process by which CO2 is removed directly from the atmosphere rather than from higher concentration point sources. This proves to be quite challenging as the concentration of  $CO_2$  in the atmosphere is only ~400 ppm <sup>[5]</sup>. Nonetheless, it is important to develop methods to capture low-concentration atmospheric CO2 since capturing all emissions from point sources would fail to accomplish even an 80% emission reduction by 2050 [6], while direct air capture would be able to target the CO<sub>2</sub> from the billions of small point sources which account for 1/3 to 1/2 of society's  $CO_2$  emissions [7].

Currently, sorbent-based DAC technologies are under development at a pilot scale, including solid sorbents and liquid solvents <sup>[8][9]</sup>. These two technologies rely on absorption/desorption technologies, which require high energy inputs and large location-dependent installations. In addition, these processes often involve the use of chemicals and, therefore, introduce added environmental and safety risks <sup>[5][9][10][11][12]</sup>. Liquid solvent DAC utilizes contactors where the gas encounters a basic solution. The resulting compounds need intense heating to release captured CO<sub>2</sub> <sup>[8][11][13]</sup>. Because of the use of strong bases, the sorbent liquids are usually no more than 30% concentrated, which greatly decreases their binding potential with CO<sub>2</sub> <sup>[14]</sup>. The use of strong chemicals, e.g., KOH, also risks a negative environmental impact in the form of spills. In addition, liquid solvents use 1–7 tons of water to capture 1 ton of CO<sub>2</sub> <sup>[9]</sup>. Recent research on liquid solvent-based DAC focuses on lowering the consumption of energy and water, e.g., IPDA (3-(aminomethyl)-3,5,5-trimethylcyclohexylamine) liquid to solid carbamic acid conversion for CO<sub>2</sub> which can capture low (400 ppm) CO<sub>2</sub> with >99% removal at a lower desorption temperature of 333 K <sup>[15]</sup>. Solid sorbent methods involve pushing air into a specially designed sorbent until it is saturated. The sorbent is then heated and/or vacuumed to desorb CO<sub>2</sub> <sup>[14]</sup>. Solid sorbents have been made of several different materials like metal-organic frameworks (MOFs), mixed metal oxides, poly(ethylenimine) etc. <sup>[16]</sup>. Metal-organic frameworks are formed through the linkage of organic and inorganic constituents, which form highly structured and microporous materials with high free volumes. The performance of solid sorbent DAC depends on the

conditions of the air being processed, including temperature and humidity. High temperatures have been shown to increase energy requirements, leading to a loss of efficiency and an increase in cost [17]. These factors lead to location dependence for DAC installation for both technologies. The source of energy used to power these sorbent-based DAC plants must also be considered when evaluating their level of negative emissions and may limit the location even more [9]. The KOH liquid absorption method reportedly requires 8.81 GJ of natural gas or 5.25 GJ of gas and 366 kWh of electricity for every ton of CO<sub>2</sub> captured [11]. Solid sorbent energy requirements are around 6 GJ of thermal energy and 1.5 GJ of electricity per ton of CO<sub>2</sub> [14]. These energy demands arise primarily due to the desorption steps. Although sorbent-based DAC technologies being developed to a plant scale is a great start and is paving a path for DAC, the impact on the environment should not be underestimated, and other environmentally friendly approaches should be explored.

The idea of m-DAC was proposed twenty years ago <sup>[18]</sup>; however, only recently has a more detailed study been reported that proved that membrane processes could be considered as a new DAC approach <sup>[5]</sup>. It is a new and rather exciting area of research that shows promise for lower-cost direct air carbon capture and can lower the risk of environmental impact associated with sorption technologies <sup>[5]</sup>. Theoretically, considering the process only requires energy to blow air through the membranes, advances in membrane materials should drastically decrease the cost of operation, especially given that thermodynamic energy requirements are 20–30 times lower than that of the best DAC methods currently in use <sup>[19][20]</sup>. However, presently, m-DAC will not be a competitive option to sorbents-based DAC unless major breakthroughs are made in increasing membrane selectivity for the CO<sub>2</sub>:N<sub>2</sub> gas pair and CO<sub>2</sub> permeance. Currently, it is widely accepted that m-DAC could play an active role in hybrid system designs that incorporate other DAC technologies. In the past few decades, large amounts of funding have been allocated worldwide for the R&D of membrane-based CO<sub>2</sub> capture from point sources, and a vast number of published reports related to high permeable polymeric materials for CO<sub>2</sub> capture membranes could shed light on the selection of DAC membrane materials.

## 2. Membrane-Based Direct Air Capture Application

Once CO<sub>2</sub> is captured by DAC, it can be stored or recycled for use in several different downstream applications, as summarized in Figure 1. One important parameter for any CO<sub>2</sub> utilization after capture is the percent purity of CO<sub>2</sub>. The most common method of CO<sub>2</sub> storage is geological sequestration; generally, geological storage of CO<sub>2</sub> requires CO<sub>2</sub> gas at a high purity (more than 98%) [5][21]. Currently, a purity over 90% is not possible to achieve by m-DAC efficiently in 1 stage; therefore, geological storage is an unlikely application of m-DAC without several stages or pairing with other CO2 capture approaches [5][12][16]. A simulation-based study using a membrane with a CO2 permeance of 1850 GPU and CO<sub>2</sub>/N<sub>2</sub> selectivity of 80 for hybrid membrane cryogenic (HMC) capture showed a 9% reduction in capture cost at a capture ratio of 85% compared to conventional monoethanolamide (MEA) carbon capture [22][23]. Similarly, another HMC process using a membrane with a  $CO_2$  permeance of 1000 GPU and  $CO_2/N_2$  selectivity of 100 was shown to reduce the energy requirement compared to MEA capture from 4.409 GJ<sub>th</sub>/t<sub>CO2</sub> to 3.25 GJ<sub>th</sub>/t<sub>CO2</sub> from a stream of 15% CO<sub>2</sub> and a pressure ratio of 11.11 achieving a capture ratio of 85% and a purity over 89% [23][24]. Unfortunately, there is a lack of research on hybrid separation systems using membranes alongside other DAC methods, which have the possibility for efficient cost reductions. A recent engineering parametric study, which investigated the impact of material performance, process design, and operating conditions on membrane-based DAC, shed light on the future of this technique. The study concluded that with existing commercial membrane materials, the maximal CO<sub>2</sub> output concentration from a single-stage separation would be  $\sim 2\%$ . A similar two-stage process could increase this to  $\sim 50\%$ , noting that O<sub>2</sub> and water would be copermeated. High-performance materials (not commercialized) could achieve ~12% in a single stage and up to ~99% in two stages [16]. For these high-performance materials in a two-stage process, costs and energy fall in the affordable range, e.g., 103 to 104\$ per tCO<sub>2</sub> with a first-order optimized energy requirement of 101 GJ per tCO<sub>2</sub> [ $\frac{16}{1}$ ]. Currently, multistage membrane modules are still needed if high-purity outputs are desired since the performance might worsen due to pressure drop and concentration polarization [16]. Hence, it could be an efficient approach to produce high-concentration CO<sub>2</sub> via a hybrid system, which combines m-DAC and other CO<sub>2</sub> capture systems, although more research is needed in this area.



Figure 1. Examples of post-capture utilization pathways for CO<sub>2</sub> depending on purity.

With m-DAC, the contaminants impacting CO<sub>2</sub> purity are gases like O<sub>2</sub> and N<sub>2</sub>, not NO<sub>x</sub> and SO<sub>x</sub>, which are picked up by flue gas capture. It seems only agricultural applications can use dilute CO<sub>2</sub> <sup>[5]</sup>. Biological fixation through photosynthetic organisms is the planet's natural method for CO<sub>2</sub> recycling; photosynthetic microorganisms offer fast reproduction, adaptability, and efficient conversion of CO<sub>2</sub> into sugars and typically require low CO<sub>2</sub> (<~40%) concentrations <sup>[16][25]</sup>. With currently commercially available membranes, the 2% CO<sub>2</sub> concentration could be of interest for the intensification of greenhouses or algae ponds. Captured high-purity CO<sub>2</sub> can also be used to enhance oil recovery. It can be used for welding, dry ice, soda, and feedstock for greenhouses and other agricultural installations. Furthermore, CO<sub>2</sub> can be used for conversion to several commercial chemicals such as ammonia for fertilizer, plastics which reduce the use of petrochemical products, formic acid, synthetic fuels by methanation, and methanol, to name a few <sup>[25]</sup>. In that event, multistage membrane units or hybrid processes could be of interest <sup>[26]</sup>. Although most electrochemical reduction of CO<sub>2</sub> uses pure CO<sub>2</sub>, recent studies have shown that CO<sub>2</sub> reduction to CO can be achieved with low CO<sub>2</sub> purity, indicating another realistic use for m-DAC CO<sub>2</sub> <sup>[27]</sup>. The CO produced can be used to produce useful hydrocarbons for downstream applications. For all the aforementioned uses, the source of energy (renewable or not) for conversion and the processes' emissions should be considered to determine the overall environmental impact and the extent of negative emissions.

Currently, since m-DAC is rather expensive with current membranes, the most attractive selling point is the modularity. Fujikawa et al. showed through process simulation that a 4-stage separation module using current highly permeable membranes can fit into 0.01 m<sup>3</sup> and capture 1 kg-CO<sub>2</sub> per day <sup>[12]</sup>. Dittmeyer et al. proposed DAC-integrated AC units that could convert captured CO<sub>2</sub> into hydrocarbon fuels. Their paper provided perspective examples of towns fueling their cars using the fuels generated by negative emission technologies. This approach could add an incentive for the public to get involved in DAC technology <sup>[28]</sup>. Small-scale m-DAC installations have the potential to be installed in office buildings and schools where the CO<sub>2</sub> concentration reaches up to 1000 ppm <sup>[29]</sup>. Areas with elevated CO<sub>2</sub> concentrations compared to the atmosphere would increase the capture efficiency of m-DAC. Moreover, the location independence of m-DAC allows for installation near CO<sub>2</sub> storage and recycling sites. This process can avoid the construction of pipelines needed to transport the CO<sub>2</sub> recovered from location-dependent capture sites to storage sites <sup>[Z]</sup>. This also avoids the energy required to compress the gas for transport. Using the previously mentioned utilization of CO<sub>2</sub> as an agricultural feedstock as an example, m-DAC modules could become a standard installation in every greenhouse.

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