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STATE OF THE ART OF THE VIABILITY OF CARBON CAPTURE TECHNOLOGIES

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Abstract. *The IPCC report AR6 (2021) presents a scenario in which the replacement of fossil fuels and improved efficiency of energy systems would not be sufficient to ensure an overall average temperature increase of 1.5°C above pre-industrial era level by 2040. To reduce the level of CO_2 in the atmosphere is the objective carbon capture devices development. This paper aims to review the research with carbon capture advanced materials (CCAM) and the most recently used and promising conversion routes. Carbon capture requires a gas flow and physical-chemical reactions, for which a minimum energy expenditure is expected in order to carry out the process. Therefore, an exergetic and thermo-economic analysis would be essential to evaluate and compare options. The most used materials for chemical process by absorption are the monoethanolamines (MEA) and diethanolamines (DEA) and their derivatives. They yield high capture rate but take 3.5 GJ per ton of captured CO_2. Amine solvents blends and similar can improve this consumption range down to 2.5 to 2.9 GJ per ton. Alternatively, in the realm of adsorbents, one finds activated carbon, minerals zeolites, metal organic frameworks (MOF) as well as promising nanomaterials with high adsorption capacity. For instance, graphene has a CO_2 adsorption capacity of 0.07 mol/g, which is ten times higher than MOF. Mineral carbonation, in which metal oxides react with carbon to form carbonates, has been shown to be an economically viable alternative but the rate of reaction is low. Recent studies with nanoparticle reaction kinetics show the smaller is the nanoparticle the greater the rate of reaction of the carbonates. Uses of membranes for molecular separation is also explored with better flow configuration, study of membrane properties and improvement of mass transfer in conjunction with application of chemical solvents (MEA). Other processes such as vortex tube for thermomechanical separation and direct air capture at cryogenic temperatures are also covered by this review. On the biological routes, the literature addresses artificial photosynthesis, in which besides making carbon capture, it would still be possible to generate photovoltaic energy. There are still enzymatic methods that mimic the photosynthesis of nature inspired by cellular metabolism that creates an efficient source of CO_2 conversion. Each process and material under research has its advantages and disadvantages, generating the need for a trade-off between local and overall energy expenditure and conversion capacity.*

Keywords: *Energy, Carbon Capture and Storage, Advanced Materials, Indirect Mineral Carbonation.*

1. INTRODUCTION

According to the report of the Intergovernmental Panel on Climate Change (IPCC AR6) carbon dioxide (CO_2) emissions during the period 2011 to 2019 increased by 5.0%. Historical CO_2 emissions between 1850 and 2019 were estimated at about 2,390 (± 240) $GtCO_2$, from which 210 $GtCO_2$ were emitted between 2015 and 2019 (Friedlingstein et al., 2020). That means a possible increase in CO_2 emissions in last years. The concentrations of CO_2 in the atmosphere that were on average 278 ppm before the industrial era (~1750) are now around 410 ppm (IPCC, 2021), the influence of the increase in emissions of CO_2 and other gases in the atmosphere in recent years has increased the effective radiative forcing (ERF) that cause the greenhouse effect. Economic and population growth are the most important drivers of increased emissions from fossil fuel combustion. CO_2 emissions from the combustion of fossil fuels and industrial processes contributed around 82.4% of total emissions between 2010 to 2019.

Anthropogenic activities that dedicated to remove CO_2 from the atmosphere and store it in a lasting way in geological, terrestrial or oceanic reservoirs, or in derivatives are known as Carbon Dioxide Removal (CDR). Carbon dioxide is removed from the atmosphere by increasing biological or geochemical carbon sinks or by directly capturing CO_2 from the air or emitting sources. Emitting countries that accept the agreement to impose a limit on global warming between 1.5 °C and 2 °C normally assume the use of CDR proposals in combination with reductions in greenhouse gas emissions (GhG – Greenhouse Gas). CDR projects can be used to offset residual emissions from sectors where decarburization is difficult or expensive. In this case, there is a scientific gap where it is possible to develop and apply solutions through devices to capture carbon, mainly CO_2. (IPCC, 2021).

There are some actions to reduce CO_2 emissions mainly replacing energy production from fossil fuels with other carbon-free or clean and renewable energy sources, for example, the use of solar energy, wind energy and the use of biomass. These actions depend on sophisticated equipment and limited efficiency, so it is necessary to develop simple, effective, low-cost strategies with mild conditions to alleviate global climate change caused by CO_2 emission (Chen *et al.*, 2021).

Therefore, the objective of this paper is to present the state of the art of the development of carbon capture devices, showing their advantages and disadvantages, their efficiencies and deficiencies.

2. METHODOLOGY

The methodology used consists of searching through combined keywords for each process or method of carbon capture. The results have been refined through the inclusion of articles dating back to the last 10 years, and to bring out the very latest and most innovative regarding the topic of carbon capture. The results of the keywords were combined in resulting blocks, applying the theorem of intersection or union of sets (Venn diagram) in order to filter the results for a more restricted number of articles. The degree of importance of each article is taken into account: by the number of citations, by the degree of efficiency and performance of carbon capture demonstrated, and if it was applied in a laboratory test or if it is a computer simulation.

The scientometrics is defined as research quantitative methods applied on the science development as an information process (Goerlandt, *et.al.*, 2021). Two categories of scientometric were used to prepare this paper the co-word analysis and authorship analysis. The co-word analysis was used to visualize the interaction between search topics. The authorship analysis was used to check the cooperation between co-workers and find more papers related to the topics, and also to the check the primary sources used in the papers. The tools Web of science, Google Academics and Scopus were widely used for the research, and covering the entire databases. The main keywords searched were: CO_2 or carbon dioxide, capture or remove, design and combustion. After was included the keywords related to technologies: absorption, adsorption, membranes, carbonation, cryogenic and Vortex Tubes. And then was done the relationship between keywords for each case. Finally, were read the abstracts and selected the required papers and were put away the papers non-relevant.

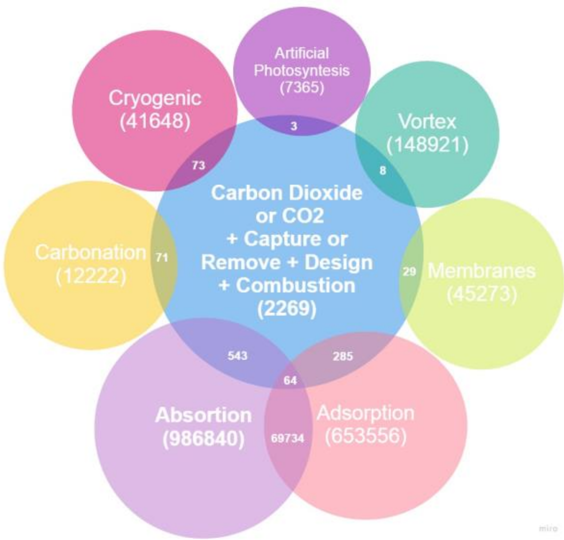

Figure 1. Cientometric Analysis of the Reasearch. Source: The Author.

3. REVISION OF LITERATURE

Projects for the development of systems for capturing and storing CO_2 (CCS) have advanced around the world. Several processes have been studied, among which: storage, which consists of providing geological storage, in the ocean or even using the mineral carbonation; the capture processes that are divided into three main approaches: a) industrial processes of oxyfuel combustion or gasification of pre-combustion fuels to generate pure or almost pure carbon dioxide, b) industrial processes with a gas discharge in a plant or factory where post combustion separation is applied to capture CO_2, or c) the direct capture in the air of a CO_2 stream through a chemically stable by-product. Each process has its advantages and disadvantages, oxy-combustion is a technology developed and available but a very large modification is necessary in the plant, generating a very high cost, pre-combustion requires less energy for capture and compression on the other hand there are critical issues associated with the temperature and efficiency of the hydrogen gas turbine, post-combustion systems have several different methods but in a generic way it can be said that there are well-developed technologies that have high installation and operation costs (Rackley, 2010).

3.1 Geological Storage

There are a great number of projects in progress for CO_2 storage, including in Brazil. There are geological storage fields, mainly those developed by Petrobras in the exploration of oil in the Pre-Salt basin where natural gas and carbon dioxide are extracted from the wells and then the CO_2 is separated and reinjected into the well (Ketzer *et al.*, 2016). According to the forecast of the IEA (International Energy Agency) around 90 gigatons of storage capacity will be needed in 2050, if CCS contributes up to 12% of emission reductions, this is equivalent to approximately 6 gigatons per year (Consoli *et al.*, 2016), in addition to being a method that requires a lot of investment, it also has a series of physical limitations and high energy consumption (Mouedhen *et al.*, 2018).

3.2 Post Combustion:

The post combustion capture process consists of removing CO_2 from the exhaust stream the products of combustion reactions, from plants or industries before emitting to the atmosphere, the exhaust gases are mixed with the proportion of CO_2 around 5 to 15 %. An important detail is the issue of CO_2:N_2 ratio selectivity, as they are two gases with very similar molecular diameters, carbon dioxide has an average diameter of 0.33 nm and nitrogen 0.35 nm, which makes difficult for gas separation (Chen *et. al.*, 2021). Post-combustion carbon capture systems are better options for retrofitting existing plants (Leung *et al.*, 2014). Post-combustion carbon capture processes can be classified by (Wee, 2013) the presence of water (wet process) or its absence (dry process). It can also be classified by the number of processes involved (Ji *et al.*, 2017): direct, where the reactions occur simultaneously or indirect, where the reactions occur in steps. The indirect route is initiated by the dissolution of mineral species in an aqueous medium to extract the metals alkaline earths such as calcium and magnesium. Another classification employed is due to the type of fundamental technology: adsorption, absorption, mineral carbonation, membrane separation and cryogenic separation (Sreenivasulu *et al.*, 2017).

3.3 Pre-Combustion:

In the process of pre-combustion, the decarburization by gasification of the fuel takes place and not the burning by combustion itself. Normally, coal or biomass is used as fuel and based on its own chemical reactions, hydrogen is produced through a combination of partial combustion, reforming and water-gas displacement and the separation of CO_2 from the stream resulting from the reaction products. According to Leung *et al.* (2014) with coal this process involves a gasifier under low oxygen level forming syngas that consists mainly of CO and H_2. Then the syngas undergoes a water-gas shift reaction (WGSR) with steam forming more H_2 while the CO gas will be converted into CO_2. If the fuel is natural gas the process is called reforming and CO and H_2 are obtained after the displacement reaction.

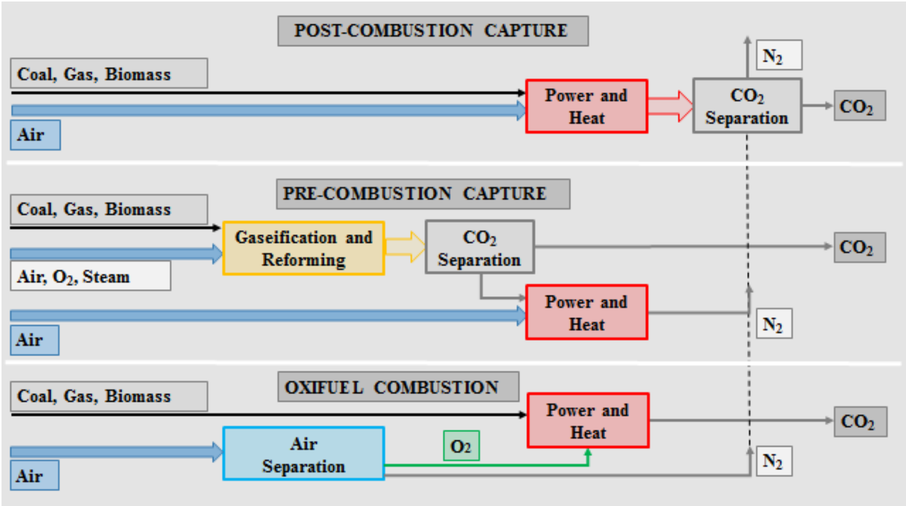

Figure 2. Approaches to CO_2 capture from power generation plants.
Source: adapted from Rackley (2010)

4. TECHNOLOGIES

Power generation plants or industries inevitably generate CO_2 as a combustion product when they use any carbon-based fuel. The removal of this CO_2 from combustion processes or energy generation led to the development of several technologies such as: adsorption, absorption, membrane separation, loop chemical combustion, cryogenic separation, among others.

$$Fuel + Air \xrightarrow{exothermic\ reaction} H_2O + CO_2 + N_2 + gases + heat \quad (1)$$

Large scale gas separation technology is as old as separation of natural gas from other impure gases (1930 patent by R. Bottoms). The first purification process was based on amines, which are the basis for current carbon capture devices of today (Smit *et al.*, 2014).

4.1 Absorption:

The CO_2 absorption technology is based on two distinct processes: chemical absorption when the solvent chemically reacts with sorbate (CO_2) and forms new chemical compounds after which recovery occurs when CO_2 is released, or physical absorption, where the process is chemically inert and the sorbate is absorbed without a chemical reaction (Rackley, 2010). Chemical absorption uses a wide range of solvents: alkanolamines (MEA, DEA, DMEA, TEA, DGA, DIPA), ammonia, methanol (Rectisol), dimethyl ether polyethylene glycol DEPG (Selexol), N-methyl-2- pyrrolidone (NMP), propylene carbonate (PC) and water (Osman *et al.*, 2021 and Cesari *et al.*, 2021). More recent studies of solvent mixtures (blends) show that the monoethanolamine-methanol solvent (30% by weight) has a faster CO_2 absorption rate and lower regenerative energy consumption compared to the monoethanolamine aqueous solution. The mixtures were created to apply the best characteristics of each product. A physical absorbent must have the following features: exceptional reactivity and absorptivity with CO_2, stability at high temperatures; chemical stability, moderate vapor pressure, low environmental impact and cost-effectiveness to apply (Osman *et al.*, 2021). Shuangchen *et al.* (2016) applied Piperazine Cyclo Amine as a promoter to produce carbamates with carbon dioxide and obtained an absorption rate of 72% using bubbling reactor. The mixture of 2-amino-2-methyl-1-propanol and piperazine investigated by Khan *et al.* (2016) reduced the regeneration energy and reached a CO_2 absorption rate of ~99% with a purity of ~96%. Wang *et al.* (2019) synthesized spherical pellets of potassium carbonate (K_2CO_3) compounded with alumina (Al_2O_3) and also urea (CH_4N_2O), and it reached a CO_2 removal potential of ~0.0031 mol CO_2/g with excellent resistance to compression and corrosion.

4.2 Adsorption:

Adsorption is a process that occurs between a gas and the surface layer of a solid material, where the adsorbed ions, atoms or molecules remain adhered to the surface of the sorbent forming a film. The binding of the adsorbate to the surface can be through a chemical bond (chemical adsorption) or a weak physical force of attraction (physical adsorption) (Rackley, 2010). One of the best adsorbent known is activated carbon. New techniques with pyrolysis at high temperature and pressure of carbonaceous substances produced activated carbon with large surface area and heterogeneous pore structure, low energy and regeneration temperature (Osman *et al.,* 2021). On the other hand, the capacity and selectivity are limited due to weak interactions between the material and the CO_2 molecules (Chen *et al.,* 2021). The results with carbon nanotubes are more promising with good storage potential when they are doped with nitrogen and encapsulated with metallic salts (Osman *et al.,* 2021). Zeolites, due to negative charges on their surface, have stronger physical interactions and with CO_2 molecules, this material has high porosity and surface area and regeneration capacity. Both activated carbon and zeolites are low-cost materials, but the selectivity of CO_2 does not allow them to be competitive with chemical sorbents (Chen *et al.,* 2021). The nanomaterials of the Metal Organic Framework (MOF) class are good candidates for capture, as their high nitrogen content renders good selectivity for CO_2, as it also has a high surface area and porous structure. The adsorption capacity of the known material ZIF-8 reaches about 29 $mg.g^{-1}$ under atmospheric pressure and room temperature (Chen *et al.,* 2021). Another innovative nanomaterial is boron nitride composite foam chemically bonded with vinyl alcohol. It exhibited high CO2 absorption due to its improved porosity, surface area and mechanical properties. On the other hand its working pressure is approximately 54 bar (Owour *et al.,* 2021). Another promising nanomaterial is MXene due to its excellent electronic properties, which is fundamental for the electrostatic interactions between CO_2 molecules, and it shows a large surface area and porosity as well (Chen *et al.,* 2021). The moisture swing adsorption process provides a new approach to cost-effective capture of CO_2 from the air. Anion exchange resin sorbent binds CO_2 when dry and releases it when wet. A thermodynamic model with coupled phase and chemical equilibrium was developed to study the complex H_2O-CO_2-resin system (Chen *et al.,* 2021).

4.3 Carbonation:

The simplest mineral carbonation reactions occur when a metal oxide reacts with CO_2 to form a carbonate, calcium and magnesium are alkaline earth metals that are ideal for this purpose and their carbonates have low solubility in water (Wilcox, 2012). Many minerals and rocks are studied with capacity and abundance as possible candidates for carbon capture and storage, and many processes are analyzed and could be basically divide them into two segments: direct and indirect carbonation. The direct process use solid-gas reactions in the dry base or can use the aqueous base. Indirect can use acid extraction or molten saline extraction (Olajire, 2013). An advantage of carbonation is to take advantage of solid waste generated in the coal combustion processes (fly ash), which have a high amount of CaO and MgO in the exhaust gases. These oxides are essential for natural carbonation due to their high reactivity as a function of the temperature of the exhaustion (JI *et al.,* 2017; Ukwattage *et al.,* 2015; Wee, 2013). In this process, carbon in gaseous form (CO_2) is converted into stable solid forms of carbonates through mineral sequestration (Ukwattage *et al.,* 2017). According to Kemache *et. al.* (2017) the rate of reaction speed of carbonation of the system does not follow the rate of emission of gases from energy generators, which is a chronic problem that lacks economic and commercially acceptable development for the process (Olajire, 2013). Research and efforts from the scientific community are therefore needed to find solutions for these opportunities for technical design improvements with high kinetic reaction rate, high CO_2 removal efficiency and low energy consumption for government and industry to subsidize the design of equipment (Ben-Mansour *et. al.,* 2016). According to Wilcox (2012) the advantages of mineral carbonation are: The possibility of CCS as a single process, permanent sequestration with minimal leakage potential, stabilization of harmful pollutants associated with mineral matter. The mineral carbonation processes are thermodynamically favorable. However, the reaction rate, process efficiency and capture percentage do not offer advantages to this technology. Camerini, *et. al.* (2019) studied the kinetics of carbonation using commercially available dispersed calcium hydroxide ($Ca(OH)_2$) nanoparticles and used the Boundary Nucleation and Growth Model (BNGM) to analyze the process of carbonation in the surface area of the molecules. They used the wet route for the experiment with a faster conversion rate at temperatures of 30 °C, the larger the nanoparticle and the smaller its surface area, the lower the rate at which the porosities are filled with the reaction products in the case of the carbonates.

4.4 Membranes:

For porous membranes, the higher the mass transfer coefficient, the greater the absorption performance of the membrane, wetting the membrane can reduce the mass transfer coefficient (Cesari *et al.,* 2021). Membranes using molecular sieving technology can increase selectivity, where it occurs through a combination of diffusion within the pore space and adsorption of CO_2 and surface diffusion across pore surfaces. It is believed that this technology will be economical and viable, there is a lot of research for chemical modification and new materials for the molecular sieve (Olajire, 2010). Non-porous membranes operate through the mechanism of solution diffusion (Fick's law) and normally consist of a thin, dense layer polymeric membrane with a less dense, porous layer at the base (Rackley, 2010). The spiral membrane consists of a central perforated tube through which the permeated gas flows through the various sheets of membrane wrapped around it, each sheet is an envelope that has a feed spacer, the polymeric membrane and the permeation spacer, the flux flows through the permeator to the tube center (Rackley, 2010). The hollow fiber membrane is made up of fiber bundles that end in a pressure vessel, with the gas flow passing outside the fibers, the purge flow passes inside the fibers carrying the permeated CO_2 with it (Rackley, 2010). The effect of pressure drop in hollow fibers increases the energy requirement in the gas absorption process, a trade-off between process intensification and the amount of energy must be made to validate the approach of this material (Cesari *et al.*, 2021).

4.5 Criogenic and Vortex Tubes:

The separation of gases through distillation and cryogenic systems is based on different boiling points and volatility of gases (Wilcox, 2012). The temperature and pressure of the gas mixture influence the extraction process through the phase changes of the gases. Dual column processes use pretreated ambient air through filters and compressed to remove moisture and CO_2, which is then cooled to cryogenic temperatures using series heat exchangers that feed distillation columns to separate oxygen, nitrogen and also the argon. Oxygen can be used in oxyfuel combustion to capture carbon (Rackley, 2010). High performance and purity process control while ensuring safe and reliable operation and energy efficiency are important for CO_2 removal. To treat large volumes of air, cryogenic distillation is the most economical technology, while for smaller volumes, pressure swing adsorption (PSA) is more effective. What determines the cost associated with the distillation process is the desired purity of the gases (Wilcox, 2012).

The Vortex Tube can be analyzed as a new method for carbon capture, although the technology and its applications already exist since the 1930s, thermomechanical processing (compression and subsequent cooling) and changes in the thermodynamic state of CO_2 present in a mixture of gases. To separate carbon dioxide by liquefaction, it is necessary to change its thermodynamic state until it reaches the vaporization curve below the dew point The system proposed by Matos (2021) is composed primarily by a compressor for the air, followed by a heat exchanger, a first stage Vortex Tube, plus a heat exchanger, a liquid separator and finally a second stage Vortex Tube, presented a theoretical removal potential of 0.163 kg-CO_2/kg-combustion gases with a removal rate of 90%. Ratermann *et. al.*, (2001) developed a Ranque-Hilsch Turbo Vortex for carbon dioxide separation and built a prototype and test bench in 2001 to extract CO_2 from flue gases in the range of up to 15% using DEA as an absorbent. Kaya (2020) carried out an experiment with Ranque-Hilsch Vortex Tube with different inlet pressures for gas separation, obtaining an excellent performance of the vortex tube with a working pressure control factor of 79.5%.

4.6 Photosynthesis:

The mention the most common technology for removing carbon dioxide from the atmosphere is through photosynthesis. It has the capacity to remove about 120 Gt-C per year. Photon energy is used to carry out a chain of complex chemical reactions that take place in plant cells known as the Calvin cycle that takes place inside chloroplasts and the enzyme called RuBisCO catalyzes the fixation of CO_2. Artificial systems that mimic the natural process of photosynthesis have been developed and some of them present experimental results. In electrochemical cell processes a current is applied using metallic electrodes to reduce CO_2 so the fuel produced will be oxidized to take advantage of its energy potential with the generation of CO_2 and H_2O. The next step is to convert that CO_2 into other products within a synthetic gas or convert it into other hydrocarbons like methane. Another option is the photocatalytic reduction of CO_2 using titanium oxide (TiO_2). It has an energy transition band of 3.2 V which is activated by the ultraviolet (UV) region leaving the reduced CO_2 so that it binds with molecules of hydrogen and oxygen and forming hydrocarbons that facilitate the biocatalysis of carbon (Wilcox, 2012). Roy *et. al.*, (2019) developed artificial photosynthesis devices including thermocatalysts, photocatalysts, electrocatalysts and combined catalysts, they analyzed physical and chemical aspects of the process pH, temperature, electrolytes and environment, they demonstrated that in addition to capturing carbon it is also possible to generate photovoltaic energy. Long *et. al.*, (2017) created an enzymatic method inspired by cellular metabolism, with an efficient CO_2 conversion due to its improved selectivity.

5. CONCLUSION

In this paper, we presented a concise overview of the main routes that can be used to reduce carbon emissions or to remove it from the atmosphere altogether. The study of the energy penalty for carbon capture is necessary, but without neglecting solutions that may be more expensive today but may become viable in the future. Carbon capture and storage is still a technology in the research phase to make it viable economically and energetically in large scale in a way that would timely address the issue of greenhouse gases in the atmosphere. There have been many advances in recent years and many articles have been published, but expressive results still seem far from being achieved.

6. ACKNOWLEDGEMENTS

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