Artigo técnico

CO_2 utilization: a brief review of main routes and the potential to Brazilian scenario industry

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Abstract

Within the chemical and fuel production chains, four raw materials are basically used as a source of carbon: oil, natural gas, coal and biomass, the latter being a renewable source. But, taking into account the objective of reducing the effects caused by greenhouse gases (GHG), it is necessary to develop processes and technological concepts that aim to recycle carbon dioxide (CO_2) emitting mainly by large stationary sources. In addition to carbon capture and storage, the concept of "CO_2 utilization" makes room for recycling CO_2 avoiding its atmospheric emission and, in addition, a new carbon building block for chemicals and fuels. In this context, the Brazilian scenario stands out for industrial cases with high CO_2 purity emissions, such as the sugar-energy sector where new technologies for converting CO_2 into valuable chemicals can be tested. Thus, this review presents an overview of the main routes developed for the conversion of CO_2, ranging from those with low level of technological readiness (TRL) such as photochemistry and plasma catalysis to the most advanced ones such as thermocatalytic and biological conversion, polymerization and mineralization.

1 Introduction

The reduction of greenhouse gases emissions is the main factor that must be taken into account in the design and development of the future processes that will be applied in the next decades. The industrial scenario has been collaborating with the goal of sustaining the increase in average global temperature up to 1.5 °C compared to the pre-industrial period (COP 26, Summary Report). According to SEEG data ("Greenhouse Gas Emissions Estimation System"), in 2020, in spite of Corona Virus pandemic situation, Brazil had increased its greenhouse gases emission in 9.5% against the world situation where had pointed out a reduction. Implementation of CCS (carbon capture and storage) technologies may be a practical and emerging alternative for much of the industrial sectors, but the most promising technologies are too expensive to implement and operate. The conversion of CO_2 into value-added products ("utilization") can significantly change the economic parameters of the CO_2 destination route instead of emitting the gas directly into the atmosphere (Zhu, 2019). This work shows a brief review of the main sectors in Brazil with the potential to capture CO_2 or obtain CO_2 streams with a high level of purity in the industrial sector, what are the most recent advances in the conversion of CO_2 into chemicals or fuels, and their respective level of technological development with potential application in the Brazilian scenario.

2 CO_2 emissions in Brazilian industry

Some industrial sectors can emit streams of CO_2 with high purity. It is important because the separation of CO_2 of some process like power plants and combustion process can increase expressively the cost of capture of CO_2 process and consequently make the final product (chemical or biofuel) more expensive (House et al., 2011). Some of the most relevant industrial processes for emitting high-purity CO_2 streams are ethanol production by fermentation, hydrogen production, ammonia processing, ethylene oxide production, and natural gas processing and treatment (Bains et al., 2017). In 2021, Brazil achieved the highest production of natural gas of the country history, reaching the average annual production of 134 million m³/day (ANP, 2021). CO_2 concentrations in natural gas from pre-salt reservoirs range from 10 to 45% and after the treatment process to remove acid gases and CO_2, the CO_2 content must be removed to a maximum of 3% mol/mol according to the criteria of the ANP (*Agência Nacional do Petróleo*). The separation of CO_2 is usually an effort in oil plants, implying large separation costs (made in most cases by processes with membranes) and, after separation, it is reinjected. (Maleski; Ritter, 2021). Petrobras has already surpassed the mark of 4.5 million tons of separated and reinjected CO_2 (Almeida et al., 2017).

3 Status of CO_2 utilization and conversion routes

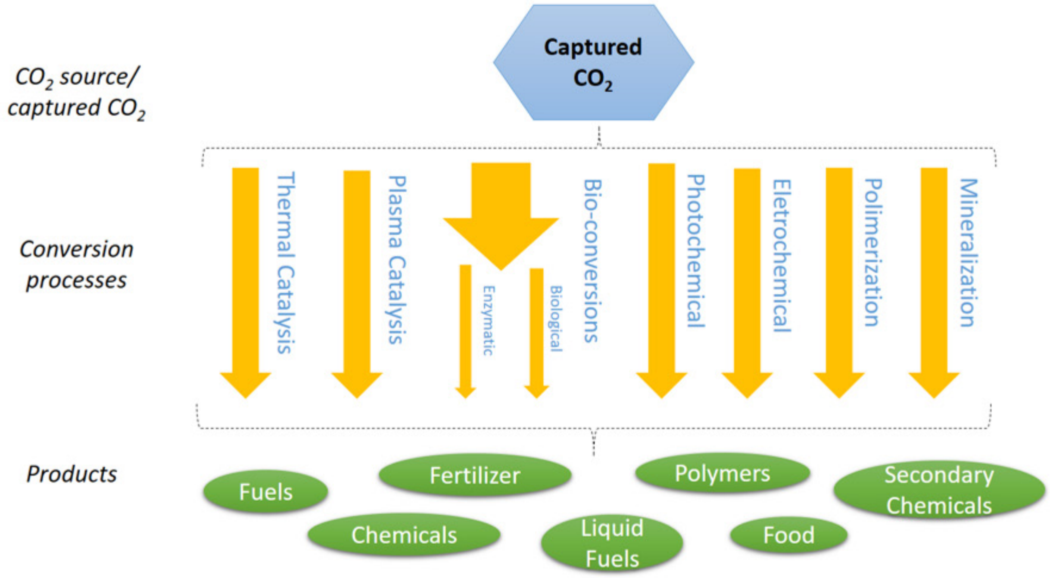
Worldwide, about 230 Mt of CO_2 are used, the main source of use being the production of urea, corresponding to about 130 Mt CO_2 per year, followed by the oil sector with a consumption of 70 to 80 MtCO_2 for enhanced oil recovery (EOR). Urea ($CO(NH_2)_2$) or carbamide is an important nitrogenous compound for the agricultural industry as a fertilizer. In recent years, the production of urea has been around 190 Mt/year, and around of 120 Mt of CO_2 was needed for this. However, in the Brazilian scenario, the production of this chemical is deficient, nearly 80% of the fertilizer used in Brazil is currently imported. (Pérez-Fortes, 2014) The commercial production of urea occurs through the Basaroff reactions, as shown in **Equation 1** and **Equation 2**.

$$2NH_3 + CO_2 \leftrightarrow NH_2COONH_4 + 117\ kJ/mol \qquad \textbf{(1)}$$

$$NH_2COONH_4 + 15{,}5\ kJ/mol \leftrightarrow NH_2CONH_2 + H_2O \qquad \textbf{(2)}$$

This process takes place at temperatures around 185°C and pressure of 150 bar. According to key performance parameters, net use of CO_2 in urea production is 0.74 tonCO_2/tonurea and electricity is 0.023–0.16 MWh/tonurea (Jarvis; Samsatli, 2018). But one of the reagents for the Urea synthesis is ammonia (NH_3) which is produced from the reaction of N2 and H2. Hydrogen production is the bottleneck because it is normally produced from fossil sources (such as natural gas, petroleum derivatives, etc.), resulting in an increase in greenhouse gas emissions. The need to intensify the use and diversify the matrix of products generated from CO_2 recycling has meant that in the last decades a series of conversion routes have been developed for this and reached different levels of technological readiness (TRL). Of these technologies, catalytic synthesis to convert CO_2 into chemicals is the most advanced conversion route. Electrochemical and photochemical processes are less technologically mature, but due to the direct use of renewable sources, they can be more efficient in CO_2 reduction (Kapetaki; Barbosa, 2019). **Figure 1** shows a schematic drawing showing the main CO_2 conversion routes studied and applied at different scales.

Figure 1 – General mapping of uses and products derived from CO_2



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3.1 Thermal Catalyst

One of the ways to get around the cost and technology problems associated with the recovery of CO_2 is its conversion into fuels using ways such as catalytic routes. Process to convert "CO_2into fuels" using thermal catalytic technologies has been explored as a potential solution. For example, conversion of CO_2 into methanol, methane and hydrocarbons fuels is already technically explored.

The catalytic conversion route of CO_2 to methanol is one of the most promising routes of recovery and use of CO_2 mainly because methanol (CH_3OH - MeOH) is an important molecule due to its wide applicability in the production of fuels and chemicals. In China, for example, the development of methanol platforms will play a crucial role in the development of clean coal technologies. (Xinbao et al., 2021). Methanol production occurs between a slightly exothermic reaction between CO_2 and H_2 as shown in Reaction 3.

$$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O \quad \Delta H_{298K} = -11{,}9\ kcal/mol \qquad \textbf{(3)}$$

One of the successful parameters of CO_2 hydrogenation is mainly in the characteristics of the catalyst used, its potential for selectivity, resistance to deactivation, promotion of activity and stability of active sites (Galadima, 2019). The catalyst most successful in direct conversion of CO_2 in to MeOH are Cu-based. Liu et al. (2016) analyzing the importance of MgO in the mixed support of Cu based using only TiO_2 as based suport (Cu/TiO_2), achieved MeOH yield's under 30% wt, but when putting a content of 5% wt of MgO in the support ($CuO/MgO\text{-}TiO_2$) the MeOH yield achieved 56% and selectivity above 85%. In fact, much of the research has shown that Cu-based catalysts exhibit high selectivity activity in the synthesis of CO_2 to MeOH. In addition, different promoters (ZrO_2, ZnO, and LaOx, etc.) have been evaluated to improve the activity of Cu-based catalysts. Despite the different promoters, a significant part of the studies points to ZnO as the best alternative for the dispersion and stabilization of Copper. Under the process conditions, the CO_2 to MeOH reaction is exothermic and therefore thermodynamically unfavorable at high temperatures, being carried out around 220-270 °C with some processes operating up to 600 °C as in the case of the CAMARE process of direct hydrogenation that uses Ga_2O_3 as a promoter of copper (Xinbao et al., 2021, Samiee, 2019). In terms of technological maturity, the production of methanol via CO_2 is indicated in TRL 6-7, the process having already reached, in some cases, commercial status. The economic values of the CO_2 to methanol route depend on the catalyst technology used (yields, stability and selectivity), the cost of obtaining H_2, methanol separation and electrical energy. In 2008, the Japanese company Mitsui Chemicals Inc installed a pilot plant to produce 1000 tons of methanol per year from CO_2 hydrogenation (Jarvis; Samsatli, 2018).

In 2012, The Carbon Recycling Internation (CRI) commissioned the first industrial-sized unit for the production of methanol from CO_2 hydrogenation, with a production capacity of 5 million liters per year (4000 ton/year). The process was based on conversion using a Cu and Zn based catalyst with the reactor operating at 250 °C and pressures up to 100 bar. This process was called ETL "Emissions to liquid" and the CO_2 feedstock was obtained from the capture of the flue gas nearby geothermal power plant (Harp, 2015; Zhu, 2019). Regarding the economic parameters, the production of methanol through direct hydrogenation of CO_2 has competitive values compared to the conventional route, which is obtained via syngas (~666 €/t compared to ~ 401 €/t for a conventional process) (Jarvis; Samsatli, 2018). In a context where CO_2 can already be obtained with high purity, another relevant synthesis is methanization (production of CH4) from CO_2, which is extremely relevant, especially in the European scenario, which already has pipeline lines installed for operation with natural gas and about 50% of the natural gas consumed in Europe today is imported from Russia. The global reaction of hydrogenation of CO_2 to methane (**Equation 4**) is called the Sabatier synthesis.

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O \quad \Delta H_{298K} = -165\ kJ/mol \qquad \textbf{(4)}$$

The Sabatier synthesis presents stoichiometric conditions of CO_2:H_2 and temperature and pressure different from those of the synthesis of methanol from CO_2, in addition to the desired catalytic properties. This process usually occurs using catalysts based on noble metals such as Ni, Rh or Ru and different supported oxides such as Al_2O_3, SiO_2, TiO_2, CeO_2 and ZrO_2 in temperature ranges of 200 - 450°C (Müller et al., 2013; Galadima, 2019; Brooks, 2007). Ahn et al (2021) evaluated and simulated a PtG (power to gas) pilot process of CO_2 methanization in a sewage disposal plant in Korea. This pilot plant has the capacity to produce around 250 Nm³/day of CH_4 produced from the hydrogenation of CO_2. It was obtained from anaerobic digestion and H2 from an electrolytic process respectively. The methanization reaction took place after preheating the CO_2+H_2 mixture (up to 250°C) and entering a fixed bed reactor with Ni–0.2Ce–0.1Zr catalyst cylindrical pellets with external diameter of 1.5 cm. The results indicated a stable methane production at this scale. The largest Power to gas plant in the world is located in Wertle, Germany. The Audi e-gas plant has the capacity to produce around 100 t/year of methane gas associated with the recycling of around 2800 t/CO_2. In this process, H_2 used is obtained through three alkaline electrolysers, totaling about 6 MWe and with the CO_2 coming from a biodigestion and biogas production plant (Götz et al. 2016). KPI's indicate that Sabatier's synthesis has TRL in the range of 8-9 already with commercialization potential. The investment cost (CAPEX) in a methanization unit from CO_2 with hydrogen produced from renewable sources can be in the range 35.8–38.8 €M with a production rate of 311 m³/h. Furthermore, the cost of producing hydrogen tends to be the major operating cost (Götz et al., 2016; Jarvis; Samsatli, 2018).

3.2 Plasma technologies

Plasma is defined as the fourth state of matter, whose temperature scale imposes the solid state on the lowest, followed by liquid, gases and then plasma. Plasma is technically a gas in an ionized state where electrons are turned off from the electronic layer, having as a parameter of plasma formation or its degree of ionization, that is, fully ionized or partially ionized, transforming the gas into an ion with positive charges (Snoeckx; Bogaerts, 2017). The first step in CO_2 conversion is the breaking of the strong carbon-oxygen C-O bond (783 kJ/mol) that makes the CO_2 molecule a highly stable molecule. In this sense, the plasma can accelerate the atomic separation mechanism of the C-O atoms bonds, providing the conditions for the dissociation process by exciting the electrons and increasing the vibration energy of the CO_2 until it reaches the breakage level, that is, overcoming the dissociation enthalpy (Çoskun; Prakash, 2015). Commonly, three types of plasma have been used aiming at the development of technologies for the conversion of CO_2, as shown in **Table 1**.

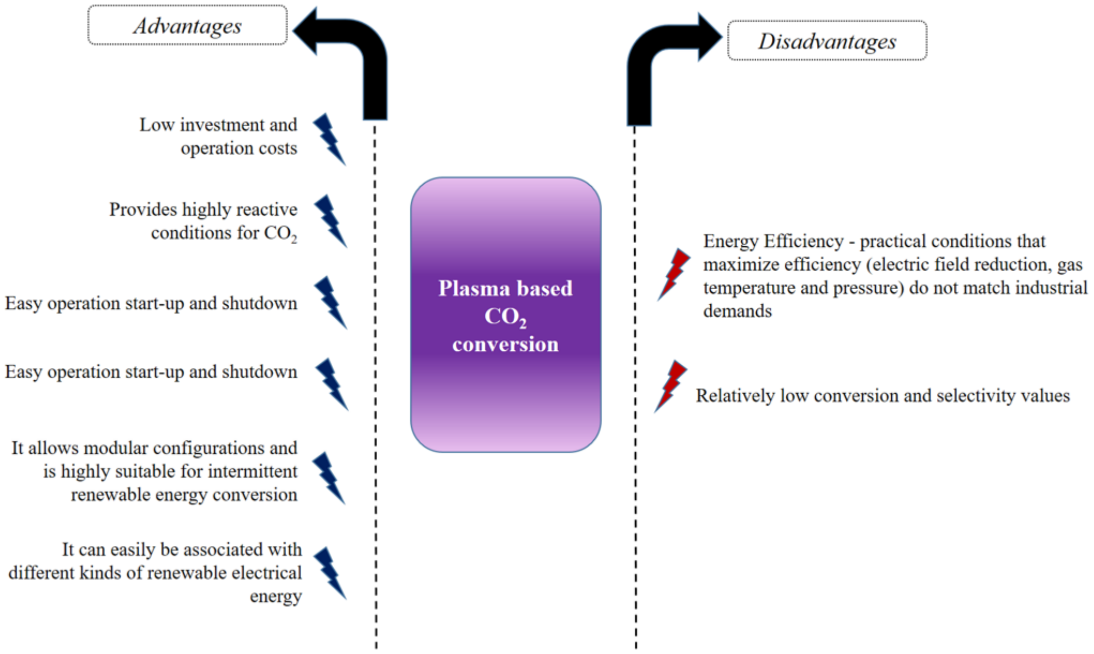
Table 1 – Plasma types commonly used for CO_2 conversion

Kind of Plasma	Electron densities, cm^{-3}	Electron temperature, eV[a]	Gas temperature (neutral), K	Pressure, Pa	Type of discharge[b]
Cold Plasma	≤1011	∼ 2	∼ 300 - 400	≤100-105	GD or DBD
Warn Plasma	1011-1012	1-2	∼∼ 1500 - 3000	∼103 - 105	GA, MW or RF
Thermal Plasma	≥ 1013	1-2	≥ 4000	≤105	ARC, MW or RF

[a]: 1eV = 11.605 K. b: GD: glow discharge; DBD: dielectric barrier discharge; GA: gliding arc; MW: microwave discharge; RF: radio frequency discharge; ARC: alternating-current or direct-current arc discharge
Source: adapted from Yin et al., 2021

In the operation with thermal plasma, the analogies with the macroscopic thermochemical processes are acceptable because the temperature of the electrons is very close to the vibrational and gas temperatures, and it can be assumed that the thermodynamic equilibrium has been reached. Cold plasma (or non-thermal plasma) has a significant gradient between the electron temperature and the gas temperature, the latter of which can almost be assumed to be room temperature. Whereas warm plasmas are a form transitional phase between non thermal and thermal plasma system showing characteristic of a non-equilibrium system where the vibration temperature remains above the gas temperatures (Gutsol et al. 2011; Çoskun, 2015). Non-thermal plasma has been regarded as the most promising plasma technology for CO_2 conversion. In non-thermal plasma, reactions are driven mainly by the action of energetic excitation of electrons and of the reactive species generated and not specifically by the action of heat, that causes reactions that are unfavorable from the point of view of thermodynamic equilibrium to occur under ambient conditions (Li et al., 2021; Ashford; Tu, 2017). **Figure 2** shows some advantages and disadvantages of using plasma in the dissociation of CO_2 in order to generate other products.

Figure 2 – Advantages and disadvantages of CO_2 plasma conversion



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In addition to the reported disadvantages, such as low energy efficiency and little selectivity in the products generated, the technologies that emerged to evaluate the direct conversion of CO_2 with plasma are complex and difficult to master. A parallel route that emerged in order to sustain the advantages of plasma reactors was the use of solid nanostructured catalysts to overcome these challenges (Bogaerts; Centi, 2020). In plasma catalysis for the conversion of CO_2 there are a number of synergistic effects that must be taken into account considering the interaction of plasma on the solid catalyst and catalyst on the generated plasma as shown in **Table 2** (Snoeckx; Bogaerts, 2017).

Table 2 – Relation between catalyst and plasma in plasma-assisted catalytic processes

Plasma effects on the catalyst	Catalyst effects on plasma
Reduction of the activation barrier	Formation of microdischarges within the pores of the catalyst leading to different characteristics in relation to the bulk
Change in physicochemical properties (change in catalyst oxidation state, reduction in coke formation, improvement in adsorption performance, etc.)	Improving the properties of the electric field
Changing reaction surface properties	Change in the type of discharge due to the presence of surfaces with insulating properties
Formation of points with overheating attributed to the formation of the various microdischarges	Species concentration in the plasma due to the residence time of the species adsorbed on the catalyst
Activation by photon irradiation	

Source: prepared by the authors

A series of parameters associated with the type of discharge used, temperature, pressure and reactor configuration can affect the performance of plasma-catalytic systems. Li et al. (2021) evaluated the capture and conversion of CO_2 and a DBD (dielectric barrier discharge) plasma reactor packed with hydrotalcite as an adsorbent to obtain CO for the generation of syngas and its respective conversion into liquid fuels. The conversion of the reaction had a peak at the beginning of the process and showed a decrease over time, presenting an average value of 41.14%. The data also indicated that this can be a sustainable solution for the "Power to gas/liquid" cases, integrating thermoelectric plants, for example, the generation of plasma and electrolytic processes for the production of CO and H_2 respectively. Also aiming to observe the use of plasma-assisted catalysts in the hydrogenation of CO_2 into MeOH, Chen et al (2018) tested the Pt/γ-Al_2O_3 and Cu/γ-Al_2O_3 performance in a DBD plasma reactor at 30 °C and 1 atm. The Cu-based catalyst showed the best results with a yield of 11.3% in MeOH and a selectivity of 53.7%. Although the reaction parameters are relatively low, the authors point out that this can be an alternative for converting CO_2 into MeOH with low processing, avoiding high demands on temperature and pressure, as in thermal catalysis routes. Yao et al. (2020) evaluated the conversion of mixtures of CO_2 and steam to CO + hydrogen. It was found that the presence of H_2O inhibits the conversion of CO_2 to CO. In the presence of spherical NiO catalysts and with non-thermal plasma it reached CO_2 conversion values of 30.2% and CO yield of 28.9% in addition to 1022 mg/L of H2 in the output composition. Plasma catalysis technology appears as an innovative and differentiated field of technologies aimed at the conversion, recovery and recycling of CO_2. However, the process efficiency values are still the bottlenecks for its commercialization. Thus, in order to make plasma technology more competitive with other routes developed for the reuse of CO_2, its advantages such as the flexibility to adapt to different and intermittent electrical sources and reactivity in ambient conditions should be further explored, such as the development of new catalytic structures that improve the parameters of selectivity and yields into CO and MeOH (Liu et al., 2019).

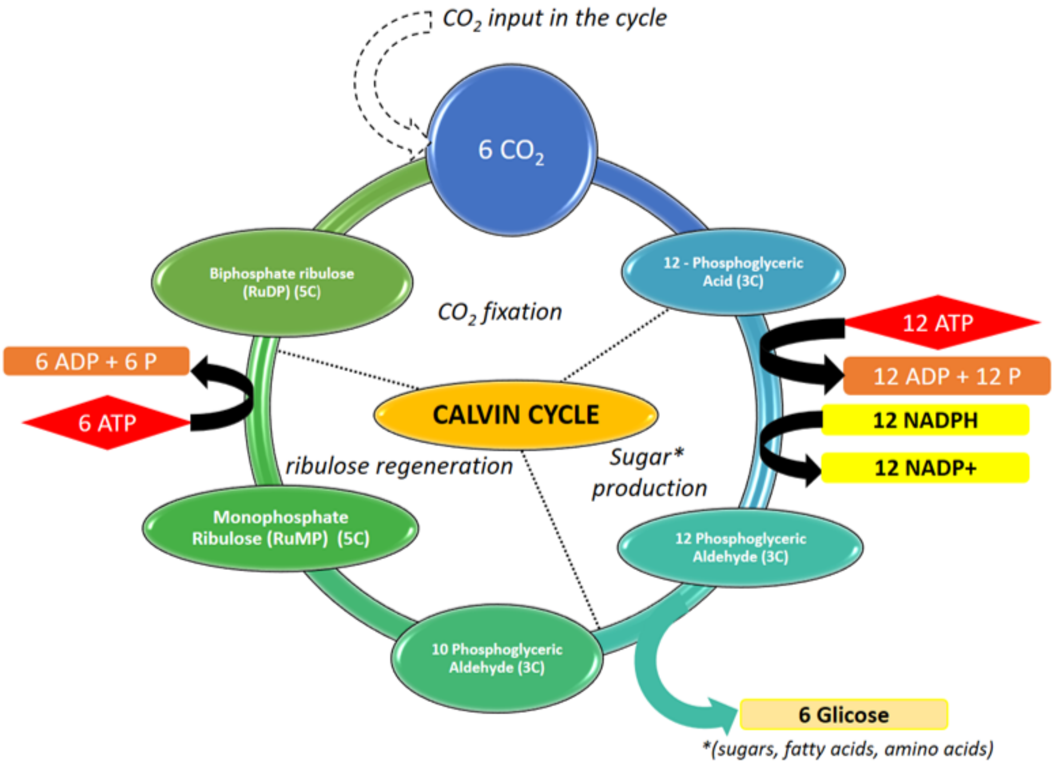
3.3 Bioprocess

Another possible route of CO_2 recovery is using bioprocess technologies where the conversion is done through a biological agent, either a microorganism or an enzyme (non-photosynthetic conversion). Furthermore, the potential of using algae (photosynthetic conversion) as a source of biofixation also stands out as it provides a form of direct sequestration and production of algal biomass as an intermediary for the production of other forms of biofuel. Biometabolic fixation of CO_2 can be done by six routes, which include (Shi et al., 2015):

a) calvin cycle;
b) citric acid reductive cycle;
c) acetyl-CoA reductive pathway;
d) 3-hydroxypropionate cycle;
e) 3-hydroxypropionate/4-hydroxybutyrate cycle; and
f) dicarboxylate/4-hydroxybutyrate cycle.

Of these, the Calvin cycle **(Figure 3)** is the most important on Earth because it is used by organisms (such as algae, plants, cyanobacteria and other anaerobic and facultative anaerobes) to fix and convert CO_2 in the carbon cycle of cells.

Figure 3 – Calvin cycle – steps and carbon balance



Source: prepared by the authors

Regarding the conversion of CO_2 using enzymatic catalysis, some research has analyzed the potential of using single enzymes or multi-enzymatic reactions in the sequestration and use of CO_2. Shi et. al. (2015) observed a set of reactions by two main sets of enzymes: the oxidoreductases and the lyases. In the set of oxidoreductases enzymes, he observed the enzymatic aspects of the conversion of CO_2 into formate and methane by the action of dehydrogenase and into methane by the nitrogenase. In relation to the lyases the two highlighted syntheses were the conversion of CO_2 into biodegradable chemicals by the action of decarboxylases and bicarbonate (or minerals) by carbonic anydrase (CA). The combined use of the CA enzyme in the CO_2 sequestration process associated with the formation of salts gained prominence in other studies where it presents a detailed description of the use of CA from thermophilic microorganisms as a biocatalyst in the process of CO_2 absorption from combustion sources (CO_2 Solution - Quebec, Canada) (Savile, 2011). However, the enzymatic conversion still needs optimization and improvements in the routes, use of appropriate techniques for immobilization and recycling of enzymes, the use of alternative cofactors to the most frequent ionic cofactors of enzymatic reactions (NADH and NADPH) for the use to be effectively extended in the industrial scales such that most technological advances in enzymatic conversion of CO_2 are still located in TRL's 3 (Chauvy; De Weireld, 2020, Shi et al., 2015).

Another possibility associated with the conversion of CO_2 through bioprocesses is the use of microalgae. The use of microalgae enables the concept of sequestering and converting CO_2 in a single stage through biofixation of CO_2 in algae that are considered the raw material for the production of third-generation biofuels (Silva, 2019). Despite the large-scale cultivation of microalgae being relatively complex and relatively expensive, this can be one of the viable options for the anthropogenic conversion of CO_2 and enable the generation of algal biomass that is the raw material for a series of chemical products with high added value (fuels, protein-rich food, medicines, animal feed etc) making this route highly attractive (Anguselvi, 2019). Some species of microalgae such as Chlorella have shown promising results in the biofixation of CO_2 from flue gases. The data has been promising to the point of indicating that not only the removal of CO_2 is possible, but cultures of this algae have also been beneficial for the removal of NO_x (nitrogen oxides) and SO_2 (sulphur dioxide) in the flue gases, in addition to that the presence of CO, in the order of mg/L, does not harm the growth of this algae. Research has indicated that with Chlorella yield data, 4.4 kg of CO_2 are needed to produce about 1.0 kg of dry biomass, in other words, photobioreactors with the appropriate algal cultures can be an attractive route for the decarbonization and partial cleaning of combustion gases, reducing costs for the implementation of this route. However, data indicate that the installation of algal photobioreactors in series with high capacity power plants would require extremely high implementation areas (Iglina, 2022; Doucha, 2005).

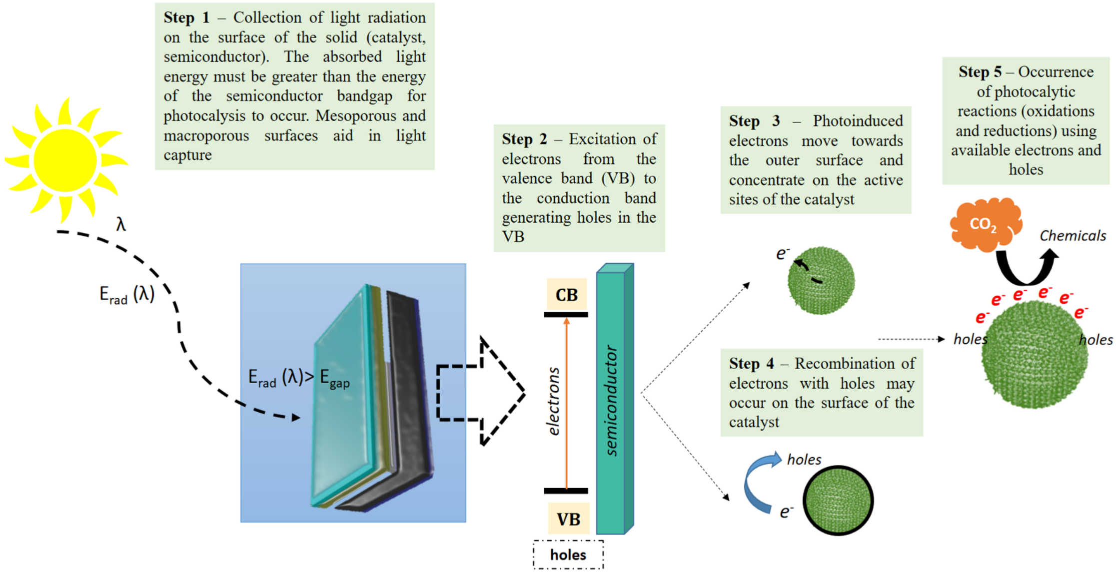
Non-photosynthetic biological CO_2 conversion such as aerobic or anaerobic fixation pathways has been used for the conversion of CO_2 into products such as formic acid, ethanol and methanol (Roger et al., 2018; Erşan; Park, 2020). Acetogenic fermentation, cultures with E. coli, mixotrophic fermentation and microbial electrosynthesis, for example, are pointed out as promising routes for the production of value-added alcohols and acids, but both metabolic engineering and process engineering challenges still need to be overcome in this route (Gonzales et al., 2019, Erşan; Park, 2020; Modestra et al., 2020). However, the most prominent biochemical process is the gaseous fermentation of the CO_2/CO/H_2 mixture for the production of ethanol. Lanzatech has developed a demonstration scale fermentation process using a specific acetogenic bacterium for the production of alcohols (ethanol and 2,3-butenediol) with high yields with the potential to produce other chemicals such as acetone and isopropyl alcohol with selectivity values of up to 90% of these molecules. It is noteworthy that the sources of raw materials for this route can be diversified and mixed as flue gases, biomass gasification gas and urban solid waste. In addition, studies on the life cycle analysis of this process indicate negative values for the carbon footprints along this route. (Dubois, 2021, Zhu, 2019, Liew, 2022).

As a notable example of the larger-scale technology of CO_2 bioconversion was the first off-gas to bioethanol conversion plant resulting from the partnership between Indian Oil Corporation and LanzaTech for the production of 4000 m^3 per year of ethanol from off-gas from a refinery. In this process, the carbon balance indicates that about 50% of the carbon present in ethanol comes from CO_2. In addition, the use of CO_2 in the production of alcohols can be directly associated with the production of other fuels such as SAF (sustainable aviation fuel) using technologies of the same nature, such as the LanzaJet project (Zhu, 2019; Teixeira et al., 2018; LanzaTech, 2022). Finally, biological processes have a wide range of sub-routes for CO_2 reuse. Although some processes have shown to be highly promising with application even in the pre-commercial stage involving gas fermentation, most of the technologies under development for this route are found in TRL close to 4 (Roh et al., 2020).

3.4 Photochemical

In the recovery and recycling of CO_2 into higher value products or intermediates, there is a class of reactions that convert carbon dioxide through its reduction, which can generate a chain of products such as CO, MeOH, CH_4, among others. These reduction reactions, however, consume considerable amounts of energy that can be supplied by a thermal, electrical source or via irradiation/photons (Alper; Orhan, 2017). When the latter is the main energy matrix of the CO_2 conversion process, the process is said to be photochemical in nature. Fundamentally, a photocatalytic conversion process takes place in a vessel called a photoreactor where, in addition to the conversion with photochemical kinetics, heat and mass transfers and momentum in the design must also be taken into account radiation transfer via photons. **Figure 4** shows a summary of the steps involved in a heterogeneous photochemical conversion (Khan; Tahir, 2019).

Figure 4 – Step by step of a heterogeneous photocatalytic reaction



Step 1 – Collection of light radiation on the surface of the solid (catalyst, semiconductor). The absorbed light energy must be greater than the energy of the semiconductor bandgap for photocalysis to occur. Mesoporous and macroporous surfaces aid in light capture

Step 2 – Excitation of electrons from the valence band (VB) to the conduction band generating holes in the VB

Step 3 – Photoinduced electrons move towards the outer surface and concentrate on the active sites of the catalyst

Step 4 – Recombination of electrons with holes may occur on the surface of the catalyst

Step 5 – Occurrence of photocalytic reactions (oxidations and reductions) using available electrons and holes

Source: prepared by the authors

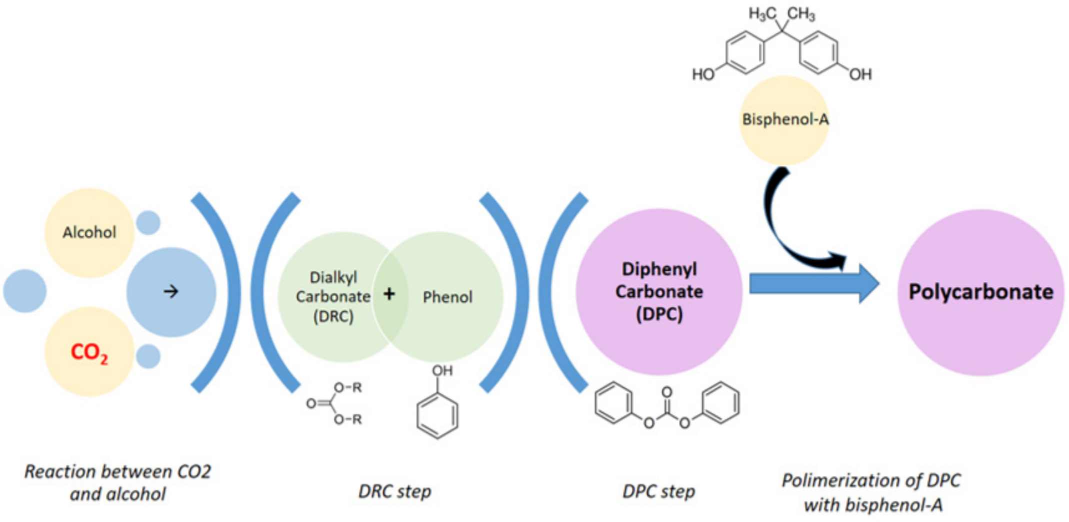
Recently, studies on the photocatalytic reduction of CO_2 on semiconductors have been widely studied in the hope of improving the energy efficiency values that prevent the scaling up of this route. TiO_2 is the most studied photoactive material and technological efforts have focused on narrowing the band gap (~3 eV). Other semiconductor oxides such as Cu_2O and CuO have received more attention in this regard because they have a lower bandgap (~ 2.0 eV) that allows the use of these materials. The design of a hybrid system using photovoltaic cells associated with photoelectrochemical cells has shown promising results as it allows separating the light absorption system and the reduction/oxidation reaction into two subsystems and allowing their optimization separately. In addition, it allows breaking some restrictions in the choice of cell materials while maintaining high values of energy conversion efficiency of solar energy into fuel without the use of precious metals (Kim; Kwon, 2019). Despite presenting a relative ease of adapting renewable energy sources in its process, the photochemical routes of CO_2 reduction to higher value chemicals are still situated in various scales of technological maturity, presenting TRL's of 3-4. (Kapetaki; Miranda Barbosa, 2019; Jarvis; Samsatli, 2018).

3.5 Polimerization

Carbon dioxide can be seen as an extensive carbon source for the synthesis of polymers or intermediates used in the synthesis of polymers. The use of CO_2 as a raw material for the synthesis of polymers such as polycarbonates, which can have a series of applications such as composites, biomedical materials, adhesives, among others, has already been industrially demonstrated in such a way that the synthesis of polymers using CO_2 as raw material has a radical environmental advantage over the usual synthesis of polymers from fossil sources (Ballamine et al., 2022). There are two approaches to using CO_2 as a raw material for polymer synthesis. The first is called the direct approach, in which carbon dioxide is used directly as a carbon source for the formation of polymers. The second is the so-called indirect approach, in which carbon dioxide is used to form monomers from which polymeric synthesis can be carried out (Langanke, 2015). The Japanese company Asahi Kasei Corporation has developed an industrial process for the synthesis of polycarbonate from CO_2 without the traditional use of the toxic agent phosgene ($COCl_2$), which is obtained from the chlorination of carbon monoxide, resulting from the partial oxidation of fossil coke. In this developed process, the raw materials involved are ethylene oxide (EO), CO_2, which is a by-product obtained directly from the EO production process, and bisphenol, which react in four reaction steps using high selectivity catalysts and separation processes, such as reactive distillation. As a result, two important products are produced, monoethylene glycol and polycarbonate (Fukuoka, 2007, Zhu, 2019).

More recently, Asahi published the test results in a demonstration unit, with a capacity of up to 100 ton/year of polycarbonate, with continuous operation of the DCR process (dialkyl carbonate process). This process, as indicated in **Figure 5**, takes place in two stages where, in the first stage, a specific catalyst is used to react the CO_2 with an alcohol and obtain the DRC. In the next stage, the DRC reacts with the phenol to obtain the diphenyl carbonate (DPC). Finally, in the final step, DPC reacts with bisphenol-A to obtain polycarbonate. In addition to the operational stability of the process observed from the demonstration test, the data indicated effective use of CO_2 reduced emissions and energy consumption compared to the traditional polycarbonate process with the use of bispheno.

Figure 5 – DRC process to synthesis of Diphenyl Carbonate by Asahi Kasei



Source: prepared by the authors

The DRC process is a clear example of the indirect approach of using CO_2 for downstream polymer synthesis. As an example of direct synthesis, there is a pilot plant for the production of polyether carbonate polyols built in Bayer in Leverkusen, which is one of the raw materials for the production of polyurethanes, which is a plastic with high elasticity and wide application in the market. The reaction between CO_2 and epoxide is highly complex, mainly due to its high exothermicity, where the catalytic reactor design must provide adequate heat removal from the system to ensure selectivity and adequate conversion on double metal cyanide catalysts (Langanke, 2015, Langanke et al., 2014)

Thus, despite the need for specific advances in relation to the synthesis processes, the copolymerization route for the use of CO_2, both by the direct and indirect approach, despite the indirect route presenting greater flexibility of use, there are indications, in relation to the assessment of the carbon cycle, where there may be a limitation on how much carbon present in the final product comes from the CO_2 fed in the route. Finally, the use via copolymerization of CO_2 is one of the most advanced routes to use CO_2 on a large scale, in parallel with other processes using hydrogenation and electrochemical reduction (Laganke, 2015; Costa et al., 2021).

3.5 Mineralization

The use of CO_2 in mineralization processes consists of chemically storing CO_2 in solid form through its interaction with minerals, such as silicates and aggregates used in the cement sector. The development of CO_2 recycling technologies for this sector is highly strategic, as they are responsible for about 7% of CO_2 emissions of an anthropogenic nature (Strunge et al., 2022). Chemically, the mineralization process is based on exothermic reactions where CO_2 reacts with silicates bound to alkali metals or alkaline earth metals, producing carbonates and silica, as shown in **Equations 5 to 7** (Sanna et al., 2014).

$$CaSiO_3 + CO_2 + 2H_2O \rightarrow CaCO_3 + H_4SiO_4 \quad \textbf{(5)}$$

$$Mg_2SiO_4 + 2CO_2 + 2H_2O \rightarrow 2MgCO_3 + H_4SiO_4 \quad \textbf{(6)}$$

$$Mg_3Si_2O_5(OH)_4 + 3CO_2 + 2H_2O \rightarrow 3MgCO_3 + 2H_4SiO_4 \quad \textbf{(7)}$$

With favorable thermodynamics, the carbonates derived from these mineralization reactions are stable and can be considered important products with "stored" CO_2 in their structure. China has been a reference country in CO_2 mineralization demonstration projects, but instead of using natural sources of alkaline ores such as olivine, basalt, wollastonite and serpentine, the projects have aimed to use industrial solid waste as raw material for mining reactions and use of CO_2, such as, coal fly ash, steel slag, phosphogypsum, blast furnace slag, carbide slag, chromic slag, etc. Assessed at TRL 6, China conducts a series of pilot-scale projects considering the mineralization reaction, mainly through the use of fly ash coal and phosphogypsum generating products such as $CaCO_3$, concrete brick and $(NH_4)_2SO_4$ (Meng et al., 2021). Some mixed finance projects have been done using mining reactions around the world. In **Table 3** some of the most relevant are listed.

Table 3 – Example of CO_2 based mineralization process

Cooperative Units/ Companhies	CO_2 features	Raw Material	Products	References
Carbon8 Systems (UK)	CO_2 liquid	Cement dusts, steel slags, oil-shale ash, incinerator ash or paper ash and contaminated soils	rounded aggregates	(Gunning, 2014)
Carbon Upcycling process (UCLA - University of California, Los Angeles,)	Flue gas of power Plants	Calcium hydroxide (Ca(OH)2)	"CO_2NCRETE"	(Akmal, 2018)
Carbstone Innovation NV	CO_2 liquid	Steel slag	concrete, bricks	Carbstone Innovation NV, 2022
Sinochem Fuling Chongqing Chemical Industry Co., Ltd. and Chinese Academy of Sciences	Ammonia synthesis plant	Phosphogypsum	$CaCO_3$, $(NH_4)_2SO_4$	Meng, 2021

Source: prepared by the authors

Research points to two major potential benefits of the mineralization route, the first that it can be viewed as a chemical storage of CO_2 and, secondly, capable of generating products with potential use of increment and/or replacement of cement and aggregate. Current data show that photoprint carbon reduction can reach from 0.4 Gt CO_2 to 1.5 Gt CO_2 per year, globally, through the capture, mineralization and use of the products generated in this route (Ostovari et al., 2020). Mineralization is one of the most promising emerging technologies for large-scale use of CO_2. CO_2 mineralization curing (CMC) was tested on a large scale in Jiaozuo city in China with consumption of 10,000 ton/year. This process was carried out to replace the autoclaved curing process aimed at recycling CO_2 in the production of concrete. During this process, CO_2 diffuses through the microporous structure of the concrete, where it reacts, carbonating the calcium and silicon structure, forming microcrystals of $CaCO_3$, significantly improving the properties of the cured concrete, such as increasing its density. This process is mainly controlled by the diffusion of CO_2 and its partial pressure in the system and, as these reactions are exothermic, the slight increase in temperature that occurs in the cameras improves the kinetics of these reactions in addition to causing a heat exhaustion in the system. In this plant, CO_2 conversion values of the order of 98% were recorded. In addition, the data from the life cycle analysis show that in relation to the traditional autoclaved curing process, the CMC promotes a reduction in emissions of 182 kg CO_2EQ/m³ product, equivalent to a 65% reduction in CO_2 emissions effectively sequestered in concrete (Wang et al., 2022). However, positive investments in CO_2 mineralization are possible under two essential conditions. Firstly, the binding of CO_2 in minerals must be suitable for obtaining emission credit certificates and, in addition, the products generated must be suitable for use in combination with cement in the construction industry, such as use in buildings, houses, bridges beyond the marketing of products generated through the mineralization of CO_2 etc. (Strunge et al., 2022). The link between the industrial routes of CO_2 use associated with the civil production sector is of intense commercial attractiveness, as this sector is responsible for about 1/3 of the greenhouse gas emissions emitted by humanity (Fortunato, 2019). Finally, in industrial terms, technologies involving the use of CO_2 for mineral carbonation and construction materials have already reached a high level of technological readiness, with some cases, such as concrete curing, already identified as TRL 8, that is, final level of engineering.

3.6 Eletrochemical

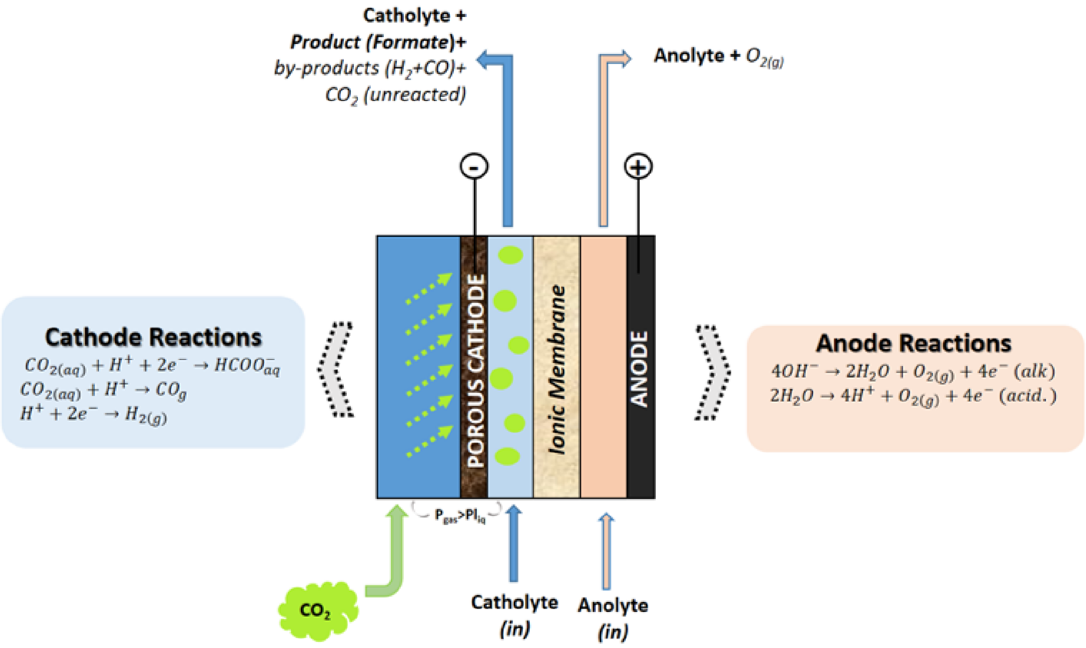
The electrochemical processes for using CO_2 are based on the fundamental method of this process, where the electrons discharged on the surface of the electrodes lead to oxidation-reduction reactions on their surface, leading to the electrochemical reduction of CO_2 in a diverse range of products within which: methanol, synthesis gas, ethylene, formic acid, etc. (Adamu et al. 2020). Production of formic acid through electro-reduction of CO_2 is possible. Formic acid (CH_2O_2) has a number of applications, ranging from a chemical raw material, application in industry and even as a fuel. CO_2 reduction (**Equation 8**) occurs at the cathode while water oxidation (**Equation 9**) occurs at the anode, with electron exchange, H+ migration and O_2 evolution in the system (Jarvis and Samsatli, 2018).

$$Cathode: 2CO_2 + 4H^+ + 4e^- \leftrightarrow 2CH_2O_2 \qquad \textbf{(8)}$$

$$Anode: 2H_2O \leftrightarrow O_2 + 4H^+ + 4e^- \qquad \textbf{(9)}$$

From a thermodynamic point of view, the water oxidation reaction occurs at a potential of 1.23 V, while CO_2 reduction occurs at a potential close to zero, which significantly hinders the reduction half-reaction, which makes the development of the elements involved in electrochemical reaction engineering indispensable, such as electrode technologies, membranes, improvements in mass transfers in the system and electrolytes (Lu; Jiao, 2016; Jarvis; Samsatli, 2018). The ECFORM Process, created by Norwegian company DNV GL, was developed for the production of formic acid and formate salts. The principle of this technology was based on the development of a pressurized gas-liquid-solid cell where the performance of different Sn-based electrocatalysts for CO_2 reduction and formate salt formation was evaluated, as illustrated in Figure 6. Faradaic efficiency data (up to 70%) and CO_2 balance in this system indicate that for every ton of CO_2, just over 1 ton of formic acid/formate can be produced. This technology has already been tested and proven on a pilot scale, proving the scaling potential of this technology, however, it is still necessary to overcome technological barriers, such as the reduction in the consumption of chemicals and energy in the activation of the catalysts, as well as the market, such as competition with the consumption of fossils (Rode et al., 2016, Agarwal et al., 2011).

Figure 6 – Eletrochemical Reduction of CO2 to Formic Acid (ECFORM Process)



Source: adapted from Rode, 2016

Electrochemical reduction of CO_2 could also be a possible route to the production of other valuable chemicals and fuels such as methanol, natural gas and hydrocarbons. In China, for example, 3 routes are applied to convert and recycle CO_2 into methanol, as shown in **Table 4** (Li, 2022).

Table 4 – Electrochemical pathways for converting CO_2 to methanol

Route designation	Route model reaction	Basic description
CO_2 hydrogenation	1st step: $H_2O \rightarrow H_2 + 0.5O_2$ 2nd step: $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$	Water electrolysis is already a commercial technology (AEC fuel cells, for example). The 2nd step is as described in 3.1 topic.
Electrochemical Reduction	$CO_2 + 2H_2O \rightarrow CH_3OH + 1.5O_2$	Still under laboratory development (low TRL). Electrochemical process parameters such as electrolyser selectivity, electrolyte type and faradaic efficiency still need to be optimized.
Co-electrolysis (CO_2+H_2O)	1st step:CO_2 + H2O → CO + H_2 + O_2 2nd step: $CO + 2H_2 \rightarrow CH_3OH$	The bottleneck is the development of the 1st step (simultaneous electrolysis of water and CO_2) where pilot and demonstration prototypes showed good results. The 2sn step "syngas to methanol" has been applied for decades in the industry.

Source: prepared by the authors

A major project in the electrochemical conversion of CO_2 to methanol was jointly developed and commissioned by Carbon Energy Technology (Beijing) Co., Ltd., Inner Mongolia Yitai Chemical Co., Ltd., Tianjin University and Zhongke Synthetic Oil Engineering Co., Ltd. The process is based on the co-electrolysis of CO_2 and H2O at low temperature using an electro-catalyst with high selectivity to reduce CO_2 and a 3D electrode with high permeability. The project uses CO_2 from the capture of a coal processing unit. The test started in 2020 operated steadily for more than 1900 h meeting the researchers design expectations. This plant can process up to 30 ton/year of CO_2 and produce more than 45 kNm³ of syngas, with a molar ratio of 0.52:1 ($CO:H_2$) in addition to generating as a by-product about 22.5 Nm³ of oxygen (Sohu , 2022; Li, 2022). The production of natural synthetic gas from CO_2 is also a prospect of high technical and environmental potential, for example, for the European scenario until 2030, where the substitution of fossil natural gas for synthetic natural gas can lead to a reduction of 1 kg of emission CO_2/kg SNG. In this context, CO_2 electro-reduction can reach prices of 0,143 €/kg SNG through the development of the process called Power to Synthetic Natural Gas (PtSNG). Some technological challenges need to be solved on this route, for example (Gonzales, 2022):

a) elevation of the partial current density of CH_4 to values of the order of 800 – 1000 mA/cm²;
b) energy efficiencies greater than 60%; and
c) recovery of by-products such as O_2, association of the production of other chemicals (such as biomass gasification).

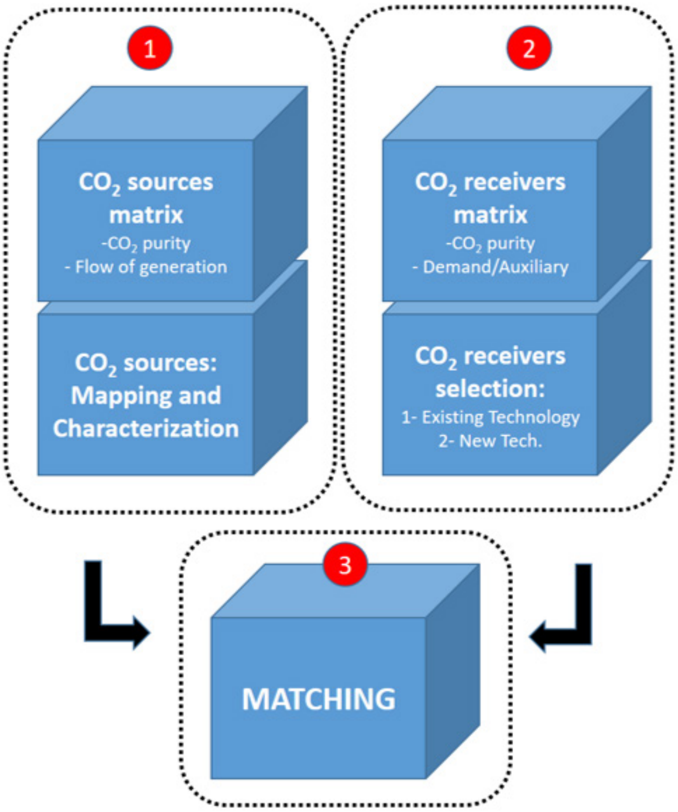
Some companies, mainly in Germany, have already applied in medium scales the capture of CO_2 and its conversion into CH_4 using mainly alkaline water electrolysis and the hydrogenation of CO_2 to produce CH_4. The two most prominent cases were the project carried out by the German ETOPAS to upgrade biogas. The 250 kW pilot plants produced hydrogen by associating photovoltaic cells with alkaline water electrolysis. The generated hydrogen reacts with raw biogas produced in an agricultural biogas plant without separation, enriching the methane contents of the natural gas significantly. A very similar process is the plant installed at Audi e-Gas in Wetle, Germany. This plant, however, has a greater capacity with 3 alkaline electrolysers of 2 MW capacity and this process showed an efficiency of around 54%, producing an SNG whose content energy is 13.85 kWh/kg. The annual production of about 1000 t allowed the consumption and recycling of about 2800 t/CO_2 (Bailera, 2017; Benjaminsson, 2013; Bard et al., 2012). Finally, electrochemical CO_2 reduction is an emerging technology with great potential for implementation, mainly because it is flexible and generates value-added chemicals and fuel such as methanol, CH_4, formic acid, etc.

4. Conclusions and aspects of the CO_2 utilization in Brazil industry

This work addressed different technological routes for using and converting CO_2 into products of interest to society in order to ensure carbon recycling, preventing massive emission of greenhouse gases.

Among the processes addressed, plasma and photochemical CO_2 conversions still have a low TRL, between 2-4, and for their large-scale application a series of technical challenges need to be overcome. At the other extreme, routes that involve thermo-catalytic and biological conversions, polymerizations and mineralizations already have great relevance in the European and Chinese scenario, already with a high degree of technological maturity, for the production of CO_2-based materials and chemicals such as methanol, SNG, urea, concrete curing, salicylic acid, polycarbonates, among others (Chauvy; De Weireld, 2020; Meng et al., 2021). However, the use of these routes may eventually be related to the consumption of H2, where production is mostly still from fossil sources, or demands CO_2 with high levels of purity and pressure, making the capture costs for its use onerous. Therefore, the installation of CO_2 recycling units and generation of CO_2-based products in the Brazilian scenario depends on the mapping and combination of pillars of the generation sources, generation values and the demands of the receivers, etc., as illustrated in the diagram in **Figure 7**. (Patricio et al., 2017).

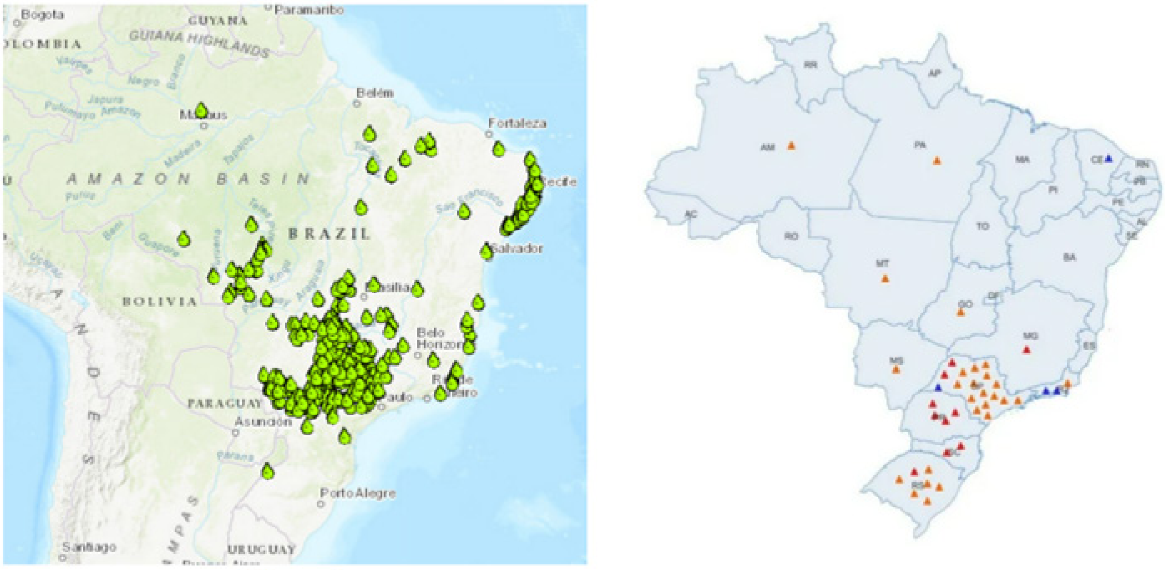
Figure 7 – Illustration of the integration of blocks of CO2 sources, uses and conversion technologies



Source: prepared by the authors

The costs for implementing CCU technologies are mainly centered on the process of capturing and generating renewable electrical energy (Roh et al., 2020). In Brazil, when mapping the availability of CO_2 sources (sources matrix), it is already possible to visualize the possible poles of installation of CO_2 units in Brazil, without considering the thermal power plants where the purity of CO_2 from combustion processes is not so high. But the production of ethanol followed by the growing units of generation of biomethane from biogas leverage the main sources of generation of high purity bio-CO_2 mainly in the state of São Paulo. The CO_2 of fossil origin comes mainly from the production of H2 in refineries from Natural Gas. **Figure 8** presents a mapping of the main units of bio-ethanol and bio-methane (sources of CO_2).

Figura 8 – Map of production of Ethanol and biomethane in Brazil



Ethanol

Bio-CH_4

Source: adapted from (EPE and EPR).

In this way, it is seen, mainly, the sugar and alcohol sector with immense potential to expand its biorefinery capacity by incorporating the production of bio-based CO_2 materials, using both the CO_2 from fermentation and that obtained in the methanization of biogas. In addition, the H_2 currently produced in Brazil is mostly called "gray", obtained mainly in the refining parks of Petrobras. The application of CCU routes associated with the production of H_2 in refineries can make the production of hydrogen transition to the "blue" scale, which can minimize the impact of emissions associated with this production of hydrogen and give survival to the use of gas as a raw material, until the production of green hydrogen is consolidated. Finally, with most of the emerging technologies described so far, from the use of CO_2 to produce chemicals such as methanol, urea, organic acids, polymers, among others, which are currently imported into the Brazilian consumption matrix, and the availability of large sources of CO_2, leveraged mainly by sugar-alcohol plants and oil refineries, open scope for more detailed investments by the industrial sector to invest in CCU technologies. In addition, other sectors that involve significant GHG emissions, such as civil, can significantly contribute to the emission reductions associated with the broad benefits of the circular economy.

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