

Prospecting Adsorption Technologies for Carbon Capture

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Currently, the method of post-combustion in industries that uses the adsorption technique to capture and separate carbon dioxide from the flue gas is widely studied due to energy efficiency, ease of handling, lower cost, and environmental risk compared to other separation techniques. Regarding the adsorbents used in adsorption, zeolites are one of the most promising because they are one of the most efficient materials with high adsorption capacity due to their unique properties. However, despite the promising performance, the adsorbents need studies that enable a lower cost, more efficient, and selective control to better understand and validate utilization as a material for flue gas CO₂ capture.

Keywords: Post-combustion. Zeolites. Separation Methods. Adsorption. Selectivity.

Introduction

The impacts caused by the greenhouse effect have environmental and health problems that directly impact the global economy, directly affecting the world GDP by about 5% to 20% due to this phenomenon [1]. Gases such as carbon dioxide (CO₂) represent about 74% of polluting gases in the atmosphere, in addition to methane (CH₄) and nitrous oxide (N₂O), which represent 17% and 6.2%, respectively, of the total emissions produced by man. Emissions of greenhouse gases that trap heat from the sun are constantly increasing, leading to global warming and climate change. According to the United Nations, such effects are linked to fossil-based energy generation, deforestation, industrial and manufacturing flue gas emissions, transportation, and food production [2].

Despite all the incentives and technological advances, the global energy matrix still depends on the use of fossil fuels. According to the International Energy Agency (IEA), more than 80% of the world's electricity production is made up of fossil fuels, emphasizing the panorama of dependence on

sources that generate more significant emissions of greenhouse gases. In addition, the context of technological development grows and generates an ever-increasing energy demand, which leads to a vicious cycle of greenhouse gas generation [3]. Thus, several capture processes are being developed to treat gases in the industry, such as pre-combustion, oxy-combustion, and post-combustion. These methods are studied and applied to separate and recover polluting gases, mainly carbon dioxide. However, the financial infeasibility, reduced performance of thermoelectric plants, and other factors make applying these practices difficult. In this context, there is a clear need to study techniques to mitigate carbon dioxide emission and reduce its concentration in the atmosphere. Therefore, the objective of this article is to understand the adsorption technology used to capture carbon from post-combustion gases and to conduct a comparative study of the primary adsorbent materials.

Materials and Methods

A technological prospection of the leading carbon capture processes was initially carried out to achieve the proposed objective. After studies on the technical feasibility of carbon capture technologies for the various gas generation processes (pre-combustion, oxy-combustion, and post-combustion), the application of carbon capture technologies in the post-combustion process was selected because it is a process, relatively

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easier to implement and with less intervention in the existing industrial layout. Furthermore, it is possible to implement different carbon capture technologies in post-combustion processes. This work selected the adsorption method due to its very high efficiency, primarily through microporous materials. There are several adsorbent materials under study and others with high technological maturity. Zeolites is an established material on the market, however, needs to be better studied and compared due to their properties, such as high selectivity and versatility. Figure 1 shows the method sequence used in this work, ranging from the study of technological prospecting of the various carbon capture technologies to the use of zeolites as adsorbent materials in capturing carbon from post-combustion gases.

Results and Discussion

Carbon capture technologies can be implemented at different stages of an industrial process. However, the simplest way, with fewer structural modifications of an industrial plant already in operation, is the implementation of carbon capture technologies in the post-combustion process. In this process, channeling the flue gases to a carbon capture unit is sufficient. In this unit, different carbon capture technologies can be used.

Carbon Capture Methods

Among the CO₂ capture methods, the most relevant and economically viable technologies

for separating carbon dioxide from the flue gas are chemical absorption, adsorption, cryogenics, and membrane separation. Table 1 shows these methods' main differences and characteristics that separate carbon dioxide from flue gases [4].

Of the methods showed in Table 1, the adsorption method was one of the most efficient, cheap, and currently used, easy to handle, with less environmental risks, and requires less energy to regenerate adsorbent materials [1].

Adsorption

It is the physicochemical process where atoms are retained on the surface of a given material and can vary between chemical adsorption (chemisorption) or physical adsorption (physisorption). The first refers to the interaction between the molecules and the solid adsorbent material, which rearrange themselves and change the shape of the electronic orbit, even partially. It is an almost always exothermic process and similar to a chemical reaction. The second occurs through interactions through weak and long-range Van der Waals forces that are physically attached to the adsorbent, and this process is always exothermic and reversible. [8] Figure 2 shows a schematic of a fixed bed adsorption process. The flue gas enters through the lower part of the adsorption tower at 25°C and 0.0059 atm, where adsorption occurs in the porous adsorbent material. The flue gas that contains CO₂ interacts with the adsorbent material while the other flue gas components permeate through the bed and exit the process through the top of the tower.

Figure 1. Flowchart of the method used in this study.

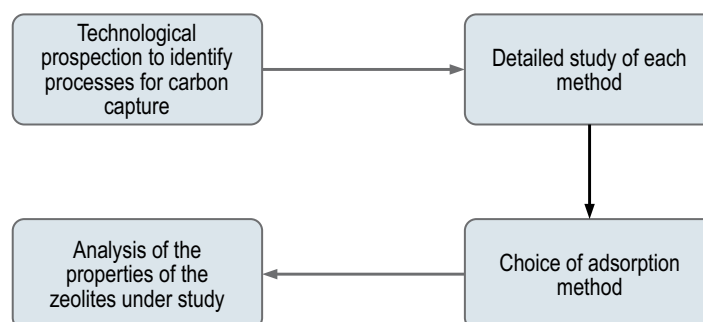


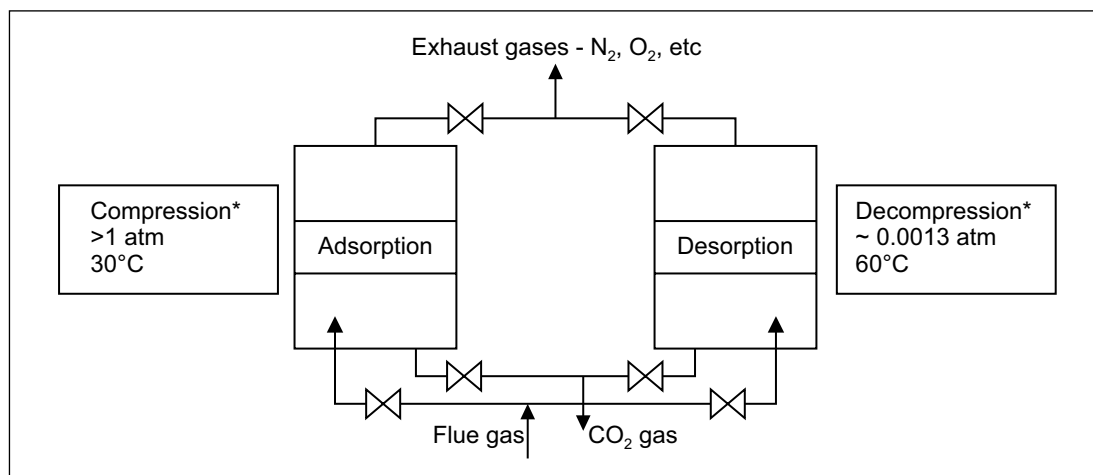
Table 1. Separation methods.

Separation Methods	Features	Process Conditions	Ref.
Adsorption	It is the physicochemical process where atoms are retained on the surface of adsorbent material. This method is very efficient and is one of the most used for CO ₂ capture, especially with zeolites. Usually, for CO ₂ capture, the adsorption technology is typically used with amine solvents to optimize the process.	Adsorption process: P = 0.04-1.97 atm; T=25°C-30°C Desorption Process: P= 0.001-0.008 atm; T= 40°C -60°C	[1] [4] [5]
Absorption	A physical or chemical process in which molecules are introduced into another component's medium and fixed. It is one of the most promising methods to capture CO ₂ due to its ease of application, efficiency, and low operating cost, and CO ₂ adsorption is usually used with amines.	Absorber: P= 2.24 atm T= 38°C-50°C; Regenerator: P=1 atm; T=100°C-121°C.	[1] [4] [6]
Cryogenic	The technique that causes CO ₂ to be desublimated from the process stream through refrigeration and/or expansion of this gas. CO ₂ can be recovered with 99% purity despite the high energy consumption associated with cooling the flue gases by refrigeration.	Vapor-liquid phase change: T=217 K-304 K; P=630 kPa- 7396 kPa	[1] [4]
Membranes	The physical barrier of ceramics or polymers through which the CO ₂ -rich gas is forced by the partial pressure difference at the entrance and exit of the permeable and selective membrane, its main problems are selectivity, permeability, and regeneration energy. Calcium oxide (CaO) membranes stand out for their crystalline structure and high porosity.	Permeate relative pressure: 0.928-11.23 bar; Input current pressure: 28 to 111 bar; T: 40°C -60°C	[1] [4] [7]

Therefore, only carbon dioxide is adsorbed due to the selectivity of the adsorbent material. This adsorbent material, after its saturation, will leave the base of the adsorption tower to the desorption tower under a temperature of 40°C and a pressure of 0.0013 atm. However, this process may vary

according to the adsorbent material used. After this step, the CO₂ will be desorbed so that the CO₂ can be recovered at the top of the desorption/regeneration tower, and the adsorbent material can be reused [5].

The adsorption process is considered one of the cleanest methods for capturing CO₂. It has

Figure 2. Adsorption tower [5].

advantages over the absorption process, such as energy efficiency and regeneration, that can be easily manipulated through pressure and temperature changes. Furthermore, this method generates less toxic residue than the absorption process that typically generates alkanolamines, whose disadvantages are the toxicity and environmental damage of the solvent degradation compounds (nitrosamines) [9].

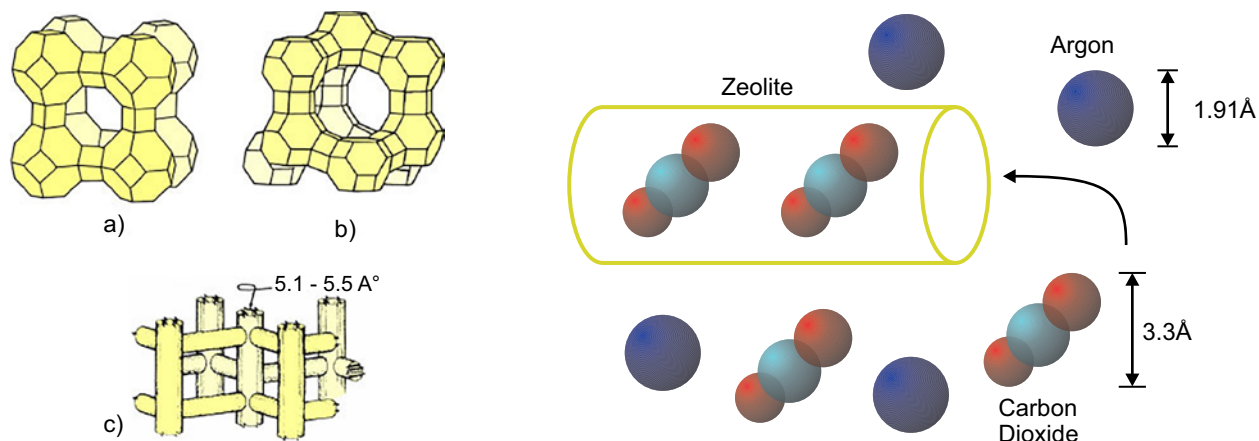
Zeolites

In 1756, the first mineral zeolite (stilbite) was discovered by Baron Cronstedt in Sweden; however, it was only in 1926 that its adsorbent characteristics came to be widely discussed due to its microporous internal structure that allows selective adsorption [10]. Its application for several processes has been carried out; in industry, zeolites have been used mainly as adsorbents for gas purification and as ion exchangers in detergents, but they are extremely useful as catalysts in petroleum refining, petrochemistry, and synthesis of organic products whose molecules have a kinetic diameter of less than 10 Å [11]. These zeolites are natural and/or synthetic minerals, usually microporous with three-dimensional crystal lattice structures. Their vertices are joined by an oxygen atom and form a TO₄ tetrahedron (T = Si, Al, B, Ge, Fe, P,

Co...). Its structure is like a molecular sieve, and its microporous properties allow selectivity and high adsorption capacity with the transfer of matter between intracrystalline spaces that are limited by the diameter of the pores [12]. In addition to the properties mentioned above, it has a high specific surface area and the ability to model the electronic properties of active sites and pre-activate molecules within the pores, thanks to high electric fields and molecular confinement. Finally, it has acidic and basic properties widely used in most hydrocarbon and organic compounds reactions [13].

According to the IUPAC, zeolites are classified by ring diameter as small (less than 4 Å), medium (from 4 to 6 Å), significant (from 6 to 8 Å), and very large (from 8 to 20 Å) [14]. Regarding pressure, zeolites, generally used with amines, adsorb better at high pressures above 2 bar without water vapor and low temperatures below 30°C [15]. Among the zeolites most used in the industry, type X (faujasite) and type A stand out due to their stable crystalline structures and large pore volumes [16]. The zeolites used in this article are A, X, Y, and ZSM-5 types because of the more than 150 zeolites that have been synthesized. The most common in commercials are them because of their unique adsorption, ion exchange, molecular sieve, and catalytic properties [17]. Figure 3 (i) represents the structures of the zeolites discussed, respectively: (a) zeolite A, (b)

Figure 3. Structures of zeolites (i) and zeolites in CO₂ adsorption(ii) [18,19].



zeolite type X, Y, and (c) zeolite ZSM-5. In (ii), the entry of CO₂ into a zeolite is represented due to the reduced diameter.

It is evident the excellent adsorption capacity that allows the capture of CO₂, a molecule that, having 3.3 Å in diameter, allows mobility between the CO₂ molecules that will be trapped inside the zeolites that have a larger diameter, 5 Å for the 5A zeolite and 7.8 Å for 13X zeolite, Ar whose molecule has a diameter of 1.91 Å, on the other hand, is not captured.[20] Table 2 shows the characteristics of the leading commercial zeolites.

Conclusion

After the analysis of several methods, post-combustion proved to be cheaper and easier to access the technology in order to be the most applied and developed in the industry. Among the

post-combustion processes, adsorption is evident due to studies that point out that solid adsorbents potentially offer a greater capacity for capturing and separating gases in a reduced space with energy efficiency and low cost compared to other technologies. However, there is still a need to improve performance, in addition to being easy to handle and low environmental risk. Among the adsorbent materials, zeolites are most used due to their microporous structure, which has a very high effectiveness in CO₂ selectivity and requires studies that enable applications aimed at mitigating carbon dioxide emission in the atmosphere.

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Table 2. Characteristics of the main commercial zeolites.

Zeolites	Structure	Pore diameter(Å)/ Micropore size	Description	Application	Adsorption capacity (120oC and 1 ATM)	Silica/ Alumina ratio	Structural symbol/ Dimensionality	Ref.
A	$\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}] \cdot 27\text{H}_2\text{O}$ (Type 5A)	4.1 / Small	They are formed by a simple cubic arrangement with the union of two rings of four tetrahedra and the other by a truncated octahedron combining 24 tetrahedra, called cavity β or sodalite cavity. They filter branched structures passing linear molecules, and types 3A, 4A, and 5A are defined by the position of the cations in the zeolitic structure; the effective pore diameter can vary depending on the compensating cation.	Detergent manufacturing and water hardness removal	~0.38 mol/kg	2-5	LTA / 3	[15] [11] [10] [21]
X, Y	$\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot \text{H}_2\text{O}$ (Type 13X)	7.4 / Big	Type X and Y zeolites belong to the Faujasites group and have a topologically similar structure. Its unit cells have cubic structures with a dimension of about 25 Å, containing 192 tetrahedrons of (Si, Al) O ₄ . It is compatible with many industry reagents because it has the largest pore diameter among microporous sieves, making it a significant research focus.	Catalytic cracking and hydrocracking	~0.70 mol/kg	3-6	FAU / 3	[22] [11] [10] [21]
ZSM-5	$\text{Na}_{41}\text{Al}_5\text{Si}_{36}\text{O}_{192} \cdot 16\text{H}_2\text{O}$	5.2×5.8 / Medium	ZSM-5 zeolite is synthetic and is a suitable adsorbent for CO ₂ adsorption due to its high surface area and thermal and mechanical stability. In addition, it has a high Si/Al ratio that generates format selectivity, high thermal stability, and acidity, as well as moderate hydrophilicity and high hydrophobicity.	Xylene isomerization, benzene alkylation, catalytic cracking, catalyst dewaxing, and methanol conversion	~0.38 mol/kg	30-200	MFI / 3	[23] [11] [10] [24]

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