

Review

## Converting CO<sub>2</sub> from a Harmful Gas to a Renewable Source of Matter and Energy: A Review

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### Abstract

The emission of greenhouse gases, specifically CO<sub>2</sub>, has reached non-acceptable levels causing global warming with adverse effects. Owing to rigorous ongoing research, these harmful substances might be converted to beneficial sources. The main objective of this study was to review the most effective processes that might utilize carbon dioxide to produce various substances, chemicals, and energy. For this, different existing and projected short-term and long-term strategies have been presented and discussed. Specifically, processes like the artificial tree of Lackner to capture CO<sub>2</sub>, chemical looping combustion (CLC), the application of CO<sub>2</sub> in the food and processing industry, wastewater treatment, supercritical and refrigerant CO<sub>2</sub>, hydrogenation of CO<sub>2</sub>, the cultivation of microalgae, thermolysis, electrolysis, and photoelectrocatalysis techniques for producing hydrogen and biofuels, based on thermochemical processes, are the most promising ways to reduce and reuse CO<sub>2</sub>. Such behavioral changes can lead to the exchange of CO<sub>2</sub> between natural reservoirs and help to maintain CO<sub>2</sub> equilibrium among the atmosphere, the upper mixed layer of the sea, and the deep sea. Consequently, the mean global temperature and the climate are directly affected.



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## Keywords

Greenhouse gases; climate change; CO<sub>2</sub> capture; CO<sub>2</sub> applications

## 1. Introduction

Solving the problem of greenhouse gases, especially that of CO<sub>2</sub>, is very challenging. The concentration of atmospheric CO<sub>2</sub> is increasing, causing global warming, which has adverse effects on the climate and the composition of the environment, i.e., soil, air, water, and living beings [1]. However, new ideas are emerging to use CO<sub>2</sub> for generating energy, useful chemicals, and organic and inorganic materials in the building industry [2]. In 2014, 36 billion tons of CO<sub>2</sub> were released into the atmosphere by anthropogenic activities [3]. The atmospheric concentration of CO<sub>2</sub> was around 320 ppm in 1970, which reached about 380 ppm by 2000, and increased to about 420 ppm in 2021 [4]. The majority of the emitted CO<sub>2</sub> comes from different types of industrial plants that burn fossil fuels, such as coal, natural gas, and petroleum. Generally, CO<sub>2</sub> from combustion is mixed with nitrogen (non-reactant gas). Hence, the chemical looping combustion (CLC) technique was used to separate CO<sub>2</sub> from nitrogen before cooling and locking the carbon dioxide in a convenient material for future use [5-8]. The use and valorization of CO<sub>2</sub> can be performed by three methods: direct use, chemical transformation, and biological transformation. However, the actual time required for industrial installation and the effectiveness of these methods depend on many technological, economic, political, and regulatory factors. Hence, the first industrial recovery facilities should wait for the complete control of industrial storage projects.

## 2. Dynamics of CO<sub>2</sub> Exchange between the Atmosphere and Other Natural Reservoirs

Problems related to greenhouse gases appeared in the 1970s due to the imbalance of the carbon cycle that was triggered by the large-scale use of fossil fuels. Craig's diagram shows the natural reservoirs, the duration of interaction during CO<sub>2</sub> exchange between the reservoirs, and the relative capacities of such reservoirs [9]. The entire system, according to this diagram, consists of the atmosphere, the upper mixed layer of the sea known as the thermocline, with a mean depth between 50 and 100 m [10], the biosphere that consists of land plants (vegetation and humus), and finally, the deep sea [9]. The mixed layer and the deep sea contain about 1.2 times and 58 times the quantities of carbon present in the atmosphere, respectively. The mixed layer and the deep sea contain 2% and 98% of the total carbon present in the sea, respectively [11]. Based on Craig's model [9], the time required for the exchange of carbon between the four reservoirs was estimated as five years from the atmosphere to the mixed layer of the sea and six years in the opposite direction, 33 years from the atmosphere to the land and 40 years in the opposite direction, four years from the mixed layer to the deep sea and 300 years in the opposite direction. Thus, restoring the balance of a disrupted carbon cycle is very difficult. Only a small quantity of CO<sub>2</sub> that enters the sea remains as dissolved gas is ready to be exchanged with the atmosphere [12]. Some of the CO<sub>2</sub> reacts with magnesium and sodium to form the respective carbonates; CO<sub>2</sub> is sequestered in chemical solutions in this manner. Due to the dissolution of CO<sub>2</sub> in the sea, an increase in 0.6% CO<sub>2</sub> in the sea yields a 10% increase in the partial pressure of atmospheric CO<sub>2</sub>. Consequently, about 20% extra CO<sub>2</sub> might

be emitted from the ocean into the atmosphere, whereas the deposition of some of the oceanic carbon as carbonates on the seabed requires more time. The dynamic exchange of CO<sub>2</sub> between the natural reservoirs can be studied based on the radioactivity of C<sup>14</sup>. Two types of measurements of carbon isotopes allow calculation of the exchange rate through the sea-atmosphere interface relative to the mixing rates of the water masses in the oceans. Hence, the apparent C<sup>14</sup> age of marine materials and the effects of the combustion of industrial fossil fuels on the atmospheric C<sup>14</sup> concentration (a dilution) can be distinguished [13]. The marine and atmospheric carbon reservoir, as a closed system in equilibrium, can be mathematically expressed as follows:

$$\frac{\tau(sea)}{\tau(atm)} = \frac{k_1}{k_2} = \frac{S_0}{A_0} \quad (1)$$

Here,  $\tau(sea)$  is the average lifetime of carbon in the sea before it becomes atmospheric CO<sub>2</sub>,  $\tau(atm)$  is the average lifetime of CO<sub>2</sub> in the atmosphere before it dissolves in the sea,  $k_1$  is the annual rate of CO<sub>2</sub> transfer from the atmosphere to the sea,  $k_2$  is the annual rate of CO<sub>2</sub> transfer from the sea to the atmosphere,  $S_0$  represents the total carbon of the marine carbon reservoir at equilibrium at instant zero, and  $A_0$  is the atmospheric CO<sub>2</sub> carbon at instant zero. An increase in atmospheric CO<sub>2</sub> was shown to be predominately due to anthropogenic disturbances caused by the accelerated release of CO<sub>2</sub> by the combustion of fossil fuels and associated with a strong decrease in  $\Delta C^{14} = -20\%$  between 1890 and 1950. Furthermore, only  $\Delta C^{14} = -3\%$  was due to natural processes, such as changes in the natural production of C<sup>14</sup> due to solar and geomagnetic variations, and -17% was attributed to the dilution of C<sup>14</sup> due to the CO<sub>2</sub> produced by the combustion of fossil fuels (this mechanism is known as the Suess effect) [14, 15].

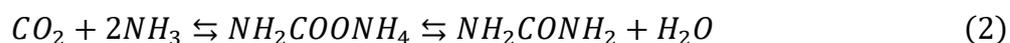
### 3. Converting CO<sub>2</sub> from a Harmful Gas to a Renewable Source of Matter

The main objective of scientists and political, social, and economic decision-makers, who participate in the various world summits, is the reduction of greenhouse gas emissions, where CO<sub>2</sub> is the main factor. Other strategies have emerged to clean the atmosphere of excess CO<sub>2</sub> and consider atmospheric CO<sub>2</sub> as a source of raw materials. The estimates show four distinct paths: the already industrialized paths, the short-term paths, the medium-term paths, and the long-term paths.

#### 3.1 Already Industrialized Route of CO<sub>2</sub>

Besides the burial technique, Lackner [16] developed a process known as artificial trees to directly capture atmospheric CO<sub>2</sub> for a net-zero carbon economy. However, this technique requires further refinement before being implemented widely on an industrial scale. Another technique for capturing CO<sub>2</sub> from the smoke of factory chimneys has also been developed, where CO<sub>2</sub> is dissolved at an acidic pH in basic baths [17, 18]. Liu et al. [14] showed that CO<sub>2</sub> can be captured from the flue gas of an industrial installation plant fed with coal in a semi-batch using aqueous ammonia at different concentrations. The plant performs quick reactions, is highly efficient and has a high loading capacity of CO<sub>2</sub>. The researchers concluded that the optimum ammonia concentration is between 5 and 10%. Xiao et al. [18] conducted a study on the absorption of CO<sub>2</sub> in a mixture of 2-amino-2-methyl-1-propanol (AMP), monoethanolamine (MEA), and water. The solubilities and

diffusivities of N<sub>2</sub>O were studied in the amine systems, and the analogy between N<sub>2</sub>O and CO<sub>2</sub> was applied to estimate the solubilities and the diffusivities of the latter gas. The researchers concluded that the addition of small quantities of AMP and MEA could increase the CO<sub>2</sub> absorption rate significantly. Moreover, enhanced hydrocarbon recovery based on a novel gas-gas separation method known as condensed rotational separation (CRS) is widely used for upgrading natural gas contaminated with H<sub>2</sub>S/CO<sub>2</sub> [19]. Also, CO<sub>2</sub> can be stored naturally or captured from industrial fumes (e.g., the Weyburn project) [20-23]. Urea is the most convenient product for fixing nitrogen. It also has the highest nitrogen content among solid fertilizers (46%) and is easy to produce as granules. It can be stored and transported easily. Additionally, no salt residues are left after it is applied to crops. Urea decomposes on boiling and is soluble in water-based solvents. It is commercially known as carbamide and is composed of carbon, hydrogen, oxygen, and nitrogen with the formula CON<sub>2</sub>H<sub>4</sub> or CO(NH<sub>2</sub>)<sub>2</sub>. The raw materials required to produce urea are ammonia and CO<sub>2</sub>. The reaction is as follows:



The first reaction is fast and exothermic, but the second one is slower and endothermic. The conversion (on a CO<sub>2</sub> basis) is in the order of 50-80%. The rate of conversion increases with an increase in the temperature and/or NH<sub>3</sub>/CO<sub>2</sub> ratio and decreases with an increase in the H<sub>2</sub>O/CO<sub>2</sub> ratio [24].

This reaction is conducted in a special manufactory, which includes four units: synthesis unit, recirculation unit, evaporation and finishing unit, and wastewater treatment unit [25]. Another path for the green production of urea requires the generation of hydrogen via biomass gasification and PV electrolysis, while nitrogen is used as the raw material from an air separating unit, which separates nitrogen and oxygen by a cryogenic process. CO<sub>2</sub> is derived either from the ammonia plant or from the flue gas of the power plant. Nitrogen and hydrogen react in the plant to form ammonia, and then, ammonia and CO<sub>2</sub> react to produce green urea in the urea plant. A more economic and sustainable approach comprises the underground coal gasification (UCG) method. A high calorific Syngas mainly consisting of methane, hydrogen, and carbon dioxide is required. Hence, the required feedstock for the urea process can be supplied for the UCG-Urea coupled process [26].

Similarly, CO<sub>2</sub> can be used for carbonate and polycarbonate materials. For example, Asahi Kasei used ethylene oxide, its by-product CO<sub>2</sub>, and bisphenol-A to produce large quantities of high-quality polycarbonate and highly pure monoethylene glycol [27]. Moreover, Qin et al. [28] used a simple and renewable process for synthesizing a functional CO<sub>2</sub>-copolymer (polyurea) with a multiblock structure. Polyurea exhibits a spherulitic morphology as a typical black cross pattern formed by many concentric circles characterized by different shades of light and dark. Additionally, CO<sub>2</sub> be fixed into a polymer to produce a highly valuable and biodegradable plastic, mainly polypropylene (PPC). This product is unique among conventional plastics not only because of its biodegradability and unmatched CO<sub>2</sub> application but also because it has already been industrialized [29]. Using the same pathway, Kamphis et al. [30] reported that the reaction between CO<sub>2</sub> and epoxides could form different and valuable products, such as cyclic and polymeric carbonates. Such products can be used effectively to produce polymer-based products, energy storage devices, and biomedical and pharmaceutical materials.

### **3.2 The Short-Term Paths for the Application of CO<sub>2</sub>**

CO<sub>2</sub> is currently used in the food industry (e.g., soft drinks, deep freezing, etc.). According to Moritaka et al. [31], the effect of soft drinks, with gas volumes between 1.5 and 2.7, was tested on the linguopalatal swallowing pressure, perception of intraoral carbonation, and the maximum speed of the movement of the bolus through the pharynx in healthy women of 20-21 years. The results showed that the CO<sub>2</sub> dissolved in soft drinks influenced the activity of taste receptors in the mouth and induced neuromotor responses of the volunteers. Moreover, CO<sub>2</sub> in different states (solid, liquid, gas, and supercritical) exhibits advantageous characteristics such as inertness, non-explosiveness, non-corrosiveness, high volatility, cooling ability, and low cost. Hence, CO<sub>2</sub> can be applied in different domains, and particularly, in the food and processing industry for preserving fruits, vegetables, food grains, liquid foods, meat, fish, inactivating decomposition by microorganisms, oil extraction, and for flavoring and coloring [32]. The application of CO<sub>2</sub> is evolving in water treatment and the chemical industry, such as wastewater treatment pathways, increasing environmental and economic benefits via microbial, electrochemical, and phototropic processes [33, 34]. Kyung et al. [33] developed a mathematical model to estimate the emission of CO<sub>2</sub> from any type of water treatment plant (conventional or advanced), irrespective of the turbidity level. Similarly, Lu et al. [34] captured and utilized carbon using different processes and demonstrated that wastewater management could counterbalance the greenhouse gas footprint and produce negative carbon emissions. However, these industrial applications remain potentially limited since only around 10 million tons of CO<sub>2</sub> are used worldwide annually. New techniques based on supercritical or refrigerant CO<sub>2</sub> are being improved further with the development of carbohydrates, which are environment-friendly compared to the conventional refrigerants currently used [35-37]. Moreover, processes such as the industrialization of salicylic acid or urea are already underway. However, the major objective currently is the development of polycarbonates that are mainly based on CO<sub>2</sub> and epoxy [38, 39]. A second method, which exists in a few pilot units around the world, involves the hydrogenation of CO<sub>2</sub> and the cultivation of microalgae in open basins to produce biofuels. Hydrogenation of CO<sub>2</sub> allows the production of methane and methanol. However, the production cost is higher than that required for the conventional production of methane [40]. The culture of microalgae by capturing the CO<sub>2</sub> of the fumes is more profitable at a small scale than at a large scale [41].

### **3.3 The Medium-Term Paths: Microalgae Cultivation and Methane Reforming as Examples**

Despite significant scientific advancements, the techniques of microalgae cultivation and methane reforming remain undecided due to a lack of control over productivity and energy expenditure. This is the case, for example, with the cultivation of microalgae in photo-bioreactors to produce biofuels [42, 43]. González et al. [44] conducted an experiment using three autochthonous microalgae using two different culture techniques, which included Arnon culture and agriculture fertilizer-based liquid medium, to evaluate the growth of microalgae. They concluded that the medium affected biomass productivity and the growth rate. Additionally, the algae elemental analysis and the high heating value (HHV) were independent of the culture medium, while their contents of sugar and lipids strongly depended on the species of algae and the culture medium. One of the selected species "la Orden" had a lower lipid content in the photo-bioreactor than that in the laboratory. The collected biomass fed to a batch-type digestion process produced

296 ±23 L CH<sub>4</sub> kgVSS<sup>-1</sup> of biogas. A photo-bioreactor (PBR) based on microalgae works under illumination, where CO<sub>2</sub> and the substrate dissolved in water are consumed, and oxygen is produced [45]. This process requires the continuous flow of wastewater through the reactor. A series of PBR used together significantly reduces CO<sub>2</sub> and the substrate. A PBR can also be modeled with differential equations based on the concentrations of dissolved substitutes and biomass algae, and the internal cell quota of the substrate to biomass. Each PBR has a certain volume and irradiation. The absorption rate of substrate into the cells can be modelled using Monod kinetics and the biomass growth rate can be modelled using Droop kinetics knowing that a minimum and a maximum internal cell quota are assumed [45]. According to Diehl et al. [45], the model showed a unique steady-state solution for all PBRs considered. Moreover, a wash-out solution with no algae in the system forms another stable steady-state. Unfortunately, analyzing the models of such phenomena by conventional methods is very difficult. Many problems emerge during numerical evaluation as the results do not have physical meaning and are strongly affected by the initial conditions [42]. The process consisting of feeding algae-based systems by the flue and exhaust gas showed some drawbacks such as the destruction of chloroplasts, the disruption of photosynthesis, and other problems related to metabolic functions that negatively influence the uptake of CO<sub>2</sub>. The photo-bioreactors that were used to capture CO<sub>2</sub> also showed limitations due to the low concentration of biomass. The immobilization of algae in a trickle bed reactor to capture CO<sub>2</sub> from the flue and exhaust gas is an innovative process [43]. In this experiment, Dębowski et al. [43] enriched the ambient air with CO<sub>2</sub> at a concentration of 25% v/v. The immobilized algae produced biomass of about 100 g DM/dm<sup>3</sup>. They found a correlation of approximately 40% between CO<sub>2</sub> removal rates and gas volume flux for a feed gas of 25 dm<sup>3</sup>/hour. Dry reforming of methane (DRM) is a well-known process; however, it is limited by issues of catalyst and energy consumption [46, 47]. This process has gained much attention because of its capacity to reduce greenhouse gases (GHG), such as CO<sub>2</sub> and CH<sub>4</sub>, from the atmosphere as follows:



With  $\Delta H^0 = 247.3 \text{ kJ} \cdot \text{mol}^{-1}$  and  $\Delta G = 61770 - 67.32T \text{ kJ} \cdot \text{mol}^{-1}$ .

Besides reducing GHG, this process produces a mixture of CO and H<sub>2</sub> that are the main components of the Syngas and required for Fischer-Tropsch synthesis (presented later). Thus, this process is better than steam reforming for the transmission of chemical energy. The Ni-based catalysts supported by Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> and promoted with Ce/ZrO<sub>2</sub> are suited for the DRM process [46]. However, carbonaceous deactivation of the catalysts is a major problem during such a process [46]. The steam reforming process (SRP) of natural gas, mainly composed of CH<sub>4</sub>, is the cheapest and the most used technique to generate around 8 kg CO<sub>2</sub> per kg H<sub>2</sub>. The mechanism of the reaction is as follows:



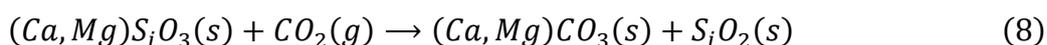
Details regarding the rate of reaction, the kinetic parameters, the equilibrium constant, and the adsorption constant have been published [48].

### 3.4 The Long-Term Paths: Thermolysis, Electrolysis, and Photoelectrocatalysis Techniques as Examples

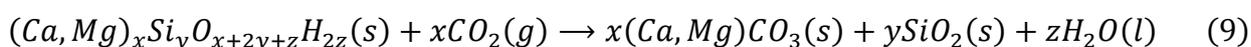
The last route still requires scientific and technological investigation. Although there is sufficient information available, the development of mineralization is adversely affected by obstacles such as energy consumption and low outlets. Seifritz [49] suggested binding CO<sub>2</sub> chemically via an exothermic reaction to a silicate to form a stable substance according to the following reaction:



The thermochemical process (for example, the solar oven) can be implemented to produce hydrogen from water [50]. Considerable progress was made by using solid alkaline metals for CO<sub>2</sub> mineralization, as reported in some studies [49, 51, 52]. This process is similar to the natural weathering of silicate minerals, where CO<sub>2</sub> reacts with oxides of alkaline or alkaline-earth metals (e.g., CaO and MgO) to produce carbonates, as shown in the following reaction:



Also, direct CO<sub>2</sub> reduction by mineralization and accelerated carbonation can be performed as follows [52]:



According to classical methods, hydrogen production relies on carbonaceous sources, and the thermochemical splitting of water is based on metal oxide redox reactions. This route might be the most effective one for the long-term production of H<sub>2</sub> for its direct utilization in fuel cells or other targets, such as synthetic liquid hydrocarbon fuels. Metal oxides, which have high efficiency, are volatile (ZnO/Zn, SnO<sub>2</sub>/SnO) and non-volatile redox pairs (Fe<sub>3</sub>O<sub>4</sub>/FeO, ferrites; CeO<sub>2</sub>/CeO<sub>2-δ</sub>, perovskites). The energy for such processes is provided by concentrated solar energy. The process is divided into two steps [50, 53]: (1) the endothermic high-temperature reduction step to release hydrogen:



(2) the exothermic hydrolysis step producing hydrogen that can be used as a clean energy carrier for the generation of heat/electricity or their co-generation:



However, studies on the combined thermolysis of CO<sub>2</sub>/water are rare and require a deeper understanding of the intervening mechanisms [54]. A thermochemical water-splitting cycle operates at much lower temperature than direct water thermolysis while obtaining the same water decomposition yields [50]. Moreover, the solar thermochemistry of the two-step water splitting

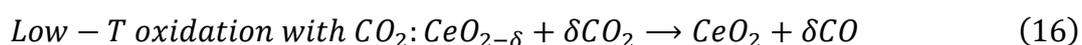
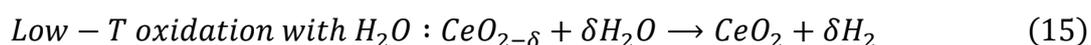
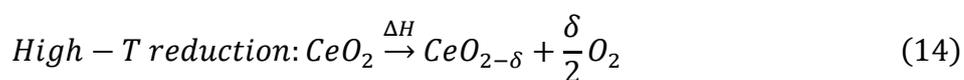
process, which is based on metal oxide redox reactions represented in Eq. 10 and Eq. 11, has advantages. The cycle temperature (between 1,200 and 1,600 °C) is relatively low and compatible with concentrated solar energy. Water and heat are the only inputs, and hydrogen and oxygen are the only outputs. The other substances are continually recycled in the closed process. The hydrogen produced is pure and can be used directly. Conversely, conventional electrolysis also generates pure hydrogen and is limited by a low overall energy conversion efficiency, especially as it first requires the generation of electricity, making the global energy conversion efficiency drop below 20% [50]. Moreover, thermolysis of water can be coupled with CO<sub>2</sub> by direct air capture (DAC) to produce CO<sub>2</sub>, H<sub>2</sub>, O<sub>2</sub>, and electricity. The process is based on a sodium-manganese-carbonate (Mn-Na-CO<sub>2</sub>) thermochemical water-splitting cycle [54]. The authors concluded that it is possible to facilitate several cycles of the complete water-splitting reaction system with the designed reactor. Also, the DAC tests showed that alkaline slurries of NaMnO<sub>2</sub> could efficiently remove CO<sub>2</sub> from the air, even from ultra dilute solutions. Furthermore, this process is inexpensive when CO<sub>2</sub> removal from the atmosphere is combined with water splitting to produce a gas stream of CO<sub>2</sub>/H<sub>2</sub> for generating renewable chemicals. Moreover, under the water splitting conditions (in the high-temperature process), CO<sub>2</sub> can also be decomposed to CO with H<sub>2</sub> to form the Syngas. The hindrance of carbonate formation during CO<sub>2</sub> splitting can be overcome by choosing the correct experimental conditions. The difference between CO<sub>2</sub> and H<sub>2</sub>O splitting can be summarized in the following points: (1) CO<sub>2</sub> splitting above 1,100 K is more favorable (thermodynamically). (2) The water-gas shift (WGS) reaction (eq. 12) and the reverse water-gas shift (RWGS) reaction (eq. 13) are alternative approaches to liquid fuel production via Syngas generation. (3) H<sub>2</sub> production by the low-temperature WGS reaction is more favorable due to the crossover stability [55]. Through a similar reaction, solar Syngas can be produced from H<sub>2</sub>O and CO<sub>2</sub> using a two-step thermochemical cycle based on cerium oxide redox reactions (eq.14 - eq.16) [56]:



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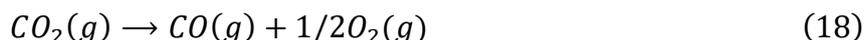
The process occurs in two steps. The first endothermic step occurs at 1,800 K, where CeO<sub>2</sub> is reduced to an oxygen-deficient state. The second exothermic step occurs at 1,100 K, where the Syngas is generated by re-oxidizing CeO<sub>2-δ</sub> by a mixture of H<sub>2</sub>O and CO<sub>2</sub>.

Additionally, there is another part, where the bonds of CO<sub>2</sub> are broken by electrolysis, photoelectrocatalysis, or biocatalysis [57-59]; the productivity and cost of these processes need to be evaluated. Similarly, the photoelectrocatalytic (PEC) reduction of CO<sub>2</sub> could be investigated as a

promising technique for using solar energy in value-added chemicals. The photochemical process is based on visible light irradiation of solutions such as  $Ru(2,2' - bipyridine)_3^{2+}$ , cobalt (II) chloride, and  $CO_2$  in acetonitrile/water/triethylamine) [60]. The following example of a catalytic system that performs the photoreduction of  $CO_2$  to  $CO$  under visible light irradiation is composed of two reactions (two-electron water-splitting and  $CO_2$ -splitting):



This reaction has a free energy  $\Delta G^0 = 56.6 \text{ kJ/mol}$  and a standard redox potential  $\Delta E^0 = 1.23 \text{ V}$ .



This reaction has a free energy  $\Delta G^0 = 61.4 \text{ kJ/mol}$  and a standard redox potential  $\Delta E^0 = 1.33 \text{ V}$ .

Here, the triethylamine donates electrons to  $Ru(2,2' - bipyridine)_3^{2+}/Co^{2+}$ . The quantity of Syngas produced and the selectivity ratio  $CO/H_2$  depend strongly on the composition of the system. Also, the addition of free pyridine strongly decreases  $CO$  generation but increases  $H_2$  production [60]. Such a technique usually lacks a performing catalyst characteristic of the photocathode. Besides, three-dimensional p-n heterojunctions like C/N-doped of  $Znx:COy@Cu$  can successfully be used as photocathodes in the PEC reduction mechanism while producing paraffin. Such materials integrate heterojunctions formed by semiconductors of p-type such as  $Co_3O_4$  and n-type like  $ZnO$  on  $Cu$  foam. These heterojunctions exhibit multiple active sites which have excellent C-C control during the reduction of  $CO_2$  [61]. Wang et al. [61] concluded in a study that the best catalyst was  $Zn_{0.2}:Co_1@Cu$ . Indeed, the paraffin was produced at a rate of  $325 \mu\text{g}\cdot\text{h}^{-1}$  and  $O_2$  was released at a rate of  $41 \mu\text{mol}\cdot\text{h}^{-1}$  under  $-0.4 \text{ V}$  compared to the saturated calomel electrode in the absence of the release of  $H_2$ . The apparent quantum efficiency of  $Zn_{0.2}:Co_1@Cu$  reaches 1.95%. However, Pan et al. [62] developed a novel photoelectrocatalytic catalyst by modifying a copper catalyst with flower-like cerium oxide nanoparticles ( $CeO_2$  NPs as n-type semiconductor) and copper oxide nanoparticles ( $CuO$  NPs as p-type semiconductor) for the reduction of  $CO_2$  to methanol. The rate of methanol production was  $3.44 \mu\text{mol cm}^{-2} \text{ h}^{-1}$  at an applied potential of  $-1.0 \text{ V}$  (vs. SCE) under visible light irradiation. This rate of methanol production was around five times higher than that produced by using a  $CuO$  NPs/ $Cu$  catalyst. Zhang et al. [63] investigated the hydrophilic-hydrophobic  $Cu-SnO_2/ZIF-8$  composite catalyst to resolve the problem of poor solubility and the intense competition of the reaction to generate hydrogen, which can considerably restrict the activation of  $CO_2$ . They concluded that when the overpotential was around 364 mV, the Faraday efficiency of formic acid reached about 69%, and the maximum current density reached  $12.8 \text{ mA cm}^{-2}$  at  $-1.4 \text{ V}$  versus the  $Ag/AgCl$  electrode.  $ZIF-8$  promoted electron transfer, while  $Cu-SnO_2$  provided additional active sites.

#### 4. $CO_2$ as a Renewable Source of Energy via Biogas Products

Although green plants that perform photosynthesis are less efficient transducers of solar energy compared to an array of solar cells, they gained importance in the last decade because they are cheap and can develop with a judicious supply of water, nutrients, and in the presence of  $CO_2$  that they transform into stable organic compounds. Also, due to the excessive emission of greenhouse gases, governments worldwide decided, in previous world summits (Montreal, Kyoto, Madrid, Rio,

Paris, etc.), to diversify the range of fuels in use by 2050. Such a policy is based on biomass conversion. The reasons why biofuels should be selected for this purpose are as follows:

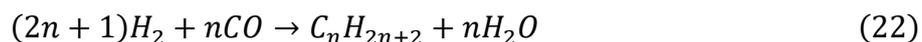
- They are simple
- They can be prepared with well-known agriculture methods
- They can mitigate global warming without changing the old energy conversion systems
- They can be used in complicated engines like conventional turbofans (used in aerospace) [64, 65]
- The regulation of practices worldwide through directives and normalizations
- They are available throughout the year, are inexpensive, and are distributed uniformly worldwide, unlike oil, coal, and gas
- They can bring about improvement of rural areas and easily generate employment

Biofuels are liquid, gas, and solid fuels that are produced based on a wide variety of techniques and mechanisms from biomass. They include bioethanol, biomethanol, biodiesel, vegetable oils, biogas, bio-syngas bio-oil, biochar (obtained after biomass pyrolysis), Fischer-Tropsch (FT) liquids, and biohydrogen (produced by gasification). Gasification is a thermal process that can be conducted using the framework of char gasification (during which the char is prepared by pyrolysis before gasification) or by the continuous pyro-gasification of biomass in a macro-TG. Countries and organizations that have adopted an energy policy based on biofuels showed a high economic growth during the 21<sup>st</sup> century [66].

Biogas can be produced from lignocellulosic biomass by two processes. The first process requires microbial fermentation, where polysaccharides are converted to alcohols, specifically, to bioethanol or biomethanol [67-69]. In the second process, raw plant biomass is converted via anaerobic fermentation to biomethane [70, 71]. However, the latter process is slow due to the low availability of energy to microorganisms, which limits the amount of methane formed [72]. However, even small-scale devices along with agriculture residues and human wastes that are converted to methane could significantly improve the living conditions of rural/urban communities [73, 74].

The second process for biogas production is based on the thermochemical conversion of lignocellulosic biomass into a synthesis gas characterized by a high HHV called Syngas, which is a mixture of CO, H<sub>2</sub>, and C<sub>n</sub>H<sub>m</sub> mainly composed of CH<sub>4</sub>. Along with Syngas, various liquids composed of bio-oils and tars are also generated [75-80]. Hence, in this method of Syngas production, a large amount of CO<sub>2</sub> is used as a gasifier mixed or not with dry and heated water steam (at about 180°C) during the char gasification [75-77, 80]. The formation of methane from CO<sub>2</sub> has been reported in previous studies [81]. The catalytic reduction of CO<sub>2</sub> to methanol or methane using renewable energy (mainly solar as mentioned above) is considered to be a viable alternative, as the process can minimize the cost and depletion of fossil fuels. Thus, the next processes should involve the Fischer-Tropsch (F-T) process (established during World War II to replace oil). Such a process allows the conversion of biomass to Syngas that can be converted into fuels or chemicals when using coal at a H/C ratio of 0.8 to 1 [82]:





Furthermore, biomass is more reactive than coal, and it is gasified at a temperature between 550 and 1,500 °C with different heating rates depending on whether biogas, bio-oils, or biochar needs to be produced. The process can be slow, rapid, or instantaneous. The process can occur at atmospheric pressure or under high pressure ranging between 4 and 30 bars [83, 84].

The installations used for Syngas production via biomass gasification are called Macro-TG. They consist of an electrically heated furnace and either a manual or an automatic system, which allows the samples to be placed inside the furnace at a certain time [80, 85-87]. Plasma technology can be used to achieve the same goal. The temperature-induced by the electric arc in hydrogen plasma is high (~1,500 °C), resulting in the production of syngas (CO and H<sub>2</sub>) with a conversion rate of about 100% [85-87]. The efficiency of generating electricity and hydrogen-based on hydrogen plasma and carbon fuel cell technology varies between 87% and 92%, which is more than twice that of the installations fed with coal and based on conventional steam. Moreover, the reduction of CO<sub>2</sub> using plasma technology is about 75% per unit of electricity [88, 89].

The F-T process mainly produces aliphatic hydrocarbon chains, and thus, it has gained attention for the production of transportation fuels and chemicals. Such a technique has many advantages as it can produce fuels of different molecular lengths (typically < 15 C) from any carbonaceous feedstock (coal, natural gas, etc.) [90]. The synthetic fuels produced by F-T have several advantages:

- They can be used in the existing transportation systems
- They are compatible with the existing vehicles
- They can be mixed with the available derivatives of petroleum [91].
- FT diesel is of high quality, has a very high cetane number, and is free of sulfur, nitrogen, aromatics, and other contaminants found in petroleum products.

However, F-T has a high cost of investment and low energy efficiency compared to the energy efficiency of alternative fuels [92].

## 5. Conclusion

A disequilibrium exists among the natural reservoirs (atmosphere, thermocline, and the deep sea) of CO<sub>2</sub>. In this study, the conversion of CO<sub>2</sub> from a harmful gas to a beneficial source of energy and matter was shown. CO<sub>2</sub> can be used in the food industry in soft drinks and for deep freezing. R744 can be used as a refrigerant in the future. Lackner tree and the dissolution of CO<sub>2</sub> in basic baths using aqueous ammonia could be investigated as suitable processes to capture CO<sub>2</sub>. Urea, commercially known as carbamide, could be widely and easily produced either by the reaction between CO<sub>2</sub> and ammonia or by the reaction of hydrogen (generated by biomass gasification) with nitrogen after its separation from atmospheric oxygen via a cryogenic process. Microalgae have recently received much attention as they can capture CO<sub>2</sub> and utilize it in renewable energy. They have several advantages over the use of other plant feedstock, including (1) high photosynthetic conversion, (2) rapid production, (3) a high capacity to produce a wide variety of biofuel feedstock, (4) high capability for environmental bioremediation, such as CO<sub>2</sub> fixation from the atmosphere/flue gas and water purification, and (5) no competition for land with crops or other food sources. Nickel-based catalysts are commonly used for the DRM process due to their low cost but are prone to deactivation at high temperatures; hence, bimetallic catalysts were introduced. The synergetic effect of two metals enhances the activity of the catalyst. Ni-Co bimetallic catalysts have been

investigated intensely for the DRM process. Several supports such as Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, MgO, SiO<sub>2</sub>, YSZ, SBA15, etc., have been investigated under the DRM process, and Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and SBA15 have been found to perform well. Moreover, water thermolysis can be coupled with CO<sub>2</sub> through a direct air capture (DAC) method to produce CO<sub>2</sub>, H<sub>2</sub>, O<sub>2</sub>, and electricity. Additionally, it is feasible to produce solar Syngas from H<sub>2</sub>O and CO<sub>2</sub> when using a two-step thermochemical cycle based on the cerium oxide redox reaction. Catalytic systems that perform the photoreduction of CO<sub>2</sub> to CO under visible light irradiation consist of two reactions (the two-electron water-splitting reaction and the CO<sub>2</sub>-splitting reaction). Finally, CO<sub>2</sub> acts as a good gasifier during biomass gasification for the production of Syngas.

### Author Contributions

The author did all the research work of this study.

### Competing Interests

The author has declared that no competing interests exist.

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