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Renewable Methanol Production Using Captured Carbon Dioxide and Hydrogen Generated through Water-Splitting

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Abstract

The global warming issues associated with fossil fuels have forced the world to shift towards environment-friendly alternatives. The studies on the capture and storage of CO_2 have gained significant research attention, and to attract the world towards CO_2 capturing and storing, it is necessary to find suitable applications for this captured CO_2. Methanol is one of the products which can be produced by utilizing the captured CO_2 and hydrogen that can be produced by water splitting. Keeping in view both these green fuel production processes, this study proposes a combined application of both these technologies for the production of methanol, which is an important chemical used in manufacturing industries. This review paper presents a brief study of both carbon capture and hydrogen production technologies. It also provides research trends, economic aspects, and methods of incorporating both these technologies to produce methanol. Additionally, the prospects of the approach in Oman have also been presented.

Keywords

Renewable Energy, Captured Carbon Dioxide, Hydrogen Production, Electrolysis, Green Methanol

1. Introduction

According to International Energy Agency (IEA), fossil fuels are still considered the primary source of the current world's energy system. A large amount of carbon dioxide can be produced by this colossal use of fossil fuels, leading to an increase in climate change. Therefore, to reduce the emissions of CO_2 associated with fossil fuels, it is necessary to find a technology that enables the capture of

CO_2 and reuses it to produce value-added compounds or an alternative energy source instead of fossil fuels. According to IEA, the most attractive product that can be produced from CO_2 is methanol. Where the first renewable methanol production plant started operation in 2011 by Carbon Recycling International (CRI), where it used CO_2 conversion to produce methanol, which is different from natural gas-based production. However, the same catalysts such as $Cu/ZnO/Al_2O_3$ or $Cu/Zn/SiO_2$ are used in both methods. Still, methanol production from CO_2 has resulted in higher purity [1]. In addition to the low cost of methanol, it degrades faster than fuel. It meets the latest emissions standards and can be used as a feedstock in manufacturing gasoline, biodiesel, MTBE, DME. As the price of oil and gas fluctuates and greenhouse gas emissions increase, the interest in methanol production from renewable energy sources has increased [2].

The purpose of this current work is to present an overview of the various methods of producing methanol. The main efforts focus on renewable methanol production using captured carbon dioxide and electrolyzed hydrogen, highlighting the recent development of chemical conversion methods and the processes of CO_2 hydrogenation. Major studies on the improvement of new catalyst system targeting $Cu-ZnO-Al_2O_3$ Catalysts. It also provides an overview of the difference between using syngas and chemical conversion to produce methanol.

2. Methanol

Methanol is used in commercial industries as a raw material in many fuels, and chemical products include the production of aromatics, ethylene, formaldehyde, methyl tertiary butyl ether (MTBE), acetic acid, and other chemicals [3]. As methanol is flexible liquid, different feedstocks can be used in methanol production, such as waste, natural gas, captured CO_2 with green hydrogen. Moreover, according to the methanol institute, methanol is considered as a sustainable and clean fuel rather than a petrochemical. It is aligned with climate change policies and becomes a net carbon-neutral fuel that can lower greenhouse gas emissions. Nevertheless, methanol is liquid at room temperature and at everyday pressures. It has a small molecule, unlike LNG and hydrogen, that takes a more significant amount of energy to be produced compared to methanol [4]. It is considered a harmless fuel as it has lower emissions while the combustion process in marine or land vehicles as reported by the methanol institute.

However, methanol is also considered a toxic chemical that can be harmful to the skin and must be handled carefully. Besides, it is relatively expensive to be produced as it requires electricity, and the equipment used needs significant investment [4].

In general, there are five primary sources of renewable feedstocks that are used to produce renewable methanol, namely forestry residues, municipal solid waste (MSW), agriculture waste, carbon dioxide (CO_2), and renewable hydrogen [5]. Using two different routes: electricity or sustainable biomass (called bio-methanol) [5] (**Figure 1**).

In the biomass method, the organic matter is fermented in a reactor with a high temperature in the absence of air to produce synthesis gas, which is then formed into bio-methanol. While in the electro-fuel, hydrogen is extracted from water by electrolysis and reacts with the captured carbon dioxide to create methanol [5]. Researchers find green methanol produced by captured carbon dioxide and hydrogen is the most attractive option for stabilizing the earth's climate because it reduces the amount of carbon dioxide in the atmosphere and forms a clean and safe fuel time.

The first technique used in methanol production is the distillation of vinegar on wood; after that dry wood distillation technique was used. After that, the catalytic processes have been discovered and developed, e.g., partial oxidation of biomass (wood or solid waste) used commonly as it is relatively cheaper than the other expensive and harmful techniques at the same time. The amount of methanol produced by this method is comparatively large as it is estimated to be 185kg per metric ton of solid waste [6].

In the 1920s, the German chemical company BASF started to study the catalytic processes for methanol production; where the first methanol was produced as by-products in the ammonia production plant with an iron-oxide catalyst which led the researchers in BASF to invest more in the catalytic methanol production process and they created a selective catalyst made of zinc and chromium that works under high pressure of 350 bar and a temperature of 400˚C [6].

Imperial Chemical Industry (ICI) has developed a catalytic process using copper instead of chromium with lower pressure ranges between 25 to 55 bar and a temperature of 200 to 300˚C. Nowadays, $Cu/ZnO/Al_2O_3$ is considered the highest and most selective catalyst for methanol production, and it is used frequently in methanol production from hydrogen and carbon dioxide. As shown in Table 1, all the catalysts used in methanol production are made of zinc oxide, copper oxide, and more stabilizer compounds [6].

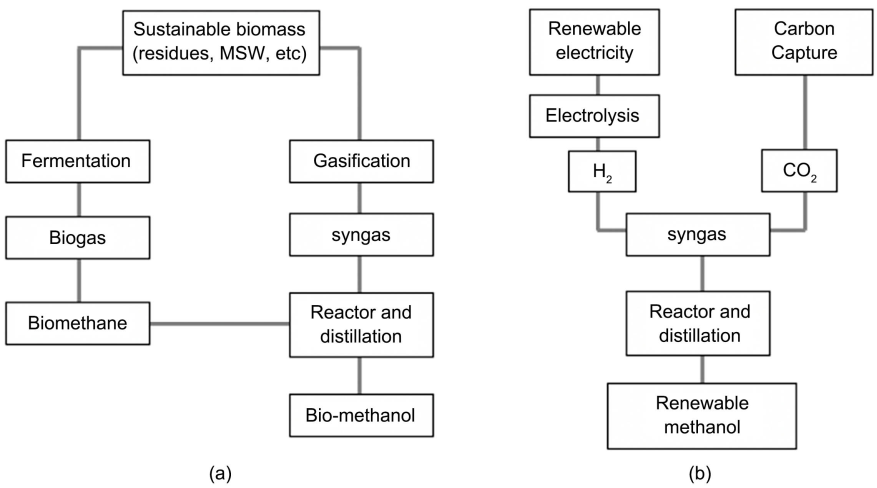

Figure 1. (a) Bio-methanol production processes (b) Renewable methanol production processes from different feedstocks. Reproduced from: [5].

Table 1. Typical composition of methanol synthesis catalysts (Reproduced from: [6]).

Producer	Cu (%)	Zn (%)	Al (%)
SUD CHEMIE	65 - 75	18 - 23	5 - 10
BASF	65 - 75	20 - 30	5 - 10
DUPONT	61	30	9
HALDOR TOPSOE	50 - 60	21 - 25	15 - 28

Methanol is the world's most-shipped chemical commodity, with more than 95 billion liters Per year of products using methanol such as plastics, cosmetics, paints, and fuels. It can be produced by the conventional method using fossil fuels, e.g., natural gas or coal (Methanol Institute, 2019). However, the main drawback of the conventional method is that fossil fuels are non-renewable materials and it is expected to deplete in the near future. Nevertheless, burning fossil fuels causes an increase in the amount of acid rain and photochemical smog, which increases the value of carbon dioxide that results in global warming. Yet, it is still the most common and commercialized technology used [7].

3. Carbon Dioxide Capture

As stated by International Renewable Energy Agency (IRENA), the amount of CO_2 needs to be reduced by more than 70% from 35 Gt (in the current levels) to 9.7 Gt by 2050. Consequently, to reduce the emissions of CO_2 associated with fossil fuels, it is necessary to find a technology that enables the capture of CO_2 and reuses it to produce value-added compounds [8]. To reach this target, 7% - 32% of CO_2 generated from the energy production using fossil fuels must be reutilized by 2050, which means that 155 megatons of CO_2 emissions will be reduced by 2030. Many chemical products at the industrial scale can be produced using CO_2 as a feedstock, e.g., methanol, formaldehyde, methanol, carbamates, polymer-building blocks, and methanol formic acid. The synthesis of methanol and urea are the chief consumers of CO_2, with more than 110 megatons of CO_2 annually used in the production industries of these two chemicals [8].

Carbon dioxide can be produced from exhaust streams, for instance, power plants, cement and steel factories, distilleries, and others. In 2016, around 32.045 billion metric tons of CO_2 were released into the atmosphere, and it raised by 1.4% in 2017, which is equivalent to having 170 million cars on the road [5]. Carbon dioxide is considered the most dangerous greenhouse gas that absorbs solar energy and keeps heat close to the earth instead of being released to space [1]. Nevertheless, the emission of carbon dioxide in 2018 reached 6677 million metric tons (**Figure 2**).

Carbon dioxide emissions driven by human activities pose a threat to the whole planet, where the average surface temperature has risen about 1.18 degrees Celsius in the last two years [10]. This has led government institutions, science, and industry to search for clean fuels produced by using renewable feedstocks to reduce greenhouse gas emissions. Therefore, they turn to using green methanol that is produced by renewable raw materials as a clean alternative source for fossil fuels [5].

Many technologies have been used to capture CO_2 from an industrial source, including post-combustion capture, pre-combustion capture, and oxygen fuel or oxyfuel combustion. Other new technologies are under research and development, e.g., adsorption, absorption, solid sorbent, and membrane separation technologies [11]. Nevertheless, CO_2 can be captured directly from the atmosphere, called Direct Air Capture (DAC). Currently, there are 15 direct air capture plants around the world, capturing more than 9000 metric tones of CO_2 per year, including Carbon Recycling International (CRI) which produces 4000 metric tons of renewable methanols by mixing up 5600 metric tons of captured carbon dioxide every year with renewable hydrogen [5]. According to Sustainable Development Scenario (SDS), this amount will be scaled up by 2030, where 10 million metric tons of carbon dioxide per year will be captured using DAC technology. **Figure 3** shows CO_2 capture by direct air capture in the SDS, 2010-2030 [12].

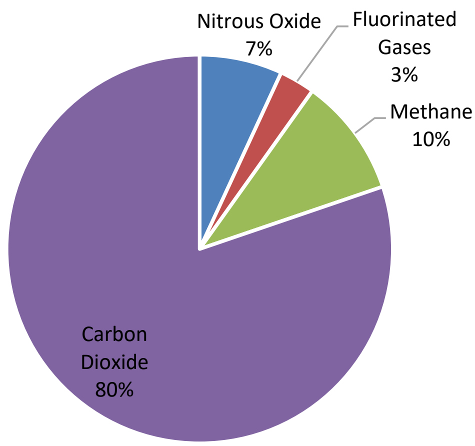

Figure 2. Overview of greenhouse gas emissions (Reproduced from: [9]).

After CO_2 is extracted from the air, it can be stored in deep geological formations or used in food processing, or combined with hydrogen to form value-added chemicals such as methanol. There are two different types of systems used to capture carbon dioxide from the atmosphere: liquid and solid direct air capture technologies. In the liquid system, the air passes through chemical solutions, e.g., a hydroxide solution that absorbs carbon dioxide, and the rest of the gases are turned back into the atmosphere. The solid technology uses sorbent filters that bind with carbon dioxide chemically, where the filters are heated to collect the concentrated CO_2, which can then be captured for use or storage [12].

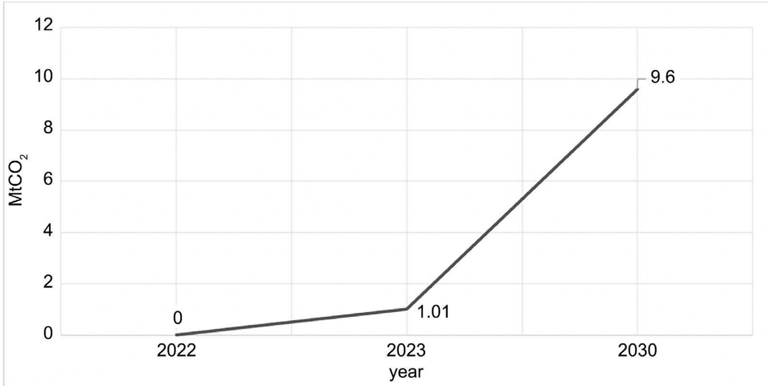

Figure 3. CO_2 capture by direct air capture in the SDS, 2010-2030. Reproduced from: [12].

4. Hydrogen Production: Electrolysis

Hydrogen fuel has shown great potential in helping the world tackle the global warming issue and, at the same time, help meet the global energy requirements effectively, using a sustainable approach. Although there are several approaches available for the production of hydrogen, such as electrical, solar-based electrical, biological and chemical, currently electrolysis or electrical hydrogen production systems are the most profitable and sustainable. The study justified the claim by using 3S mode of evaluation for hydrogen production technologies [13].

Electrolysis is the easiest and the most appropriate option for hydrogen production from renewable resources, e.g., water. In this process, water is split into oxygen and hydrogen by using electricity. The reaction occurs in an electrolyzer unit that can differ in size from large-scale, central production facilities to small-scale distributed hydrogen production [14]. As with any fuel cell, electrolysers consist of a cathode and an anode separated by an electrolyte. There are many electrolyser types, e.g., alkaline electrolysers, solid oxide electrolysers, polymer electrolyte membrane electrolysers, etc. These electrolysers work differently depends on the type of electrolyte material involved [14]. Not minding the type of technology employed, the electrolysis process involves the introduction of water into the reaction environment. The solution is then subjected to an electrical current, causing dissociation. The separated hydrogen and oxygen atoms are made to accumulate in their individual physical streams by putting them through an ionic transfer mechanism [15]. In **Figure 4**, it presents a diagrammatic example of an electrolyzer.

As a clean energy source, H_2 can be derived from both renewable and non-renewable sources [17]. Moreover, H_2 can be generated using an electrolyzer by connecting the fuel cells in the reverse mode through either water or methanol, or any other hydrogen carrier. An illustrative example of the generation of hydrogen and methane is the dark fermentation process with anaerobic digestion of residual algae biomass [17]. Even though the electrolysis method of hydrogen production is more expensive than the steam reforming of natural gas [15], the transition to a hydrogen economy will rely greatly on the electrolysis process.

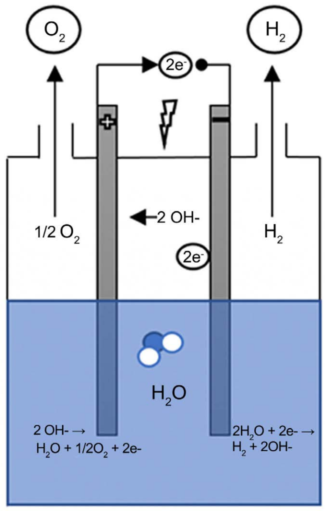

Figure 4. An electrolyzer (Reproduced from [16]).

This is because, with electrolysis, small facilities can be built and used against what is obtainable with other methods.

There are two main water electrolysis technologies: proton exchange membrane (PEM) solid polymer and potassium hydroxide (KOH) technologies. Further researches are also ongoing on other modes of water electrolysis, construction of cells, construction and selection of electrodes and electrolytes, and other parameters for another improvement of water electrolysis systems [18] [19].

5. Methods for Chemical Conversion of CO_2 to Methanol

5.1. Electrochemical Reduction of CO_2 to Methanol

The electrochemical reduction method is used to convert carbon dioxide to valuable fuels and chemicals using different electrocatalysts, conditions, and energy, which is electricity. The effectiveness of the method chosen depends significantly on the catalyst that is selected and the conditions of the reaction. Therefore, a huge effort must be applied to choose the appropriate electrode for the electrochemical reduction of CO_2 to reduce carbon dioxide's selectivity at high rates and low over potential without lowering water. Whereas water is used as an electrolyte and proton source, metals with a high hydrogen evolution reaction (HER) are used as an electrocatalyst.

Table 2 shows the products that can be produced electrochemically from CO_2, where the formed product depends on the reaction conditions and selection of catalyst [20].

Electroreduction allows the methanol to be produced in only one step by reducing CO_2 directly in the electrolysis cell. This can be done by using different types of electrodes such as semiconductors, metal oxide, homogeneous catalysts and other types. In 1983, many semiconductors such as n-GaAs, p-GaAs and p-InP were used to produce methanol directly from CO_2. However, the current densities and faradaic efficiencies (FEs) are relatively low. Many other studies

Table 2. Standard potentials for CO_2 reduction (Reproduced from [20]).

HALF-CELL REACTION	E° VS. SHE
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	+0.17
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	+0.131
$CO_2 + 4H^+ + 4e^- \rightarrow CH_2O + H_2O$	−0.028
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	−0.10
$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	−0.11

have been carried out to increase the faradaic efficiency and current density of the process. For example, pyridinium ion, a homogeneous electrocatalys, has been utilized for CO_2 reduction, then pyridine was discovered and used as a co-catalyst to create the active pyridinium species. Recently, it has been found that the two-electron reduction products like CO show higher current density than the one-electron reduction products of CO_2. The direct electrochemical reduction of CO_2 still has not yet been applied in industrial processes successfully but it is used widely on a laboratory scale [20].

The electrical chemical reduction has many advantages, e.g., it can be recycled, which significantly reserves chemicals and reduce waste. It also has a flexible and controllable reaction. It is considered a green and clean process as it uses a green source of energy, such as tide, wind, and solar power. Nevertheless, this method does not consume a large amount of hydrogen [21] [22].

Many studies have been done on developing the electrocatalysts and the reactor configuration/electrode in methanol production by electrochemical reduction to accelerate the production process and increase the selectivity [23]. However, this method has some drawbacks, e.g., the low current density, overpotential, stability, and it have not yet been applied in the industrial processes successfully. Still, it is used widely on a laboratory scale [20], making it unconvincing for commercial applications.

5.2. Photochemical Reduction of CO_2 to Methanol

The photocatalytic or photochemical method is a combination of photophysical and photochemical processes. Solar energy such as laser or light is used to transfer the captured carbon dioxide into methanol and other various products. This method is relatively similar to the electrocatalytic method of CO_2 reduction, where both ways use molecular catalysts. Recently, the photochemical process has been considered a promising method for CO_2 conversion. However, the selectivity of methanol is low compared to the other methods. The major limitation in this method is the sacrificial hydride source that must be added to the solution to substitute the anode, for example, amine, 1-benzyle-1, 4-dihydronicotinamide, and ascorbic acid. In **Figure 5**, it presents a simple schematic of the photocatalytic reduction of CO_2 [20].

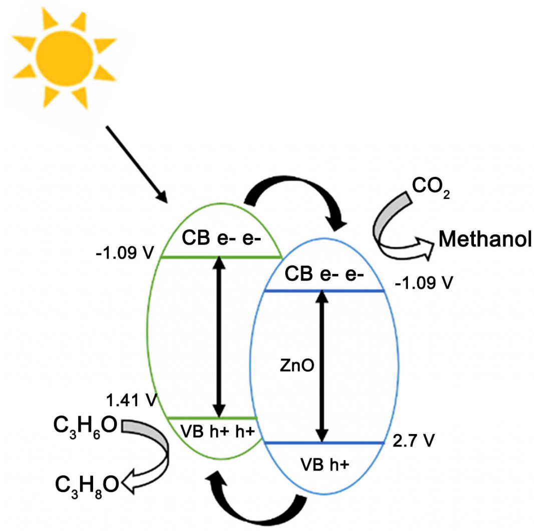

Figure 5. Schematic of photocatalytic reduction of CO_2 system [24].

Many experiments have been done to examine the ability of metal oxides and semiconductors to convert CO_2 to methanol, including NiO, ZnO, TiO_2, silicon carbide, and others. They can be either used alone or by adding them to other heterogeneous catalysts. However, the main drawback in producing methanol by solar energy and semiconductors is that the formation reaction is reversible. Therefore, it is essential to find other strategies to mitigate methanol oxidation to reach the desired industrial process. Photochemical reduction of CO_2 is considered the most attractive method for CO_2 conversion, even if the selectivity of methanol is relatively low in this method [20].

However, many other undesired products such as carbonates, formic acid, elemental carbon, and oxalic acid can be formed simultaneously in methanol production using photocatalytic CO_2 reduction, leading to a lack of selectivity. Some of these products can be poisoning for the photocatalyst, quenchers, and even cause degradation and produce CO_2 back. At the present stage, this method faces a lack of understanding the factors of controlling the products and modifying the direction of the whole process to produce only one desired product. Thus, the recovery of the non-gaseous products and the product distribution can cause a deactivation on the photocatalysts' surface. Scientists think that the leading cause of the problem is the differences in the potential products' chemical and physical properties formed from carbon dioxide. As a result, the whole CO_2 reduction should be mass balanced to avoid any solid phase deposition. Nevertheless, photocatalytic studies have to focus more on the factors and reasons behind other undesired products' formation [25].

Photocatalytic reduction is an attractive method to use. Still, at the same time, it constitutes a real challenge as it needs a lot of modifications and development in photocatalysts' effectiveness. The thermodynamics and kinetic requirements need to be developed; for instance, electrons and protons simultaneous transfer.

5.3. Photoelectrocatalytic Reduction of CO_2 to Methanol

The Photoelectrocatalytic CO_2 reduction method combines the electrocatalytic and photocatalytic techniques. Many semiconductors have been tested with different materials that are used as photoelectrode to transform CO_2 effectively by applying solar energy in PEC cell. Still, none of them met the desired efficiency and stability. This method uses around 1.5 eV of thermodynamic energy input. Thus, more significant energy input is needed for the PEC cell to make up for the losses that are caused by the overvoltage potentials, resistance losses, and band bending. Solar irradiance of semiconductors is used as a photocathode, and it helps generate hydrogen ions and electrons. The electrons will be excited to transfer it from the semiconductor to the conduction band, then move until it reaches the cathode counter electrode through an external electrical wire. After that, the produced electron-hole pairs will be split by the semiconductor to make oxidation and electrochemical reactions injected into the electrolyte. In **Figure 6**, it shows a photoelectrocatalytic cell to reduce CO_2 [26].

Despite the importance of photoelectrochemical method economically and socially, only a few studies have been done on developing this method. However, the main drawback of the photoelectrochemical CO_2 reduction is the susceptibility of semiconductors materials to degrade and oxidize the semiconductors surface, which results in creating holes on the surface of the semiconductors itself. This leads to thermodynamic instability toward anodic photodegradation [27].

It is required to understand some mechanisms to get good results in using PEC in CO_2 reduction; 1) understand the mechanisms of CO_2 reductions and water oxidation over the surfaces of photocathode and photoanode; 2) the dissolution and evolution of carbon dioxide in some organic solvent that can be dissolved in water such as monoethanolamine; 3) the interacting of the photocathode and photoanode materials with polymers; 4) study the corrosion of non-oxide semiconductors in solar irradiance and the passivation of the materials of semiconductors. 5) understand the behavior of ions and electrons of organics and the catalysts transferring in the photoelectrochemical cells. 6) integrate all the systems related to the CO_2 conversion to methanol in photoelectrochemical cells [28].

5.4. Chemical Conversion

Catalytic hydrogenation of CO_2 with hydrogen is the most usable and most straightforward method for methanol conversion. During the 1920s and 1930s, hydrogen and carbon dioxide were used widely in methanol production plants in the USA and were operated at high pressure and temperature using different oxide catalyst types, especially a mixed Cr_2O_3-ZnO material. Then, a new process was developed using a Cu/Zn/Al_2O_3 catalyst, which operates at lower pressure and temperature, with a desulphurization unit in front to remove sulfur as Cu is very sensitive. The first commercial plant that used this type of catalyst was built in 1966 [20]. This method has two different systems, heterogeneous and homogeneous catalysts systems:

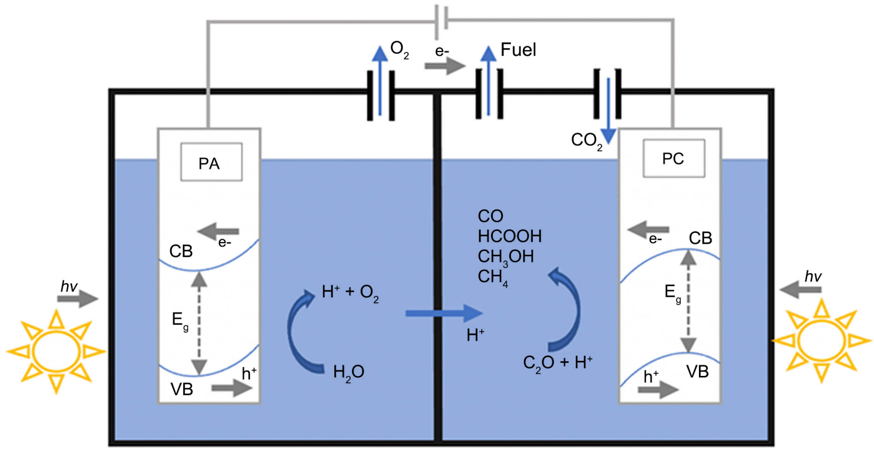

Figure 6. Photoelectrocatalytic cell for CO_2 reduction (reproduced from [26]).

5.4.1. Homogenous Catalyst

The first study on the carbon dioxide hydrogenation method by using homogeneous catalysis and the proper type of the used catalyst was carried out in 1995 by [29]. [29] proved that the $Ru_3(CO)_{12}$-K for CO_2 conversion works better than the other transition metal carbonyle catalysts, for example, $Fe_2(CO)_9$, $W(CO)_6$, $Ir_4(CO)$ and $RH_4(CO)_{12}$. Instead of the six electrons process, the cascade process has been used for CO_2 conversion [20].

The Cascade process using homogeneous catalysts includes three steps, which are hydrogenation of CO_2 to formic acid, then in the next step, formic acid will be esterified to generate formate esters, and in the final step, formate ester will be hydrogenated to produce methanol [30].

The reaction is undergone around 135˚C of temperature and 40bar of pressure. However, these numbers differ on the catalysts that are used in each step. The main two agents that help reduce the carbon dioxide in homogeneous chemical conversion are silanes and hydrides, with organocatalysts, e.g., N-heterocyclic carbenes (NHC). In addition to the high cost of silanes, Zhang proved that the NHC-catalyst could reduce carbon dioxide by reducing methoxides under ambient conditions [30].

The application of frustrated Lewis pairs for CO_2 reduction to methanol is another example of metal-free catalysis. In the first step of the reaction, that formatoborate derivative is produced by the reaction of CO_2 with [TMPH] + [HB(C6F5)3]-. Then in the next step, the latter reacts with [TMPH] + [HB(C6F5)3]- to formaldehyde acetal derivative and methanol [30].

However, the biggest challenge in the homogeneous catalysts is the separation process; in some cases, the catalyst cannot be separated from the product as they have the same phase. In other cases, the products are volatile, making it difficult to separate them by distillation. Moreover, compared to heterogeneous catalysts, homogeneous catalysts' thermal stability is relatively low, where the operating temperature ranges between 80˚C to 100˚C and rarely reaches near 200 in some pincer-based catalysts [31].

Homogeneous CO_2 hydrogenation to methanol is still in its infancy and needs to be developed more to become practical. Nonetheless, more studies need to be done to improve homogeneous catalysts' efficiency, especially non-noble metals (e.g., Fe, Cu, Mn, Co, etc.) to increase the produced quantity of methanol to make this method industrially valid [32].

5.4.2. Heterogenous Catalyst

Heterogeneous catalysts are more effective than homogeneous catalysts, separating the fluid from solid catalysts easily. It can also be recycled and used in various reactors, such as fluidized and fixed reactors. Many studies have proven that the Cu-based catalysts with multiple additives, for example, ZrO and ZrO_2 show more stability and efficiency than the other types [20]. Methanol is produced using the commercial methanol catalyst, a heterogeneous mixture of alumina, copper, and zinc oxide. Consequently, much research focuses on developing the performance of catalysts to increase the amount of produced methanol. Nevertheless, these researches aim to improve catalysts' activity and stability over time to sustain high plant output. CO_2 hydrogenation into methanol is an exothermic reaction (ΔH 298 k = −49.5 kJ/mol), which involves catalytic conversion at relatively low operating temperatures between 230˚C and 270˚C [20].

Figure 7 presents the heterogeneous catalytic process for converting CO_2 to methanol using Cu/ZrO_2 and $Cu\text{-}ZnO/ZrO_2$; where the formal structure-insensitive character of CO_2 transformation can be determined by the dual-site nature of the reaction path [20].

5.5. How $Cu\text{-}ZnO\text{-}Al_2O_3$ Catalysts Work

CuZnAl ($Cu/ZnO/Al_2O_3$) was developed firstly by Dalian Reak Science and Technology Co., Ltd. The studies have been conducted on hydrogenation of CO_2 fixed-bed continuous-flow reactor in high pressure. Before catalysts are placed on the stainless-steel floor reactor, it is diluted with quartz sand (0.8 mL, 20 - 40 mesh). Catalysts are also being kept for one hour at 250˚C with the hydrogen flow of 20 $mL \cdot min^{-1}$ in a phosphoric pressure. After cooling the vessel, the reactor is introduced with feed gas and H_2/CO_2 in a ratio of 3/1 with adjusting pressure to 3 MPa, which is further followed by keeping the temperature at 200˚C initiating their reactions. A thermocouple is used to control reactions by keeping the temperature at 200˚C and pressure at 3 MPa and H_2/CO_2 = 3 with gas hourly space velocity (GHSV) = 9000 h^{-1}. The collection of data from the reaction from 10 hours of operations using a thermal conductivity detector and using a flame ionization detector. Reactions in various stages mainly after H2 reduction, after ten h and 720 h, found no diffraction peaks of Al_2O_3 during multiple stages of using the CuZnAl catalyst. This is due to the high dispersion of catalysts and low content of Al [33].

Aggregation of Cu particles is the main reason for the deactivation of Cu-based catalyst in methanol synthesis [11]. After 10 hours of reaction, the size of Cu particles has decreased from 11.7 to 7.9 nm, and this might be due to the

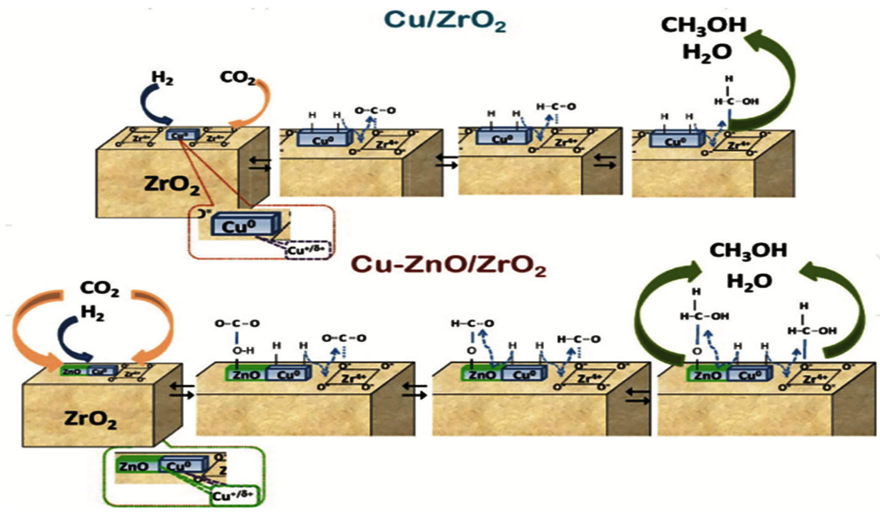

Figure 7. Heterogeneous catalytic process for conversion of CO_2 to methanol using Cu/ZrO_2 and $Cu-ZnO/ZrO_2$ (adopted from [20]).

reconstruction of Cu species [34]. Usage of conventional Cu-ZnO catalysts leads to complete reduction of partial reduction of Cu when it contacts with ZnO. The other by-products are also formed as part of methanol synthesis by this conventional catalyst [35]. Creating Cu-ZnO interphases is very important to get an active catalyst in the methanol synthesis process. Optimization of hydrogen partial pressure, heating rate, the temperature can play a crucial role in determining the optimal catalyst [36].

A different nanomorphology used for the synthesis has resulted in the best catalytic results from ZnO. Based on this study, the mechanism that has been widely accepted for bringing improvements in the catalyst is $Cu/ZnO/Al_2O_3$ formulation. The use of $Cu/ZnO/Al_2O_3$ in methanol synthesis from CO_2 brings significant improvements [36]. Partial or complete production in Cu is observed when Cu-based conventional catalysts get in contact with ZnO or even partial reduction in ZnO_x. The critical role of ZnO is that it helps the stabilization and dispersion of Cu sites and also helps in more absorption of the CO_2, which influences the performance of the catalyst [37]. The use of Al_2O_3 in the catalyst is that it helps improve the stabilization and dispersion under various reaction conditions of Cu-active centers.

The commercial preparation of $Cu/ZnO/Al_2O_3$ catalyst is based on a three-stage process, which includes precipitating precursors in hydroxy carbonates. These hydroxycarbonate precursors are calcinated in a controlled manner to produce dispersed CuO-ZnO. This process also produces residual carbonates, which maintain porosity on surface areas. The third stage of ZnO/Al_2O_3 catalyst precipitation includes reducing the oxidized phases to get active catalysts such as Cu+ nanoparticles or Cu for ZnO [38].

In catalyst synthesis, hydroxycarbonate precursor synthesis is the main stage as the final catalyst depending on the early stages in the progression of the catalyst [39]. Catalyst precursors need to have controlled precipitation which helps in preparing an efficient catalyst for hydrogenating CO_2. The final catalyst has desired properties with a large Cu surface area, better Cu-ZnO interaction, and even forming surface Cu-Zn partial oxidized materials. In the co-precipitation process, minimal contamination takes place from alkali metals (Na+). Controlling the parameters is required in the hydroxycarbonate precursors' vision progression by considering the aging time, temperature, and pH [39] (**Figure 8**).

5.6. Feasibility Analysis of Methanol Synthesis

The idea of synthesizing methanol using captured CO_2 and hydrogen is a unique approach that is needed for a feasibility analysis as both it is a quite new and expensive technology. In this regard, an important economic study has already been carried out by researchers in [40], and our entire feasibility portion will be based upon this predictive cost analysis study.

The study carried out the economic feasibility analysis of the production of renewable methanol utilizing captured carbon and hydrogen generated through electrolysis of water. The study employed Aspen Hysys 9, a simulation software, to evaluate technical analysis and predictive cost analysis of the project.

It was found that methanol cost for industrial-scale production of 100 tons per day will cost 0.48 $ per kWh of energy consumed. The cost of renewable methanol cannot reach the cost of present methanol production facilities which costs around 0.065 $ kWh^{-1} [40]. The main cost driving parameter for Methanol production is hydrogen which can cost up to 5 $ kgH_2^{-1}.

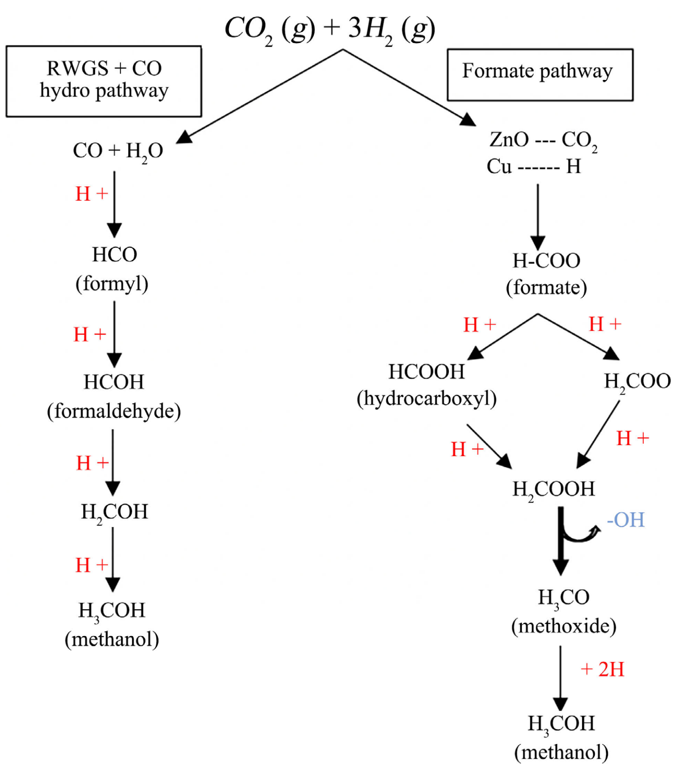

Figure 8. Pathways of methanol production from CO_2 hydrogenation over Cu-based catalysts (Reproduced from [1]).

The cost of hydrogen is also a challenging factor that has limited its applicability so far and research is ongoing to reduce it to \$2 to \$3 per kg [41].

However, the added environmental benefits and the ban on fossil fossils in the future can make this technology a good alternative. Also, with the advancement of research in this field of renewables, the costs will surely decrease in the future.

5.7. The Difference between Using Syngas and Chemical Conversion to Produce Methanol

Equation (1) shows the industrial production of methanol by syngas, a combination of monoxide and hydrogen, where the syngas is produced by using steam reform fossil fuels. It consists of a small percentage of carbon dioxide (CO_2). While the second equation is the industrial production of methanol by heterogeneous chemical conversion with using of $Cu/ZnO/Al_2O_3$ as a catalyst at a high temperature of 200˚C - 300˚C and high pressure of 5 - 10 MPa.

$$CO + 2H_2 \geq CH_3OH \;\; \Delta H = -90.8 \text{ kJ}\cdot\text{mol}^{-1} \tag{1}$$

$$CO_2 + 3H_2 \geq CH_3OH + H_2O \;\; \Delta H298K = -49.5 \text{ kJ}\cdot\text{mol}^{-1} \tag{2}$$

The process of generating methanol is less exothermic in Equation (2) rather than in using syngas. The two significant differences between producing methanol from pure CO_2 or syngas are the exothermicity of both processes and the formation of water in the synthesis that causes the deactivation of the catalyst prematurely [35]. Methanol synthesis from syngas takes place with higher exothermicity based on Equation (1) which creates the need for considering the reactor design to remove additional heat produced in the reaction. The convention plants producing methanol from syngas are based on the boiling water reactor type as it facilitates dissipating produced heat. Thermal control can be more accessible due to the low heat generated compared to the other process. There is no need for a boiling water reactor, whereas a simple tube reactor is good enough to control the temperature of methanol, which can improve the operation's efficiency and lower the cost [42]. To carry out methanol synthesis from syngas, the conventional catalysts used are mainly Cu combined with ZnO. One of the significant problems with the traditional catalyst is that it is less effective, where it can only convert 20% or less of CO_2 [43].

Additionally, synthesis from CO_2 produces a higher level of water and causes problems as it accelerates crystallization in ZnO and Cu particles. This leads to the deactivation of the catalyst and produce unwanted substances such as some hydrocarbons. Cu-ZnO catalysts are commonly used for methanol synthesis and hydrogenation of CO_2. However, it has some drawbacks, and most studies are on the improvement in the properties of catalyst in terms of physicochemical properties that are related to the efficiency of the catalysts [44].

5.8. Prospects in Oman

The economic assessment was based on historical fuel prices, energy expenses, and fuel economy. A life cycle analysis was used to assess carbon dioxide emissions. It was discovered that exclusively using green methanol as a fuel reduces CO_2 emissions from well to wheel when compared to fossil fuels [45]. It was established how much methanol could be produced using recycled garbage and wind power. Its yearly output ranges between 7.21 to 40.2 million tonnes [45].

Renewable methanol decreases carbon dioxide emissions by up to 95%, nitrogen oxide emissions by up to 80%, and sulphur oxide and particulate matter emissions entirely in Oman as compared to traditional fuels. Methanol is increasingly being seen as a clean and sustainable fuel rather than only a petrochemical [46]. Methanol becomes a net carbon-neutral fuel when made from renewable feedstocks such as collected CO_2 or garbage, aligning with climate change initiatives to reduce greenhouse gas emissions.

Oman is a country that earns a large portion of its income through the oil and gas industry. Owning to the shifting trends of the world, because of the harmful environmental effects of fossil fuels such as global warming, the world is shifting towards renewable energy sources to fulfill its energy demands. In terms of chemical production, the use of green chemicals is getting attention and conventional petroleum-based chemicals are also expected to be replaced.

So oil-based countries have to look for alternative income sources, which although they are already doing, such as increasing tourism, etc., but also have to look for other energy production means to fulfill their energy requirements. Although methanol is already being produced in Oman, this methanol is being produced from natural gas which is not considered a very environment-friendly way. With the expected ban on petroleum-based chemicals in the coming future, this method is not long-lasting.

There are several important uses of methanol, such as biodiesel, adhesives, and solvent production, which will increase its demand in the coming future. The demand for the downstream products of methanol such as methyl lactate, which is referred to as a green solvent, is also increasing owing to the trends in the world. But to ensure the sustainability of the downstream products, methanol has to be derived through environment-friendly methods. In other words, the introduction of this project will open pathways for several other downstream industries, ensuring the sustainability of the processes, and will help Oman not just in terms of the environment but will also help it in playing an important role in supplying green chemicals in the future.

However, there are several companies in Oman that produce methanol using the traditional way; for example, Oman methanol, Salalah methanol that is owned by OQ, and others. However, there are also projects under review that aim to produce methanol using green hydrogen and carbon dioxide.

5.8.1. Salalah Methanol Co. LLC

Salalah Methanol Company LLC, a subsidiary of OQ Company, was founded in 2006 with the goal of constructing a cutting-edge methanol manufacturing plant in the Salalah Free Zone. It is a chemical firm with between 201 and 500 people. Methanol is made from dry sweet natural gas, which is provided by the Ministry of Oil and Gas through existing pipeline networks. They already have the underlying infrastructure and the majority of the industrial facilities needed to create ammonia in their methanol plants. Ammonia was a commercially appealing product, allowing us to fund the project wholly through the refinancing of existing Salalah Methanol Company assets rather than depending on shareholder stock [47].

5.8.2. Oman Methanol Co. LLC

In 2004, Oman Methanol Holding Company LLC, a part of Omar Zawawi Establishment (Omzest), and Methanol Holdings International Limited created a joint venture (MHIL). The OMC Plant is located at the Sohar Port Complex on the Gulf of Oman, having maritime access to international markets. The methanol plant and facilities started producing refined methanol in December 2007 and now produce over 3000 tonnes per day. A team of highly skilled and capable individuals with vast expertise in the petrochemical industry staffs and runs the company. The bulk of OMC's employees are Omani nationals who get rigorous training that are tailored to each person [45].

6. Discussion

The concept of renewable methanol production is unique as it employs CO_2 captured from industrial processes or the atmosphere and hydrogen produced by splitting water. Hence, an idea of manufacturing methanol from raw materials which are not derived from petrochemicals has been presented. This approach will help in resolving the problem of storing a large volume of CO_2, which by this approach can be utilized for green fuel production.

Hydrogen fuel, itself can be used as a fuel which by this approach can be utilized for forming a chemical instead of energy, which will increase the applications of water-splitting technology in the manufacturing sector increasing the speed of development of the technology.

This approach will also allow the petroleum-based manufacturers of Methanol, who already have a well-established market for the product, to shift towards renewable methanol production.

7. Conclusion

As renewable energy sources can help greatly minimize environmental pollution and global warming issues, several modes of preparation of renewable energy have been employed by the researchers. Especially the production of renewable methanol that is used as an alternative where it reduces emissions of manufacturing industries that are caused by fuel combustion as it is considered the main source of climate change. Great progress has been made in the field of electrolysis and photochemical processes and the processes have attained high efficiencies which are comparable to the commercial processes. Still, significant research is needed on the subject from the effective capturing and separation of CO_2 to the manufacturing of methanol, especially on the economics of making renewables feasible for industrial-scale manufacturing.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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