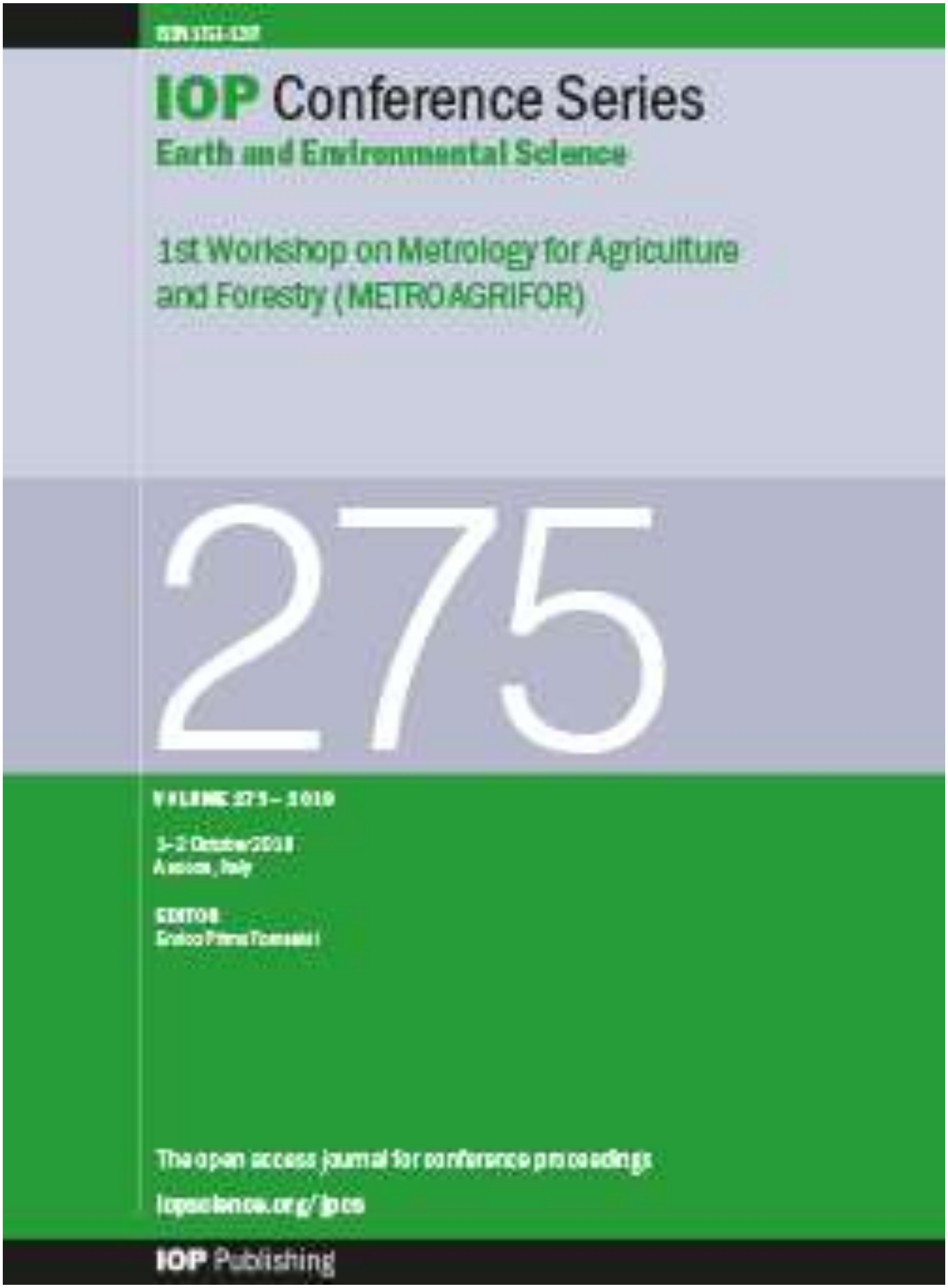

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# Perspectives in advance technologies/strategies for combating rising $CO_2$ levels in the atmosphere *via* $CO_2$ utilisation: A review

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# Perspectives in advance technologies/strategies for combating rising $CO_2$ levels in the atmosphere *via* $CO_2$ utilisation: A review

N Joshi[1,2], L Sivachandiran[1] *, A. A. Assadi[3]

[1]*LPCP, Dept. of Chemistry, SRM Institute of Science and Technology, Chennai, India.*
[2]*School of Chemical Sciences, Goa University, Taleigao Plateau 403206, Goa, India*
[3]*Laboratoire Sciences Chimiques de Rennes - équipe Chimie et Ingénierie des Procédés, UMR 6226 CNRS, ENSCR-11, allée de Beaulieu, CS 508307-35708 Rennes, France.*
E-mail : sivachal@srmist.edu.in (Dr.L. Sivachandiran)

*Keywords*: Carbon dioxide, Mitigation, Non-thermal plasma, $CO_2$ conversion, Dielectric barrier discharge (DBD), Value added products

## Abstract

This review provides exhaustive literature on carbon dioxide ($CO_2$) capture, storage and utilization. $CO_2$ is one of the greenhouse gas, emitted into the atmosphere and has reached an alarming level of well above 400 ppm. The consequences of rising $CO_2$ levels and global warming are visual in day today life such as floods, wildfires, droughts and irregular precipitation cycles. Several reviews, focused on a particular topic, have been published since the 19th century and recently. However, in this review, we have attempted to cover all the $CO_2$ mitigation techniques available for their advantages and disadvantages have been discussed. The blooming technology of carbon capture and storage (CCS) and the pros and cons of $CO_2$ capture, transportation and storage techniques are showcased. Interestingly the transportation of captured $CO_2$ to the potential storage sites requires more than 50% of the total energy budget, therefore, this review is dedicated to the onsite $CO_2$ conversion into value-added chemicals. Various technological advancements for $CO_2$ conversion into other products by the solar thermochemical, electrochemical and photochemical processes have been analysed. From the extensive literature, it's demonstrated that NTP (Non-Thermal Plasma) is one of the emerging techniques for the direct conversion of $CO_2$ into value-added products as it is energetically efficient. The mechanisms of $CO_2$ activation by thermal and NTP-catalysis have been discussed. Moreover, the benefits of DBD to obtain oxygenates like methanol, aldehydes, acids, and hydrocarbons from direct one-pot synthesis are discussed. The production of such value-added chemicals from $CO_2$ is of prime importance as it will be our step towards a carbon-neutral economy which is the need of the hour. This review has also attempted to compare the cost-effectiveness of current existing techniques for $CO_2$ capture and utilized solar to fuel efficiency to compare distinct technologies available for the utilization of $CO_2$ to value-added chemicals.

## 1. Introduction

Globally air pollution has gained immense attention among scientists. Especially air pollution its sources, and its impacts on human life were widely studied. The prime pollutants responsible for air pollution are VOCs (Volatiles Organics Compounds, $CO_2$, NOx, $SO_2$ and PM (Particulate Matter) etc. Notably, $CO_2$ is one of the GHG (greenhouse gases), which contributes to about 25% of global warming [1]. GHGs also have an impact on climate change because they trap heat in the atmosphere. GHGs, in particular, allow the sun's UV (ultra-violet) light to flow through the atmosphere unhindered and reach the earth's surface. IR (Infrared) radiation is reradiated back into the atmosphere, where it is absorbed by GHGs, and part of this energy is absorbed into the surface. When IR radiation contacts GHG molecules like $CO_2$, the bonds flex and vibrate, allowing the molecule to absorb part of the energy and then reradiate it *via* vibrations in all directions. This leads to the storage of heat and a phenomenon called global warming [2].

According to the IPCC (International Panel on Climate Change) AR5 report, for the decade of 2000 to 2010, GHG emissions grew on average of 1 Gt (Gigaton) carbon equivalent. The report states that GHG emissions reached an enormous amount in the year 2010 which was $49.0 \pm 4.5$ Gt $CO_2$ equivalent/year. Out of this amount, $CO_2$ itself constitute about $38.0 \pm 3.8$ Gt. In 2015-Dec, France hosted the 21st COP (Conference of Parties), where 195 countries signed an amendment to control their GHG emission. The main aim of this amendment is to control global temperature rise below 2 °C for the upcoming century. The 26th COP meeting was held in Glasgow in November 2021. In the past 6 years from the Paris agreement in COP 21, about a 76% drop in the number of new coal plants planned globally was observed. Furthermore, COP 26 also focussed majorly on the reduction of coal and driving the economy based from coal to renewable energy sources. As shown in Figure 1 India and China, are major contributors to $CO_2$ emission which lies at top of the tally table along with the USA. China has assured to move towards net-zero carbon emissions by the year 2030 whereas, India has committed to reaching net-zero carbon emissions by 2070. China and India are coal-driven economies and the transition would be slower and time-consuming. $CO_2$, apart from being a pollutant, is an important component in the carbon cycle and is a necessary ingredient in the life cycle of animals and plants. In the natural carbon cycle, 750 Gt of $CO_2$/year is recycled, out of which about 30-32 Gt of $CO_2$/year emission is contributed from anthropogenic sources [3]. There are increasing concerns about global warming and keen interest worldwide, in reducing the emissions of gases, particularly $CO_2$ [4].

Figure 1 shows the emission trends of various countries between 1990 and 2014. The $CO_2$ emissions tell a lot about the country's economic status. For instance in developing nations where the economy has just started to grow, more emissions of $CO_2$ are evidenced. Developing countries have significantly increased $CO_2$ emissions over the years. It is observed that, from 2010 to 2014, China emitted about 10.5 billion tons of $CO_2$ which is nearly three times more than the amount emitted by $EU_{28}$. GDP per capita is gross domestic product divided by midyear population and no wonder the GDP per capita has increased from 4550$ to 7679$. However, in India, the GDP per capita has increased from 18.70$ to 22.60$ which is small in comparison to China [5]. Several factors were correlated to $CO_2$ emission namely: colder winters, economic recession, growth per capita income, natural disasters like the volcanic eruption and occupation of the people (agriculture, industrial sector) and many other sources.

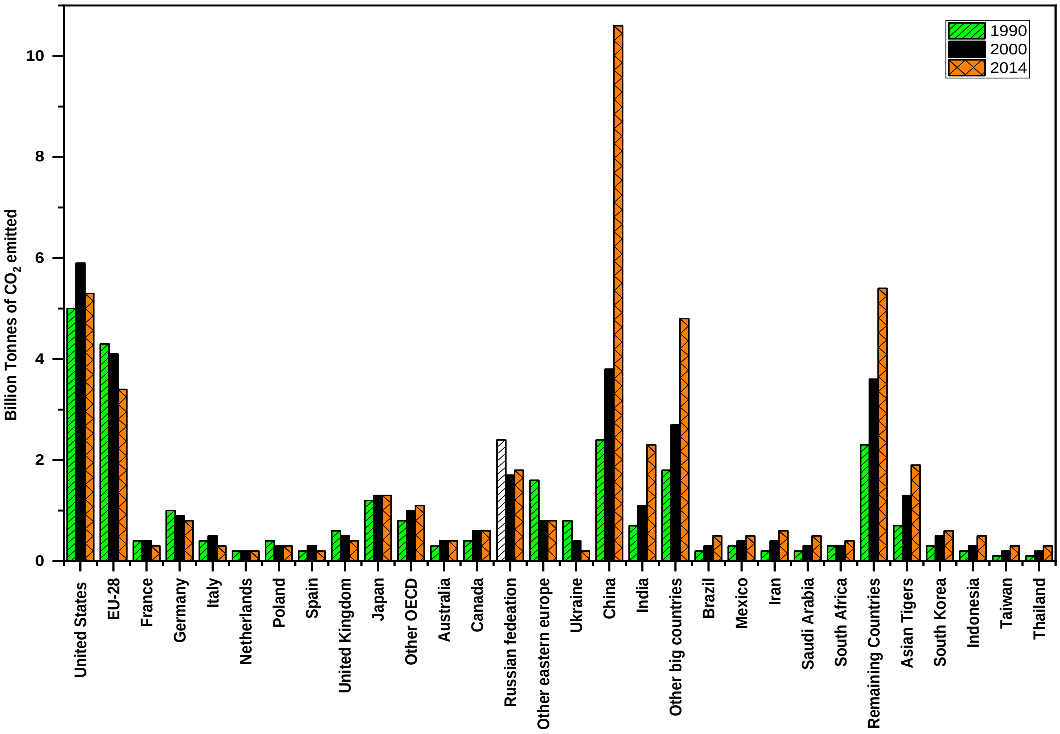


**Figure 1.** The amount of $CO_2$ emitted, over 3 decades, by various countries (Adapted from [6]).

Figure 2(a) & (b) shows the global major contributors to $CO_2$ emission and the composition of the pollutants emitted from fossil fuel combustion for the year 2010, respectively. About 49 ± 4.5 Gt $CO_2$ equivalent/year is emitted, out of which six major contributors are China 30%, the United States 15%, $EU_{28}$ 9%, India 7%, Russian Federation 5%, and Japan 4%. As shown in Figure 2(b), it is evidenced that fossil fuel combustion constitutes a majority of the emission with the following composition: $CO_2$ 73%, $CH_4$ 18%, $N_2O$ 7% and fluorinated gases 2%.

$$\boldsymbol{CO_{2(g)}} \rightarrow \boldsymbol{CO_{(g)}} + \boldsymbol{O_{(g)}} \qquad \Delta \boldsymbol{H^0} = +\mathbf{282.92}\,\frac{\boldsymbol{kJ}}{\boldsymbol{mol}} \qquad \text{Equation 1}$$

As reported in Equation 1, $CO_2$ is quite a stable molecule in the atmosphere because it is the most oxidized form of carbon and the enthalpy of dissociation is very high. At room temperature the $CO_2$ conversion is non-spontaneous, however, at high temperature (~1600 K) the dissociation is spontaneous [3,7].

It is observed that the $CO_2$ concentration ramped from 370 ppm (December 1999) to an alarming concentration of 408 ppm in January 2018, according to the NOAA (National Oceanic and Atmospheric Administration). The situation becomes even more threatening since, the IPCC report has predicted that if necessary policies, for $CO_2$ mitigation, are not implemented, then the year 2100 will witness about 600 ppm of $CO_2$ concentration [8]. The increase in $CO_2$ concentration increases the global temperature due to the radiative effect which leads to global warming of the atmosphere. It is reported that over the last 5000 years the temperature rise is about 4 °C to 7 °C [9,10]. The IPCC [11] and IEA (International Energy Agency) [12] reports together stressed reducing the global anthropogenic emission of $CO_2$ to a value well below 60 Gt of $CO_2$/year consequently curbing global raise in temperature by 6 °C in comparison to the preindustrial era [13].

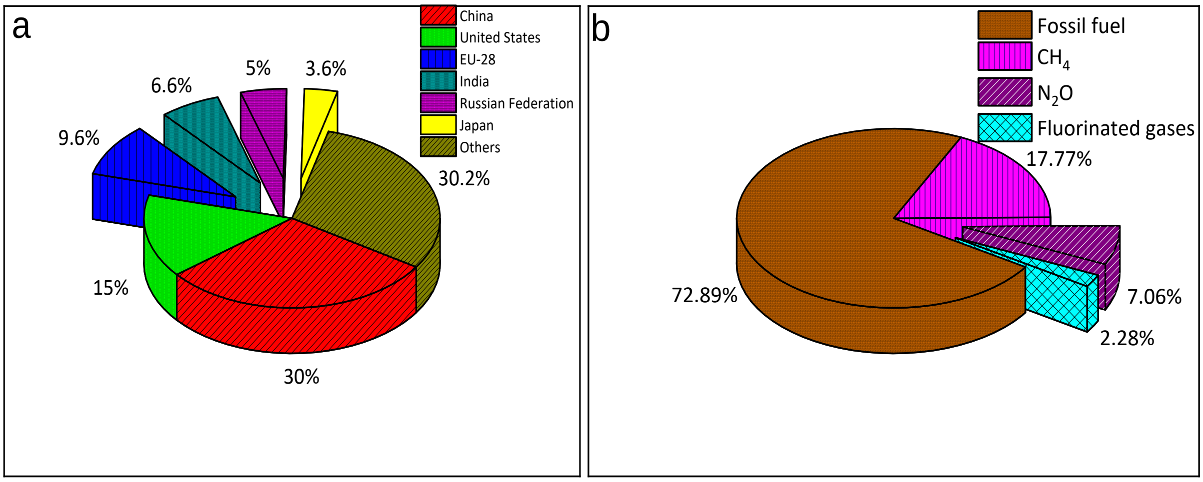


**Figure 2.** (a) Major contributors to $CO_2$ emission; (b) The composition of pollutants emitted by fossil fuel combustion in 2010 (Adapted from [6]).

### 1.1 Consequences of Rising $CO_2$ levels

Readers are well aware of the impact of $CO_2$ on human, plant and animal life. The rising levels of $CO_2$ lead to a rise in global temperature and thus lead to a rise in water levels across the globe. Especially plants which are the primary source of food for humans and animals are also affected. It is noteworthy to mention that the, rising $CO_2$ level increases the photosynthesis rate but negatively impacts plant physiology and growth, which alters the genetic pattern of plants. Since 1970, global surface temperatures have increased by roughly 0.6 °C (about 1 °F) and are now increasing at a pace of 0.29 °F per decade [14]. Due to rising $CO_2$ emissions, ocean acidification has increased by roughly 0.1 units, equal to about a 30% increase in hydronium ($H^+$) ion concentration, since pre-industrial times. The $CO_2$ is regularly exchanged between the atmosphere and the oceans, and as atmospheric $CO_2$ concentrations rise, the oceans absorb more $CO_2$. Increased acidification lowers the carbonate ion concentration in seawater, which has an impact on coral and other marine calcifiers [15]. During the 20th century, 4.8-8.8 inches elevations in sea level are reported over the world. As temperatures surge melting of glaciers, ice caps, and ice sheets is prominent and the sea level rises.

To put the rising $CO_2$ levels in context, total worldwide anthropogenic $CO_2$ emissions are around 30-35 Gt of $CO_2$/per year. $CO_2$ injection and storage conditions are typically operated at 10 MPa and 40 °C, resulting in a $CO_2$ density of 600 kg $m^3$. This equates to more than 1,033 MMbbl (million barrels) of $CO_2$ that is produced. However, the current oil production rate is at 87–91 MMbbl per day [16,17]. This indicates that worldwide $CO_2$ output is around a ratio 10-fold higher than global oil production, and could be 20-fold higher in 2050 if the present growth rate continues [18].

In this review, we have summarized important literature to show readers some of the important aspects of $CO_2$ removal by various methods. Important technological advancements have been discussed which can be of great importance to the deal with $CO_2$ and global warming. State of-art techniques and comparative studies for $CO_2$ utilisation are presented and discussed based on various parameters obtained from the literature. Indeed, more attention has been paid towards the utilisation of $CO_2$ to produce value-added chemicals via different available methodologies. Non-thermal plasma (NTP) is an emerging technology that is dealt with in detail in this review. More emphasis is played on the conversion of $CO_2$ to oxygenates, hydrocarbons, syngas and allied products using a heterogeneous catalytic process.

## 2. Methodologies for Removal/ Controlling Emission of $CO_2$

The energy sector contributes majorly towards the total $CO_2$ emissions. Out of which burning coal to drive electricity produces 950 g $CO_2$ is emitted per KWh of $CO_2$ of electricity. This amount is huge thus an alternative to the direct burning of coal is implemented. Herein coal is gasified to produce CO and $H_2$ which is a syngas mixture, this method not only emits lower $CO_2$ but also can be used to produce value-added chemicals. Similarly, if one wants to abolish non-renewable energy sources like coal and petroleum products major emphasis will be on renewable energy resources. COP 26 which was held in Glasgow majorly played emphasis on the reduction of the use of non-renewable energy sources like coal and moving towards renewable energy sources. The use of a renewable source of energy is an environmentally friendly technique, which involves the use of hydro, solar (thermal), and wind power. These techniques are efficient as the $CO_2$ emission is eliminated and/or reduced to a very low amount.

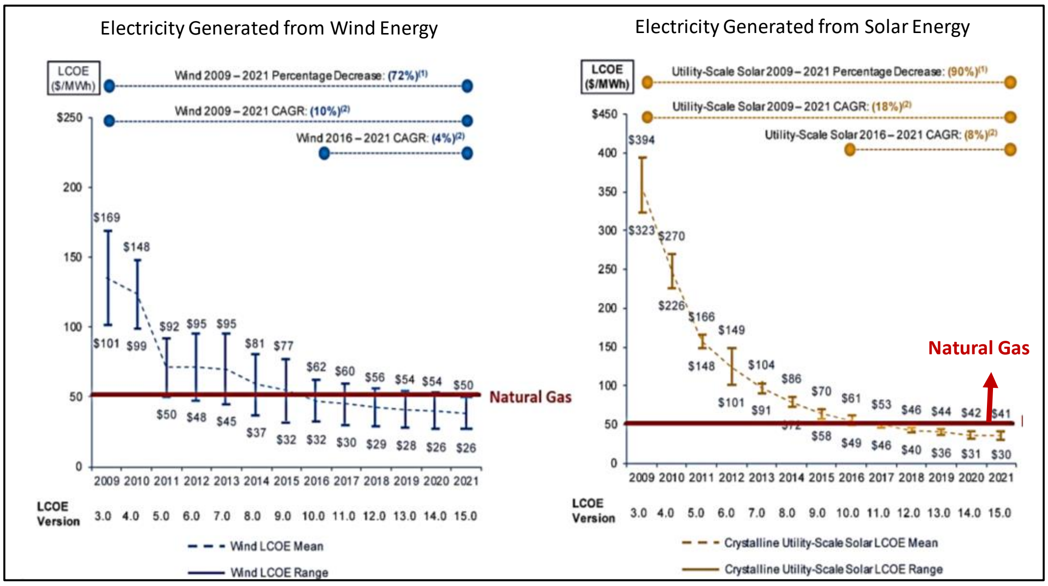


**Figure 3.** The energy cost for renewable energy sources. *Reproduced from reference [19].*

Over the last preceding decades, the energy turnover was lower than installation and implementation costs. However, as can be seen from Figure 3 nowadays, the cost of production of electricity from solar and wind energy is competing with other electricity production sources like natural gas [19]. Apart from these alternatives, nuclear-driven processes are the most efficient to produce electricity from nuclear reactions. The most efficient source to generate energy is the nuclear reactor; here energy output is high with zero $CO_2$ emission. Indeed, nuclear power plants are associated with very high-risk factors, such as nuclear meltdown and disposal of nuclear waste etc., thus their widespread use is of concern. Additionally regarding on-the-go technology nuclear energy is still not developed.

Since humans depend on transportation to commute no wonder that transportation is one of the biggest sectors, which emits GHG. Looking at upcoming fuel shortages and energy crises EVs (electronic vehicles) are a suitable choice for the short-distance commute. Apart from the complete shift of engines from gasoline to electric PHEVs (plug-in hybrid electric vehicles) and hybrid vehicles are present in the market. A report published by the US department of energy shows that EVs emit the lowest $CO_2$ which is 1800 kg of $CO_2$ equivalent per year which is 3 fold lower than gasoline-based vehicles as seen in Figure 4. EVs can tremendously bring down $CO_2$ emissions, however, this may not be a complete story. They also rely heavily on the charging of EVs and the electricity is generated from the burning of coal and natural gas, which emits $CO_2$.

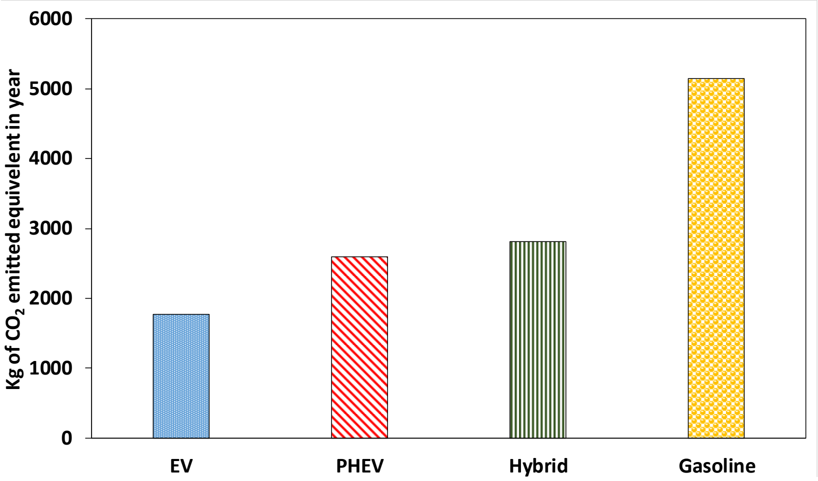


**Figure 4.** The $CO_2$ emission profile for various commute modes. Adapted from reference [20,21]

According to a study published by Leard and McConnell [22] one percent of all passenger vehicles in the US on the road today are EVs. The heavy truck EVs are in development, they have not yet entered the market in significant numbers. Thus, EVs even though has huge potential to reduce GHG emissions till now they have had little impact on overall GHG emissions. On a positive note, the demand for EVs is increasing along with their sales which will bring new players into the market. Thus, a lot of research-driven works are carried out for improving the technical knowhow of EVs [23,24].

The $CO_2$ emitted into the atmosphere or before being emitted into the atmosphere can be trapped by the following techniques.

### 2.1 Reducing $CO_2$ Levels During Combustion

#### (i) $CO_2$ removal in the pre-combustion process

Coal is a major source of non-renewable energy. Coal originates from fossils of flora and fauna buried underneath the earth. The influence of high pressure, temperature and low oxygen content lead to the formation of coal. The energy yielded upon the combustion of coal is enormous however apart from energy, harmful gases are emitted from the coal once burned. One simple way to reduce $CO_2$ emissions is by using the gasification technique. According to the coal utilisation research council, 2016 the term gasification is defined as *"the reaction of solid fuels with air, oxygen, steam, carbon dioxide, or a mixture of these gases at temperatures exceeding 800 $^oC$ in a reducing environment where the air: oxygen ratio is controlled* ". The influence of heat and pressure breaks down chemical bonds in coal, to produce CO and $H_2$. The reaction product has the potential towards (1) an energy source, or (2) a raw material (syngas) for the production of chemicals, liquid fuels, or other gaseous fuels and/or a combination of these. Synthesis gas (syngas), is composed of CO and $H_2$. The chemical composition of the gas produced depends on coal composition and rank, coal preparation (specifically particle size distribution and ash content), gasification agents (oxygen: air: steam ratios), gasification conditions (heating rate, residence time, temperature, pressure), and plant configuration (flow geometry, feed form, mineral behaviour, syngas cleaning). For instance, as reported in Equation 2 & 3, coal is forced to undergo a gasification process in low oxygen levels at high temperatures and high pressure to form syngas (CO and $H_2$). The syngas thus produced, can be used to synthesise other products like $CO_2$, and $CH_4$ as given in Equation 3&4. The gasification technique has huge imprints on $CO_2$ emission as using coal to generate electricity an average of 950 g $CO_2$ is emitted per kWh whereas upon the gasification process only 497 g $CO_2$ is emitted per kWh [3]. As given in Equation 3, CO formed reacts with water (water gas shift reaction) and produces clean $CO_2$ and $H_2$. In this process, about 5 to 15% $CO_2$ concentration of $CO_2$ is formed. Thus this process enhances the purity of the emitted $CO_2$; therefore, it can be easily separated. Similarly, as shown in Equation 4, the natural gas mainly $CH_4$ can be reformed to syngas and the $H_2$ content can also be raised by using a suitable catalyst**.**

$$\mathbf{Coal_{(S)}} \xrightarrow{\textbf{Gasification}} \mathbf{CO_{(g)} + H_{2(g)}} \qquad \text{Equation 2}$$

$$\mathbf{CO_{(g)} + H_2O_{(g)}} \xrightarrow{\textbf{Water-gas shift}} \mathbf{CO_{2(g)} + H_{2(g)}} \qquad \text{Equation 3}$$

$$\mathbf{CH_{4(g)} + H_2O_{(g)}} \xrightarrow{\textbf{Reforming}} \mathbf{CO_{(g)} + H_{2(g)}} \qquad \text{Equation 4}$$

It is worth mentioning that in the above-said techniques the widespread application is restricted due to added cost and deactivation of the catalyst.

However even though the limitations, plants are put up all around the world that focus on coal gasification. The Sasol process in South Africa is a notable example, where the plentiful low-grade, high-ash coal makes the Sasol-Lurgi Fixed Bed Dry Bottom technology (formerly known as the Lurgi Dry Ash process) particularly appropriate (Erasmus and Scholtz, 2002). The GreatPlains Synfuels plant in North Dakota, USA, employs the same method to manufacture lignite-based replacement natural gas. Apart from this British Gas Lurgi (BGL), and ConocoPhi, are some of the other operational plants in the world.

### ii) Oxyfuel Technology

Oxy-fuel combustion deals with carrying out the combustion process by removing $N_2$ from the air. The $O_2$ content in the combustion chamber is higher than 21%. The Oxyfuel combustion technology typically enhances the efficiency of the $CO_2$ capture process. In this process a pure blend of oxygen is used instead of air, therefore, the combustion considerably reduces the $NO_x$ emission [25]. The gases emitted are only $CO_2$, $SO_2$, water and particulate matter. The electrostatic precipitation or desulphurisation process is used to remove $SO_2$ from the exhaust flue. Thus, relatively pure $CO_2$ is emitted which makes it easier for separation and reduces the cost of separation of other gases from the mixture. The $CO_2$ thus produced is clean and can be used for storage or can be used for other purposes, however, the requirement of a pure blend of $O_2$ increases the capital and energy investment by 7% [26,27]. When it comes to the implementation of Oxyfuel technology plants at a piolet scale Callide power Station in Queensland Australia, Schwarze Pumpe Power Station in Spremberg, Germany, and the CIUDEN plant in Cubillos del Sil, Spain are some of the facilities available.

### iii) $CO_2$ removal post-combustion process

An interesting method to reduce $CO_2$ emission in the atmosphere is the post-combustion process. In this method, $CO_2$ is removed from the exhaust flue gas. The removal of $CO_2$ from the exhaust stream could be achieved by techniques like adsorption, absorption, membrane separation, cryogenic distillation etc. This process is very efficient as fewer or no modifications are required in the existing working plant. The method is reported to be successful for lower scales where 800 tons of $CO_2$ is recovered per day [27]. The major disadvantage of the combustion process is the amount of $CO_2$ formed is very low (<15%) along with other constituents like $SO_2$, and NOx [26,27]. The estimate provided by US NEA (National Energy Agency) showed that the use of the post-combustion treatment technique would certainly lead to an increase in the electricity cost of the overall process.

### iv) Chemical looping combustion

The CLC (Chemical Looping Combustion) technique uses the dual fluidised bed system. The metal oxide is used as catalytic material owing to its oxygen-donating capability in a combustion reaction. During this process, metal oxide undergoes reduction to metal and oxygen removed from the metal oxide is used in fuel combustion as reported in Equation 5 & Equation 6. The reduced metal is then re-oxidised in the oxygen-rich condition in the air stream and the cycle continues. The CLC technique is also an alternative to the carbon capture method.

$$M_{(s)} + O_{2(g)} \rightarrow MO_{(s)} \qquad \text{Equation 5}$$

$$C_{(s)} + 2MO_{(s)} \rightarrow CO_{2(g)} + 2M_{(s)} \qquad \text{Equation 6}$$

Different metal oxide like $Fe_2O_3$, NiO, CuO, and $MnO_3$ and their effectiveness are studied for oxygen transfer fuel combustion [28,29,30,31,32,33]. These metal oxides are reduced by a mixture of hydrocarbons and then it is oxidised in the air reactor. Natural gas is partially oxidised in the fuel reactor which leads to the formation of CO, $CO_2$, $H_2$ and $H_2O$. Bayham *et al.* [34] used hematite ore as an $O_2$ carrier due to its high stability and resistance to mechanical attrition. The authors studied methane cracking using steam. $H_2$ is bye product other than CO. Figure 5 summarises the pros and cons of different techniques under study.

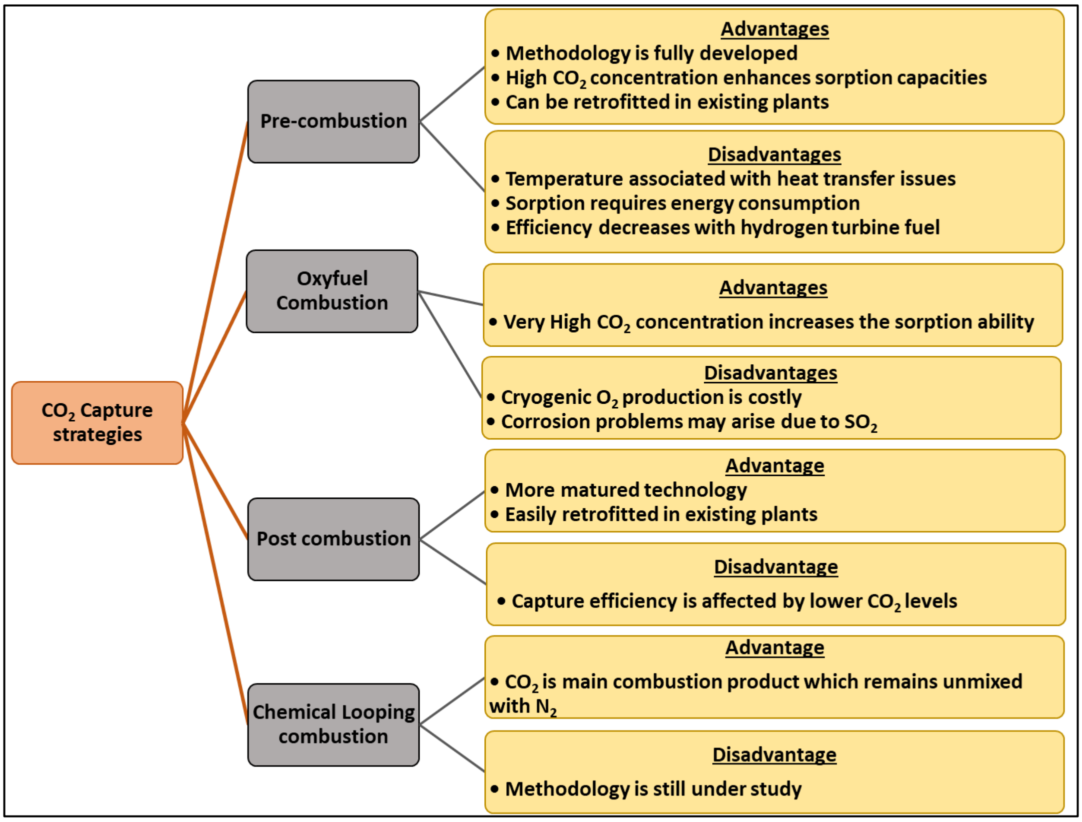


**Figure 5.** Pros and Cons of Strategies for $CO_2$ capture.

## 2.2. Removal of Emitted $CO_2$ From The Atmosphere

The $CO_2$ emitted in the environment or the $CO_2$ coming from the combustion process in the industry is impure. The composition of $CO_2$ in flue exhaust is around 15-25% [27]. The $CO_2$ can thus be not used directly it needs to be purified and separated from other gases the below-mentioned techniques are widely used for improving the quality of $CO_2$.

### i) Adsorption process

The adsorption process is an efficient method for $CO_2$ capture. The best adsorbent is the one that possesses (i) high surface area, (ii) higher selectivity towards $CO_2$, (iii) high thermal stability lesser and (iv) easy $CO_2$ desorption at lower energy input. The PSA (Pressure Swing Adsorption) and TSA (Temperature Swing Adsorption) are methods widely employed for the regeneration of the adsorbent. For instance, in PSA the $CO_2$ is adsorbed at high pressures and when pressure is reduced to atmospheric pressure it facilitates desorption.

In TSA, the adsorbed $CO_2$ molecule is desorbed by elevating the temperature of the system or by using steam injection. The $CO_2$ regeneration time is very slow as compared to PSA. Indeed, the released $CO_2$ is highly pure (95%). An estimate of 80-150 $ is required per ton of $CO_2$ captured. Generally, PSA is more efficient than TSA as it requires lower energy demand and higher regeneration rates. In TSA the cost of separating $CO_2$ is 27.8 $/ton $CO_2$ [35]. The implementation of the adsorption technique on a bigger commercial platform is limited due to the irreversible and competitive adsorption of other gases which poison the catalytic surface.

### ii) Absorption process

The absorption process utilises an effective scrubber solution or sorbent solution for $CO_2$ sorption. The most commonly used sorbents are monoethanolamine (MEA), diethanolamine (DEA), piperazine, anion-functionalised ionic liquids and others [36]. A review by Aaron *et al.* [37] concluded that the best sorbent for $CO_2$ is MEA, which has an efficiency of 90% for $CO_2$ sorption. Interestingly, piperazine reacts with $CO_2$ faster than MEA, however, owing to high volatility its application is limited. Moreover, the MEA undergoes degradation with an increase in temperature, to form nitrosamine and nitramine products which are harmful to human life and causes fatal accidents. The MEA itself can be very dangerous if escapes into the atmosphere. An alternative safer sorbent is the chillier ammonia process which is comparatively safer and a substitute for MEA. In this process, ammonium salts have been used for $CO_2$ storage [38]. The average cost for $CO_2$ storage including operative and maintains cost is 40-70$/ton of $CO_2$ separated [39,40].

### iii) Membrane separation technique

Composite membranes are permeable to $CO_2$ and separate other gases from flue like $O_2$, and NOx. Audus [41] and Gielen [42] exhibited membrane separation technique can provide an efficiency of 82 and 88%, respectively. Ceramic and metallic membranes were developed by Aaron and Tosuris [37] with a motive to increase $CO_2$ separation. The ceramic membranes have pores that are selective for a certain size of molecules and thus restrict the entry of higher-sized molecules. Apart from the permeable membranes researchers have also developed gas-absorbing membranes. Herein $CO_2$ selectively diffuses across the membranes and is captured/removed by liquid adsorbent [43]. The the thicker membrane higher the permeability for gas it possesses [44]. Yave *et al.* [45] developed a polymeric membrane that showed enhanced $CO_2$ separation using poly(ethylene oxide)-poly(butylene terephthalate) multiblock copolymer. These membranes showed higher $CO_2$ permeability up to five folds higher without loss in selectivity. Brunetti *et al.* [46] in their comprehensive review of membrane separation techniques have concluded that membrane separation is strongly affected by the concentration of $CO_2$ in the flue gas. Membrane separation suffers from major drawbacks due to its lower permeability and selectivity. The estimated cost for $CO_2$ separation from the exhaust gas is 50-70 $/ton [47].

### iv) Hydrate-based separation

Hydrate-based separation technique infers that the flue gas is exposed to high water pressures to form hydrides and $CO_2$ gas is selectively caged in the hydride structure. Hydrides are ice-like structures. Wherein water forms a cage that can effectively trap $CO_2$. The main principle runs on phase equilibrium where $CO_2$ can form hydrides more easily than $N_2$ due to which $CO_2$ can be easily separated from flue exhaust gases. The energy consumption for $CO_2$ capture is as low as 0.5 KWh/Kg-$CO_2$ [48]. Nevertheless, the capture efficiency is affected by hydrate formation and the operating pressure for instance $CO_2$ hydrides do not form below 4 bar at above 10 °C. This method is restricted due to impractical conditions like cooling flue gases, and pressurization of gases. These processes are energy exhaustive. The tetrahydrofuran (THF) has a water miscibility property and forms solid clathrate at low temperatures. Thus, it is used as a thermodynamic promoter for hydrate formation. The presence of a small amount of THF is reported to have reduced hydrate formation pressure and thus it makes it easier to capture $CO_2$ at medium pressure [49]. The United States, DOE (Department of Energy) has classified hydrate technology to cage $CO_2$ as the most promising technology for upcoming years.

### v) Cryogenic distillation

In cryogenic distillation, the complex gas components of the flue gas are separated and removed except $N_2$ and $CO_2$. Once the components are separated the remaining gas is passed to the cryogenic chamber which operates at low temperatures and high pressure. In this method, $CO_2$ undergoes de-sublimation at (-100 to 135 °C) to remove other gases and compress at high pressures of 100-200 atm. At the triple point of $CO_2$ (-56.6 °C and~7.4 atm), it undergoes sublimation whereas $N_2$ remains in the gas state. The amount of $CO_2$ recovered from flue gas can reach 90-95 %. Göttlicher and Pruscheck [50] estimated that about 660 kWh of energy is spent per ton of $CO_2$ capture. Burt *et al.* [51] and Tuinier *et al.* [52] have patented technology for $CO_2$ capture cost-effectively. For separation on an average of 32 $/ton, $CO_2$ is required.

These methods discuses above deal with the separation of segregation of $CO_2$ from possible flue exhaust of industry. The separated material needs to be transported to storage sites for safe storage. This is a prime step in carbon capture and sequestration which can enhance the cost. Figure 6 summarises the distinct techniques discussed previously.

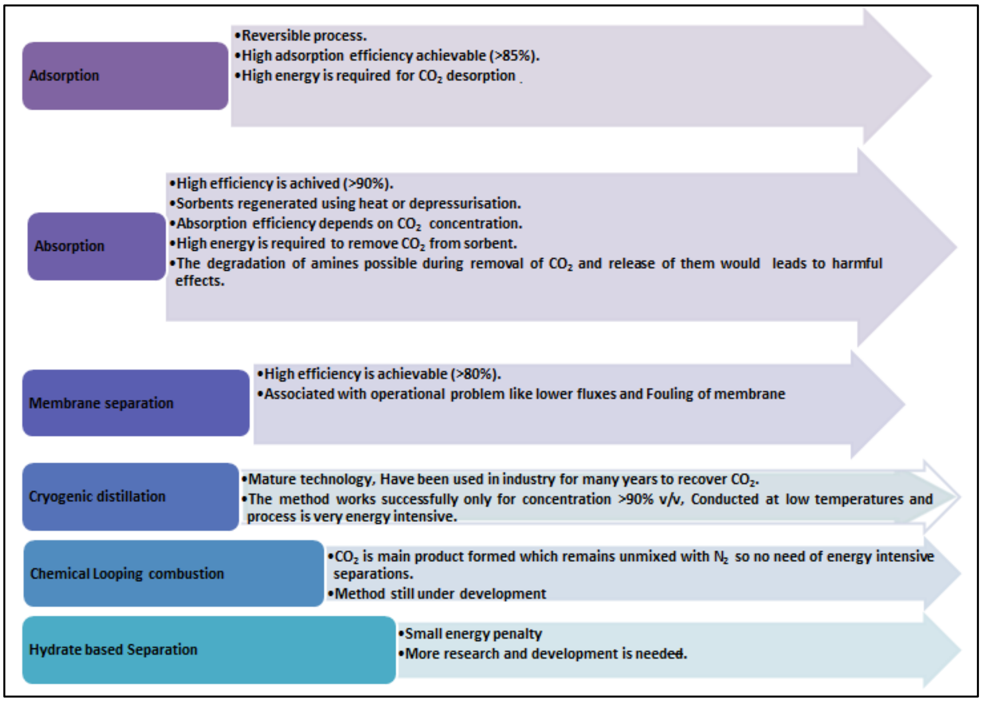


**Figure. 6.** Separation techniques for $CO_2$.

## Post-$CO_2$ capture Carbon capture and sequestration (CCS)

### i) Transportation of Captured $CO_2$ to necessary sites

As one could see from Figure 7 the $CO_2$ captured at emission sites, is transported to appropriate sites for safe storage. Usually, based on the volume of $CO_2$ captured, different transport means have been adopted like pipelines, ship tankers, truck tankers etc. Indeed, among the different ways, the best method is pipeline transportation. Svensson *et al.* [53] estimated that when CCS (Carbon Capture Sequestration) is performed on a larger scale, pipeline transportation is the only efficient method that can be used for the transport of $CO_2$ from one place to another. Gao *et al.*[54], after a detailed case study in China, compared the cost for different methods of transport, and concluded that about 12.64 $ /ton $CO_2$ by railway tankers, 7.48 $/ ton $CO_2$ by using ship containers and 7.05 $/ton $CO_2$ for 300 km pipeline and interestingly about 4000 ton of $CO_2$ is transported per day. The pipelines are maintained at 85-150 bar and 13 to 44 °C. Due to operational conditions frequency of accidents has increased to 0.76/year for every 1000 km and the total pipeline drawn is 5800 km [55]. However, the frequency of accidents caused, by $CO_2$ transportation, is lesser than that of natural gas pipelines.

### ii) $CO_2$ storage

Moving from the sequential steps of $CO_2$ production, separation, capture and transport now let's address the literature available for $CO_2$ storage. In this section, readers will be briefed about the $CO_2$ storage sites and reservoirs. $CO_2$ is generally stored in potential locations where the place has no practical application. For example, unused oil and/or gas reservoirs, un-minable coal bed storage, storage in saline aquifers, and deep-sea ocean storage. Solomon *et al.* [56] and Bachu *et al.* [57] have reported the general requirements for the geological sites. The $CO_2$ storage potential of the deep alkaline reservoir is 400-10000 Gt, whereas 920 Gt is the potential storage capacity of depleted oil or gas fields and 15 Gt is for un-minable coal seams.

Figure 7 shows the storage of $CO_2$ in reservoir sites. $CO_2$ can be pumped into depleted air/gas reservoirs for storage. Blunt *et al.* [58] reported that about 40% of residual oil left in the reservoirs can be extracted, after primary production, by pumping down $CO_2$. Similarly, $CH_4$ trapped in the porous structure of seams can be extracted by injecting $CO_2$ into coal beds. This process is called $CO_2$-enhanced coal bead methane ($CO_2$-ECBM). White *et al.* [59] reviewed the potential storage capacity, storage integrity, physical and chemical processes, environmental health and safety of the $CO_2$-ECBM process. It is worth mentioning that $CO_2$-ECBM sites are actively working in New Mexico, USA [60].

The $CO_2$ can also be stored in saline aquifers 700-1000 meters deep, where a highly saline brine solution is formed. Statoil's Sleipner project in the North Sea is the best example of saline aquifers. It holds 1 Mt $CO_2$/year, whereas the Utsira Sand formation, which extends 1 Km below sea level, has the potential to store 660 $\times 10^6$ $m^3$ of $CO_2$ [61]. The $CO_2$ stored in saline aquifers is quite safe and has an impact on the environment. The deep ocean reservoirs provide the best place to store $CO_2$. The process can be carried out in a deep depth of 3 Km where $CO_2$ undergoes liquefaction and since it is denser than saline water it settles down. The implementation of this technique possess several threats to the marine ecosystem as the pH of the water will decrease and could potentially affect the marine habitat [62]. An estimate shows that about 38000 Gt of $CO_2$ can be stored in saline aquifers at the rate of 1.7 Gt/year [63].

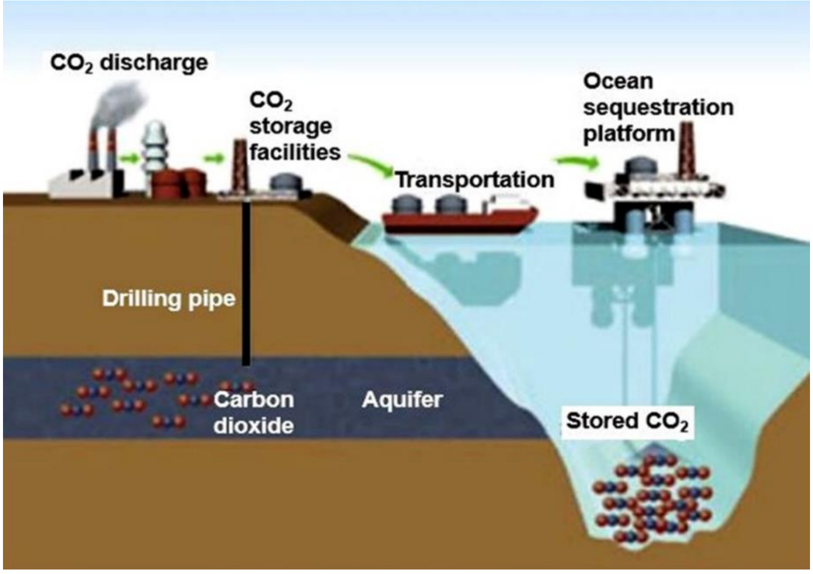


**Figure 7.** Generalised schematic for CCS technology. *Reproduced from reference [64] with permission from the IOP publishing, Copyright 2020*

It is expected that 120–160 Gt $CO_2$ would need to be stored *via* CCS over the period till 2050, with similar trends expected by the end of the century, to regulate atmospheric $CO_2$

concentrations at a level of 450 ppm, with a high likelihood of not temperature not exceeding 2 °C globally [65].

We have more than enough $CO_2$ storage capacity to meet this goal, and even without the discovery of additional storage sinks, we will have enough to meet even the most ambitious $CO_2$ sequestration needs well into the next century, allowing ample time for the likely lengthy transition away from fossil fuels. The world's first commercial CCS-equipped power plant, the Boundary Dam facility in Saskatchewan, Canada, has begun operations, with the second project in Alberta, where Shell is capturing $CO_2$ from $H_2$ production, now in operation. CCS is an undeniably well-understood, mature technology that can now be used at a commercial scale [66].

Apart from the storage of $CO_2$, it would be wise to utilise it as a reactant to derive products as global demand for the potential products, such as methanol, appears healthy [67].$CO_2$ could be used in various ways to obtain products of strategic importance. $CO_2$ recirculation, apart from being cost-effective, is also an environmentally friendly route. CCU (Carbon Capture & Utilisation) technology uses $CO_2$ as feedstock apart from conventional applications. $CO_2$ is already being employed in the synthesis of several chemicals namely urea, urethane, polycarbonates and others.

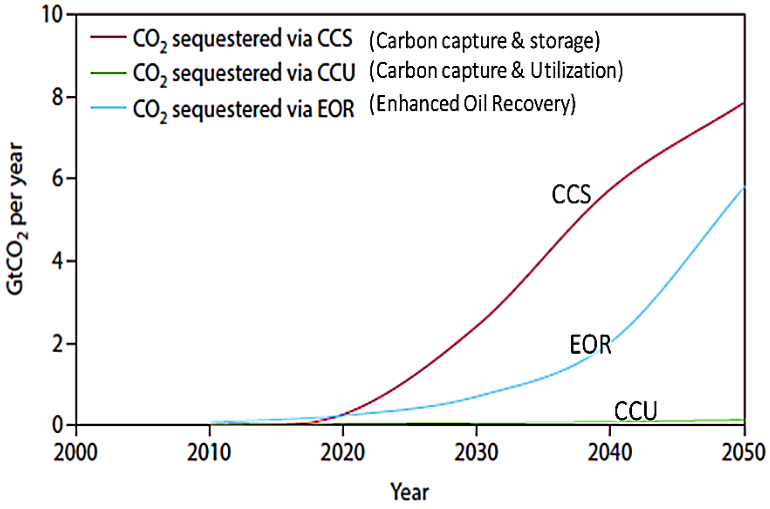


**Figure 8.** The Scenario of $CO_2$ mitigation via different techniques *Reproduced from reference [13] with permission from Springer Nature, Copyright 2017.*

Figure 8 shows the different techniques for the mitigation of $CO_2$ and their potential to do so. When it comes to reducing our emissions of $CO_2$ into the atmosphere the techniques namely the CCS and CCU and EOR (Enhanced Oil Recovery) are the major players. It is predicted that by the year 2050 the $CO_2$ mitigated *via* CCS and EOR is expected to be around 8 Gt/year and 6 Gt/year it is disappointing to see that the CCU technique is still underdeveloped and by the year 2050 will contribute <0.5% towards mitigating rising $CO_2$ levels. This could attribute to immature technologies at the prototype level or the ones which are at the lab scale. Big technological leaps are needed to achieve efficient mitigation of $CO_2$ and become a competition with other techniques. Furthermore as stated in Figure 8, by the year 2050 CCS will lead the battle against rising $CO_2$ levels. The $CO_2$ which is captured by material be it ionic liquids, or heterogeneous materials like MOF, clays and others suffers from lower desorption efficiency. For the sorption study, TSA (Temperature swing adsorption) and PSA (Pressure Swing Adsorption) are employed. Ionic liquids undergo thermal decomposition due to lower thermal stability.

## 3. $CO_2$ A Feedstock For Chemical Synthesis

$CO_2$ mitigation involves both extractions and making useful chemicals out of them. The $CO_2$ utilization can be carried out in the following ways: (1) the use of $CO_2$ in chemical processing based on unique physical and chemical properties, (2) to remove of the hazardous impact of some chemicals and replacing them with $CO_2$-based solvents, and (3) to produce value-added chemicals for the industrial sector. The $CO_2$ gas finds its applications in refrigerants for food preservatives, beverages carbonation agents, inert medium (such as fire extinguishers), pressurizing agents, supercritical solvents, chemical reactants (urea), neutralizing agents, and as gas for greenhouses [3,68]

$CO_2$ is the highest oxidized form of carbon with a +4 oxidation state. As shown in Figure. 9, it can be utilized in various ways depending upon its oxidation states and Gibbs free energy of formation ($\Delta G_f$). In carboxylic acids, the oxidation state of C is +2, thus the conversion into other products with different oxidation state is thermodynamically achievable. The reduction of +4 oxidation states to +3 or +2 requires the energy push. This energy can be supplied from electrons (generated from $H_2$, metal radiation) or by heat depending upon the reaction parameters. Aresta *et al.* [3] have classified the $CO_2$ conversion reactions into two types based on the oxidation state: (i) the $CO_2$ oxidation state is maintained at +4, and (ii) with an external energy push, the $CO_2$ oxidation state has been reduced from +4 to +2 or lower oxidation states as reported in Figure. 9.

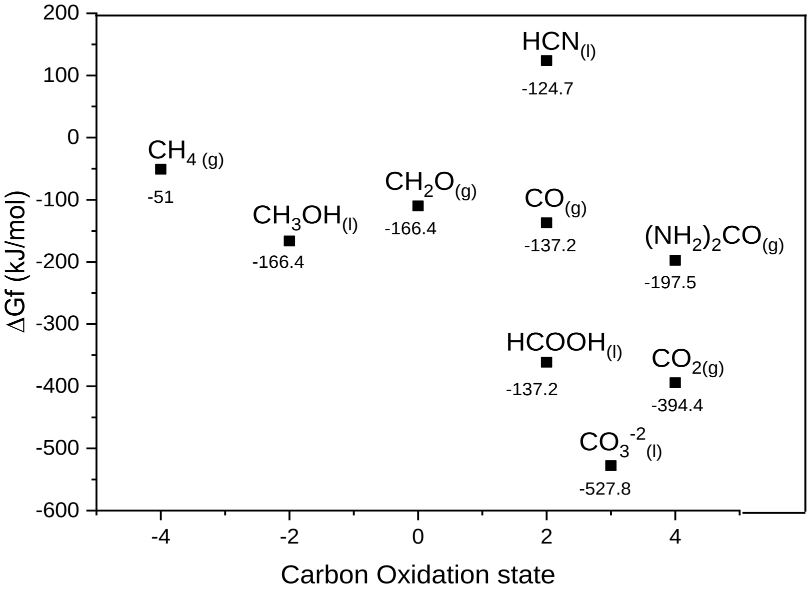


**Figure. 9.** The Gibbs free energy of the formation of different species could be produced from $CO_2$. (Adapted from [3]).

### 3.1. Physical Properties of $CO_2$ and Its Influence on Stability

At room temperature and pressure, $CO_2$ exists in a gaseous state. $CO_2$ solidifies under normal temperature by application of pressure. $CO_2$ may be converted to a liquid by compressing it to the liquefaction pressure and eliminating the heat produced at temperatures between triple point and critical temperature. At temperatures more than 31.1 °C and pressures greater than 73.9 bar, $CO_2$ is in a supercritical state (sc-$CO_2$), in which it acts like a gas. The physical and chemical properties of $CO_2$ are summarized in Table 1 [69,70,71].

Although $CO_2$ is a non-polar molecule with two sets of orthogonal orbitals, it is a linear 16-electron molecule with two polar C=O bonds. The distance between two bonds between C and O atoms is 1.16 Å. $CO_2$ has a 13.73 eV ionisation potential and a 3.8 eV electron affinity, making it a poor electron donor and an excellent electron acceptor. As $CO_2$ is a very stable molecule, it requires a lot of energy and highly active metal catalysts, which are mainly transition metals. In the $CO_2$, there are two different reaction sites.

An electrophilic core is a carbon atom with a Lewis acid character, while a nucleophilic centre is an oxygen atom with a weak basic Lewis character. Most catalytic processes need the activation of both acidic and basic centres for carbon and oxygen atoms to interact with metal catalysts. Furthermore, the electrons in two C=O bonds can interact with the d electrons in transition metals. The acceptance of an electron in the $CO_2$ orbital leads a molecule to bend (the OCO angle is close to 133°), resulting in a shift in molecular energy and an increase in the bond length between the carbon and oxygen atoms.

$CO_2$ has the lowest energy content of any carbon-containing binary-neutral species. It is also the result of any organic compound combustion process, together with water, and so exists in a potential energy well, as shown in Table.1. Exothermic processes that do not require energy input include reactions in which $CO_2$ combines with $OH^-$ ions, amines, or olefins ($CO_2$ is formed into organic molecules and the C atom does not alter its oxidation state) and thus are used for the $CO_2$ removal process. The general synthesis of value-added chemicals from $CO_2$ requires a lot of energy investment thus a suitable catalyst is desirable to lower the energy investment. The conversion of $CO_2$ into useful organic chemicals such as carboxylates and lactones (RCOOR'), carbamates (RR'NCOOR'), ureas (RR'NCONRR'), isocyanates (RNCO), or carbonates [(ROC(O)OR'], is of prime importance as it offers an alternative to more polluting methods for synthesis now in use. [28].

The reactions in which a reduced form of $CO_2$ is obtained as a product are endothermic processes and thus require the input of energy in the form of heat, electrons or other radiation. By applying these processes, it is possible to obtain formates (HCOO-), oxalates $[C(O)O]_2^{2-}$, formaldehyde ($H_2CO$), carbon monoxide (CO), methanol ($CH_3OH$), dimethyl ether ($CH_3OCH_3$) and methane ($CH_4$).

**Table 1.** Physical properties of $CO_2$.

| **Property** | **Value and Unit** |
|---|---|
| The heat of formation at 25ºC | -393.5kJ/mol |
| The entropy of formation at 25ºC | 213.6 J/mol |
| Gibbs free energy of formation at 25ºC | -394.3 kJ/mol |
| Sublimation point at 1 atm | -78.5ºC |
| The triple point at 5.1 atm | -56.5ºC |
| Critical temperature | 31.4ºC |
| Critical pressure | 72.85 atm |
| Critical density | 0.468 g/cm$^3$ |
| Gas density at 0 °C and 1atm | 1.976 g/L |
| Liquid density at 0 °C and 1atm | 928 g/L |
| Solid density | 1560 g/L |
| Specific volume at 1 atm and 21ºC | 0.546 m$^3$/kg |
| Viscosity at 25ºC and 1 atm | 0.015 cp |
| Solubility in water at 25ºC and 1 atm | 0.1449 g $CO_2$/100g $H_2O$ |

With its linear structure, $CO_2$ is a thermodynamically stable molecule with a calculated bond strength of D = 532 kJ/mol. Table 1 illustrates the various physical and chemical properties of $CO_2$. The standard heat of formation (ΔH°) and standard Gibbs free energy of formation (ΔG°) of $CO_2$ are the two most important characteristics, as shown in Table 1. As a consequence, the ΔH° and ΔG° values are the most crucial criterion for estimating a reaction's thermodynamic feasibility. The bulk of the associated reactions is found to be thermodynamically unfavourable after evaluating the Gibbs free energy of exothermic $CO_2$ hydrogenation. Indeed, they are less advantageous since the ΔG° values are more positive than the equivalent ΔH° values. As an outcome, only a handful of processes have negative ΔG° and H° values. $\Delta G° < 0$ values either relate to hydrogenation processes or reactions with products having C-O bonds. The generation of water is connected to favourable values of ΔG° in the hydrogenation reaction as $H_2$ must be created at the expense of input energy, none of these processes can reduce $CO_2$ emissions [72].

When $CO_2$ is used as a single reactant, it necessitates more energy because $\Delta G^0$ is -394.4 kJ/mol. The reaction becomes thermodynamically more feasible when $CO_2$ is used with another reactant that has a higher $\Delta G^0$ as seen from Equations 7 and 8. For example, $CH_4$, carbon (graphite), and $H_2$ are some co-reactants that have higher (less negative) $\Delta G^0$. The dissociation of $CO_2$ to CO where $CO_2$ is used as a single reactant and in the hydrogenation of $CO_2$ by $H_2$ (where $CO_2$ is recycled as a co-reactant) 10-fold lower values for $\Delta G^0$ is seen. Moreover, the heat of the reaction is less in the case where $CO_2$ is used with other co-reactant [73].

$$\mathbf{CO_{2(g)} \rightarrow CO_{(g)} + \frac{1}{2}O_{2(g)}}, \qquad \text{Equation 7}$$

$$\mathbf{\Delta H^0 = +293\ kJ/mol, \Delta G^0 = +257\ kJ/mol}$$

$$\mathbf{CO_{2(g)} + H_{2(g)} \rightarrow CO_{(g)} + H_2O_{(g)}} \qquad \text{Equation 8}$$

$$\mathbf{\Delta H^0 = +51\ kJ/mol, \Delta G^0 = +28\ kJ/mol}$$

With these basic concepts now let's see different techniques available for $CO_2$ conversion to value-added products. As can be seen in Figure 10, different techniques can use $CO_2$ to build value-added substances. Several research groups are effectively transforming $CO_2$ into value-added chemicals *via* photochemical, biochemical, thermochemical, electrochemical, and hybrid approaches. The application of solar energy conversion to chemical energy is underlined in photosynthetic processes and photochemical and photo-electrochemical conversion. The methodology is cost-effective considering silicon photovoltaics could provide a Levelized cost of $0.05/kWh and an energy efficiency of 20%. [74,75]. The biochemical approach relies on the electrolysis of water to produce $H_2$ gas [76,77]. Although, the $H_2$ gas produced by water electrolysis can be employed thermo-chemically to hydrogenate $CO_2$ into a final product, however, there are energy losses in $H_2$ compression, product separation, and yield. [78]. Single-step electrochemical approaches that convert $CO_2$ and water straightforwardly into small-molecule products have the potential to prevent some of these losses. This can be done by operating under milder conditions with higher selectivity but, they have their drawbacks of system stability and feedstock contaminant intolerance [79,80].

The purpose of these $CO_2$ utilisation techniques is idealistically to disrupt a $5 trillion economy [81,82] by producing fuel and commodity chemicals at a price point lower than petrochemicals can afford while maintaining environmental sustainability.

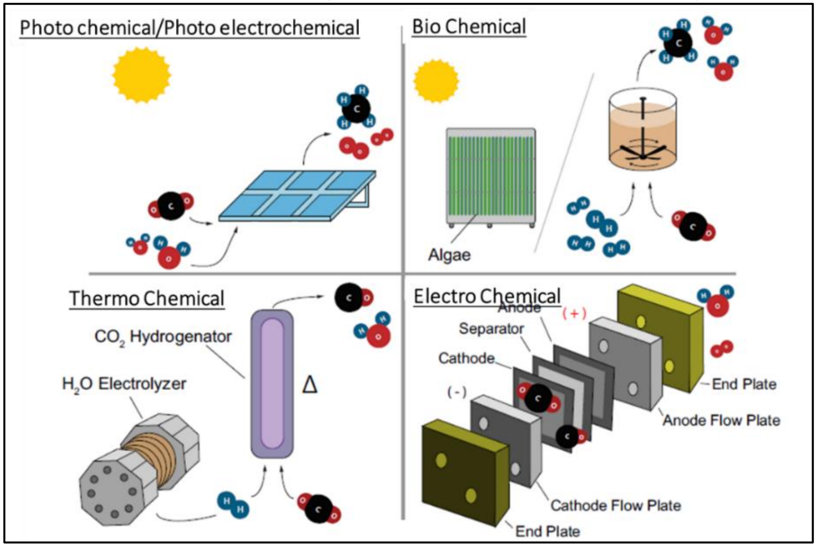


**Figure 10.** Methodologies to mitigate $CO_2$. *Reproduced from reference [83] with permission from Elsevier, Copyright 2018.*

Due to their intrinsic reactivity, most $CO_2$ conversion approaches rely on using rare earth metals; nevertheless, the use of rare-earth metals increases the overall cost of the technique, which competes with the commercialization aspect. As a response, increased attention is placed on avoiding rare earth metals and achieving competitive product yields using new technologies. Thermal catalysis, electro-catalysis, and photo catalysis are some forms of catalytic techniques that are extremely similar to each other. These catalytic techniques are variants of catalysis in which the central concept is the production of reactive species on the catalyst surface, facilitating subsequent conversion. In contrast to previous approaches, plasma catalysis is persistent to produce reactive species in the gas phase and subsequently interacting with the catalytic surface.

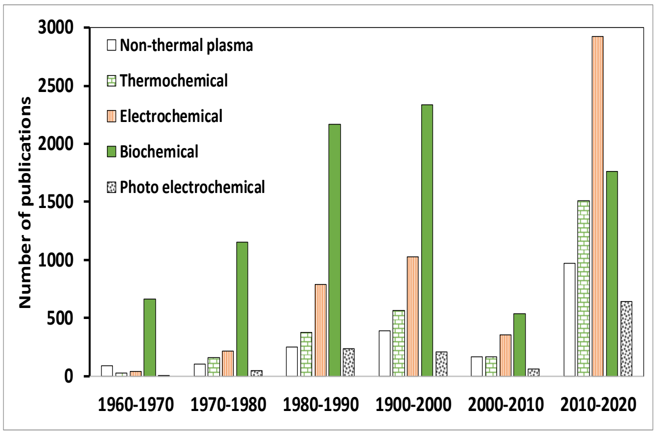
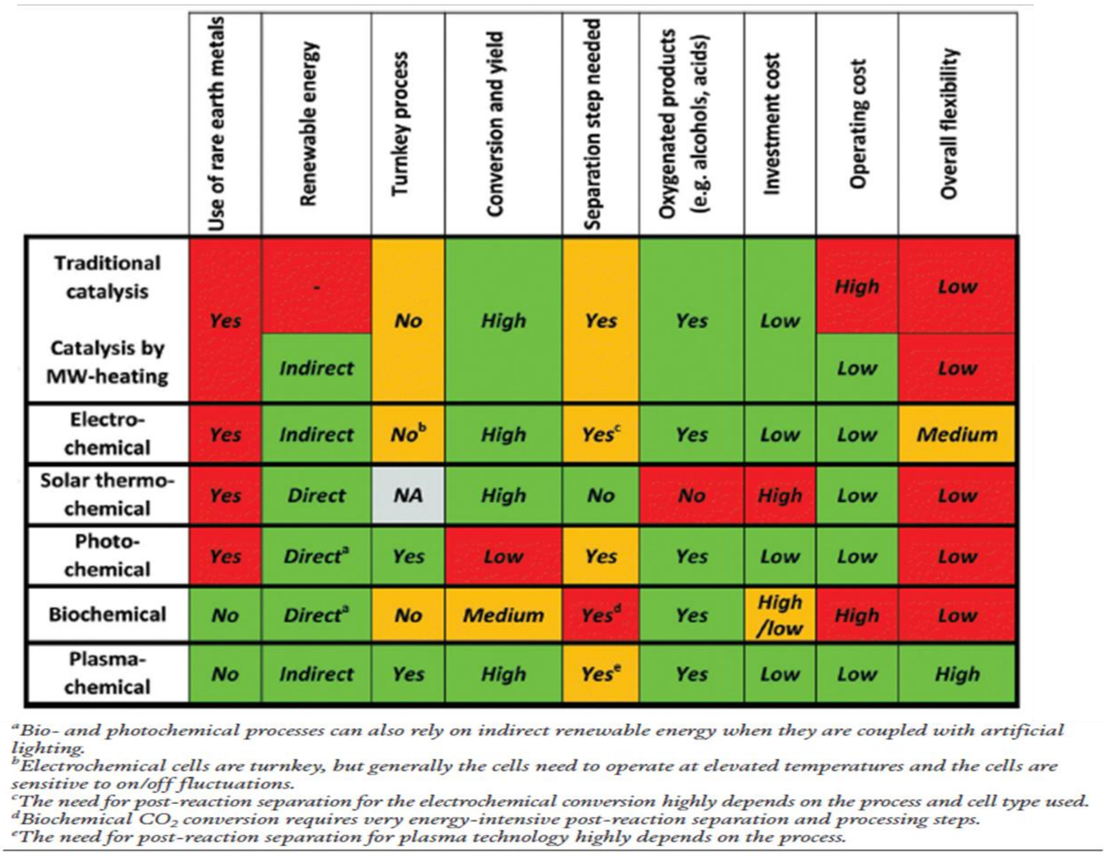


**Figure 11.** Number of articles published from 1960-2020 for $CO_2$ conversion (source Science Direct; the key word "$CO_2$ conversion using non-thermal plasma/Thermochemical/Electrochemical/Biochemical/Photo electrochemical")

Figure 11 depicts the number of research articles published from 1960-2020 which deal with $CO_2$ conversion using various approaches. It can be seen that there is growing concern and attention on $CO_2$ conversion recently. There is growing interest among researchers to catalyse $CO_2$ at ambient conditions and thus many publications are published dealing with electrochemical, non-thermal plasma and biochemical routes.

Bogarts *et al.* [7] have investigated thoroughly different techniques based on qualitative characteristics such as i) use of rare earth metals, ii) renewable energy, iii) process turnkey, iv) method conversions and yield, v) post-reaction separation of products, vii) total cost and viii) process flexibility. Based on a comparison, as shown in Figure 12, it is possible to deduce that plasma chemical-based conversion is the most promising. The main justification for this conclusion was that plasma could be created using electricity generated *via* renewable energy resources. More importantly, plasma catalysis does not rely on rare earth metals to accelerate reactions, cutting the overall cost of the process. Unlike other techniques, plasma-based conversions are simple to turn on and off and produce high conversion and yield. As the mechanism of plasma chemical conversion proceeds primarily *via* electron excitation and collision, the energy involved is minimal, and hence the operational cost is low. When it comes to processing flexibility, plasma-based techniques are adaptable, with the capacity to scale up from laboratory to industrial scale with little adjustments.



| | Use of rare earth metals | Renewable energy | Turnkey process | Conversion and yield | Separation step needed | Oxygenated products (e.g. alcohols, acids) | Investment cost | Operating cost | Overall flexibility |
|---|---|---|---|---|---|---|---|---|---|
| **Traditional catalysis** | *Yes* | *-* | *No* | *High* | *Yes* | *Yes* | *Low* | *High* | *Low* |
| **Catalysis by MW-heating** | | *Indirect* | | | | | | *Low* | *Low* |
| **Electro-chemical** | *Yes* | *Indirect* | *No*[b] | *High* | *Yes*[c] | *Yes* | *Low* | *Low* | *Medium* |
| **Solar thermo-chemical** | *Yes* | *Direct* | *NA* | *High* | *No* | *No* | *High* | *Low* | *Low* |
| **Photo-chemical** | *Yes* | *Direct*[a] | *Yes* | *Low* | *Yes* | *Yes* | *Low* | *Low* | *Low* |
| **Biochemical** | *No* | *Direct*[a] | *No* | *Medium* | *Yes*[d] | *Yes* | *High /low* | *High* | *Low* |
| **Plasma-chemical** | *No* | *Indirect* | *Yes* | *High* | *Yes*[e] | *Yes* | *Low* | *Low* | *High* |

[a] *Bio- and photochemical processes can also rely on indirect renewable energy when they are coupled with artificial lighting.*
[b] *Electrochemical cells are turnkey, but generally the cells need to operate at elevated temperatures and the cells are sensitive to on/off fluctuations.*
[c] *The need for post-reaction separation for the electrochemical conversion highly depends on the process and cell type used.*
[d] *Biochemical $CO_2$ conversion requires very energy-intensive post-reaction separation and processing steps.*
[e] *The need for post-reaction separation for plasma technology highly depends on the process.*

**Figure 12.** Comparison of different techniques available for yielding value-added products from $CO_2$. *Reproduced from reference* [7] *with permission from the RSC, Copyright 2017.*

Recently, innovations for $CO_2$ reduction and improved efficiency have been devised. NTP (Non-Thermal Plasma) is one such innovation with immense prospects for chemical $CO_2$ conversion into value-added chemicals. Several plasma technologies for $CO_2$ conversion have been investigated in the literature. The concept of NTP, particularly the DBD (Dielectric Barrier Discharge), is true of significant interest to readers. The NTP can be generated at room temperature and pressure, making it ideal for large-scale and immediate deployment. However, much study is required, and as of now, it is merely a utopian dream and is far from reality. The $CO_2$ conversion and product selectivity have been significantly improved by coupling NTP and suitable catalysts. Even though the best conversion of $CO_2$ is achieved in microwave plasma but the study was carried out in supersonic flow conditions and reduced pressure which makes it inefficient in terms of energy efficiency and thus, undesirable for implementing in the industry [84,85]. The NTP-assisted $CO_2$ transformation research has majorly concentrated on $CO_2$ splitting to CO and O rather than the direct synthesis of value-added products. This is due to the non-selectivity of NTP plasma. However, since NTP could be operated at ambient conditions makes it a very good contender for industrial applications. As a result, the superiority of the NTP-heterogeneous catalytic process over other established $CO_2$ mitigation approaches is discussed in the following sections.

The NTP can be used with $CO_2$ capture technology; rather than storing collected $CO_2$ in geological reserves, plasma can be used to break down the molecule to form carbon monoxide (CO) and oxygen and later hydrogenated using $H_2$ to produce a variety of chemicals. In this way, we can minimize its effects on climate change.

If we look at the thermal splitting of $CO_2$ the process is endothermic with the standard heat of formation of ($\Delta H^o$) +283 kJ/mol as seen from Equation 1. The equilibrium yield is just 1% with 2000 K, and it reaches about ~60% when the temperature is raised from 3000 to 3500 K [86]. As shown in Figure ***13***, thermal splitting even though gives good conversion of $CO_2$ suffers from lower energy efficiency. Following the Le Chatliers principle, the continuous removal of one of the products would drive the equilibrium of the reaction in the forward direction as shown in Equation 1 and thus, one could lead to the improved conversion of $CO_2$. This can improve the energy efficiency of the process. To achieve the improved $CO_2$ conversion calcium stabilized zirconia membrane is used in the $CO_2$ splitting reaction and about 21.5% conversion of $CO_2$ has been attained at 1954 K [87]. It is demonstrated in Figure 13, to heat one mol of $CO_2$ from 300 K to 2000 K about 92 kJ/mol of energy has to be applied, which implies that the $CO_2$ splitting is favoured at a higher temperature. At 3500 K, about 47% of energy efficiency is observed, whereas only 4.4% is obtained with 2000 K [88,89,90]. It is worth mentioning that the $CO_2$ conversion, at room temperatures, is poor due to non-comparable conversion and low energy efficiencies [91,88]. Thus, rather than using $CO_2$ for its splitting, it is used for reforming $CH_4$ rather than the direct route of $CO_2$ splitting which operates at much lower temperature conditions. Plasma, on the other hand, is well known to activate $CO_2$ at much lower temperatures *i.e.* at room temperature in comparison to thermal splitting.

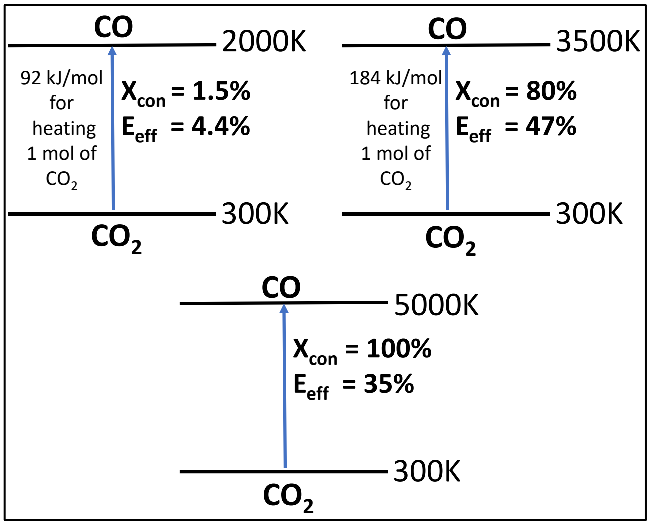


**Figure 13.** Thermal splitting of $CO_2$ and corresponding energy efficiency Adapted from [7].

### 3.2 Conversion of $CO_2$ into Value-Added Products Using Plasma

This section deals with the application of NTP for $CO_2$ conversion. Plasma is commonly called the fourth state of matter. The composition of the plasma is quite complex which includes neutral molecules, positively charged ions, electrons, radicles and others [92,93]. Crudely plasma can be classified as natural plasma-like lightning, auras etc. and artificial (manmade plasma). The man-made plasmas are classified based on the equilibrium of species as thermal and non-thermal plasma. In thermal plasmas, a local thermodynamic equilibrium (LTE) between all species in plasma over a localized area is observed. The non-thermal plasma (NTP) is characterized by species (electrons, ions, neutral molecules, etc.) having different temperatures in a localized area and thus they distort from equilibrium and are called non-equilibrium plasmas or cold plasma. Apart from this plasma which lies at two extremities, there exists another type of plasma called warm plasma which is intermediate between the two. These types of plasma lie in the boundary between non-thermal plasmas and thermal plasmas [93]. In these types of plasmas, the electron temperature is higher than the gas temperature but the gas temperature (or transitional temperature) is above room temperature 2000 to 3000K. Thus, these plasmas can use the advantages of non-thermal and thermal plasmas. These types of plasmas are interesting not because of temperature but as discussed in later sections the electron energy is majorly used in the vibrational excitation of $CO_2$ molecules. Concerning plasma catalysis for $CO_2$ hydrogenation, there are only a handful of reports (as discussed below). Nevertheless, it exhibits great potential since plasma can operate at ambient temperature and atmospheric pressure. The later sections show the authors various ways in which $CO_2$ can be utilized with aid of various types of plasmas.

### 3.3. Dielectric Barrier Discharge (DBD)

Dielectric barrier discharge also called DBD is another type of cold plasma which is extensively applied to dissociate $CO_2$ into a variety of products. As depicted in Figure 14, in most DBD experiments copper or stainless steel mesh wounded around a glass tube or quartz tube (dielectric material) acts and the ground electrode and metallic rod act as the main electrode. A potential is applied between the two electrodes which creates ion and electron. In DBD, one or both electrodes are separated by a dielectric material like ceramics, glass, quartz and catalysts. The dielectric material accumulates charges, these charges form an opposite electric field that opposes the electric field generated on the electrode. This restricts the current flow through the reactor from one electrode to another, the process occurs in a sub-microsecond regime which gives micro discharges These electrons due to virtue of their less mass are accelerated towards electrodes of opposite charge. This accelerated electron encounters stable molecules like $CO_2$ with which it collides and dissociates $CO_2$. Upon dissociation *i.e.*, ionization of any molecules more secondary electrons are generated which avalanches and sustains plasma.

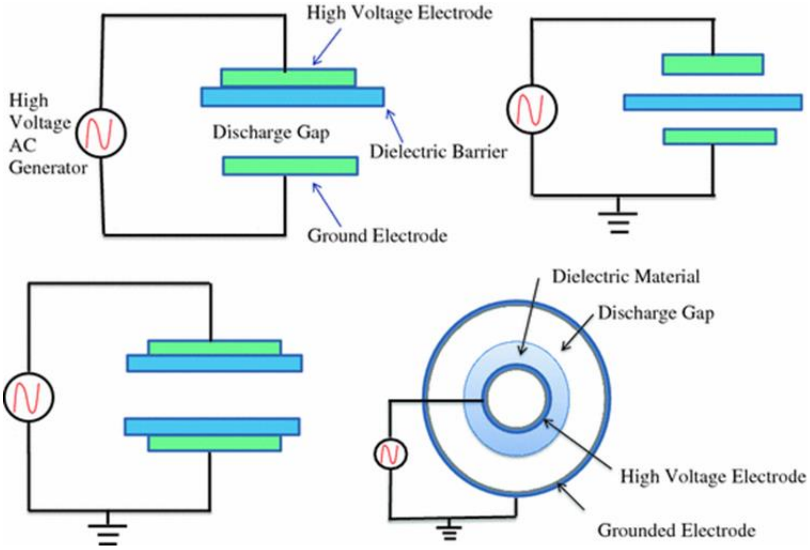


**Figure 14.** Schematic dielectric barrier discharge. *Reproduced from reference* [94] *with permission from the RSC, Copyright 2017.*

$CO_2$ dissociation can occur *via* a variety of channels or modes. As stated in earlier sections, electrons in the non-thermal plasma, particularly in DBD reactors, have more energy and transmit energy to other molecules through collisions. As collisions, in addition to delivering energy, also lose energy, this causes energy redistribution across multiple channels, culminating in $CO_2$ dissociation. Excitation, ionisation, and dissociation are the three pathways. A normalised unit termed a reduced electric field (E/n) is used to analyse the energy distribution between these different channels. The reduced electric field is a ratio of the electric field in plasma to the density of neutral gas.

For each type of plasma, the reduced electric field has different values. In DBD plasma, the reduced electric field value is above 200 Td ($1Td=10^{-21}$ $V/m^2$) whereas microwave and gliding arc plasma operate above 50 Td and below 200 Td respectively. In a region above 200 Td the detailed energy distribution is given in Figure 15 (b). As can be seen in Figure 15 (b), over 80% of the energy in DBD plasmas is used for electronic excitation, whereas, only 5% of total energy is used for $CO_2$ dissociation by ionisation and 10% of total energy is used for vibrational excitation. However, at lower electric field strengths, roughly 80-90 % of total energy is transmitted to dissociate $CO_2$ *via* vibrational excitation. Energy is supplied to the $CO_2$ molecule in vibrational excitation mode, as illustrated in Figure 15 (a), and it follows a ladder-climbing process to conduct $CO_2$ dissociation, which needs 5.1 eV of the threshold. In the case of electron impact dissociation mode surplus energy of 2 eV additional needs to be supplied for $CO_2$ dissociation due to elastic and inelastic energy losses. This makes electron impact dissociation mode less energy-efficient and thus DBD reactors and NTP reactors suffer from lower energy efficiency problems.

The trade-off between conversion and energy efficiency is always there. As vibrational excitation is a key step in $CO_2$ dissociation, the conversion of $CO_2$ in the DBD technology is much less productive than in microwave plasma. Additionally, the vibrational temperatures in DBD are substantially lower than those in microwave plasma, which has an impact on $CO_2$ conversion efficiency. Indeed, readers will be drawn to the fact that $CO_2$ conversion is appealing in microwave plasma. However, the easy operational design ability to work at atmospheric pressure and reactors modification (*i.e.* type of electrodes, catalyst integration facility, and usage of different operating parameters) make DBD more suitable for large-scale use [95,96].

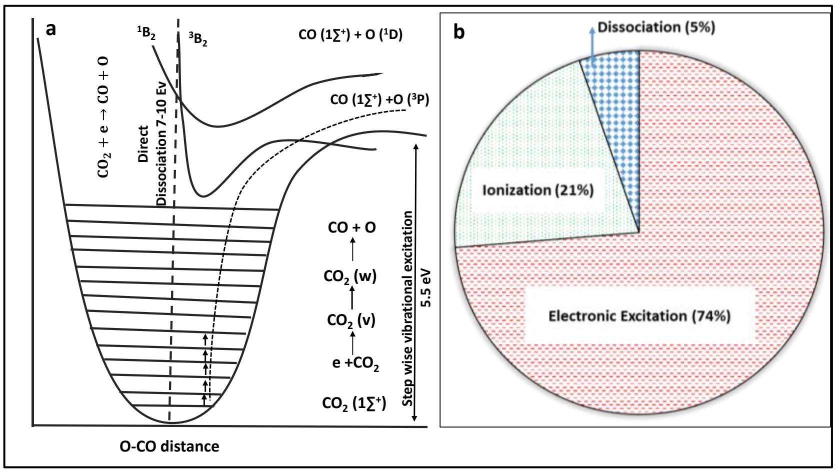


**Figure 15.** (a) Vibrational and electronic excitation levels of $CO_2$ molecule (not to scale). The stepwise excitation of $CO_2$ molecule and direct dissociation mechanism and $CO_2$ (v), and $CO_2$ (W) are different vibrational levels. (b) Distribution of total energy in NTP discharge at reduced electric field higher than 200 Td. Adapted from [7].

Further, microwave plasma which is a type of warm plasma is most suitable for $CO_2$ conversion however, it is operated under pressure constraints and the only reported products are CO and O from $CO_2$ dissociation. Nevertheless, in the case of a gliding arc GA's discharge plasma can yield maximum energy efficiency of more than 50% as observed by Kim *et.al* [97] nevertheless, the process suffers from low conversions due to the limited amount of gas flowing through the reactor due to the high flow rate required to sustain glow discharge. In comparison to both methodologies, a DBD reactor is a simplistic design that does not have constraints of gas flow and necessary operational pressures constrain. The low energy efficiency of the DBD reactor could be overcome by optimizing the parameters of the reactor or by incorporation of catalyst in the reactor bed. In upcoming sections, the reactor parameters are studied which could be optimized to obtain the best results from the DBD reactor.

The benefit of working with DBD is the possibility of incorporating catalytic materials in the plasma region. The incorporation of the catalyst opens new avenues and the possibility of product distribution. Furthermore, a variety of products ranging from oxygenates to others are reported to be produced via DBD coupled with catalysts. The yield and selectivity of products are considerably higher when plasma is coupled with a catalyst in-situ. Catalytic materials, usually metal oxides, can be placed upstream (*in-situ* plasma) or downstream (*post-plasma*) as shown in Figure 16. It is widely reported that depending upon the position of the catalyst, the species interaction on the catalyst surface could be controlled. Even though plasma-directed catalysis and conventional catalysis look similar, indeed, they are functionally different. [98,99,100,101,102].

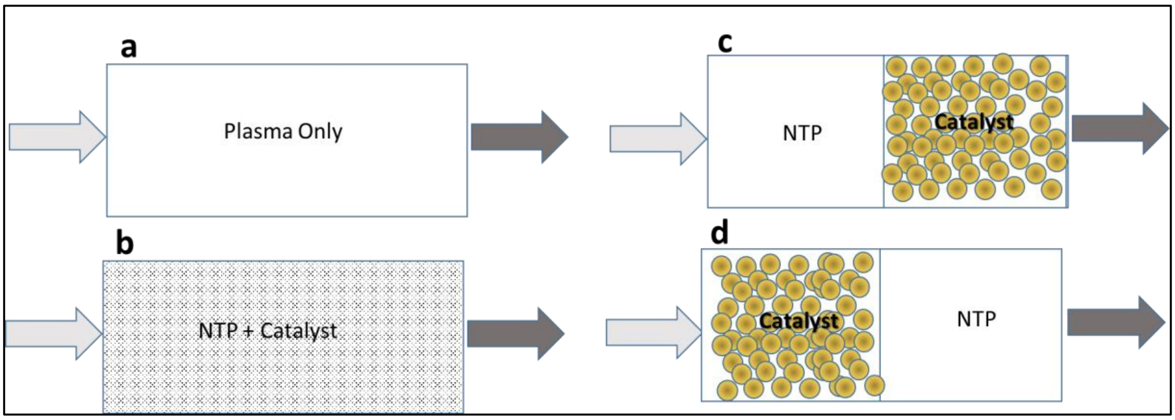


**Figure 16**. Different types of plasma-catalytic reactor configurations. (a) Plasma only, (b) IPC (in-situ plasma catalytic), (c) PPC (Post plasma catalytic), (d) p-PPC (pre-plasma catalytic system).

Plasma catalysis is more beneficial as it does not require the employment of rare earth metals as in the case with the conventional catalyst. Table 2 shows the descriptive comparison between plasma catalysis and conventional catalysis.

**Table 2.** Comparison between plasma-catalysis and conventional catalysis.

| Plasma Directed Catalysis | Conventional Catalysis |
|---|---|
| ❖ **Radicals species were generated mainly due to the interaction of plasma streamers with a molecule** | ❖ Radicals were generated by dissociative chemisorptions on the catalyst surface |
| ❖ **Energy expenditure is lower for radical generation** | ❖ The energy required for the radical generation was much more than plasma-directed catalysis |
| ❖ **At lower temperatures Eley-Rideal mechanism for the reaction** | ❖ No such mechanism occurs at a lower temperature( only follows the Eley-Radial mechanism at a higher temperature i.e thermal catalysis) |

Plasma-assisted $CO_2$ dissociation is one viable approach for reducing greenhouse gas. When it comes to the synthesis of value-added products from $CO_2$ synthesis of syngas ($CO+H_2$) is played more emphasis on. The reason being it is used to produce other products ranging from oxygenates, $CH_4$, polymers and others. The aim of the review is not to provide extensive literature on syngas production *i.e.* direct $CO_2$ dissociation but to exhibit how $CO_2$ could be directly converted to oxygenate and others in a single step which has high calorific values and is of thus prime importance.

### 3.4. Methanol ($CH_3OH$) production

Figure 17 displays the energy density of several fuels. We can see that jet fuel and diesel have the highest energy density per volume, while liquid $H_2$ is the most promising fuel in terms of energy density per mass. $CH_3OH$ is a good contender, as shown in Figure 15 since, it is midway between natural gas, gasoline, and diesel. One may underestimate $CH_3OH$ potential over other fuels, but one must also remember that fuels generated from fossilised material are restricted in terms of supply. Thus, it is possible that shortly, the depletion of fossil fuels would result in energy shortages, and $CH_3OH$ to gasoline (MTG) or $CH_3OH$ to olefin nature of product (MTO) technologies will be prioritized. However, $CH_3OH$ was utilised as a gasoline mix, and it could also be used to generate electricity from methanol fuel cells.

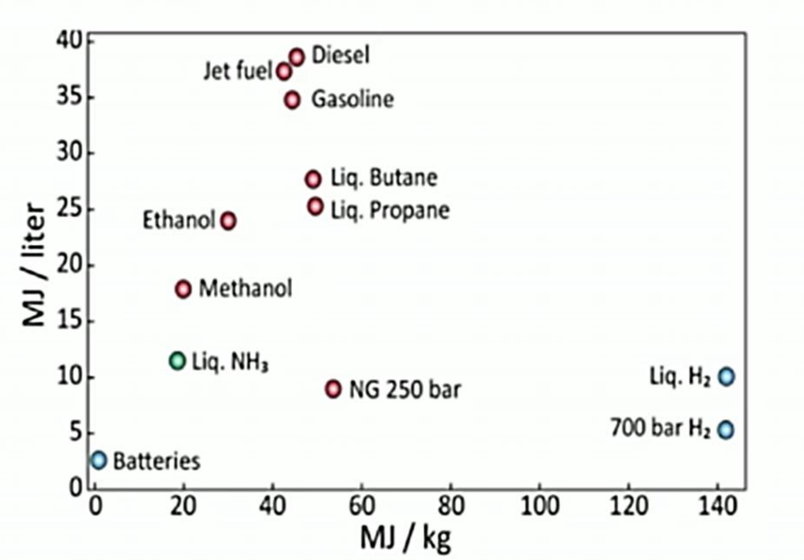


**Figure 17.** Energy density profile for different energy technologies/fuels.

When it comes to the synthesis of $CH_3OH$ *via* plasma only the DBD reactor is proven to achieve respectable $CH_3OH$ production. The $CH_3OH$ production proceeds via the mechanism given in Figure 18. The mechanism is validated by Eliasson *et al.* [103] and Coteron *et al.* [104] have proposed a systematic mechanism for $CO_2$ conversion into $CH_3OH$ on Cu (111) surface as reported in Figure 18.

$$\mathbf{CO_{2(g)}} + \mathbf{H_{2(g)}} \xrightarrow{\textbf{Reverse Gas-water shift}} \mathbf{CO}_{(g)} + \mathbf{H_2O}_{(g)} \qquad \text{Equation 9}$$

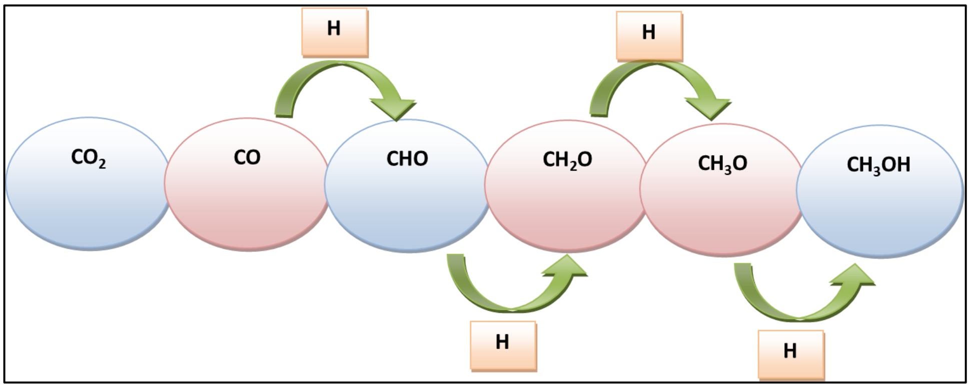


**Figure 18.** Mechanism of $CH_3OH$ formation on Cu (111) surface.

In regards to $CH_3OH$ production, a plant is set up by George Olah in Iceland to convert $CO_2$ to $CH_3OH$ following Equation 11. The $CH_3OH$ production from $CO_2$. Equation 11 is exothermic and is catalysed at 50-100 bar pressure and reaction temperature at 500-543K. The enthalpy of the reaction is -49.5 kJ/mol. Thus if one wants to convert $CO_2$ to $CH_3OH$ at ambient conditions *i.e*. at lower temperatures one has to lower the ΔS (entropy) or decrease the ΔH (enthalpy) to drive the reaction from the reactant side to the product side in accordance to Le Chateliers principle.

$$\mathbf{CO + H_2O \xrightarrow[\rightarrow]{\text{Water gas shift reaction}} CO_2 + H_2} \qquad \text{Equation 10}$$

$$\mathbf{CO_2 + 3H_2 \xrightarrow{\substack{\Delta\ 500-543K \\ 50-100bar \\ Cu/ZnO/Al_2O_3}} CH_3OH + H_2O;\ \Delta H^{O}{}_{298K} = -49.5\ kJ/mol} \qquad \text{Equation 11}$$

As shown in Equation 9 reaction we need to minimise the gas phase production of CO and more CO adsorption on the catalyst surface. In addition to that, the water gas shift reaction is also needed to be quenched as the water in the gas stream at high operating conditions may react with CO to produce $CO_2$ and $H_2$ as shown in Equation 10.

It is evident from Equation 11 that 1 mol of $CO_2$ produces about 1mol of water, which is economically not preferred as useful $H_2$ is wasted to produce water. The water destabilizes the plasma discharge and the effective adsorption of water on the catalyst will reduce the activity of the catalyst. Adding to that water needs to be separated from $CH_3OH$ which can add up to the overall cost of $CH_3OH$ production. Apart from using $CO_2$ for $CH_3OH$ production, $CH_4$ could also be used for $CH_3OH$ production as seen in Figure 19.

In the DBD reactor, $CH_4$ and $CO_2$ were used to synthesize $CH_3OH$, however, a very low yield was obtained even after using metal oxide catalysts [105]. Indarto [106] investigated the $CH_4$ oxidation with $O_2$, $H_2O$ and $CO_2$. It is noticed that $CH_3OH$ production was negligible with $CO_2$ reforming, whereas, the partial oxidation of $CH_4$ with oxygen, in a 4:1 ratio, yields $CH_3OH$ selectivity of 12% in a catalyst-free environment. Rajanikant *et al*.[107] have reported $CH_4$ reforming with water using altered inner electrodes and reported that the barbed wire electrode was efficient for $CH_3OH$ synthesis. Different approaches for $CH_3OH$ synthesis are described in Figure 19 depending upon the temperature, pressure and functionalities of the material introduced.

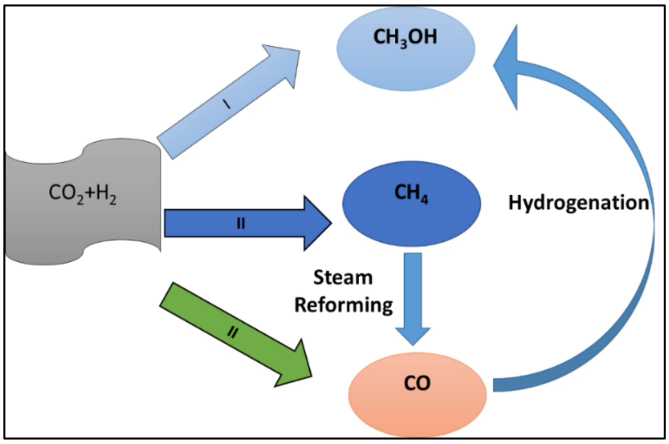


**Figure 19.** Different approaches for $CH_3OH$ synthesis.

As reported in Table 3 Wang *et al.*[108] reported a room-temperature synthesis of $CH_3OH$ employing a DBD system with water as a ground electrode, yielding 7% $CH_3OH$. Furthermore, when the catalyst was placed into the reactor at 10 W input power, 9 kHz frequency, and 40 mL/min, the yield rose by several orders of magnitude. As seen in Figure 19, the production of $CH_4$ during direct $CH_3OH$ synthesis is undesirable since it eliminated any potential of $CH_3OH$ formation The space-time yield of $CH_3OH$ is 0.3 $mmolhr^{-1}gcat^{-1}$ and the energy efficiency of 280 mmol $kW^{-1}hr^{-1}$ is attained. Indeed, methods such as steam reforming might be applied to generate CO. The $CH_3OH$ reaction pathway involves several intermediate species. Ihara *et al.*[109] have explored the synthesis of $CH_3OH$ using microwave reduction of $CO_2$ using $H_2O$ and discovered that around 60 kWh of energy is required to create 1 L of $CH_3OH$.

**Table 3.** Literature report available for $CH_3OH$ formation directly from $CO_2$ using DBD.

| Packing material/catalyst | Input Power (W) | $CO_2$ Conversion (%) | $S_{CH3OH}$ (%) | $CH_3OH$ Space Time Yield ($mmolhr^{-1}gcat^{-1}$) | Energy Efficiency (mmol $kW^{-1}hr^{-1}$) | Ref. |
|---|---|---|---|---|---|---|
| $Cu/\gamma\text{-}Al_2O_3$ | 10.0 | 21.2 | 53.7 | 0.3 | 279.5 | [108] |
| $CuO/ZnO/Al_2O_3$ | 500.0 | 11.0 | 1.9 | NA | NA | [103] |
| $Pd/In_2O_3$ | 30.0 | 24.9 | 36.5 | 4.5 | 74.4 | [110] |
| $Cu/ZnO/Al_2O_3$ | 30.0 | 25.6 | 35.1 | 4.4 | 73.5 | |
| $In_2O_3$ | 30.0 | 13.1 | 24.6 | 1.6 | 26.4 | |
| 15% $Co_xO_y/MgO$ | 10.0 | 33.0 | 31.0 | 5.0 | 251.2 | [111] |
| 5%$CuO\text{-}Fe_2O_3$/QW* | 2.0 | 16.2 | 32.5 | 9.3 | 1398 | [112] |
| 10%$NiO\text{-}Fe_2O_3$ * | 7.2 | 7.2 | 90.0 | 11.9 | 450 | [113] |
| * External heating of 200 ºC applied | | | | | | |

There are just a few literature accounts of direct $CO_2$ conversion to $CH_3OH$ as reported in Table 3, for example, Bill *et al.* [114] used a DBD reactor at atmospheric pressure, 400 W of input power, 50 °C gas temperature, and a feed flow of 250 mL/min to achieve a $CH_3OH$ selectivity of 0.2 %. The temperature rise lowered the $CH_3OH$ yield to 0.1 %, demonstrating that temperature impacts the spontaneity of a reaction. Eliasson *et al.* [103] have studied the impact of pressure on $CO_2$ conversion upon applying pressure 8 times higher than atmospheric pressure with 500W of input power, the gas temperature at 100 °C and feed flow of 500 mL/min $CH_3OH$ studied the impacts of pressure on $CO_2$ conversion using a pressure 8 times greater than atmospheric pressure, 500W of input power, a gas temperature of 100 °C, and a feed flow of 500 mL/min. A $CH_3OH$ selectivity of 7-10% with a $CO_2$ conversion of 12 % was obtained. Fundamental knowledge of $CO_2$ dissociation might explain the observed trends. The dissociation of $CO_2$ to CO increases the decrease of the system pressure by 1.5 times, and the use of high pressure compensates for the decrease in pressure in the reactor caused by $CO_2$ conversion. Second, high pressure causes a positive entropy shift in the system, leading to a spontaneous catalytic reaction. Lastly, high pressure ensures higher reaction rates. Men *et al.* [110] have used $Pd/In_2O_3$ for $CH_3OH$ synthesis at atmospheric pressure, 30 W input power and a feed flow rate of 40 mL/min. The selectivity for $CH_3OH$ was 36.5% and $CO_2$ conversion of 24.5% is reported. Herein, the nature of the catalyst *i.e.* oxygen vacancies on the Indium oxide surface facilitates $CO_2$ adsorption and dissociative $H_2$ absorption and $H_2$ spillover facilitates $CH_3OH$ formation. The space-time yield of 1.6 $mmolhr^{-1}gcat^{-1}$ and energy efficiency of 26.4 mmol $kW^{-1}hr^{-1}$ was achieved. As seen in Table 3 the 15% $Co_xO_x/MgO$ catalyst system is reported for the conversion of $CO_2$ to $CH_3OH$ at room temperature and atmospheric conditions [111]. The authors obtained 33% $CO_2$ conversion and 31% $CH_3OH$ selectivity achieved by using 10W of input power. The authors obtained a $CH_3OH$ space-time yield of 5 $mmolhr^{-1}gcat^{-1}$ and an energy efficiency of 251 mmol $kW^{-1}hr^{-1}$.

We have also worked on the direct conversion of $CO_2$ to $CH_3OH$ over mixed binary metal oxide of $CuO-Fe_2O_3$ loaded on quartz wool as reported in Table 3. With 2.0 W of plasma input energy and external heating of 200 °C about 16% $CO_2$ conversion and $CH_3OH$ selectivity of 32.5% and space-time yield of 9.3 $mmolhr^{-1}gcat^{-1}$ and energy efficiency of 1398 mmol $kW^{-1}hr^{-1}$ [112]. In another study, $CH_3OH$ selectivity of 90% and $CH_3OH$ space-time yield of 11.9 $mmolhr^{-1}gcat^{-1}$ is achieved with 10% $NiO-Fe_2O_3$ packed in sandwiched mode [113]. The energy efficiency which we have obtained is by far the best that is available for $CH_3OH$ production however it does not account for additional energy which is utilised for heating of the reactor. Nevertheless comparing the space-time yield of $CH_3OH$ the values which we have obtained are far better than available other literature reports as can be seen in Table 3.

The annual usage of $CH_3OH$ was 65 million tons in 2013 and is expected to increase even further [20]. The current technology uses synthesis gas obtained from fossil fuels. The reaction is mainly catalysed by Cu/ZnO-based catalysts. The new method of $CH_3OH$ production, which could help $CO_2$ mitigation is to use a $CO_2/H_2$ mixture.

The $CH_3OH$ production from CO or $CO_2$ heavily relies on the usage of $H_2$. $H_2$ production is a costly affair and is a tedious task thus, at most care must be employed to eliminate its wastage. Peters *et al.* [115] analysed different $H_2$ sources in the $CO_2/H_2$ conversion to $CH_3OH$ taking into account: (1) conventional $CH_3OH$ synthesis with $H_2$ production *via* steam reforming of natural gas, (2) $CH_3OH$ synthesis from $CO_2/H_2$ mixture with $H_2$ obtained from natural gas, (3) $H_2$ from the electrolysis of water, whereby the electricity was produced in the 2011 German power plant mix, and (4) $H_2$ from the electrolysis of water using hydroelectric power as shown in Table 4. Only in the latter case, the implementation of $CH_3OH$ production from the $CO_2/H_2$ mixture results in a net decrease in $CO_2$ emissions

**Table 4** Economical profile of utilization of $H_2$ for $CH_3OH$ production.

| **The source of Hydrogen produced** | **$CO_2$ emission associated with $CH_3OH$ Production ($t_{CO2}/t_{CH3OH}$)** | **Amount of $CO_2$ fixed (t)** | **Amount of $CO_2$ released (t)** |
|---|---|---|---|
| Steam reforming of Natural gas | 0.24 | - | +0.24 |
| Natural Gas | 1.91 | 1.38 | +0.53 |
| Electrolysis of Water (burning fossil fuels) | 5.67 | 1.38 | +4.29 |
| Electrolysis of Water (Hydroelectric Power) | - | 1.38 | -1.38 |

Thus from Table 4, it is clear that only the $H_2$ produced via the electrolysis of water provides net negative $CO_2$ emissions. Only in such a case, the process can be efficient however, electrolysis of water requires electricity to drive the reaction and is again interdependent. Thus there needs more emphasis on developing infrastructure which can harness renewable energy resources for $CO_2$ mitigation. One plant which does it efficiently is the one setup by Nobel Laureate George Olah. The plant is set up in Iceland called the Carbon Recycling International plant which harnesses geothermal energy to drive the plant's energy needs [116]. Apart from this Mitsui Chemicals plant in Singapore also synthesise $CH_3OH$ from $CO_2/H_2$ mixture.

### 3.5. Aldehyde & Acid Synthesis

The synthesis of aldehyde, using silent electric discharge, was reported in the 1930s when a central electric rod and the liquid dielectric barrier were used [100]. Synthesis of formaldehyde and acetaldehyde at room temperature was reported and high selectivity could be achieved by varying feed stock in the reactor. Luk'yanov *et al.* [117] have reported the synthesis of aldehyde and carboxylic acid with $CO_2$ and Ar mixture. The highest yield obtained for aldehyde was 1083 µmol with 0.6% of $CO_2$ and Ar acts as a dilution gas.

Liu *et al.* [118] & Malinson *et al.* [119] reported the production of liquid HCs( hydrocarbons) and many oxygenates. Indeed, about 10% $CH_3COOH$ selectivity is reached. Liu *et al.* [103] have reported in the review that improved the selectivity of $CH_3COOH$ by changing the ratio between $CH_4$ and $CO_2$. The authors have reported that, with 100 W input power and 40 mL/min feed flow rate, the mixture of $CH_4$ and $CO_2$ with a 3:1 ratio produces 4.2% of $CH_3COOH$, 0.3% of HCOOH and 1.7% of $CH_3CH_2COOH$ (Propanoic acid). As reported in Equation 15, the major reason for acid formation is $CH_3^\bullet$ and $H^\bullet$ radicles. The hydrogen radicle reacts with $CO_2$ and produces •COOH radicle, which further reacts with methyl radicle to yield $CH_3COOH$ as reported in Equation 12 and Equation 13.

$$\mathbf{CO_2 + H^\bullet \rightarrow COOH^\bullet} \qquad \text{Equation 12}$$
$$\mathbf{COOH^\bullet + CH_3{}^\bullet \rightarrow CH_3COOH} \qquad \text{Equation 13}$$

The $CH_3COOH$ formation, in a DBD, proceeds via two roots. Interestingly, DFT (density functional theory) theory showed that the pathway with CO intermediate was favoured. Moreover, if the DBD reactor was coated using starch then the acetic acid is increased to 11.2% with 75 W input power [120,121].

Ihara *et al.* [109] showed the reduction of $CO_2$ with steam, using microwave discharge, and obtained $CH_3OH$, HCOOH and $H_2O_2$. Wan *et al.* [106] have used catalysts in microwave irradiation and reported that $CH_4$, $CH_3OH$, $C_3$ and $C_4$ alcohols are obtained, interestingly, conversion has not been observed without catalyst and water. Nair *et al.* [122] have studied the $CH_4$ conversion in NTP discharge. The authors have fixed the NTP reactor, with several holes to allow air circulation, inside the FTIR cell (6.5 cm path length). It was reported that at 4-6 kV applied voltage and 600-1200 Hz, when the $CH_4/O_2$ ratio was low more oxygenates have been produced. However, due to the overlapping of water peaks, it was difficult to understand what type of oxygenates formed.

### 3.6. Dry Reforming of $CO_2$

$CO_2$ and $CH_4$ largely contribute to greenhouse gas emissions. As discussed previously in section 3.1, the extreme inertness of $CO_2$ demands a huge lump-sum energy investment. Similarly to $CO_2$, $CH_4$ is another greenhouse gas emitted into the atmosphere. $CH_4$ is gas at room temperature and atmospheric pressure conditions. The petroleum refining process acts as the main source of $CH_4$. Since the resources of natural gases are located at remote locations transport of natural gas becomes an important issue to address. $CH_4$ could be liquefied at -161.6 °C and atmospheric pressure but this is difficult to implement due to high-cost involvement. Thus more emphasis is on the conversion of $CH_4$ to oxygenate like $CH_3OH$ and $C_2H_5OH$ which can be liquefiable and easily transported. As reported in Equation 14, in NTP discharge about 10 eV/molecule has to be spent to reach 20% of $CO_2$ conversion with various dilution gases. Thus, researchers have tried the $CO_2$ conversion with hydrocarbons such as $CH_4$, $C_2H_4$ and $C_3H_6$ etc., to reduce energy consumption and this process is called dry reforming.

$$\boldsymbol{CH_{4(g)} + CO_{2(g)} \rightarrow 2CO_{(g)} + 2H_{2(g)}; \Delta H_{1073K} = 258.9\ kJ/mol} \qquad \text{Equation 14}$$

The reaction of $CO_2$ reforming with $CH_4$ is given in Equation 14. This reaction is endothermic and needs a temperature of 1073 K as the enthalpy of the reaction is ($\Delta H_{1073K}$) +258.9 kJ/mol. The drawback of this reaction is the catalyst deactivation due to carbon deposition. Therefore, the best catalyst has to be designed with high thermal stability. This process is operated commercially at 973 K temperature and 72% and 82% of $CH_4$ and $CO_2$ conversion have been reached respectively. Moreover, about 58% of theoretical energy efficiency was reported [123] .

Even though thermal catalysis yields higher conversion but still this method is not reasonable on an industrial scale as a huge lump sum of energy is utilised for obtaining respectable yields. To solve the energy scenario, researchers have developed a DBD reactor to synthesize syngas from $CH_4$ reforming with $CO_2$ [124,125,126,127]. DBD reactor due to operation at ambient conditions, simplistic design is preferred over other types of reactors. With DBD syngas production was possible even at ambient temperature and pressure, which is profitable for industrial applications. To explain the operation of DBD, Motret *et al.* [128] carried out reforming of $CH_4$ with $CO_2$. The gaseous species' rotational temperature and reactor wall temperature at atmospheric pressure were found. It was evidenced that in plasma streamer temperature reaches about 3000 K, but the mean gas temperature is about 350 K, which confirms the fact that DBD operates at ambient temperature.

The major product obtained from $CH_4$ reforming is synthesis gas (CO and $H_2$) also known as syngas. Syngas production, in plasma discharge, is dependent upon feed gas ratio and discharge power. The higher the discharge power higher is the yield of synthesis gas, however, the energy efficiency is very low. The highest reported energy efficiency is only about 7%. To enhance the energy efficiency, Tu *et al.* [129] used $Ni/\gamma\text{-}Al_2O_3$ catalyst to selectively produce CO and inhibit HCs like $C_1$-$C_4$ formation. By thermal catalysis, at 573 K, only 2% conversion is reached, while 40% conversion was obtained using an empty DBD reactor. Moreover, about 97.4% of $CH_4$ conversion was obtained by combining plasma and $Ni/\gamma\text{-}Al_2O_3$ catalyst, with 50 W input power[72]. Benrabbah *et al.* [20],[73] have reported the $CO_2$ reforming of $CH_4$ using Ni loaded-$CeO_2/ZrO_2$-based catalyst. Upon pre-treatment, with $H_2$ plasma, the catalyst showed higher $CO_2$ conversion with 5-8 W input power.

Li *et al.* [96] have investigated the effect of electrodes on $CO_2$ conversion during the $CH_4$ reforming process. It was evidenced that if feed gas was only $CH_4$ then the electrode made-up of Ti showed higher conversion. Moreover, conversion decreases in the following order Ti≈Al >Fe>Cu. It is concluded that when $CO_2$ and $CH_4$ are mixed in feed the best electrode with the highest conversion was Ti. Interestingly, Sarmiento *et al.* [130] demonstrated that apart from electrode material, the controlled roughness of the surface is necessary to sustain silent electric discharge. Zhang *et al.* [131] have reported $CH_4$ reforming of $CO_2$ using different zeolites. Interestingly, about 67% $CH_4$ conversion, and 40% $CO_2$ conversion are reached, moreover, 47% syngas yield and 34% liquid hydrocarbons ($C_{5+}$) selectivity are obtained. The reaction was carried out at 423 K, a flow rate of 200 mL/min, an input power of 500 W and a gas pressure of 100 kPa. Havran *et al.* [132] have studied the impact of zeolites on syngas production. NaY zeolite is useful for syngas production followed by quartz wool > HY- zeolite > NaX- zeolite. The HY- zeolite is used to synthesise $C_2$-$C_4$ HCs. It is observed that about 68% $CH_4$ conversion was reached with 200-700 W input power at a fixed frequency of 30 kHz.

At the lower feed ratio of $CO_2/CH_4$, the CO production was highest and oxygenates production was the least. As the feedstock ratio increases the selectivity towards oxygenates increases. At least two types of oxygen species were produced by the interaction of plasma with $CO_2$. One species was responsible for the conversion of $CH_4$ into oxygenate and other results in the formation of CO. Successful synthesis of selective polymers was possible by quenching the effect of destructive components of plasma. Recently, Bogaerts and co-workers [133] have developed an efficient model for plasma-based reactions like $CO_2$ reforming of $CH_4$, artificial photosynthesis, the impact of dilution gases on $CH_4$ conversion and others. Their model predicts the results close to the experimental results.

Gesser *et al.* [124] have reported about 50% conversion during $CH_4$ reforming of $CO_2$, with 3 min gas residence time and 25 kV applied voltage. Mei *et al.* [134] have optimized the process through response surface methodology using $Ni/\gamma\text{-}Al_2O_3$ as a catalyst for $CO_2$ reforming of $CH_4$. The authors concluded that the flow rate of $CO_2$ and discharge power plays the main role in $CO_2$ conversion, whereas energy efficiency is dependent on discharge power. The $CO_2$ conversion of 27.8% and energy efficiency of 10.2% was achieved when the aluminium foil was used as an outer electrode and screw-type inner electrode.

Li *et al.* [135,136,137] employed AC and DC corona discharge, at atmospheric pressure, and showed that with an increase in feedstock ratio of $CH_4/CO_2$, the syngas ratio increased, indeed, the syngas ratio decreased with increasing flow rate. It was also evidenced that conversion at 380 K was higher as compared to 890 K due to a feasible water gas shift reaction.

### 3.7. Steam Reforming of $CO_2$

Zou *et al.* [138] in the comprehensive review, have documented the $CO_2$ reforming using $H_2O$ to produce syngas using corona discharge. The ferroelectric material packed bed reactor is used and observed that the energy efficiency increased by decreasing water content in the reaction mixture. Indarto [106] in his review has documented that $CH_3OH$ and $C_2H_5OH$ were obtained with 12% and 4% yield using zeolite-13X in corona discharge, at 1.01 kPa. In another work, Ma *et al.* [139]reported syngas production from $CO_2$ and $H_2O$ mixture using $Ni/Al_2O_3$ catalyst. The $H_2$ and CO yields were 13.8% and 5.6 respectively with an input energy of 55.3 $J/cm^3$. In an empty DBD reactor, the $CO_2$ conversion was 16% but upon the introduction of water in form of moisture, the conversion decreased to 8.7% as seen in Figure. 21. This trend is due to 1) $H_2O$ addition leading to a decrease in the number of micro discharges and electron density 2) Rapid recombination of intermediate formed in reaction during plasma ignition. Similar observations are seen by Snoeckx *et al.* [133] where a chemical kinetic study was done with aid of a modelling approach. It was observed that effective $CO_2$ conversion decreased with a feed of $H_2O$. The products where CO and $H_2$ with no oxygenate are produced as insufficient conversion and the desired ratio for $CO/H_2$ is not attained as per Figure 20.

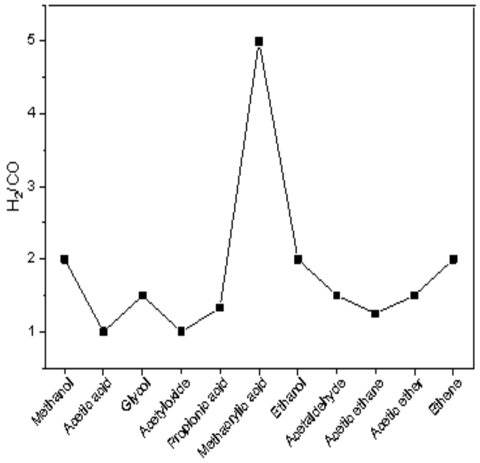


**Figure. 20**.Syngas mixture ratio to synthesize various chemicals

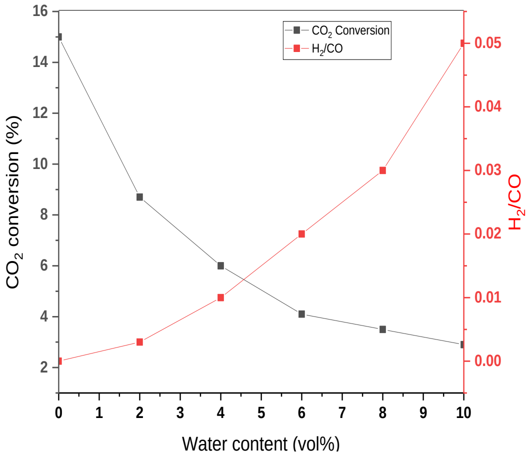


**Figure. 21.** $CO_2$ conversion profile over water content

The impact of catalyst $TiO_2$ and $Al_2O_3$ on $CO_2$ conversion was studied. Upon incorporating the catalyst in the reactor the $CO_2$ conversion rose to 20-24% for $TiO_2$ however for $Al_2O_3$ was in the range of 10-15% which is less. The difference in reactivity is due to the stronger water absorption capacity of $Al_2O_3$. The adsorbed water leads to hydroxyl radicle formation which could recombine with CO to yield $CO_2$.

### 3.8. Hydrocarbon Synthesis from $CO_2$

The reforming of $CO_2$ with $CH_4$ yields higher hydrocarbons and this is ascribed to the dissociation of $CH_4$ into methyl radicle which initiates the formation of chain growth as depicted in Equation 15 to Equation 17. The chain growth is dependent on various factors like the catalyst, applied power and others.

$$\mathbf{CH_{4(g)} \xrightarrow{Plasma} CH_3^{\bullet} + H^{\bullet}} \qquad \text{Equation 15}$$

$$\mathbf{CO_{2(g)} + 2CH_{4(g)} \rightarrow C_2H_{6(g)} + H_2O_{(g)} + CO_{(g)};\ \Delta G_{1073k} = 35\ kJ/mol} \qquad \text{Equation 16}$$

$$\mathbf{CO_{2(g)} + C_2\,H_{6(g)} \rightarrow C_2H_{4(g)} + H_2O_{(g)} + CO_{(g)};\ G_{1073k} = 0\ kJ/mol} \qquad \text{Equation 17}$$

Readers will find it interesting that the yield of $C_2H_4$ and $C_2H_6$ were significantly high as reported in Equation 16 & Equation 17 which can be attributed to the lower free energy of formation and lack of chain growth in the precursors [87]. The oxidative conversion of $CH_4$ using $CO_2$ as an oxidant in AC corona discharge. It was evident that a significant amount of CO was formed compared to $C_2$ hydrocarbon since $CH_4$ reforming was thermodynamically more favourable than oxidative coupling reactions. About 20-45% of $C_2$ HC's yield was achieved with a $CH_4$ conversion of 25-80% [85].

Hydrogenation of $CO_2$ and CO yields $C_2$ hydrocarbons. Blaustein and Fu [140] used static microwave discharge, at 1.6 - 6.7 kPa, to hydrogenate CO. Interestingly, about 90% conversion is reached, and $CH_4$ and $C_2H_2$ were quantified. To increase the energy efficiency, Mertz *et al.* [141] used a continuous flow microwave discharge reactor, working at 1.3 - 12 kPa, and reached only 4-19% CO conversion. The hydrogenation mechanism of $CO_2$/CO proceeds through hydrogen radical formation, which is the controlling step. Yoshida *et al.* [142] studied the effect of electrode material on hydrocarbon formation and reported that, among the studied materials, Cu electrode showed better performance towards $CH_4$, $C_2H_4$ and $C_2H_6$ formation irrespective of the energy applied between the electrodes. Li *et al.* [143] have reported the formation of hydrocarbons like $C_2H_2$, $C_2H_4$, $C_2H_6$, $C_3H_6$, $C_3H_8$, $iC_4H_{10}$, $C_4H_{10}$, $nC_5H_{12}$, $iC_5H_{12}$, $C_5H_{12}$ in DBD reactor with 100 W input power and 40-60 mL/min feed flow rate.

Eliasson *et al.* [144] showed that $CH_4$ and $CO_2$ react and produce about 40% syngas, 35% $C_1$-$C_5$ and 19% $C_5$-$C_{11}$ hydrocarbons(HCs), furthermore, oxygenates and plasma-polymerized films were also obtained as gas-phase products. Liquid hydrocarbons in the range of gasoline with 130 components were obtained. Out of 130 components, 87% were highly branched with high octane numbers. The chain-building up in these HCs would start from methyl radical formation and $CO_2$ acts as an oxidant in $CH_4$ conversion. The introduction of NaX-zeolites, in the discharge gap, prevents the formation of carbon black and significantly increases the selectivity of light and liquid hydrocarbons. It is reported that a high $CH_4$/$CO_2$ feedstock ratio and a narrow discharge gap assist the liquid HCs formation.

## 4 Summary & Future Perspective

Even though multiple emissions reduction solutions are available, energy cost and capital expenditure must be considered. Power generation (electricity) and transportation are the two most significant contributors to $CO_2$ emissions. Coal is a well-known source of energy, and coal-fired power stations are still in service. With the shared goal of lowering $CO_2$ emissions, the gasification of coal and subsequent use for power generation decreases $CO_2$ emissions in the atmosphere by an order of magnitude. Nonetheless, $CO_2$ is still being spewed into the atmosphere. $CO_2$ emissions in the atmosphere can be reduced by employing a variety of technologies, as detailed in the review. Figure 22 summarizes the cost required for the separation of $CO_2$. The energy cost for $CO_2$ separation by cryogenic distillation and chemical looping combustion is around 32 $/ton, but membrane separation appears to be the least cost-effective technology, requiring approximately 50-70 $/ton for $CO_2$ separation [47]. Adsorption and absorption need less capital investment than membrane separation (27.8 $/ton of $CO_2$ removed and 40-70 $/ton of $CO_2$ removed). Interestingly, even though certain methods are cost-effective, only absorption is extensively used in industry; other approaches, such as adsorption and cryogenic separation, are still on a pilot size. Indeed, the membrane separation is still being tested experimentally [145].

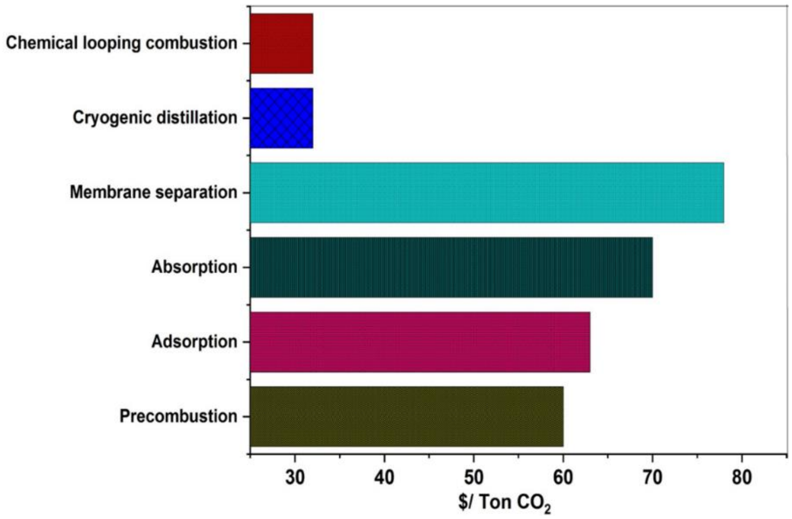


**Figure 22.** Cost efficiency of $CO_2$ separation.

Carbon capture and storage (CCS) is the most promising $CO_2$ mitigation strategy. However, this strategy is limited owing to a variety of factors such as the difficulty in locating suitable $CO_2$ storage reservoir locations, transportation costs, and the frequency of accidents. Metz [146] has comprehensively estimated the capital investment for different techniques.

Figure. 23 depicts the fraction of energy used on $CO_2$ collecting, transportation, and site monitoring. It has been demonstrated that around 86 % of total energy is used for $CO_2$ collecting and approximately 9% is spent on conveying the obtained $CO_2$. $CO_2$ capture from power plants costs around 90$/ton of $CO_2$, plus transportation and site maintenance costs 10 $/ton of $CO_2$ and 5$/ton of $CO_2$, respectively.

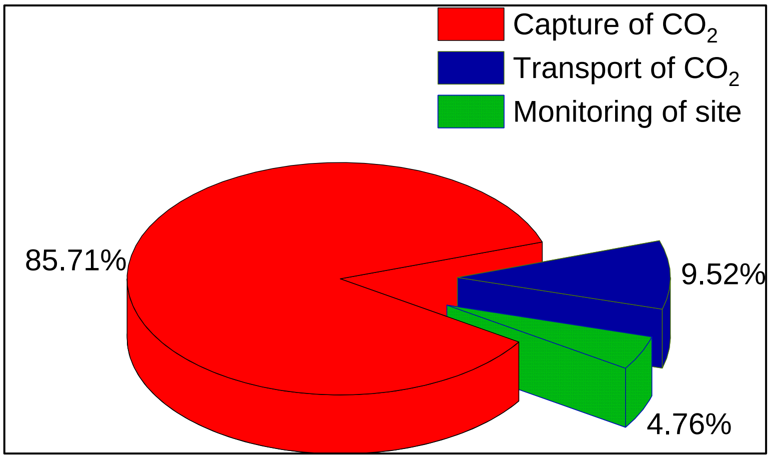


**Figure. 23.** The total cost involved in carbon capture and storage.

Based on the preceding material, readers will infer that using $CO_2$ rather than storing it is a superior method for addressing rising $CO_2$ levels. There are various $CO_2$ utilisation methods accessible, including solar thermochemical, photothermal, electrochemical reduction, and plasma catalysis. Each approach has advantages and downsides, which Snoeckx and Bogarts discuss thoroughly in their review [7]. Distinguishing methodologies only based on advantages and disadvantage is a skewed attempt. A normalised parameter is necessary to compare competing approaches. Snoeckx and Bogarts [7] used solar to fuel energy efficiency as a parameter to compare various methodologies as reported in Figure 24. Among the various technologies, plasma-based chemical conversion is the most cost-effective technology. Water electrolysis has the potential to provide maximum solar to the fuel efficiency of 60% -75%; however, as shown in Figure 24 only 15-19 % is currently achieved. Likewise, the electrochemical method has a maximum efficiency of 18%. The solar thermochemical process has maximum theoretical solar-to-fuel efficiency of 50%, whereas currently barely 7% is attained [147,148]. The photochemical process has the potential to achieve a solar-to-fuel energy efficiency of 5%; however, only 2% is currently achieved. In upcoming times dedicated research will raise the bar and it could be expected that a theoretical maximum could be achieved. Currently, the highest achievable solar-to-fuel efficiency of 95% could be achieved for plasma chemical conversions however, only around 23% is currently accomplished.

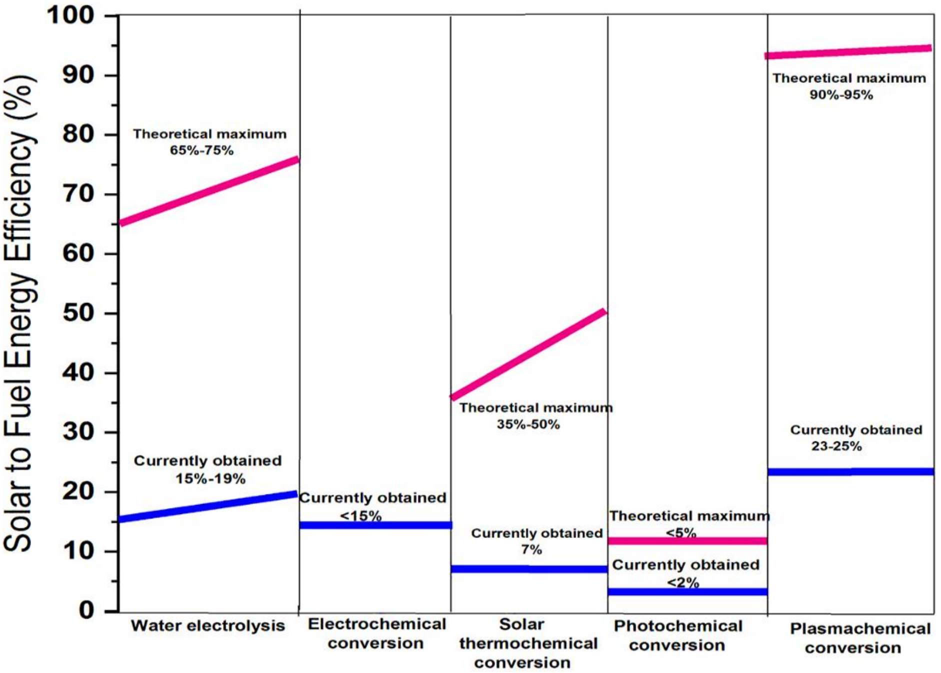


**Figure 24.**Solar to fuel energy efficiency for different techniques. *Adapted from reference [7] with permission from the RSC, Copyright 2017.*

## 5 Concluding Remarks

Despite the reality that the volume of $CO_2$ which may be converted to value-added products is relatively minimal in comparison to the amount of $CO_2$ released by various sources, $CO_2$ utilisation is an important facet of $CO_2$ mitigation processes. The ambition of commercialising $CO_2$ to value-added chemicals in ambient circumstances using DBD remains hazy. Several technologies for $CO_2$ conversion and storage have indeed been described, with some of the more important approaches addressed in this study. Rising $CO_2$ levels in the atmosphere are detrimental to us, but if $CO_2$ is used wisely, it can also be advantageous.

CCS is the lead protagonist for $CO_2$ mitigation. Indeed, the expenses of storage, transportation, and maintenance contribute to the overall cost of this system. Even though CCS is based on well-known and well-understood technical components, the transfer to wider implementation remains difficult. The funding of this transition is a unique issue, requiring a mix of strong policy and pricing signals to guarantee that low-carbon and energy-efficiency projects provide an attractive risk-adjusted return. CCU is frequently cited in the context of $CO_2$ mitigation. $CO_2$ may be converted into a wide range of end products since it is a reasonably benign substance. Various methodologies rely on using a catalyst. Catalyst deactivation decreases energy efficiency, and other drawbacks plague the use of catalysts in electro-reduction, thermochemical catalysis, and photocatalysis. The present period requires a new strategy to use $CO_2$, and we argue in this review that NTP-driven catalysis is the ideal approach with significant energy efficiency.

Looking at the favourable traits of NTP, it is possible to minimise catalyst deactivation and hence improve conversion. Most crucially, the reactions may be promoted at room temperature and pressure. On the negative side, plasma creation necessitates the use of electricity generated by the combustion of fossil fuels or *via* solar energy. However, it can be solved with the development of more efficient renewable energy harvesting devices which can serve as an indirect energy source for plasma generation. As previously stated, microwave plasma seems to have the highest solar-to-fuel energy efficiency and is also the most cost-competitive. It is important to note that the commercialization of $CH_3OH$ or any other value-added chemical production is possible if the energy efficiency of the plasma chemical reaction is more than 52% and the product yield is greater than 12%.

Indeed, a lack of understanding of the interaction of plasma and catalysts is impeding the commercialization of this technology. Readers may be led to believe that the production of plasma is a costly and energy-intensive procedure. This is not entirely incorrect; nonetheless, the need for specialised instruments raises the expense of plasma-based processes. However, it might be readily argued that obtaining value-added chemicals that were difficult or impossible to acquire in atmospheric circumstances outweighs the energy cost and instrument capital expenditure. This thorough review would provide readers with a fundamental grasp of current $CO_2$ conversion and separation methods.

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