

MOLECULAR TO PROCESS SCALE: A REVIEW OF HOLISTIC DIRECT AIR CAPTURE CONTACTOR DESIGN

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Abstract

Air-sorbent contactors are an essential part of direct air capture processes. Their design can have a great influence on the process energy demand and efficiency. Three aspects of this design have been identified and differentiated by length scale. On a molecular scale, the adsorption sites are defined by the chemisorbent-containing molecules, generally amines. The support of these amines defines the second length scale and plays an important role in mass and heat transfer. These two length scales have been studied in detail in academic literature and a short overview is given. The third length scale is the process scale, or contactor module scale. Together with the first two length scales, it is necessary to characterize the third to perform adequate process optimization. Research on this third length scale is scarce in academic literature, though it has been researched in industry. The direction of research tends towards structured sorbents due to their ability to process large volumes of air and academic research in this area should be expanded.

Keywords: Direct Air Capture, Amines, CO₂ Capture, Contactor Design

1. Introduction

Anthropogenic carbon dioxide CO₂ and other greenhouse gases (GHGs) have to date caused a temperature increase of approximately 1°C [1]. Following the current path of emissions, humankind is likely to increase this above the 2°C target set by the Paris Agreement in 2015 [2]. Consequently, an increasing number of countries have pledged to meet net-zero CO₂ emissions targets within the next 40 years. This will entail the deployment of negative emission technologies (NETs) in addition to conventional mitigation options such as reduction of emissions of GHGs [3]. A key component of these NETs is the direct capture of CO₂ from ambient air (*Direct Air Capture*, DAC) combined with the permanent storage of the collected CO₂ [4]. This offers the ability to offset the emissions from hard-to-decarbonize sectors such as agriculture, aviation, and the chemical industry, as well as offsetting emissions from the past.

DAC is currently achieved through absorption in aqueous basic solutions or through adsorption on solid sorbents [5]. The absorption of CO₂ in aqueous basic solutions is followed by a regeneration step at around 900°C to retrieve the bound CO₂ [6], [7]. In contrast, the regeneration of solid sorbents generally requires lower temperatures between 80 and 120°C [8], [9], [10]. Processes using solid sorbents therefore enable the use of lower quality heat, while additionally completely removing the need for the corrosive and volatile solvents used in absorption processes [11], [12].

Both processes face challenges to become economical. This is due to their current energy inefficiency and the low value of the product [13]. Aside from the unavoidable thermodynamic inefficiencies, which stem

from the low concentration of CO₂ in air, the air-sorbent contactor is the main source of inefficiencies in the DAC process. The energy required for the process is dominated by parasitic heat losses caused by the heating of the support material and sorbent during regeneration [14]. The large amount of air required for the process and the corresponding pressure drop also contributes a sizeable amount to the energy requirements [15], [16], [17]. On a smaller level, mass and heat transfer can affect cycle times and therefore influence the productivity of the process. It follows that there is a need to design and optimize the contactor with respect to the aforementioned aspects.

2. Contactor Design from Molecular to Module Scale

2.1 Molecular Scale

Much research has focused on developing materials for carbon capture applications. Commercial zeolites, such as 13X, are a material of choice for post-combustion capture from flue gases of between 4-15% CO₂ concentration due to their high selectivity towards CO₂ and process robustness [18]. Adsorption occurs on these materials through physisorption within the pores. However, the same adsorption sites have a higher selectivity towards H₂O. Pre-drying the gas therefore offers more efficient processing [19].

In this respect, materials for post-combustion differ significantly from materials capture for DAC applications. In comparison to industrial flue gas, ambient air contains much higher H₂O to CO₂ ratios, making pre-drying highly uneconomical. Materials for DAC processes must therefore be unaffected by the

presence of H₂O, while maintaining a high selectivity towards CO₂.

Research has focused on amine functionalized materials due to their favorable CO₂ uptake in the presence of H₂O. In contrast to zeolites and physisorbents, the adsorption mechanism on these materials is through chemisorption, the formation of a chemical bond with the primary and secondary amine groups. Different reaction pathways have been suggested in hydrous and anhydrous conditions, as depicted in figure 1 [5]. Adsorption via this mechanism is not only highly selective towards CO₂, but also enhanced in the presence of H₂O. In the absence of H₂O, two adjacent amine sites are required to bind a CO₂ molecule, whereas the presence of H₂O enables each amine site to bind a CO₂ molecule.

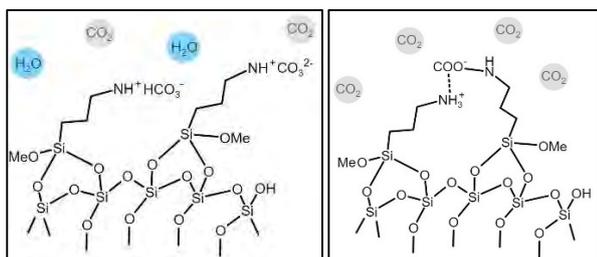


Figure 1: CO₂ capture mechanisms on silica supported amine sorbents with H₂O (left) and without H₂O (right)

As amine molecules are generally in liquid form under ambient conditions, they are tethered to solid supports to give the advantages of adsorption processes. Tethering can occur through physical impregnation via hydrogen bridges or covalent bonding, also known as grafting. Grafted amine-containing molecules are generally smaller than impregnated molecules, therefore the CO₂ adsorption capacity is generally lower [20]. However, due to the covalent bond, grafted molecules are less prone to leaching during the adsorption and desorption processes [24]. Typical materials often used for impregnation are poly(ethylenimine) (PEI) and tetraethylpentamine (TEPA), whereas silane containing molecules, such as aminopropyltrimethoxysilane (APTMS), are used for grafting. Both procedures can be accomplished in one step, though physical impregnation is generally considered the easier process [20].

2.2 Support Scale

The amine-containing molecules mentioned above must be supported on a solid material to remain in the solid phase at ambient and process conditions. The support characteristics can profoundly affect process performance. These characteristics include material, surface area, and pore structure.

The supports currently proposed in research can be divided to a large extent into oxide materials and metal-organic frameworks (MOFs). MOFs can offer extremely high adsorption capacities and are, therefore, promising candidates for DAC processes. However, their relative novelty means that more research is needed to make them industrially viable for DAC [21]. Oxide materials have been comparatively well studied and offer tunable high surface areas, pore sizes, and pore volumes [22].

Heat capacity and conductivity of the support directly influence the heat needed for regeneration. During the regeneration step, the support material is unavoidably heated together with the adsorbing molecules. This parasitic heat loss can make up almost 40% of the total energy requirement of the process [14]. A low heat capacity of the sorbent is, therefore, desirable in terms of process energy efficiency. High conductivity enables fast heating of the sorbent and, therefore, a shorter regeneration time, increasing productivity.

$$Productivity = \frac{CO_2 \text{ captured}}{\text{adsorbent volume} \times \text{process time}}$$

Isotherms define the thermodynamic equilibrium adsorption capacity at a certain temperature as a function of the partial pressure [23]. They are critical in calculating the equilibrium working capacity of a sorbent for a specific process. They correlate directly with the amount of accessible adsorption sites of a sorbent and are generally presented per mass of sorbent. For the design of process equipment, however, the per volume of sorbent values can be of more interest. In the case of amine-functionalized sorbents, the accessible adsorption sites are the accessible amine groups on the surface.

Generally, the surface area of the support directly affects the adsorption capacity per unit volume of sorbent (volumetric capacity). Intuitively, a high specific surface area is preferable to enhance the volumetric loading of the adsorbing molecules. However, it has been found that that for amine-functionalized oxides, pore size, and volume play a more important role in the number of amines present on the surface [27].

Pore size plays an important role in mass transfer. In the case of DAC processes, mass transfer is a measure of how fast CO₂ is transported to the adsorbing molecules. Faster mass transfer is desirable as shorter residence times are possible, thereby decreasing process time and increasing productivity [25]. Mass transfer can be tuned by adjusting the amount of amine molecules on the support [26]. In general, an optimum must be found between fast mass transfer and high volumetric loading, as higher loadings tend to lead to clogged pores and slow mass transfer [27]. Large pores are preferable from a mass transfer perspective and larger surface amine densities have been observed for such materials even with lower surface areas [24].

2.3 Contactor Module Scale

The above-mentioned support materials can come in various geometric configurations. The most common are honeycomb monoliths, pellets, and foams. The geometries can be either made of the support material or a different material which is then coated with the support material. Each configuration has its advantages and disadvantages, which make them more or less suited for individual applications.

Honeycomb monoliths have been used in catalysis for applications that require low pressure drops and high throughputs [28]. They have suffered from high mass transfer resistance, but recently thinner walls have

overcome this setback [29]. Compared to pellets, they have a low volumetric capacity [17].

Pellets generally offer high mass transfer rates and high volumetric capacities but suffer from higher pressure drops especially at high flow rates [17]. They are generally cheaper to produce, easier to handle, and offer a high flexibility in further geometric configurations (packed column, radial flow reactors, thin manifold beds etc.). Some examples are given in the next section.

Foams are characterized by high mass transfer due to the turbulence produced by the tortuous channels [29]. The pressure drop is, therefore, increased compared to honeycomb monoliths but decreased compared to pellets due to higher porosity. In terms of mass transfer and pressure drop, they have been found to be inferior to honeycomb monoliths [30].

3. Contemporary Contactor Design

There are many contactor configurations used or proposed for adsorption and filtration process conditions similar to those experienced in DAC. Some of these have been adapted to be used in DAC processes, whereas some may still be evaluated. This section gives an overview of some contactor designs that are already used for or could possibly fulfill the specifications of a DAC process. In all the figures, the blue arrows show the direction of the gas flow.

3.1 Diesel Particle Filters

Diesel particle filters are used to remove the soot particles from the exhaust gas of internal combustion engines. They must deal with high throughputs and offer low back pressures.

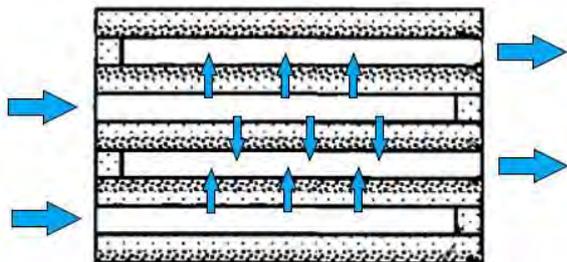


Figure 2: Diesel particle filter as suggested by Beall et al. [31].

3.2 Hollow Polymeric Fibres

Hollow fibres made of a porous polymer matrix with embedded sorbent particles offer a low pressure drop contactor for post combustion CO₂ capture. The inner duct can be used as a novel heat integration strategy for rapid temperature swing regeneration [32].

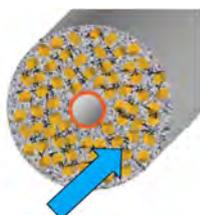


Figure 3: Porous polymer fibres as suggested by Lively et al. [32].

3.3 Radial flow adsorbers

Radial flow adsorbers have been used for a wide variety of applications and offer lower pressure drops than conventional packed beds, while still using conventional pellet sorbents. Yu and Brillman [13] suggested its use for DAC capture purposes due to high mass transfer and low pressure drop.

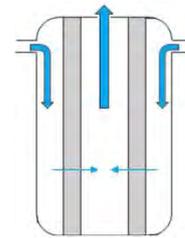


Figure 4: Radial flow adsorber suggested by Yu and Brillman [13].

3.4 Functionalized Honeycomb Monoliths

Honeycomb monoliths have been extensively used as catalyst supports in high throughput, low back pressure applications. These qualities also make them interesting for DAC applications, with MOF functionalized monoliths [34] and amine-functionalized monoliths [28] proposed in literature and in industry [35].

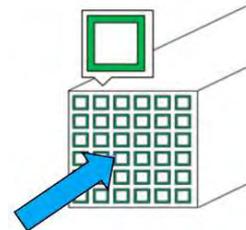


Figure 5: MOF functionalized (green) honeycomb monolith as proposed by Darunte et al. [34].

3.5 Thin manifold pellet bed

A thin bed configuration with the goal of reducing pressure drop of a pellet bed and optimizing volumetric loading within a contactor module has been patented by Climeworks [36].

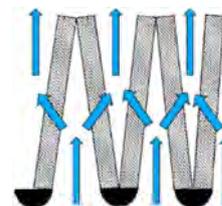


Figure 5: Manifold configuration of a pellet bed as proposed by Climeworks [36].

4. Outlook

Research in direct air capture has been mainly driven by start-ups, such as Climeworks, Global Thermostat, and Carbon Engineering. Open academic research has focused on creating novel materials, but there is a significant lack of research into optimal contactor configurations for typical DAC processes. Additionally, materials and process research has to date been conducted mostly independently, even though these are

inherently coupled. Filling the gap in academic research and combining the two main areas of DAC research is essential to further its standpoint in a net-zero future.

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