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Introductory Chapter: An Outline of Carbon Dioxide Chemistry, Uses and Technology

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1. Introduction

Carbon dioxide (CO_2) is a stable and relatively inert triatomic molecule that exists as a gas at ambient temperature and pressure. A CO_2 molecule exhibits a linear structure in which the carbon is bonded to each oxygen atom *via* a sigma and pi bond forming two $\text{C}=\text{O}$ bonds. Each $\text{C}=\text{O}$ bond has a length of 116.3 pm and $750 \text{ kJ}\cdot\text{mol}^{-1}$ bonding energy, considerably higher than the bonding energy of $\text{C}=\text{C}$, $\text{C}-\text{O}$, and $\text{C}-\text{H}$ bonds [1]. Carbon dioxide is generated naturally from various sources such as forest fires, volcanic eruptions, and respiration of living organisms. The photosyntheses of plants and other autotrophs play an indispensable role in balancing the carbon/oxygen cycle and consequently in maintaining the earth life. The global concentration of CO_2 in the atmosphere was approximately 270 ppm by volume prior to industrial revolution. Nowadays, the carbon dioxide level has reached up to 405 ppm, approximately a 50% increase. This steady increase in CO_2 emissions stems from the large consumption of fossil fuels and anthropogenic activity (power plants, oil refineries, cement, iron, and steel industries, biogas sweetening, and chemical industry and processing) in addition to the wide deforestation for land usage [2].

Pollution is regarded as the issue of our era, since dominant industries deem its control as an expense that overwhelms the domains that are beneficial to the advances of science. Finding alternatives to indispensable fields such as providing energy, food, drugs, and dyes for medicinal probes, among others, seems to conflict the innovative progress reported every day in academia and industry. The greenhouse effect is one of the utmost contemporary issues in this regard. Carbon dioxide is currently the most abundant greenhouse gas (GHG). Greenhouse gases such as ozone, nitrous oxide, methane, chlorofluorocarbons (CFCs), and CO_2 has a detrimental role in preventing the heat loss and protecting

the life on earth during nighttime. However, the increased concentrations of GHGs, particularly CO_2 , are believed to cause drastic changes such as global warming and ocean acidification [3].

Global warming refers to the increase in the average global temperatures, mostly noticeable in the melting of ice caps in polar regions and the rising of sea levels. Specifically, the greenhouse effect of CO_2 relies on its asymmetric stretching and bending vibrational modes, which allow this gas to absorb and emit infrared radiation at wavelengths of 4.26 and 14.99 μm , respectively [1, 4]. On the other hand, ocean acidification refers to the ongoing decrease in the pH of water in seas and oceans. About 30–40% of the anthropogenic CO_2 are dissolved in oceans and seas forming carbonic acids to achieve chemical equilibrium. Consequently, the formed H^+ ions are leading to decrease the pH of earth water from slightly basic conditions toward neutrality or even acidity in the long term, hence affecting the life cycles of marine organisms and the subsequent food chains [5].

Several international conventions and governmental protocols have been formulated to reduce the CO_2 emissions such as *The Kyoto Protocol*, *the UN Framework Convention on Climate Change*, and *the Intergovernmental Panel on Climate Change*. To date, there is no universal agreement on these laws, and many countries and industries do not abide by these conventions. Therefore, immediate actions and solutions are demanded to circumvent the potential influence of the yet high CO_2 emissions on the climate. In general, the total CO_2 emission can be controlled by reducing the energy intensity, limiting the carbon intensity, or by improving the CO_2 sequestration. In the short term, carbon-based fossil fuels will persist to be the main source of energy. Thus, there is an urgent need to develop economically feasible and efficient processes for capturing, separating, storing, sequestering, and utilizing the continuous CO_2

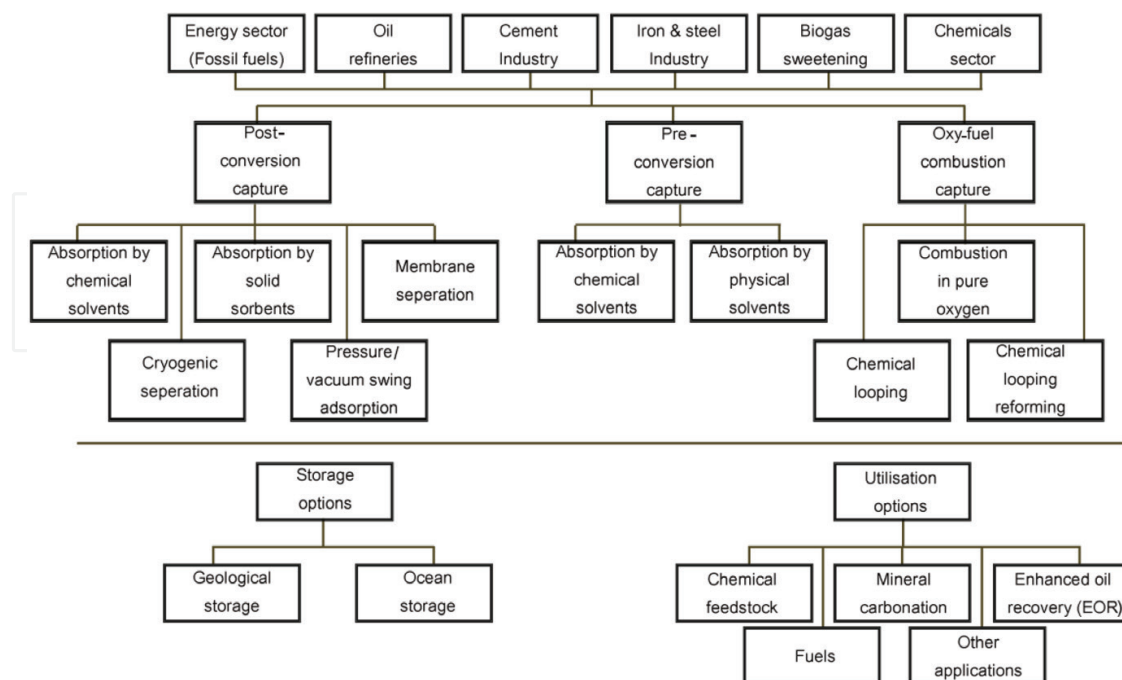


Figure 1. Major sources of CO_2 emissions and technologies used in CCS and CCU.

emissions. The future trends, however, should be directed to reduce energy consumption and dependence on fossil fuels and to develop and employ renewable and less carbon-intensive sources of energy on large scale, such as nuclear energy (e.g., H_2), biofuels, geothermal, and tidal energy [4, 6, 7].

This introductory chapter discusses the *basic properties* and the *major technologies of carbon dioxide*. **Figure 1** outlines the main sources of CO_2 emissions and the various methods used or envisioned for CO_2 capture, storage (CCS), and utilization (CCU). The most important technologies will be introduced in the next sections of this preview and will be further detailed in the separate chapters of this “Book project.”

2. Carbon dioxide capture

Carbon dioxide capture technologies involve the processes of producing relatively high purity stream of CO_2 for transport and storage, since most CO_2 emissions from electricity generation and industries are released as flue gas (4–14% by volume CO_2). Storage of flue gas is possible in principle by compression to a pressure typically higher than 10 MPa, thus requiring a huge amount of energy aside from the large volumes produced that can rapidly fill the storage reservoirs. Therefore, carbon capture and storage (CCS) technologies represent an economic solution for storage of flue gases [4, 8].

Three methods are known for capturing CO_2 in combustion systems of fossil fuels, namely *postconversion capture*, *preconversion capture*, and *oxy-fuel combustion* (**Figure 1**).

2.1. Postconversion capture

The separation of CO_2 from waste gas streams after the conversion (mainly combustion) of the carbon source is known as postconversion process. Different technologies are developed for this capture process such as adsorption by solid sorbents, vacuum swing adsorption, absorption by solvents, and cryogenic separation. These methods are still considered energy demanding. Solvent absorption is elaborated here as an example of the capture. In particular, physical absorption of CO_2 relies on its solubility based on Henry's Law without inducing a chemical reaction. Thus, low temperatures and elevated CO_2 partial pressures are needed for this application. In contrast, chemical absorption depends on the chemical reaction between CO_2 (at low partial pressure) and the used solvent forming weak bonds. The latter is more adjusted to capture CO_2 emissions in industrial processes given the flue gas conditions of ambient pressure and large volumes with varied concentrations of CO_2 , which might be low in some processes.

2.2. Preconversion capture

It involves the capture of CO_2 produced by an intermediate step in some conversions such as in ammonia synthesis. It is commonly achieved using absorption by solvents or adsorption processes. This capture also suffers from the high energy demands.

2.3. Oxy-fuel combustion capture

This technology is employed only in combustion conversions that generate flue gas rich in CO_2 but free from N_2 and NO_x products. The energy demands are lower in this capture process, but the expenses majorly stem from the need of using pure oxygen in the combustion process to avoid generating the coproducts and their separation afterward.

3. Carbon dioxide storage

Once captured, CO_2 can be compressed and transported by shipment or *via* pipelines to storage destinations in the ground (geological sequestration), oceans (still in probation phase), or as mineral carbonates (considered as both utilization and storage process) [4] (**Figure 1**).

In *geological storage*, CO_2 is injected under high pressure into stable rocks rich in pores that trap natural fluids at a depth between 0.8 and 1 km. Different trapping mechanisms, temperatures, and pressures can be employed allowing the storage of CO_2 as liquid, compressed gas, or in its supercritical condition, subject to the characteristics of the reservoir. Geological formations include unmineable coal seams, depleted oil, and gas reservoirs.

In contrast, *mineral carbonation* or metal carbonate formation involves the direct or indirect reaction between CO_2 and a metal oxide such as Ca and Mg, naturally found as silicate minerals. Aside from the availability of minerals, the advantage of this technology is the production of stable carbonates that are suitable for long period of storage that can last for centuries without leakage. The other benefit is the direct use of CO_2 from flue gas without the costly need of establishing a pure stream, since other gas impurities such as NO_x do not influence the carbonation reaction. The large-scale applications of this method are not fully developed yet and still encountering a high overall cost [4, 9].

4. Carbon capture and utilization

Carbon capture and storage (CCS) technologies suffer till now from economic and technical limitations for large-scale employment such as the huge capital investment, shortage of geological storage sites, and high leakage rates of CO_2 . Carbon capture and utilization (CCU) strategy, however, has emerged as a prospective alternative to CCS aiming to turn the CO_2 emissions into relevant products such as fuels and chemicals. Both of the technologies target capturing anthropogenic CO_2 emissions before being released to the environment, but they differ in the final destination where CCS aims at long-term storage, while CCU at conversions into useful products. CCU presents a set of advantages over CCS, namely the reduction of costs by synthesis of valuable products and the investment of CO_2 as an available, nontoxic, and “renewable” resource being constantly emitted. Nonetheless, CCU can be only a short-lived solution, which delays the release of CO_2 to later stages. Another important aspect that raises strong concerns in the large-scale application of both CCU and CCS is to ensure that the mitigation of the climate change is not achieved at the expense of other environmental issues [10, 11].

Carbon dioxide is indeed an extremely valuable molecule that can be utilized in diverse beneficial ways, as illustrated in **Figure 1** and detailed herein.

4.1. Direct utilization of CO₂

Carbon dioxide is commonly used in fire extinguishers and photosynthesis as well as a carbonating agent and preservative in food and drink industries.

In addition, *supercritical carbon dioxide* (scCO₂) has found indispensable applications in supercritical fluid technology. scCO₂ is a fluid state of CO₂ where it is held at or above its critical temperature (304.25 K) and pressure (7.39 MPa). In processes at high pressure (at or above the critical parameters), the density drastically increases, so scCO₂ can fill the volume as a gas but with a density like a liquid. scCO₂ is used in sustainable extractions of bioactive compounds and as a greener alternative for multiphase catalytic reactions, where it is employed as a promoter or modifier of liquid-phase organic reactions although not as a reactor. The dissolved CO₂ in the organic phase acts as a “promoter” by altering the physical properties of the solvent from pure organic phase into high-density CO₂ state that can dissolve gaseous reactants such as O₂, CO, H₂, thereby accelerating the involved reactions such as oxidation, hydroformylation, and hydrogenation, respectively. In contrast, the impact of scCO₂ on the chemical properties is modulated by its interactions with the functional groups of substrates and/or intermediates (whether gases or not), as proved by the *in situ* high-pressure Fourier transform infrared spectroscopy. Hence, it acts here as a “modifier” to the reactivity of these groups and, thereby, to the selectivity of the reaction (e.g., Heck reactions). It is worth noting that most of the abovementioned uses are limited to CO₂ emission streams of high purity (from ammonia production, for instance) [10, 12].

4.2. Enhanced oil (EOR) and coal-bed methane recovery (ECBM)

The injection of CO₂ in the extraction processes of crude oil (EOR or tertiary recovery) and natural gas (ECBM), respectively, from oil fields and coal deposits represent an attractive option to obtain the otherwise unrecoverable fossil fuels. These methods have been tested successfully and are being extensively researched to reduce the costs, optimize the CCS and CCU conditions, and thus to avoid the reemission of CO₂ to the environment. In EOR, the injection of CO₂ under supercritical conditions allows an efficient mixing with oil, decreasing the viscosity and consequently increasing the extraction yields by 5–15%. The ECBM employs a similar technique in which the injected CO₂ occupies the porous spaces of the coal bed and adsorbs onto the carbon at twice the rate of methane, leading to its faster displacement and enhanced recovery. It is worth noting that surfactants and other gases as well as varied methods like thermal energy processes are also applied in EOR and ECBM processes.

4.3. Conversion of CO₂ into chemicals and fuels

CO₂ represents an abundant and a safe resource of C and O, which can be employed in the synthesis of variety of useful products conforming to the principles of Green Chemistry. For instance, employing CO₂ as an alternative to toxic reactants such as phosgene and CO is attracting huge attention. The types of transformations of carbon dioxides along with

examples of the main products are illustrated in **Table 1**. They will be further discussed in this section with the exception of the biological process that will follow in the section of biofuels and the inorganic carbonate formation that was already discussed as a storage option [13].

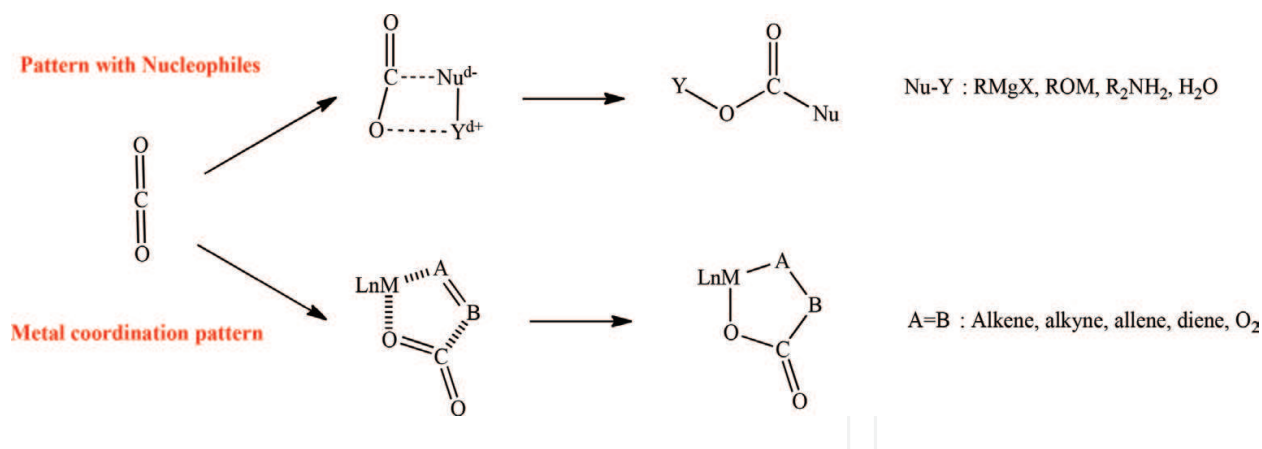
The chemistry of CO₂ can be classified into two general categories (**Scheme 1**):

- a. The “basic CO₂ transformations” depend on the polarization of C=O bonds where the higher electronegative oxygen atoms carry a partial negative charge of -0.296 and the carbon center has a partial positive charge of $+0.592$. This polarization ensures the reaction of nucleophiles (amines, Grignard reagents, phenolates, etc.) at the carbon center.
- b. The “more advanced chemical interactions of CO₂” rely on the coordination of the triatomic molecules to metals, inducing major changes in its chemical reactivity by altering both its molecular geometry (e.g., linear to more activated bent) and its electronic distribution (e.g., less electron-deficient carbon upon coordination). Various catalysts have so far been investigated to achieve this goal and activate the stable and relatively nonreactive CO₂. This area is still considered a hot topic in organometallic and theoretical research due to the various coordination modes between CO₂ and different metals [1].

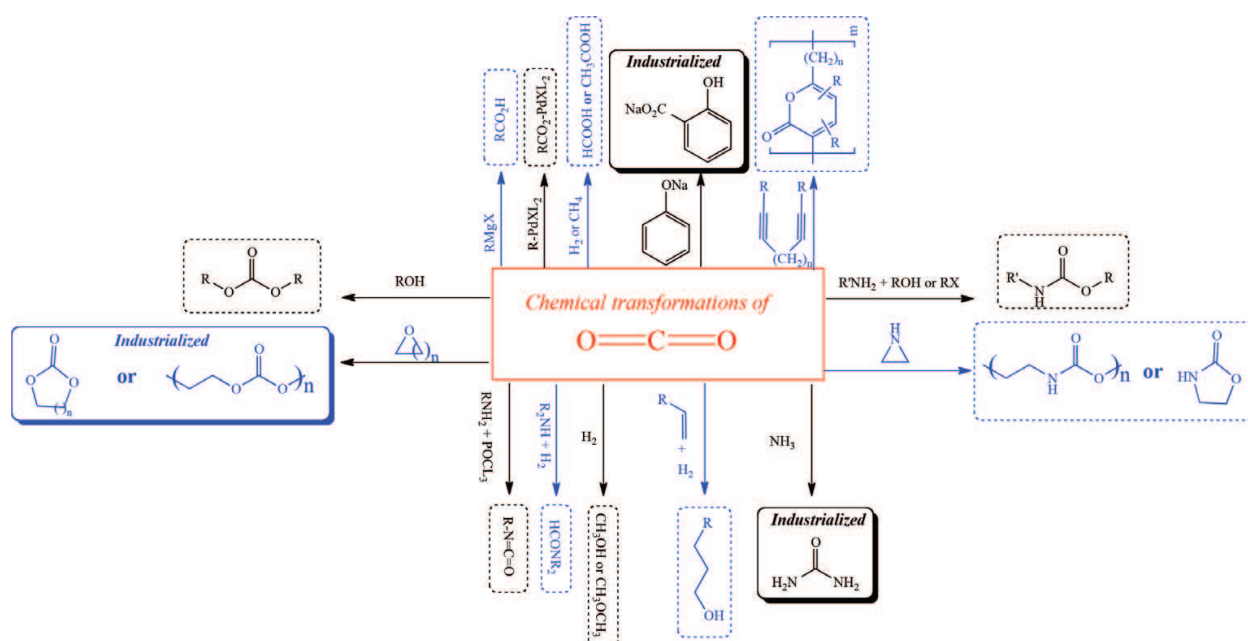
Based on these two chemistry modes, numerous transformations of CO₂ have been reported achieving a range of useful chemical products. The majority of these transformations are summarized in the pattern shown in **Scheme 2** and have been reviewed by Sakakura et al. The transformations involve either (i) using the CO₂ molecule as a precursor for organic compounds such as carbonates, carbamates, polymers, and acrylates *via* carboxylation reactions or (ii) reduction of the C=O bonds resulting in chemicals such as methanol, dimethyl ether, methane, urea (important fertilizer), syngas, and even formic acid and CO. Formic acid is a safe storage material of H₂, and CO can be transformed into liquid hydrocarbons by Fischer-Tropsch process. Some CO₂ conversions have been industrialized (**Scheme 2**) and currently play important roles in recovering the anthropogenic emissions of CO₂. The main drawbacks of these technologies are the short term of storage, intensive demand of energy, and requirement of highly selective catalysis processes due to the low chemical activity and high thermodynamic stability of CO₂ in addition to the short term of storage [13].

| Transformation | Main products |
|----------------------------------|--|
| Chemical (nonhydrogenative) | Carbamates, carbonates, urea, carboxylates |
| Chemical (hydrogenative) | HCOOH, hydrocarbons, MeOH, EtOH |
| Photochemical or electrochemical | CO, CH ₄ , MeOH, HCOOH |
| Reforming | CO + H ₂ |
| Biological | Sugar, EtOH, CH ₃ COOH |
| Inorganic | M ₂ CO ₃ |

Table 1. Types of chemical transformations of carbon dioxide.



Scheme 1. General patterns of the chemical transformations of CO₂.



Scheme 2. The major chemical transformations of CO₂.

The recent advances in all fields of catalysis (organocatalysis, photocatalysis, palladium catalysis, etc.) [14–18] were paralleled by important progress in the transformations of CO₂, particularly in *electrochemical* and *photochemical reductions* and *reforming* in both its catalytic and nonthermal plasma techniques. The design of new efficient electro- and photocatalysts consequently reflects on ameliorating the selectivity and decreasing the inherent energy requirement by using renewable sources such as solar energy.

The electrochemical and photochemical reductions of CO_2 involve varied experimental approaches, but they have essentially similar nature. They both rely on external energy stimulus to activate the chemically inert CO_2 and effectuate a thermodynamically uphill reaction. Furthermore, the surface charge transfer step in the photocatalytic reduction of CO_2 is indeed an electrochemical process and is generally promoted by adding a cocatalyst (electrocatalyst).

Both processes can proceed *via* transfer of 2, 4, 6, 8, 12, or more electrons depending on the nature of the employed catalyst and the experimental conditions, and they hence yield various products as mentioned before.

4.3.1. Electrochemical reduction of CO_2

The kinetics of the electrochemical reduction is sluggish due to the reorganization of the linear CO_2 molecule into more active bent form, which creates overpotential to the first electron transfer after the adsorption of the molecule onto the working electrode. This step is mostly identified as the rate-determining step initiating at -1.9 V, and it forms $\text{CO}_2^{\bullet-}$ anion radical that is further protonated into HCOO^{\bullet} or HOOC^{\bullet} and reduced into HCOO^- (formate) or CO , respectively. The majority of electrochemical reductions of CO_2 produce HCOOH or CO as primary products. Very few electrocatalysts (e.g., Cu) ensure the further reduction of CO into hydrocarbons, but without an elucidated mechanism till now. Various electrolytic materials have been investigated in the CO_2 reduction processes including metals (Sn, Pd, Cu, Pt, etc.), layered transition metal dichalcogenides (e.g., WS_2 , MoSe_2 , and MoS_2), and heteroatom-functionalized carbonaceous catalysts such as N-doped carbon nanofibers and graphene quantum dots [19].

4.3.2. Photochemical reduction of CO_2

The photocatalytic reduction of CO_2 has been widely studied using different semiconductors of the following types: metal oxides, sulfides, or nitrides, layered metal materials like layered double hydroxide, metal-organic frameworks, and metal-free carbonaceous materials such as graphitic carbon nitride. The photocatalytic reduction can be summarized into five steps:

- Absorption of photons by the semiconductor photocatalyst generating the hole and electron pairs.
- Charge separation of the generated electrons and holes.
- CO_2 adsorption and transfer of electrons to the CO_2 molecules.
- Surface redox reaction involving the reduction of the CO_2 and the oxidation of the common reductants such as H_2O and H_2 .
- Desorption of the products [19, 20].

4.3.3. CO_2 reforming with methane

Lastly, reforming of CO_2 and CH_4 into syngas (mixture of H_2/CO) can be performed by catalytic and nonthermal plasma methods or by the novel hybrid technique combining both. Catalytic methods still suffer from high thermal energy consumption, catalyst deactivation by coke deposition, and high costs. Selected examples of catalysts for reforming process are Pt, Pd, Ir, Rh, Ru, Co, and Ni. The general mechanism of the dry methane reforming (DRM) involves the adsorption of CO_2 and CH_4 onto the catalyst followed by dissociation of the

molecules into CO, and O, C, and H atoms. The atoms recombine forming additional CO molecule and H₂ gas, followed by desorption of the gases where the CO desorption constitutes the rate-determining step in the process.

Nonthermal plasma relies on electronic energy. Electrons are accelerated by an external electric field to collide with CO₂ and CH₄ transferring their energy to induce the dissociation of the molecules when the energy exceeds 4.5 and 8.8 eV, respectively. The dissociation generates radicals and more active species, which reform the CO and H₂ products. The main characteristic of this method is the low selectivity since the radicals can reform into side products such as hydrocarbons [4].

4.4. Biofuels from microalgae

The photosynthetic microorganisms (e.g., microalgae) constitute future alternative energy sources to fossil fuels and can serve to fix CO₂ directly from waste streams, decreasing the high existing levels. Microalgae can transform solar energy into chemical forms *via* photosynthesis and possess faster growth rate than plants. They can be cultivated in diverse environments as open or closed ponds and photobioreactors with minimum requirement of nutrients. After cultivation, the biomass content is harvested, dried, and converted into fuels by thermochemical (e.g., pyrolysis) or biochemical (e.g., fermentation) processes. The limited cultivation areas and the costs of the harvesting stage are still burdening the large-scale routes of this prospective CO₂ utilization [21].

5. Maturity of carbon dioxide technologies

The carbon dioxide technologies that have been described in this perspective can be recapitulated based on their maturity for industrial employment as follows.

- “*Mature market*,” such as gas separation and transport, EOR, and industrial transformations to chemicals like urea.
- “*Economically feasible*,” such as pre- and postconversion capture.
- “*Demonstration phase*,” such as oxy-fuel combustion and ECBM.
- “*Research phase*,” such as mineral carbonation and ocean storage.

6. Conclusion

This chapter introduced the basic properties of carbon dioxide that are used to develop the technologies for its utilization or storage in order to help in mitigating its global warming effects. The major sources of CO₂ emissions were outlined and the carbon capture storage and utilization (CCS and CCU) technologies were discussed. The chemical transformations of CO₂

were given particular emphasis as tools to reduce the high CO₂ levels and to understand the chemistry of CO₂. Within that aspect, the electrochemical and photochemical reductions and the reforming of CO₂ with methane were especially described. The chapter was concluded by the classification of the storage and utilization technologies according to their maturity in the market.

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