

Chapter 13

Progresses in Bioenergy Generation from CO₂: Mitigating the Climate Change



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13.1 Introduction

These days, the interest in the clean energy generation has been quickly expanded as a direct result of the monetary development around the world. To fulfill this developing need, a bounteous measure of non-renewable energy sources is required (Giri et al. 2020; Leung et al. 2014). The depletion of non-renewable energy sources is frequently considered as one of the dangers to nature in context of the carbon dioxide (CO₂) discharge. CO₂ is primary green house gas (GHG), present on the land surface, sea, and environment where animals, plants, and microorganisms, assimilates and produces it every day (Kapoor et al. 2020; Spigarelli and Kawatra 2013). Notwithstanding, the pattern of discharging and expending CO₂ must be adjusted essentially. To diminish the GHGs, CO₂ sequestration and conversion capacity has increased to a great extent. In any case, we must develop the techniques and measures for capturing the CO₂ as a feedstock. In this way, using CO₂ and converting it into synthetic substances, will be useful to mitigate the CO₂ emission (Peters et al. 2009). During the recent years, the transformation of CO₂ into value-added synthetic compounds utilizing various methods are getting an incredible consideration from the researchers as it results in reducing the harmful GHGs (Kumar et al. 2019; Sharma

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et al. 2020a, b). So, we need to find alternatives that uses the CO₂ present in the atmosphere and converts it into valuable products (Sharma and Kumar 2021). Methanol is one of the important product that can be made from CO₂. Methanol does not emit extra CO₂ into the atmosphere, and it has high volumetric and gravimetric energy density and is a very important fuel that is replacing the use of fossil fuels (Patterson et al. 2019). Its prime benefit is to reduce greenhouse gas emissions from vehicles. It has the highest hydrogen to carbon ratio in comparison with any liquid fuel and can be readily degraded in both aerobic and anaerobic environments. Methanol has the potential to reduce carbon emissions by 65–95%. It is highly versatile in making everyday products, and it is efficiently combustible, easily distributed, and widely available, making it affordable to use. Out of the total energy consumption of the world, 49% of it is met by fuels like gasoline, diesel, jetoils, etc. (Lewis and Nocera 2006). As compared to conventional fuels, its benefits are high as compared to gasoline and diesel. Recently, indeed, the various industries across the globe are using methanol as a crude material for making various items. Methanol is utilized in the production of solvents such as the acids. It can also be utilized in direct methanol powered devices which are utilized for the transformation reactions in the industries (Fig. 13.1). Methanol is viewed as the significant natural feedstocks that are utilized in businesses with a yearly production of 65 million tons around the world (Dalena et al. 2018). Various aspects of conversion of carbon dioxide to bioenergy based

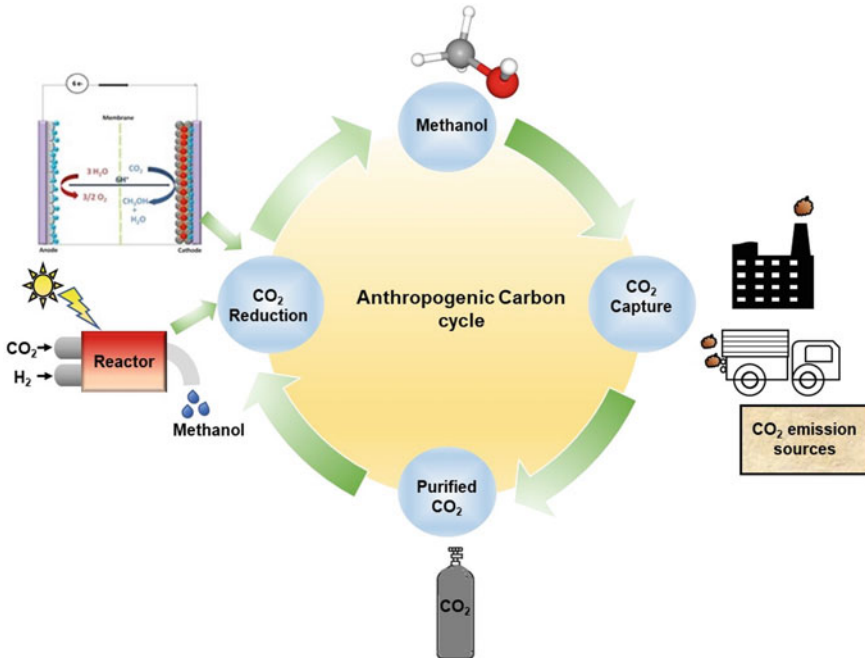


Fig. 13.1 Description of the anthropogenic carbon cycle for the production of methanol

products such as methanol and fixation of CO₂ using microbes and other biological entities have been discussed in this chapter.

13.2 Conversion of CO₂ into Methanol by Chemical Methods

The methanol production from direct hydrogenation of CO₂ is an attractive strategy, as this process has several advantages such as it requires less energy for product purification and fewer by-products formation. CO₂ can be valorized through hydrogenation, focusing on reverse water–gas shift reaction (RWGS), methanation, and methanol production (Gutterød et al. 2020). In literature, various metal organic frameworks have been reported for the CO₂ capture, and they have great potential to convert the atmospheric CO₂ in heterogeneous catalytic system. The methanol synthesis from CO₂ hydrogenation and RWGS is a thermodynamically limited reaction, and equilibrium conversion of CO₂ decreases with increasing reaction temperature; therefore, it needs a catalytic system (Kaisar and Sreedevi 2018). Methanol is also prepared by the hydrogenation of carbon dioxide by reverse water–gas shift reaction. The catalyst used is Ni/Al₁₂O₁₉, and this process is largely used in an industrial scale (Samimi and Rahimpour 2019). Lately, it has been observed that indium oxide is a highly selective catalyst in the thermal hydrogenation of CO₂ to methanol, and hydrogenation of CO₂ to methanol is being carried out commercially using heterogeneous CuZnO supported on Al₂O₃ (Chun 2020). Methanol formed by carbon dioxide via catalytic CO₂ hydrogenation is efficient for storing energy and CO₂ capture. Methanol thus formed has a neutral carbon footprint and is a clean source of energy.

In the European Union, a pilot plant was built by the MefCO₂ project that produces 500 tons of methanol per year (Bowker 2019). In Iceland, CRI has a commercial plant that has 4000 metric tons per year of methanol production capacity. They utilize this renewable methanol for bio-diesel production, automobiles, and the production of synthetic material (Olah 2013). Nonetheless, the heterogeneous catalyst has numerous focal points regarding partition, strength, taking care of, cost, and reusing of the catalyst.

13.2.1 Heterogeneous Catalytic Method

Heterogeneous catalysts for conversion of CO₂ to methanol are widely used for the industrial purposes. It generally involves the rapid separation of fluid from the solid catalyst, and the catalyst that is used can be again produced (Table 13.1). Among heterogeneous catalysts, Cu/ZnO/ZrO₂ have been mostly studied due to their high selectivity and conversion rate. In this catalyst, ZnO increases the Cu dispersion and

Table 13.1 Various methods for conversion of CO₂ into methanol

S. No.	Methods	Catalysts/Photocatalysts/Electrode	Comments	References
1	Heterogenous	Cu ZnO ZrO ₂	High selectivity and conversion rate	Zhong et al. (2020)
2	Homogenous	Ru ₃ (CO) ₁₂ Mo(CO) ₆ Rh(CO) ₁₂ CO ₂ (CO) ₈	Involves rapid separation of methanol and recycling of catalyst.	Kothandaraman et al. (2016)
3	Electrochemical	Cu Fe Mo Pt Hg	Cu is considered as a more promising electrode, utilized in conversion of CO ₂ into methanol and other value-added products	Albo et al. (2015)
4	Photochemical	CdS/TiO ₂ Bi ₂ S ₃ /TiO ₂	Reduction of CO ₂ into methanol using visible light	Gondal et al. (2013)

both ZnO and ZrO₂ improve the stability and CO₂ absorption capacity. The incorporation of metal oxides such as Ga₂O₃, Al₂O₃, MgO, SiO₂, and La₂O₃ enhances the activity and modifies the redox properties (Zhong et al. 2020). Various companies such as Sinetix, HaldorTopsoe, and Mitsubishi Gas Chemical are producing a highly stable catalyst for the production of methanol (Al-Saydeh and Zaidi 2018).

13.2.2 Homogenous Catalytic Method

Different types of homogeneous catalysts are also being used for the conversion of CO₂ into valuable compounds (Table 13.1). The catalysts for CO₂ conversion are available in the form of metal complexes, organic solvents, and ionic solvents (Zarandi et al. 2019). Referring to different studies, it has been observed that some basic heterocyclic organic compounds like pyrimidine elevate the CO₂ reduction

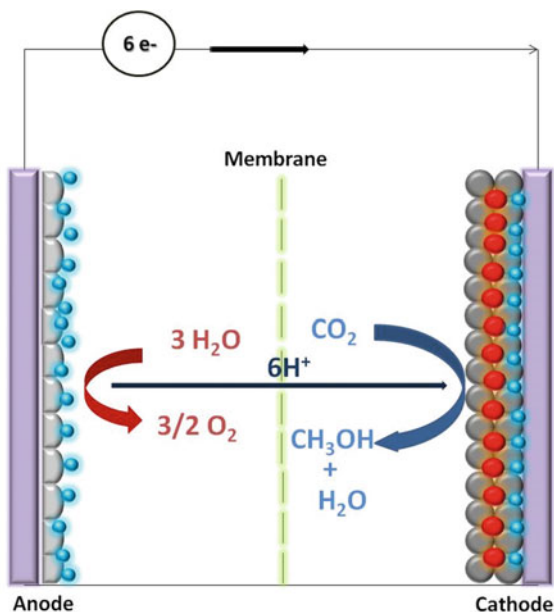
reaction and its conversion as compared to other heterogeneous catalysts. Recently, it is observed that basic heterocyclic organic compounds like pyrimidine increase the reduction reaction of CO₂ conversion as compared to other homogeneous catalysts (Albo et al. 2015). A distinctive heterogeneous catalyst was tried for immediate CO₂ conversion into methanol. In a previous study, Ru₃(CO)₁₂ catalyst in the presence of potassium iodide was studied for the hydrogenation of CO₂ to CH₃, CH₄, and methanol (Tominaga et al. 1993). Furthermore, it was reported that Ru₃(CO)₁₂KI was better for CO₂ conversion than another metal carbonyl including Fe₂(CO)₉, Mo(Co)₆, Rh₄(CO)₁₂, W(CO)₆ and Co₂(CO)₈ (Huff and Sanford 2011; Tominaga et al. 1993). Kothandaraman et al. (2016) firstly captured CO₂ directly from the air and converted it into methanol. In this process, Ru-based catalyst and polyamine were used for methanol production. After CO₂ conversion, methanol was separated and the catalyst was recycled to produce more methanol.

13.2.3 *Electrochemical Reduction of CO₂ to Methanol*

The electrochemical reduction method attracted the interest of the researcher which is eco-friendly and has economic benefits. This process is simple and can be used under ambient conditions (Zarandi et al. 2019). The electrochemical strategy is utilized for CO₂ conversion to important synthetic compounds, for example, methanol by utilizing electricity as the energy source. In this method, electric energy is applied to create a potential between two electrodes to transform CO₂ into reduced form (Yaashikaa et al. 2019). Reduced chemical species are obtained after the electrocatalytic CO₂ reduction reaction (Fig. 13.2). The electrolytes used in these reactions affect the reduction of CO₂. Solvents used also play a key role in maintaining pH, conductivity, and toxicity. Various experiments have been reported for CO₂ conversion on the terminals of metal (Kuhl et al. 2014). Various metal electrodes such as copper, ruthenium, molybdenum, titanium, iron, mercury, and platinum have been studied for electrochemical reduction of CO₂, but among them, copper (Cu) is one of the most promising electrodes (Albo et al. 2015).

The hydrogen evolution reaction (HER) is significant in the CO₂ electrocatalyst reduction in which water presents as an electrolyte. Consequently, the reported metals that have been utilized as electrocatalyst in CO₂ reduction should have moderately greater HER (Goepfert et al. 2014). In a previous study, it was found that methanol production rate was $1.2 \times 10^{-4} \text{ molm}^{-2} \text{ s}^{-1}$ on electrodeposited cuprous thin-film electrodes in potassium carbonate solution (Le et al. 2011). Moreover, MoS₂-rods/TiO₂ nanotubes electrodes were reported for electrochemical CO₂ reduction and found that CH₃OH yield reached 202.2 mgL⁻¹ at 6 h (Li et al. 2014). Qu et al. (2005) reported the RuO₂/TiO₂ nanotubes and nanoparticles for the methanol production and showed 60.5% CO₂ conversion efficiency. Wu et al. (2019) revealed that when a cobalt phthalocyanine was dispersed on carbon nanotubes, it has high selectivity and catalytic activity for the electrochemical CO₂ reduction to methanol. Modification is done in electrocatalysts to increase the reduction efficiency and increase

Fig. 13.2 Schematic representation of electrochemical system for the conversion of CO₂ into methanol



the faradaic efficiency. Recently, the catalysts are being modified and designed to control the dimensions of nanoparticles showing a mono-dispersive configuration (Zarandi et al. 2019). In most recent years, electrochemical CO₂ transformation is broadly utilized in a research field; however, it has not been effectively utilized in mechanical procedures.

13.2.4 Photochemical Reduction of CO₂ to Methanol

Normally, this CO₂ transformation technique is utilized to convert captured CO₂ to methanol and other value-added products by utilizing sunlight, (Fan et al. 2013) (Table 13.1). Nowadays, this technique has attracted the interest of people and is being considered as one of the most appealing strategies for the utilization of CO₂. The photocatalytic CO₂ transformation process is a blend of photochemical and photophysical procedures together (Gondal et al. 2013). Although this strategy has a few resemblances with electrolytic CO₂ reduction in both these methods, molecular catalyst is used. Various experiments have shown the ability of metal oxides and semiconductors such as titanium dioxide, silicon carbide, zinc oxide, and tungsten trioxide, for the conversion of CO₂ to methanol (Zhang et al. 2019). Li et al. (2012) proved that CdS/TiO₂ and Bi₂S₃/TiO₂ are promising photocatalysts to reduce CO₂ into methanol using visible light. The methanol production efficiency of TNTs-Bi₂S₃ and TNTs-Bi₂S₃ was 224.6 μmol/L and 159.5 μmol/L, respectively. In another study, the ability of Nd/TiO₂ synthesized by the sol-gel method was studied, and they found

that the maximum methanol production yield was 184.8 $\mu\text{mol/g}$ for 8 h (Luo et al. 2009). The main drawback of CO₂ reduction to methanol using the photochemical method is that the reaction is reversible. Thus, to alleviate the methanol oxidation, it is important to find new methods so it can be applied to the industrial level too.

13.2.5 MOF for CO₂ Reduction

Various classes of a porous material including zeolites, porous organic polymers, porous carbons, covalent organic frameworks (COFs), and metal–organic frameworks (MOFs) have been reported for CO₂ capture (Ding et al. 2019). Recently, MOFs are emerging out as a new class of crystalline materials due to their unique features such as large surface area, crystalline nature, handy pore structure, and chemical tunability (Fig. 13.3) (Maina et al. 2017). Debatin et al. (2010) synthesized zinc-imidazolate-4-amide-5-imidate framework, and CO₂ uptake capacity of these MOF was found to be 2.1 mmol g⁻¹ at 1 bar and 298 K. Furthermore, MOFs incorporated with nanoparticles, metal oxides, and other catalytically active species have also been studied for CO₂ conversion. As an example, Ag NPs were impregnated into the cavities of MIL-101 by a liquid impregnation–reduction method. The resultant Ag@MIL-101 materials had excellent catalytic activity (96.5%) and stability

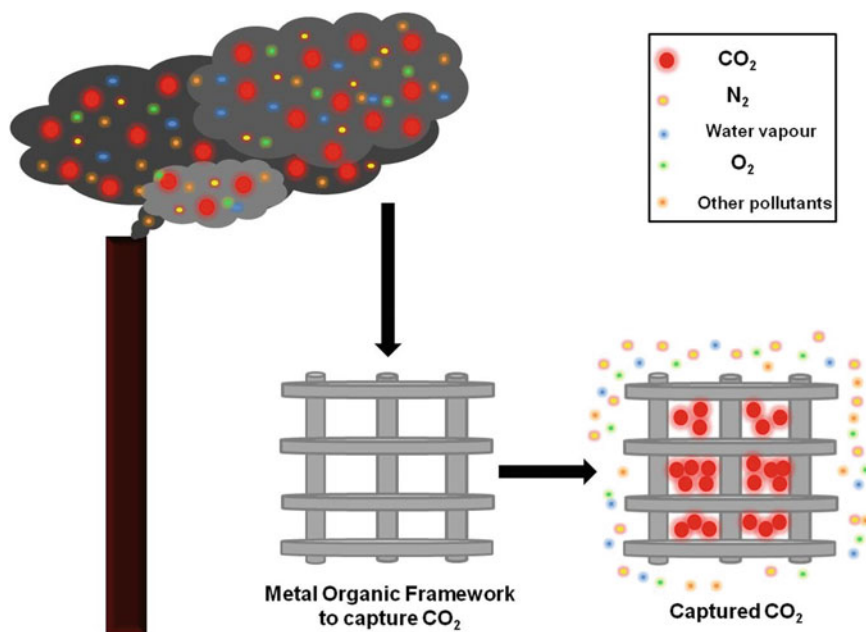


Fig. 13.3 Metal organic framework (MOF) for the CO₂ capture and conversion

at 50 °C (Liu et al. 2015 Sharma et al. 2018). Gutterød et al. (2020) studied the role of the platinum nanoparticles impregnated in ZR-based UiO-67 MOF in the hydrogenation of CO₂ into methanol using a kinetic analysis. In the resultant MOF, methanol was formed at the interface of platinum nanoparticles and linker-deficient Zr₆O₈ nodes.

13.3 Use of Biological Systems for CO₂ Capture and Utilization

Various photosynthetic microbes such as algae and bacteria can assimilate CO₂ (Table 13.2). Moreover, some of the autotrophic bacteria were also studied for utilizing CO₂. The most important advantage of microbial CO₂ conversion is the natural ability of microbes to take up CO₂ through their metabolic pathways. The CO₂ fixing routes have been developed through enzymatic processing of CO₂ by formulating C–H, C–O, and C–C bonds cleavage (Ramsey et al. 2009). The most commonly used pathways for CO₂ reduction are pentose phosphate, citric acid cycle (Peters et al. 2011). Furthermore, various microbial enzymes have been utilized for the conversion of CO₂. The direct use of microbes is affected by environmental factors, low product yield, and growth. In this context, protein engineering and synthetic biology are ideal methods for engineering the microbes, and thus making the process economically viable.

Table 13.2 Biological agents involved in conversion of CO₂

Class	Species	Comments	References
Algae	<i>Nannachloris</i> sp <i>Chlorella vulgaris</i> <i>Chlamydomonas reinhardtii</i> <i>Scenedesmus quadricauda</i>	High photosynthesis rate Rapid reproduction rate	Pavlik et al. (2017); Sharma et al. (2020a, b)
Bacteria	<i>Clostridium acetivum</i> <i>Clostridium kluyveri</i> <i>Clostridium ljungdahli</i> <i>Acetobacterium kloodii</i>	<i>Clostridium</i> is considered best for CO ₂ fixation and having numerous biotechnological applications Assorted pathway for creation of metabolites Resistance to poisonous metabolites and substrates	Jajesniak et al. 2014
Yeast	<i>Saccharomyces cerevisiae</i>	Involved in CO ₂ fixation	Zelle et al. 2008

13.3.1 Algae for CO₂ Fixation

Algae are present throughout the world and one of the most commonly researched organisms for CO₂ fixation. Algae can be found in freshwater–water or marine ecosystems individually or in a form of chains. They lack stems, leaves, or roots and have a vast range of sizes. CO₂ is utilized as a carbon source by them for photoautotrophic growth and produces over half of the atmospheric oxygen (Shi and Theg 2013). As algae use the CO₂ by the Calvin–Benson pathway and convert the inorganic carbon to organic compounds. One molecule of phosphoglycerate is diverted to focal on pathways of metabolic activity, while the other is used in the continuation of the cycle. The key enzyme for carboxylation of CO₂ is RuBisCO, and it has a high affinity for CO₂ and O₂. So, it creates a problem in an environment because of the high O₂ affinity and low fixations present in the atmosphere. Algae possess three significant constituents of CCM including dynamic bicarbonate take-up transporters, a set of carbonic anhydrases (CAs), and a subcellular small-scale compartment inside which most of RuBisCO is found. Furthermore, micro and macroalgae can fix inorganic carbon effectively. Various algal species, such as *Nannochlorissp.*, *Scenedesmus quadricauda*, *Chlorella vulgaris*, *Nannochloropsis sp.*, and *Chlamydomonas reinhardtii*, have been studied to CO₂ fixation (Pavlik et al. 2017). Microalgae have a high photosynthesis rate due to their small size, rapid reproduction rate, and synthesis of oil, pigment, etc., because of its complex metabolic reactions. Hence, making microalgae is highly efficient for converting carbon dioxide (Yen et al. 2013). *Chlamydomonas reinhardtii* and *Volvox carteri* have been genetically engineered for increasing the CO₂ fixation efficiency (Beer et al. 2009; Walker et al. 2005). To improve the CO₂ fixation efficiency of algae species, screening and domestication would be major promising strategies.

13.3.2 Bacteria for CO₂ Fixation

Various carbon-capturing bacteria are *Acetobacterium woodii*, *Clostridium aceticum*, *Clostridium kluyveri*, *Clostridium ljungdahlii*, *Rhodopseudomonas palustris*, *Rhodococcus erythropolis*, *Ralstonia eutropha*, *Syneccoccus elongatus*, *Rhodobacter sphaeroides*, etc. (Jajesniak et al. 2014). Among various bacteria reported for CO₂ fixation, *Clostridium* fixes CO₂ using the Wood–Ljungdahl pathway. They are anaerobic and gram-positive microbes, but their cultivation is difficult and expensive because of its obligate nature (Tracy et al. 2012). Numerous strains in the *Clostridium* class can fix CO₂, as a carbon source. *Clostridia* shows numerous attractive attributes for biotechnological applications such as the capacity to use a wide range of carbon substrates, assorted pathways for the creation of helpful metabolites, and resistance to poisonous metabolites and substrates (Durre and Eikmanns 2015). Typical environmental condition is normally deadly to most of its species.

Early work with *Clostridium* concentrated mostly on the creation of acidic corrosive and related items. In any case, the collection of hereditary material relevant to *Clostridia* has altogether extended after the improvement of plasmid DNA innovations and chromosomal control advances. The utilization of the portable gathering II introns for focused quality disturbance (Targetron or ClosTron) is well known for the hereditary building of *Clostridium*. The utilization of ClosTron was shown by designing *Clostridium acetobutylicum* for butanol–ethanol formation (Cooksley et al. 2012). Moreover, in the cyanobacterium *Synochococcus elongates* the carbon assimilation mechanism was studied, and it produces 2,3-butanediol from CO₂ and glucose in dark (Kanno et al. 2017). Furthermore, the various microbial enzymes has been used for the conversion of CO₂. Formate dehydrogenase enzyme is a good biological catalyst known for its reversible reduction of CO₂ (Ruiz-Valencia et al. 2020). Another enzyme used for the conversion of CO₂ is carbonic anhydrase. It is present in various organisms like eubacteria, vertebrates, algae, archaea, plants, and animals (Moroney and Ynalvez 2007; Sharma and Kumar 2020). This enzyme is efficient in capturing CO₂ in a cost-effective and eco-friendly manner as raw materials such as metal oxide ores, industrial waste, and marble mines are easily available (Bhagat et al. 2018). In recent study, carbonic anhydrase immobilized onto electrospun nanofiber is used for the conversion of CO₂ into bicarbonates, and the bicarbonate solution formed was utilized for microalgae growth (Jun et al. 2020). Moreover, an organic procedure for CH₄ formation from CO₂ is named as biogenic methane. Nitrogenase is an ATP-dependent enzyme that carries out the multi-electron reduction of an inert molecule. Fixen et al. (2016) expressed nitrogenase enzyme in an anoxygenic phototroph of *Rhodospseudomonas palustris* and found that it is capable of CO₂ reduction to methane in the presence of light under in vivo condition.

In another study, Zhang et al. (2013) expressed phosphoribulokinase (PRK) with ribulose-1,5-bisphosphate carboxylase/oxygenase (RuBisCO) in *E. coli* and converted CO₂ into a fermentation product. Microbes can be used as biocatalysts for converting CO₂ into useful products. They can be used in microbial electrochemical technologies using these biocatalysts in electrochemical cells to supply or gain electrons from various biochemical reactions that utilize CO₂ as a carbon source for the production of fuels and other products. Worldwide attempts are being made to convert methane into methanol using CO₂ as a source; due to the increase in production of methanol, its price is also decreasing and has got equal to the price of glucose (Antoniewicz 2019).

13.3.3 Yeast for CO₂ Fixation

As compared to *E. coli*, *Saccharomyces cerevisiae* has pulled in less consideration as a potential answer for anthropogenic CO₂ emanation (Guadalupe-Medina et al. 2013). To acquire a critical number of useful RuBisCO units, co-articulation of *E. coli* protein collapsing chaperones GroEL and GroES was essential. The created framework was described by a 90% decrease in the side effect glycerol development

and a 10% expansion in ethanol production, for a sugar-constrained culture (Natlesh et al. 2018). Another pertinent model is the improved creation of malic corrosive in *S. cerevisiae* by building a CO₂ focusing pathway that returns through the carboxylation of pyruvate (Zelle et al. 2008).

13.4 Bio-based Products from CO₂

13.4.1 Bioplastics

Many bacteria are capable of converting CO₂ into eco-friendly plastic, i.e. polyhydroxybutyrate (PHB) using sunlight. PHB is a biodegradable as well as biocompatible, thermoplastic as comparable to petrochemically inferred polypropylene (Markl et al. 2018). *Cupriavidus necator* is a gram-negative facultative hydrogen oxidizing bacterium; it produces single cell proteins and polyhydroxybutyrate (PHB) depending on the supply of nutrients. It can be converted into valuable products like crotonic acid and other fuels (Yu 2018). This bacterium was cultured on a mixture of gases like hydrogen, oxygen, and carbon dioxide. *C. necator* fixes CO₂ under aerobic conditions using the Calvin–Benson–Bassham cycle and has more CO₂ fixing capacity as compared to green algae. It grows on glucose and glycerol under aerobic conditions (Shimizu et al. 2015). There are certain pathways for converting inorganic CO₂ into its organic form. This has instigated an impressive enthusiasm for the business creation of this polymer. PHB is appropriate for use as nourishment bundling material taking into account its protection from water and UV radiation and its impermeability to O₂. Additionally, it is being applied in careful stitches. Significantly, PHB can be prepared to utilize previous advances and in blend with other manufactured polymers (Mozumder et al. 2015).

13.4.2 Bio-alcohol

The use of CO₂ to synthesize bio-alcohols have concentrated on ethanol using microbial genera such as *Rhodobacter spp.* The utilization of ethanol as a substitution for ordinary gas is tested by the fact that ethanol has short half life, low vitality, and is destructive to current motor and fuel foundation (Costa et al. 2015). Further, it promptly assimilates the water and weakening in the capacity tank. The natural synthesis of isopropanol is possible using microbial systems. Similarly, it can be used to esterify fat and oil for bio-diesel production, which diminishes its propensity to take the shape at decreasing temperatures.

13.4.3 *Bio-diesel*

Because of their high lipid contents and simplicity of development, the bio-diesel is used as non-inexhaustible oil-based fuel. Lipids, as triacylglycerides (TAGs), commonly provide the energy to the living cells. Once removed, the lipid can be changed into unsaturated fatty acid methyl esters (FAME) or bio-diesel through transesterification (Sharma et al. 2012; Sharma et al. 2019). The physical attributes of FAME are like those of fossil fuels. Critically, it is non-poisonous and also biodegradable. The utilization of bio-diesel as a low-mix part in the vehicle fuel does not require any progressions in the framework.

13.5 Conclusion

Carbon dioxide transformation is introducing both a chance and a test widely for the supportability of conditions. The fundamental systems of CO₂ mitigation should concentrate on the use of CO₂, reusing CO₂ with the sustainable methods. In this way, the change of CO₂ into synthetic products for example, methanol will expend an enormous conversion of captured CO₂ where the market size of methanol is possibly broad. Moreover, the synthesized methanol can be utilized rather than the non-renewable energy source, accordingly lessening the reliance on petroleum based derivative and contributing to the market development of CO₂ use. Thus, the various strategies for CO₂ transformation into methanol have been accounted in this chapter. This incorporates homogeneous/heterogeneous catalysts, electrochemical, and photochemical based methods. In any case, the superior in the CO₂ transformation procedure can be accomplished by utilizing a successful impetus. The poor item selectivity and the low/high response temperatures are viewed as the primary boundaries in the heterogeneous CO₂ conversion process. The above findings showed that among different strategies proposed for CO₂ transformation to methanol or to other value added products, the electrochemical cells are ideal over various other techniques. Also, photochemical procedures offer an appealing way to convert CO₂ to methanol utilizing sun-based energy. In future, more techniques should be discovered which use the principles of green chemistry and convert more CO₂ into methanol rather than emitting other hazardous by-products. The techniques should be cost effective and should be implanted on large scale in an environment friendly manner.

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