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# Tecnologias para mitigação da emissão de gases do efeito estufa e mudanças climáticas

*Technologies for mitigation of greenhouse gas emissions and climate change*

- 1 Rodrigo da Silveira Ribeiro
- <sup>2</sup> Carlos Alberto Galeano Suarez **D**
- <sup>3</sup>Inti Doraci Cavalcanti Montano
- 1 Universidade Federal de Goiás
- 2 Universidade Federal de Goiás
- 3 Universidade Federal de Goiás

#### **Resumo:**

Nesta pesquisa foi realizado um estudo tecnológico e prospectivo de natureza qualitativa e descritiva sobre diferentes processos e tecnologias capazes de impactar e promover a mitigação das emissões de gases de efeito estufa. Este processo de alívio envolve a possibilidade de remoção de poluentes atmosféricos, bem como a redução das suas emissões. É crucial enfatizar a importância de avanços científicos significativos para a comercialização generalizada destas tecnologias, que são essenciais para que os países atinjam os objetivos estabelecidos. Isto é indispensável para minimizar as consequências desastrosas previstas para a humanidade nas próximas décadas, como resultado do aquecimento global e das mudanças ambientais. Nesse âmbito está a utilização de métodos CCUS (Captura, Utilização e Armazenamento de Carbono) e a redução das emissões de N2O, CH4 e gases fluorados pelas indústrias, usinas, setor agrícola e o uso indiscriminado da terra. Simultaneamente, há uma necessidade urgente de políticas locais, nacionais e internacionais mais rigorosas e restritivas que promovam e imponham uma mudança gradual, sustentável, mas definitiva, na estrutura energética global.

#### **Palavras-chave:**

Legislação; Absorção química; Eficiência energética; Viabilidade economica; Separação de gás.

#### **Abstract:**

In this research, a technological and prospective study of qualitative and descriptive nature was carried out regarding different processes and technologies capable of impacting and promoting the mitigation of greenhouse gas emissions. This relief process involves the possibility of removing atmospheric pollutants as well as reducing their emissions. It is crucial to emphasize the importance of significant scientific breakthroughs towards the widespread commercialization of these technologies, which are essential for countries to achieve their established goals. This is indispensable for minimizing the predicted disastrous consequences for humanity over the next decades as a result of global warming and environmental changes. Within this scope lies the utilization of Carbon Capture, Utilization, and Storage methods (CCUS) and the reduction of emissions of  $N_2O$ , CH<sub>4</sub>, and fluorinated gases by industries, power plants, the agricultural sector, and the indiscriminate use of land. Simultaneously, there is an urgent need for stricter and more restrictive local, national, and international policies that promote and enforce a gradual, sustainable, yet definitive change in the global energy structure.

#### **Keywords:**

Legislation. Chemical Absorption. Energy efficiency. Gas separation. Economic feasibility.



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# **1 INTRODUCTION**

The issue of climate change is both present and future. Consequences of alterations in atmospheric composition and anthropogenic actions on the global ecosystem are currently observed and are expected, according to mathematical models and projections, to persist for decades and centuries (BRS Convention and MC Convention, 2021). These consequences encompass historical peaks and lows in temperature, changes in sea levels, an increase in the frequency and intensity of natural disasters, as well as significant impacts on human health, such as the rise of non-communicable diseases, nutritional problems, limited access to food and water quality, along with social imbalances. Since 1750, the climate has undergone considerable changes, heavily influenced by variations in the concentration and proportion of greenhouse gases in the atmosphere, with CO<sub>2</sub> standing out as the primary culprit, currently reaching concentrations above 400 ppm (Mikhaylov et al., 2020; Wilberforce et al., 2021).

Several factors contribute to significant dependence on fuels and carbon derived from raw materials, resulting in a positive net carbon emission. Industries play a crucial role in this scenario, with their undeniable protagonism. The burning of fossil fuels for energy generation, along with sectors such as steel and cement production, is responsible for the majority of CO<sub>2</sub> emissions on the planet. However, these sectors have substantial potential for emission mitigation through the application of carbon capture and storage technologies, given by their high-quality research and development teams and available state-of-the-art technologies (Chauvy et al., 2019; Lin et al., 2022). With the emergence of new power plants fueled by fossil fuels and industries with intensive energy consumption needs, an increase in emissions seems inevitable. Therefore, the use of CCUS (Carbon Capture, Utilization, and Storage) technologies becomes crucial. According to the Intergovernmental Panel on Climate Change (IPCC) and the IEA (International Energy Agency), CCUS will play a fundamental role in achieving net-zero objectives regarding CO2 by 2050. These technologies are viewed as the most scalable and cost-effective means for industries to effectively achieve decarbonization by 2050 (Kamkeng et al., 2021; Lin et al., 2022).

The CCUS process involves capturing carbon dioxide from emitting sources on the atmosphere, often accompanied by the separation of contaminant gases or inert components in the process. The capture and separation stages are interconnected because merely capturing the gas is insufficient. It needs to be separated and concentrated through unit operations based on chemical and physical principles. Subsequently, it is compressed and safely transported to storage or utilization sites. Another option is the storage of CO2. Intensive research is underway to identify secure sites for trapping this gas, as its current use as a raw material is insufficient (Gaurina-Međimurec and Mavar, 2019; Willberforce et al., 2021). The scarcity of comprehensive articles addressing relevant aspects of technologies and challenges for greenhouse gases (GHG) mitigation in a single text is noticeable. In this scenario, this paper attempts a broad and informative literature review, covering various aspects and stages of methods and technologies applicable to the capture, separation, utilization and storage of CO<sub>2</sub>, as well as the mitigation of emissions from other greenhouse gases. Additionally, it aims to analyze the challenges and costs associated with global needs for mitigating climate change.

# **2 METHODOLOGY**

The objective of this work is to be a technological and prospective study, focusing on the exploration of scientific literature to address both established and in development technologies that have the goal of mitigating climate change caused by the emission of GHGs. The structure of the study starts with a broad approach, initially discussing the general context of climate change and its relationship with GHG emissions.

The search criteria prioritized recent literature from 2015 to 2023, although some sources predating 2015 were used when recent authors referenced fundamental concepts. The selection of papers considered not only recency but also the number of citations to ensure the reliability and relevance of information. Key terms employed included climate change, CO<sub>2</sub> separation, absorption, adsorption, carbon capture, technologies, GHG mitigation, legislation, policies, methods, storage, CCS, CCUS, among others.

#### **3 RESULTS AND DISCUSSION**

The direct correlation between the release of chemical waste beyond the limits established by governmental agencies and climate change is widely acknowledged by the scientific community (Cachola et al., 2023). The main responsible for these emissions, which include greenhouse gases, cover a variety of industries, such as chemical, metallurgical, steel and cement industries, in addition to the agricultural and livestock sector. The highest-emitting process is notably energy consumption, representing 75% (37.6 GtCO2eq), covering activities such as transportation, electricity generation, and heat for buildings, factories, and constructions. In this sector, direct heat and electricity generation accounted for 31.8% of total GHG emissions worldwide in 2019, while transportation and manufacturing contributed 17% and 12% respectively to the overall emissions (Climate Watch Data, 2023). In this context, considering ways to alleviate or prevent impending environmental and climatic issues that will impact society, climate change mitigation initiatives have gained prominence as a response to future environmental and climatic problems, aiming to limit GHG emissions and prevent their release into the atmosphere, as discussed by Grubb et al. (2022).

#### **3.1 Climate Change and Greenhouse Gases**

One of the major gases in this harmful group is carbon dioxide. The atmospheric concentration of CO2 has increased significantly from 270 parts per million (ppm) to over 400 ppm currently, compared to the pre-industrial period, which serves as a reference for the onset of human activities impacting the climate (Ozkan et al., 2022). Even with the growth rate of emissions between 2010 and 2019 being lower than in the previous decade, the net amount of atmospheric CO<sub>2</sub> continued to rise, according to the IPCC (2022). The same source states that this increase has been consistent since 1850. Despite CO<sub>2</sub> being the primary contributor in terms of quantity, other gases are also monitored and contribute to global warming, such as methane. It has a high heat retention capacity and is considered one of the most dangerous in terms of climate impact, although it has a shorter atmospheric residence time, as well as nitrous oxide (N<sub>2</sub>O) and fluorinated gases, such as hydrofluorocarbons (HFCs), sulfur hexafluoride (SF<sub>6</sub>), and perfluorocarbons (PFCs) (Gielen and Kram, 2023).

Within the context of maintaining high levels of greenhouse gas emissions, there is growing acceptance in the scientific community regarding the irreversibility of climate changes already induced (Portner, et al., 2022). Dziejarski et al. (2023) state that optimizing fossil fuel combustion or even utilizing renewable energy will not be sufficient to counteract the continued increase in atmospheric CO<sub>2</sub>. The projection of a high probability (66%) of a global average temperature increase of 1.5°C or more by 2100 persists, with an increase of 0.6°C that occurred from 1982 to 2012 (Pathak et al., 2022). Among the irreversible impacts are rising sea levels, glacier melting, oceanic storms, species extinctions, ecosystem disruptions, as well as droughts, floods, and other crises (Mora et al., 2018; BRS Convention and MC Convention, 2021). Nevertheless, according to NASA (2023), even in the face of potential irreversibility of the climate change effects, stabilizing temperatures is feasible and would remediate unforeseeable future damages. Without a rapid and significant change, maintaining the current emission pace, projections indicate (with a lower probability, around 22%) a potential increase of up to 4°C in the global average temperature by 2100 (Pathak et al., 2022).

#### **3.2 Climate Protocols and International and National Environmental Legislation**

From the perspective of public and governmental initiatives aimed at encouraging and holding countries, governments, and their industries accountable for mitigating the broad and overall emission of gases contributing to global warming and climate change, the Kyoto and Montreal Protocols, along with the Paris Agreement, stand out. These agreements are consolidated during country meetings organized by the United Nations (UN), known as COPs. The Montreal Protocol was an agreement established in 1987, eventually signed and ratified by all countries. Its primary focus was not on the greenhouse effect but rather on banning the use of substances that were depleting the ozone layer, such as chlorofluorocarbons (CFCs). The agreement was a success, leading to a significant 99% reduction in the use of these compounds over time. This triumph subsequently inspired a notable amendment to the agreement, the 2016 Kigali Amendment, which aimed to further reduce the use of hydrofluorocarbons (HFCs). HFCs are products used as substitutes for CFCs and, while not depleting the ozone layer, are potent contributors to the greenhouse effect (Maizland et al., 2023).

The Kyoto Protocol, drafted in 1997 and enforced starting in 2005, is a legally binding agreement that compels signatory countries to reduce GHG emissions by an average of 5.2% from 2008 to 2012, compared to the 1990 baseline (Senado Federal, 2023). The main challenge was the absence of nations like China and India, along with the eventual withdrawal of the United States in 2001. The subsequent attempt was the Paris Agreement in 2015, the largest agreement up to that point. Participating countries were compelled to establish achievable goals and targets for reducing emissions, aiming to prevent an increase in the global average temperature of up to 2°C by 2100. The agreement also introduced an additional and more ambitious target of keeping the temperature increase below 1.5°C compared to pre-industrial revolution levels. The common objective is to achieve net-zero carbon emissions by 2050, meaning to absorb or remove from the atmosphere the same amount of carbon emitted (Maizland et al., 2023; Ministério do Meio Ambiente do Brasil, 2023).

Global efforts to reduce  $CO<sub>2</sub>$  emissions are, in many cases, insufficient. Despite numerous agreements, legislations, promises, and established goals, the seven largest emitters of carbon dioxide in 2018 - China, the United States, the European Union, India, Russia, Japan, and Brazil - are projected to achieve net-zero emissions between 2056 and 2086 (in the case of Russia), according to Maj and Miniszewski (2022). This is attributed to the considerable cost and time required for energy transitions, surpassing the target dates set by most Paris Agreement signatories. Therefore, the pace of change in the energy matrix is a cause for concern, with potential consequences in the coming decades. As of October 2023, according to the United Nations Framework Convention on Climate Change (UNFCCC) and the Climate Action Tracker (a website created by Climate Analytics and New Climate Institute, with German and Rockefeller group support and investment), none of the Paris Agreement signatory countries are progressing in line with their promised targets.

Brazil, having ratified the mentioned treaties and agreements, aims to achieve its established goals at the national level, as evidenced in the Nationally Determined Contributions (NDCs) (Ministério do Meio Ambiente do Brasil, 2023). Aligning with the commitments of international agreements, the Senate approved in 2021 the Bill 6539/2019, which seeks to update Law No. 12,187 of 2009, establishing the National Policy on Climate Change (PNMC). This policy formalized Brazil's voluntary commitment to the UNFCCC to reduce greenhouse gas emissions by 36.1% to 38.9% of projected emissions by 2020, compared to 2005, totaling 2.1 GtCO<sub>2</sub> emissions (Ministério do Meio Ambiente, 2023; Brazil Law No. 12,187). According to the Institute of Energy and Environment (2021), the goal was achieved at the stipulated limit.

#### **3.3 Technological Methods for Carbon Capture and Storage (CCS)**

#### 3.3.1 Overview of the Current CCS Situation

The acknowledgment of the urgency to address climate change is crucial, but finding solutions for it is even more essential for the scientific community. One of these options is carbon capture and storage (CCS) technology, which involves capturing carbon from industrial facilities, factory chimneys, or directly from the atmosphere and transferring it to locations where it will not cause a greenhouse effect (Leeson et al., 2017; Yu, 2022). Figure 1 highlights the main sectors responsible for carbon emissions, possible technological pathways for capture, and the final destinations for carbon storage or reuse.

#### **Figure - 1** Overview of Carbon Capture and Storage (CCS) versus Carbon Capture and Utilization (CCUS).



Source: Miranda et al. (2018).

This approach plays a significant role in the strategy of some countries to achieve their set goals for 2050. Some countries with the greatest potential to effectively adopt CCS technologies - even if they are not doing enough to meet their objectives - include China (potential to capture 5,700 ) and the United States (2,100 ), followed by India (1,300 ), Russia (807 ), Japan (564 ), and South Korea (403 ) (Cachola et al., 2023). These values do not indicate effective capture but rather the potential. Bibliometric studies also highlight that industries in steel, metallurgy, and cement, significant CO<sub>2</sub> emitters, have contributed significantly to scientific research in CCS (Leeson et al., 2017; Ghoneim et al., 2022; Cachola et al., 2023).

From a more technical perspective, Cachola et al. (2023) state that the most cited and utilized CCS technologies in the industrial sector are post-combustion capture using ethanolamine (MEA) or methyl di-ethanolamine (MDEA) (Bui et al., 2018; Liu et al., 2023). These processes employ the mass transfer phenomenon in absorption unit operations, where a solute from a gas mixture is transferred to the liquid solvent passing through the column. Technologies aiming to capture carbon directly from the source can be classified into four types: 1) post-combustion (PCC), 2) pre-combustion, 3) oxy-fuel combustion, and 4) chemical looping combustion or chemical looping combustion (CLC). The location for CO2 storage after capture varies depending on the available and effective options at each location, ranging from use as input for industrial plants to infiltration and storage in geological formations (depleted oil and gas reservoirs, inaccessible coal deposits, saline aquifers, among others) (Rissman et al., 2020; Fennell et al., 2021).

#### 3.3.2 Post-Combustion Capture (PCC)

PCC, as per Mondal et al. (2012), refers to the capture of carbon dioxide after the chemical reaction in the released gas stream. Two major global initiatives adopt this method: the Boundary Dam Power Station (Canada) and the Petra Nova Carbon Capture Project (USA), with capture capacities of 1 million and 1.6 million tons of CO2 per year, respectively (Carbon Brief, 2014). Despite being the most widely used and oldest method, it is costly due to the high-energy consumption required to separate carbon dioxide from other contaminant gases produced, such as nitrogen oxides and sulfur dioxide, which react with the solvent used in CO2 absorption, impacting the process efficiency. Nevertheless, it is one of the more cost-effective technologies compared to others (American Chemical Society, 2022). Therefore, desulfurization and NO<sub>x</sub> removal operations are necessary to make carbon dioxide absorption viable (Wu et al., 2020). Additionally, this method generally results in a stream with a low concentration of carbon dioxide (between 7-14%, for example, in plants using coal), as it carries much of the atmospheric nitrogen. This poses a challenge as it further compromises separation efficiency (American Chemical Society, 2022; Dziejarski et al., 2023).

#### 3.3.3 Pre-Combustion Capture

According to Dziejarski et al. (2023), the pre-combustion method primarily occurs after a hydrocarbon gasification process, typically coal or heavier fractions of petroleum, resulting in a gaseous fuel predominantly composed of  $\mathsf{H}_2$  and, eventually, other contaminants. Theo et al. (2016) explain that the process uses  ${\mathsf O}_2$ , usually at a concentration below stoichiometric, at high pressure, aiming to generate syngas. Through incomplete combustion, a stream of CO,  $\textsf{H}_{2'}$  and impurities with sulfur is generated. Other processes can also produce this mixture, such as steam methane reforming or the partial oxidation of liquid fuels. The syngas, as the synthesis gas is called, undergoes a conversion of carbon monoxide into CO2 and more  ${\sf H}_{_2}$  in a reaction with the addition of water vapor, occurring in a catalytic shift reactor (Water-gas shift reaction) (Gibbins and Chalmers, 2008). Subsequently, carbon dioxide is separated by techniques like chemical absorption, can be compressed, liquefied, and stored, while H $_{_2}$  is used as a clean fuel. A high-pressure stream with a high concentration of  $CO<sub>2</sub>$  is crucial in this process, ranging from 15% to 60%, much higher than the proportion in traditional combustion reactions (3% to 15%), facilitating the separation of other exhaust gases more efficiently and economically (Lockwood, 2017; Mora et al., 2018). The flowchart in Figure 2 allows visualizing the steps involved in pre-combustion capture.





#### 3.3.4 Post-Combustion Capture (PCC)

The oxy-combustion or oxy-fuel technique involves separating gaseous oxygen from nitrogen present in the air (over 95% O<sub>2</sub>) and burning the fuel exclusively with O<sub>2</sub>, resulting in a stream composed only of water vapor and CO2, facilitating its final disposal due to more efficient separation of its components (Mondal et al., 2012). This observation is related to the fact that, in traditional combustion using air, the high percentage of N<sub>2</sub>O results in a CO2 concentration in the combustion gas stream between 3% and 15%, depending on the type of fuel, making separation more complex and costly, as will be explained later. There is a higher energy demand to separate a less concentrated  $CO<sub>2</sub>$  stream compared to a more concentrated one (Dziejarski et al., 2023). However, the main obstacle lies in the high cost of using pure oxygen. It is worth mentioning the presence of recirculation of part of the combustion stream, aiming to dilute some of the O<sub>2</sub>, reducing the temperature reached, as most available materials would have difficulty resisting the burning temperature of coal with pure oxygen (which can reach up to 2480 °C, while with air it reaches 1730°C) (Mondal et al., 2012).

#### 3.3.5 Chemical Looping Combustion (CLC)

The CLC is a method aimed at capturing carbon dioxide without the high costs associated with producing purified oxygen and simultaneously without the need for CO<sub>2</sub> separation after combustion. In this process, an intermediate, usually a metallic solid, such as a metal oxide, is employed as an oxygen carrier. It, in its oxidized form, provides oxygen to the combustion reactor (operating at high temperatures), and during this process, it is reduced (Okoli et al., 2018). The resulting gases are CO2 and H<sub>2</sub>O vapor, while the metal oxide is recycled to the regeneration reactor, also known as the "air reactor," where it is reoxidized through the passage of air containing  ${\mathsf O}_2.$  Studies are ongoing to identify the most efficient metallic carrier, exploring elements such as Fe, Mn, Cu, Ni, and Co, as well as optimizing the reactors, both operating at high temperatures (National Energy Technology Laboratory, 2023). Following that, in Figure 3, flowcharts elucidate some of the most relevant macro steps for each of the mentioned CCS technologies.





Source: Adapted from Miranda et al (2018).

The resulting stream from the Me<sub>x</sub>O<sub>y-1</sub> processing in the combustion reactor, loaded with water and carbon dioxide, can be purified, compressed, and directed for storage or use in other applications. On the other hand, the regeneration reactor releases a very hot stream composed of  $\mathsf{N}_2$  and  $\mathsf{O}_{2'}$  making it viable for use, including in power generation through the activation of a turbine. The composition of this stream varies depending on the conversion rate of the reaction between oxygen and the metal carrier. In an ideal scenario, the depleted air would mainly consist of  $\mathsf{N}_{2'}$  with small traces of other gases

such as  ${\mathsf O}_2$ , water, and contaminants. In a study conducted by Haugen et al. (2023) with petroleum coke and lignite, it was found that this stream contained 91.1% N<sub>2</sub>, 2.2% O<sub>2</sub>, and 6.2% H<sub>2</sub>O (National Energy Technology Laboratory, 2023).

### 3.3.6 Direct Air Capture

Direct Air Capture (DAC) is performed in open-air capture units using fans. Even with the natural atmospheric composition, carbon dioxide is separated, compressed, transported, and stored, while other components return to the atmosphere (IEA, 2023; Zacari, 2023). However, similar to the methods discussed earlier, the challenge lies in the low concentration of carbon dioxide in the air, resulting in increased energy consumption to purify the output stream sufficiently (Terlouw et al., 2021; Yu, 2022). This method can be considered the most expensive carbon capture method. A solution to financial issues may arise with the development of new profitable applications for the captured and compressed CO<sub>2</sub>, such as in the production of synthetic aviation fuels (IEA, 2023). From a physicochemical perspective, two predominant approaches are utilized and researched. Solid Adsorption (S-DAC) is one, where atmospheric CO2 is extracted by adhering to a solid, at ambient on reduced pressure (under vacuum), and intermediate temperatures (80-120°C). The other approach is chemical absorption (L-DAC), mainly using basic solutions that react with the gas, absorbing it, and subsequently releasing it through a series of unit operations at temperatures ranging from 300 to 900°C (Chatterjee et al., 2020; Ozkan et al., 2022). Currently, capturing this compound from the air is more energetically costly than capturing it at the emission source, as in conventional methods. In addition to the mentioned methods, there are innovations in developmental stages and scalability, such as adsorption using electrochemical cells or zeolites (IEA, 2023). Since July 2023, according to IEA (2023) and Ozkan et al. (2022), 19 to 27 DAC plants have been licensed and are in the early stages of operation, currently capturing approximately  $0.01$  Mt CO<sub>2</sub>/yr. Figure 4 provides a simplified schematic of the DAC process.



Figure - 4 Illustration of the path taken by CO<sub>2</sub> molecules from capture to storage in a DAC unit.

CCS Brasil (Carbon Capture and Storage Brasil) reports highlights, in addition to CCS methods directly used in industries and DAC technology, the relevance of biological solutions for direct air capture. These solutions include strategies such as afforestation and reforestation, biochar and biofuel production, acceleration of weathering (bicarbonate formation through rain, chemically reacting with minerals in rocks and depositing in the ocean), and natural carbonation (a process where bubbles form through the interaction of atmospheric CO2 with a liquid) (Terlouw et al., 2021; CCS Brasil, 2023).

#### **3.4 Greenhouse Gas Separation Techniques in Industries, their advantages, and disadvantages**

Within the general carbon capture processes there is always the need to separate GHGs, such as CO2, from a stream containing other compounds (Dziejarski et al., 2023). This requires unit operations that facilitate the separation of the solute from a gas mixture. In this scope, some of the existing and potential technologies include absorption, adsorption, membrane separation, and cryogenic distillation. The choice of the most efficient method depends on separation conditions, such as the partial pressure of CO2 in the stream and the composition of the gas to be treated, which, in turn, is related to the type of fuel used. Therefore, separation methods range from those currently employed in chemical industries (for stream purification) to newer technologies still in development for future commercialization (Dziejarski et al., 2023).

#### 3.4.1 Chemical and Physical Absorption

According to Wang et al. (2011), this separation process relies on the affinity between  $CO<sub>2</sub>$  and the liquid solvent employed, leading to a reaction that forms an intermediate solution. This solution is susceptible to desorption for solvent regeneration in a reversible reaction. Among the most commonly used solvents are MEA, di-ethanolamine (DEA), MDEA, and diisopropanolamine (DIPA) (Dziejarski et al., 2023). It is estimated that the absorption method significantly contributes to current carbon capture, being widely employed commercially in various industries (Miranda et al., 2018). Ziobrowski and Rotkegel (2022) emphasize the viability and realism of the chemical absorption method in the present day. Its efficiency lies in the ability to absorb CO2 in combustion streams with low concentration and moderate pressures, reducing process costs and simplifying pre-adaptation of conditions. However, challenges are associated with the compositional characteristics of the stream. CO<sub>2</sub> removal by absorption typically requires a prior cleaning step to eliminate contaminants such as sulfur oxides (recommended concentration between 1 and 10 ppm), nitrogen, dust, and hydrocarbons. These contaminants can significantly affect the absorption column's operation and react with the amine, forming stable, non-regenerable salts, leading to continuous solvent loss. Additionally, the CO<sub>2</sub> regeneration process can corrode column materials and be financially costly due to the energy required to break chemical bonds (Rackley, 2017).

#### 3.4.2 Physical Adsorption

In separation by adsorption, carbon dioxide is adsorbed by porous solids, a pilot-phase method but promising. This cyclic process involves the adsorption and subsequently desorption of CO<sub>2</sub>. Factors such as the adsorptive capacity of the solid and the adsorption kinetics of certain gases in a mixture influence the speed of this process. The porous structure of the adsorbent is effective due to its extensive surface area, facilitating mass transfer. CO<sub>2</sub> molecules bind to the solid structure and are subsequently released for gas transport and compression, as well as for the regeneration of the adsorbent (Younas et al., 2016). However, according to Dziejarski et al. (2023), adsorption technology faces challenges related to various factors: process parameters, composition of the combustion gas, the type of industry that would use the technology, physicochemical parameters, among others. Figure 5 illustrates the stages of the described adsorption operation.



Figure - 5 Conventional flowchart of CO<sub>2</sub> separation by adsorption.

Source: Adapted from Dziejarski et al. (2023).

The choice of adsorbent depends significantly on the operating temperature and the composition of the combustion mixture. For instance, post-combustion capture (PCC) flue gases typically exit at lower temperatures (approximately 100°C for natural gas combustion and 60-150°C for coal), values that many solids can withstand. In pre-combustion methods, where the fuel results from gasification or the Watergas shift reaction, the outlet streams reach temperatures of 500-1800°C and 250-550°C, respectively. In oxy-fuel combustion, temperatures are also close to these values (Bhatta et al., 2015). In these cases, finding economically viable adsorbents capable of withstanding these extreme conditions remains a challenge for the widespread expansion of this process.

#### 3.4.3 Membrane Separation

The membrane separation involves the utilization of a driving force such as temperature, pressure, electrical potential, or gravity to conduct the separation of a solute. Depending on the size of the membrane pores, certain substances advance into what is termed permeate, while some solutes do not pass and make up the concentrated solution. Although membrane technology is under development by the industry, it is not yet marketable. Mostly, organic membranes are being tested by the industry due to their structural diversity, composition, as well as resistance to more extreme conditions such as high temperatures and pressures, or reactivity of the passing fluid. Polymers are considered efficient for separations due to high permeability, desired selectivity, and ease of pore size adjustment during manufacturing (Hou et al., 2022). In this method, two main mechanisms stand out: simple membrane separation and membrane absorption. In the first case, the process is based on dissolution and diffusion, where the gaseous solute is initially "dissolved" on the membrane surface and then diffuses through the membrane matrix until reaching the opposite surface, known as permeate. At this point, the solute is released from the solid and removed from the membrane. This separation occurs due to discrepancies in solubility within the membrane (Mondal et al., 2012; Kamio et al., 2023).

#### 3.4.4 Cryogenic Distillation

It is a method still in very early stages of development but with significant investment from the cement industry, as it can produce highly concentrated carbon dioxide streams when associated with another separation method. It involves successive compression and cooling of the combustion stream to induce phase changes in certain compounds, allowing for the separation of CO<sub>2</sub>. It is, therefore, an operation based on the dew points and sublimation of substances (Feron, 2016; Laçin et al., 2023). During this process, the separated  $CO<sub>2</sub>$  can exist in the liquid phase or as dry ice and it is removed directly. Selectivity is determined by the distinct dew points of stream components, such as SO<sub>2</sub>, NO<sub>x</sub>, H<sub>2</sub>O, CH4, CO, NH<sub>3</sub>. Separation rates and carbon dioxide purity of up to 99.99% are achievable but require a highly concentrated feed, above 50% by mass of CO2. The use of this method at low gas concentrations significantly increases the operating cost to achieve the desired purity, making it impractical (Abu-Zahra et al., 2016; Laçin et al., 2023). There are also costs associated with corrosion and fouling resulting from these components. Currently, cryogenic methods are being studied in conjunction with other carbon capture processes, such as polymeric membranes, adsorption, chemical absorption, among others (Global CCS Institute, 2021). In facilities like the cement plant in Sugar Creek, Missouri, this method is in the pilot scale and being combined with membrane techniques, as well as at the University of Illinois, where they are attempting to combine it with adsorptive processes (National Energy Technology Laboratory, 2022).

#### **3.5 Challenges and Barriers to the Implementation of Technologies in the Industry**

The implementation and widespread commercialization of several CCS technologies mentioned earlier remain uncertain and challenging, requiring considerable financial investment and innovative technological advancements. According to the IEA report, on July 11, 2023, only 40 CCS plants are operational (IEA, 2024). There is a relatively low amount of carbon captured by the discussed methods, so it is important to analyze the current situation in some sectors. Approximately 65% of the global CO<sub>2</sub> capture is carried out in natural gas processing plants, which is one of the less costly options for implementing this technology. The remaining portion is distributed among other industries and sectors. It is estimated that by 2030, units resulting from the construction or adaptation of hydrogen production plants (90MtCO2), power generation (80MtCO2), and approximately 35MtCO2 from cement and steel industries will be in operation (IEA, 2024). In this way, a crucial advancement for the effective contribution of CCS technologies to emissions reduction and energy transition is the improvement of carbon capture efficiency, currently hovering around 90% of the combustion stream. There are no intrinsic technical barriers preventing this increase; however, larger equipment, more processing steps, and higher energy consumption per ton of captured CO2 are required, leading to increased costs. Therefore, technological advancements aimed at increasing energy efficiency and integrating processes across different facilities are important steps that the market must undertake (IEA, 2024). Additionally, as highlighted by Dziejarski et al. (2023), one of the most relevant aspects when considering the present situation and future challenges in CCS technologies is the Technological Readiness Level (TRL). O TRL represents an essential measure to understand the progress of a specific process within the scientific community, as summarized in Figure 6.



**Figure - 6** The nine levels of technological maturity, Technology Readiness Level (TRL).

Source: Adapted from Subiter (2020).

In the early stage, TRL1 focuses on establishing the basic physical, chemical, and technological principles of the project. As it advances to TRL2, there is consolidation of the technical-scientific concept and a more precise delineation of the potential application of the innovation. TRL3 marks the beginning of tests in a controlled laboratory environment, where initial experiments are conducted to validate the results and confirm the proof of concept. Progressively, at TRL4, laboratory validation deepens, incorporating improvements based on previous stages (Manning, 2023). The transition to TRL5 involves creating a prototype for testing in simulated and controlled environments, though less stringent. In TRL6, the prototype must make the leap to real or near-real conditions, with real or simulated operational parameters, in a field environment (Subiter, 2020; Manning, 2023). Figure 7 illustrates the relationship between the cost of development and the stages of the project, emphasizing the importance of gradual progress for companies and investors, aiming to avoid the commercialization of ineffective or unfeasible technologies.





At TRL7, the technology undergoes a scale test, facing real operational conditions and even more severe ones, aiming to stress the prototype and identify potential failures. This stage is crucial to ensure confidence in the technology, making sure it operates as planned even under challenging circumstances. In TRL8, the technology undergoes tests at full operational scale, aiming to prove its maturity in terms of engineering, performance, and indicators, simulating its field application. Finally, at TRL9, the technology reaches the necessary maturity for construction, demonstrating economic viability and going through final stages of documentation and certification for production and operation on a large scale. These final stages are crucial to ensure that the technology is ready and efficient for its commercial and industrial implementation (Subiter, 2020; Manning, 2023).

# **3.6 Estimated Costs of Captured CO**2

One of the major challenges is related to impurities, as mentioned before. Combustion streams, in general, may contain H<sub>2</sub>S, NO<sub>x</sub>, SOx, CO, CH<sub>4</sub>, and water vapor, gases that become contaminants in the separation and isolation of CO2. This happens because they alter the physicochemical characteristics of the mixture, such as density and liquid-vapor equilibrium, impacting storage efficiency and affecting the cost, safety, and effectiveness of CCS technologies (Dziejarski et al., 2023). Now, examining the work of Cachola et al. (2023), it is possible to analyze and identify the different estimated costs of implementing

each CCS technology depending on the type of industry and sector. This is one of the main barriers to the advancement of the development and implementation of the mentioned methodologies, as they encounter the energy and financial expenditures required to meet the operating conditions indicated by research (Sun et al., 2021). According to Muslemani et al. (2020), these values are also influenced by geopolitical contexts that impact capital cost estimates, energy, and material prices, generating volatility and affecting the location of capture plants, which, in turn, alter the estimated payback calculations. Leeson et al. (2017) present cost estimates in different industrial sectors: in the steel sector, from \$54 to \$88/ tCO2 captured; in fuel refineries like petroleum, considering post-combustion absorption with MEA, about \$84/tCO2; in the pulp and paper industry, \$59/tCO2; in the cement industry, one of the major contributors to emissions, it ranges from \$40.6 to \$164.6/tCO<sub>2</sub>, depending on the technology used. Budinis et al. (2018) conducted similar analyses for other sectors: in natural gas power plants, between \$41 and \$62/ tCO2; in coal power plants, it would cost from \$51 to \$100/tCO2 captured; in cement industries, the cost would range between \$35 and \$100/tCO<sub>2</sub>, less than previously mentioned, justified by the separation of capture costs and transportation and storage operations by Budinis et al. (2018); steel and metallurgical industries would have a variable cost between \$57 and \$69/tCO2. Despite the mentioned costs, Sun et al. (2021) and Cachola et al. (2023) point out that the implementation of CCS structures has been slow not only due to cost but also due to the lack of market mechanisms and incentives. Additionally, there is insufficient penalization and accountability measures for CO<sub>2</sub> emissions by major industries and emitting countries, legal and legislative gaps, incipient influence of public opinion due to a lack of knowledge, security concerns, and uncertainties in the characterization and identification of carbon storage sites.

#### **3.7 Transport, Storage, and Utilization of CO**2

It is important to address two stages following the primary capture and separation of CO<sub>2</sub>, namely its transportation and storage or utilization. Regarding transportation, according to BUI et al. (2018), the technologies are already mature, with over 6500 km of pipelines dedicated to this purpose worldwide, both onshore and offshore, especially associated with the North American oil industry that uses them in the CO2-EOR technique (Noothout et al., 2014). The maritime transport of the substance is also relatively advanced, and these methods have already reached the technological maturity level TRL9. Regarding storage, there is consolidated knowledge in the EOR industry regarding CO<sub>2</sub> injection for oil recovery, reaching a technological maturity level of TRL9. Storing it in saline formations, as observed in the Slepner, Snohvit, and Quest projects, has also achieved the same technological maturity. However, applications in EGR and in depleted oil and gas wells are still in the demonstration phase (TRL7) (Bui et al., 2018). More innovative reservoirs, such as oceans and mineral trapping (transformation of  $CO<sub>2</sub>$ into solid mineral compounds), are still in the early stages of development, between TRL3 and TRL5. Finally, regarding the use of captured carbon, many techniques and processes have already reached technological maturity, being at TRL9, such as its application in beverage industries for carbonation, in the production of urea, methanol, and other chemicals, in mineral carbonation projects, and even as a supply for certain agricultural crops (Bui et al., 2018). Other uses still in development or demonstration but without a TRL classification were mentioned by Kim et al. (2022). These include polymer synthesis, with some final products already commercialized and others in demonstration; CO production via CO<sub>2</sub> reduction, still in testing and demonstration phases; production of light olefins; production of aromatic compounds; obtaining synthetic fuels (mainly for aviation); production of formic acid and acetic acid still in the early stages of development, as well as the construction of carbon materials with carbon dioxide as raw material.

# **4 CONCLUSION**

Throughout the paper, the issue involving greenhouse gases and the urgency to reduce their emissions or remove them from the atmosphere has been highlighted. The complexity and magnitude of the challenge to make the mentioned technologies commercially viable and scalable enough for widespread adoption in carbon-emitting facilities and other greenhouse gas sources have been emphasized. Realistically considering the coming decades, it is unlikely that the use of fossil fuels will be completely eliminated in various applications. Therefore, methods focused on directly reducing emissions at the sources are indispensable solutions. Despite advancements in technologies such as post-combustion, pre-combustion, oxy-fuel combustion, and chemical looping combustion, as well as separation methods like absorption, adsorption, cryogenic distillation, and membrane separation, significant challenges still exist. These technologies face issues related to energy efficiency, optimization, and the production of secondary pollutants. The energy input required for capture, separation, compression, and storage poses a challenge to their viability. Till significant scientific and technological breakthroughs occur, financial investment and energy demand hinder the transition of these technologies to a stage of commercial refinement (TRL8) and widespread deployment (TRL9). Therefore, the still high cost of constructing and operating these mechanisms, along with the current stage of development and maturity of some technologies, makes the challenge of mitigating emissions from these pollutants even more daunting. Promoting sustainable changes in the world, economically viable and without causing abrupt impacts on the current status quo, is highly complex and will require considerable investments and research in the coming years. Additionally, intense collaboration between industry, governments, research institutions, and overcoming international political barriers will be crucial to achieving this goal.

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