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REVIEW

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Research on biomass energy and CO_2 conversion to methanol: a combination of conventional and bibliometric review analysis

Ephraim Bonah Agyekum[1,2,3,4,5*], Paul C. Okonkwo[6] and Farhan Lafta Rashid[7]

Abstract

The use of methanol as a chemical precursor and fuel additive has increased recently on a global scale. Hence, this study combined bibliometric and traditional review methods to assess the recent trends and evolution of methanol production, as well as its use. According to the study, producing methanol on a large scale from renewable sources is still hampered by the immature technologies used in its production. For instance, methanol production via the process of biochemical conversion still remains at the laboratory level even though it has proven to be a promising production option. Cu-based catalysts, especially Cu-Zn-based catalysts, were found to be the most frequently used catalysts for the hydrogenation of CO_2 to methanol due to their superior activity. The bibliometric study shows an annual growth rate of 3.63% in research within the last decade, with 867 authors involved. China leads globally in methanol production and consumption research. The highest collaboration occurred between China and the United States of America with a frequency of six. The study proposed future research directions, including the evaluation of the environmental impact of CO_2 conversion to methanol, focusing on the entire life cycle, comparing approaches, and streamlining procedures. It is also recommended to conduct research on flow chemistry and novel reactor designs that enhance mass and heat transfer in catalytic reactors.

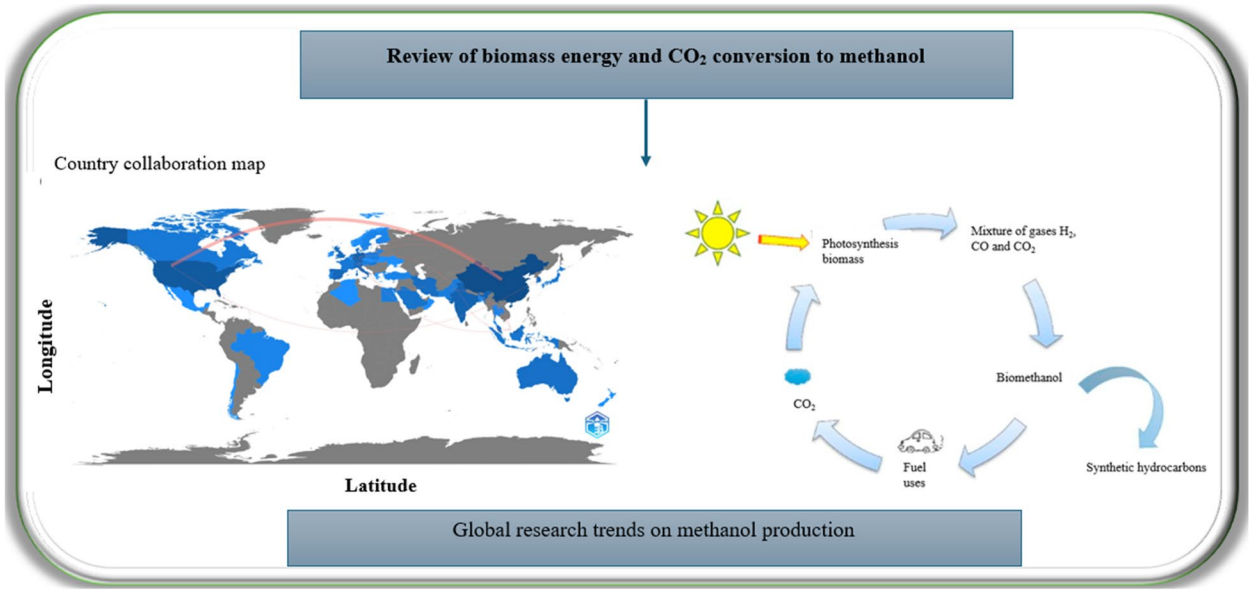
Highlights

- The review focuses on renewable methods for methanol production.
- Biomass and CO_2 conversion to methanol were discussed.
- The challenges associated with each of the methods were presented.
- Cu-based catalysts were found to be the highest used for the hydrogenation of CO_2 to methanol.
- The way forward for the development of the methanol industry was also discussed.

Keywords Renewable methanol production, Carbon capture, CO_2 hydrogenation, Biomass gasification, Methanol synthesis

*Correspondence:
Ephraim Bonah Agyekum
agyekumephraim@yahoo.com; agyekum@urfu.ru
Full list of author information is available at the end of the article

Graphical Abstract



1 Introduction

Sustainable energy supply to meet global energy needs has become a major challenge globally. Research shows that one out of every six deaths that occurred worldwide in 2019 was related to environmental pollution (Fuller et al. 2022; Wang et al. 2023). The pollution of the environment is further heightened by climate change since the greenhouse gases (GHG) that are emitted are mostly from the same sources, i.e., fossil fuels and the burning of biofuels. Global carbon dioxide emissions in 2018 were estimated to be around 33 Gt, and the atmospheric carbon dioxide concentration within that same period was also around 410 ppm, rising from pre-industrial levels of 280 parts per million (Zhong et al. 2020). To achieve the global temperature increase target set forth in the Paris Agreement, which will be 1.5 °C by 2050, global leaders have thus intensified the need to reduce anthropogenic carbon dioxide emissions by discovering alternate energy sources to meet demands in the form of renewable energy (RE) (Wang et al. 2023; Chen et al. 2024). A surge in the use of RE, particularly solar and wind power, represents a significant aspect of meeting the said ambitious target.

Nonetheless, the erratic nature of some of these RE sources remains a challenge as a result of their reliance on time of day and weather conditions. Energy storage devices have been suggested in order to solve this obstacle. The production of hydrogen from water electrolysis from the surplus generated energy from renewables for later use during high energy demands is one of the options proposed (Araya et al. 2020; Agyekum et al. 2022; Odoi-Yorke et al. 2024). Under these circumstances, the hydrogen that is produced can be employed as long-term storage, which can then be transferred as a fuel or for use in industries. Hydrogen can alternatively be transformed into electro-fuels using the concept of power-to-X, thus storing RE in the chemical bonds of liquid or gaseous fuels. Methanol is identified as one of the possible carbon–neutral electro-fuels when generated from hydrogen through electrolysis and carbon dioxide from the atmosphere, the exhaust of industrial processes, or biomass (Goldmann et al. 2018; Araya et al. 2020). The economy of methanol using green-methanol synthesis methods is proposed compared to that of hydrogen, which necessitates a massive transformation in its transportation and means of energy storage. Methanol's density is approximately half that of gasoline in terms of volume, with an octane number of 113. Blending methanol and gasoline at 10% or 90% can result in an octane number that is up to 130. The efficiency of engines powered by pure methanol can reach about 43% and sustain it beyond 40% in a broad velocity and load range (Bozzano and Manenti 2016).

Methanol, apart from being a vital alternative fuel for transportation, also serves as an intermediate for a number of downstream products, including olefins, formaldehyde, biodiesel, dimethyl ether (DME), and

acetic acid. It can be used as an efficient and safe carrier for the transportation and storage of hydrogen. Syngas, primarily composed of carbon monoxide (CO) at temperatures between 200 and 300 °C and pressures between 50 and 100 bar, is a source of industrial methanol. Hydrogenation of CO_2 and CO as well as water–gas shift reactions can also yield this product (RWGS) (Cui and Kær 2019). Although methanol and hydrogen can be neutral in terms of CO_2 emissions if their production is from renewable sources, the handling of methanol is easier and can serve as an alternative to oil directly in the chemical industry (Alberico and Nielsen 2015). Additionally, since methanol at ambient temperature is a liquid, it therefore ties the practices and infrastructure of the fossil-based economies to future RE systems, where electrolyzers and fuel cells (FC) are projected to play a major role. Through the reforming process, methanol can be converted to hydrogen, and the gas mixture, which is a product, can be used directly in high-temperature proton exchange membrane (PEM) FC or low-temperature PEM FC after purification (Araya et al. 2020). There are two primary benefits linked to the power-to-methanol technique. Some of these include the chance to produce a renewable product that can completely replace ones derived from fossil fuels and store RE in the form of a chemical. Using traditional infrastructure, e-methanol can be distributed and stored (Fournas and Wei 2022; Luo et al. 2022; Sollai et al. 2023). CO_2 hydrogenation may reduce GHG emissions by about 59% when compared to traditional methods, according to a life cycle assessment of methanol production (Assen et al. 2013).

In this study, we review renewable approaches for the production of methanol. The synthesis of methanol from biomass and CO_2 is documented in this literature. A review of methanol, its synthesis, and comparative properties with other fuels is presented. The challenges associated with the production process of methanol from both biomass and CO_2 are also presented. Next, a bibliometric analysis of clean methanol production is also presented, which presents current research trends in the last decade on methanol synthesis. The bibliometric assessments also present the evolution of studies on the topic of research over the past decade, including emerging, declining, and well-developed areas of research in the production of methanol. The way forward in terms of technical and policy directions for the development and use of methanol is also proposed. This gives researchers and academics a more refined and comprehensive understanding of the intellectual and conceptual structure of the research body.

2 Current state of methanol production and use in the world

Methanol's (CH_3OH) global production capacity as of 2021 was about 164 Mton·a^{-1}, with a projected yearly increase of about 10% for the next ten years. Methanol synthesis is traditionally obtained from the syngas of fossils, which is accomplished by steam reforming natural gas or gasifying coal. Captured CO_2 and renewable electricity are, however, gaining considerable interest globally (Campos et al. 2022). The present technology for the synthesis of methanol is largely built on the utilization of Cu/ZnO/Al_2O_3 (CZA) catalysts in either adiabatic reactors with intermediate cold syngas quenching, usually known as quench reactors (for instance, the Haldor Topsoe process, ICI, and the Casale process), or multi-tube reactors with boiling water that serves as cooling fluid, generally known as isothermal reactors (for instance, the Linde process and the Lurgi process) (Bozzano and Manenti 2016; Campos et al. 2022). Other forms that are generally not used are the Toyo process and the Kellogg process, which are adiabatic reactors with intermediate cooling (Campos et al. 2022). A scheme that shows methanol's intermediate position in the transformation of both sustainable syngas and fossil-based methanol end-use applications, as well as added-value chemicals and fuels, is presented in Fig. 1.

Methanol as a fuel constitutes about a third of the global total consumption of methanol. Its demand is estimated to increase due to the world's rising energy demand and the necessity of abandoning fossil fuel use. China, due to its coal production, leads the world methanol market with 57% utilization of the world's demand (Roode-Gutzmer et al. 2019). Currently, the emissions over a lifetime due to the production of methanol are estimated to be about 0.3 Gt CO_2 a year; this is approximately 10% of all emissions from the chemical industry. In the past 10 years, its production has almost doubled, with China having the largest share. It is forecast that its production per year could increase to about 500 metric tons by 2050 under the current production trends, which will release an estimated 1.5 metric tons of CO_2 a year if wholly obtained from fossil fuels. It costs about USD 100–250 per tonne to generate methanol utilizing fossil-based fuels. Renewable methanol that is currently produced is less than 0.2 Mt annually; it is mainly in bio-methanol form (IRENA 2021). Methanol's demand globally has already reached some 107 Mt, which is virtually a double of what existed in the past decade, and is mostly driven by methanol-to-olefin (MTO) process expansion as well as developing energy applications (Fig. 2, Sen et al. 2022).

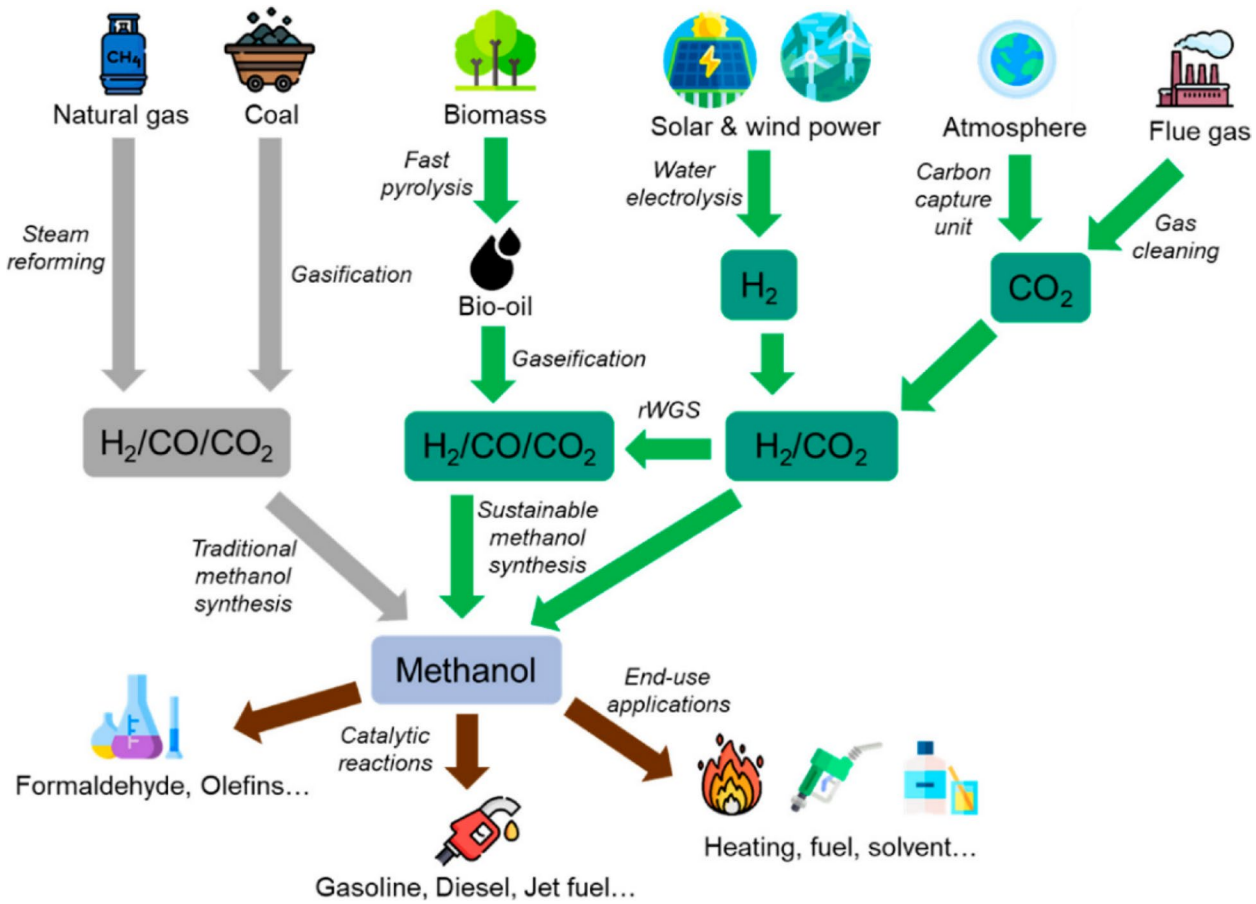


Fig. 1 Methanol's position in conversion of syngas sources and other applications (Campos et al. 2022) CC BY-NC

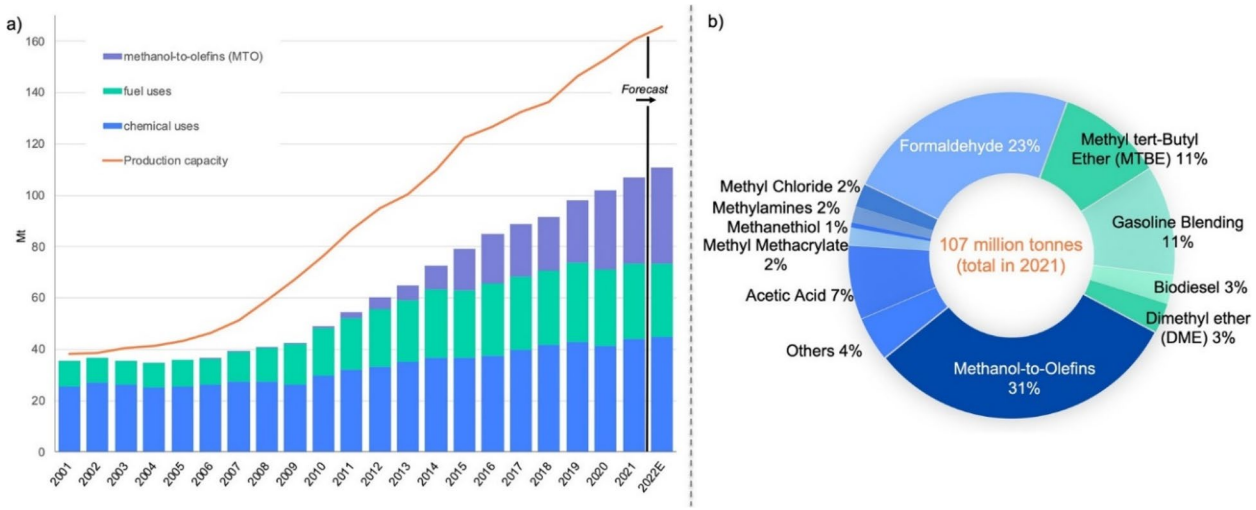


Fig. 2 **a** Methanol demand and capacity of production globally; **b**) utilization of methanol based on industrial sectors (Sen et al. 2022). CC BY-NC

3 Methanol, its synthesis, and comparative properties with other fuels

Robert Boyle first isolated methanol in 1661 through the distillation of wood, and Dumas and Peligot in 1834 first discovered its chemical composition. Production volume at that time was around 10–20 L per ton of treated wood. It was originally utilized for the purposes of cooking, lighting, and the provision of heat. Sabatier in 1905 suggested the original synthetic method of methanol production, which involves the reaction of CO and H_2 (Bozzano and Manenti 2016). Methanol's production on an industrial scale started in 1923 at BASF (Leuna Werke, Ludwigshafen, Germany). The method employed ZnO/Cr_2O_3 (a sulfur-resistant catalyst) at 320–450 °C and a high pressure between 250–350 bar (Dieterich et al. 2020). The high-pressure process was in the 1960s replaced by a low-pressure process (50–100 bar), which was originally marketed by ICI (now Johnson Matthey). The low pressure was done beyond 200 °C established by the used copper catalysts' activity and less than 300 °C restricted by its thermal stability. Today, due to kinetic observations and isotope tracing experiments, several researchers agree that the formation of methanol occurs mostly through CO_2 hydrogenation, according to the reactions presented by Dieterich et al. (2020):

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O\,\Delta H = -49.4\,kJ\,mol^{-1} \quad (1)$$

whereas the hydrogenation of CO_2 incorporates water formation, CO is transformed into CO_2 using the RWGS by water consumption:

$$CO_2 + H_2 \rightleftharpoons CO + H_2O\,\Delta H = 41.2\,kJ\,mol^{-1} \quad (2)$$

The conversion of the CO can be presented as:

$$CO + 2H_2 \rightleftharpoons CH_3OH\,\Delta H = -90.6\,kJ\,mol^{-1} \quad (3)$$

The two reactions are exothermal; therefore, they comprise a decline in volume. Therefore, the formation of methanol is supported by increased pressures and temperatures. The hydrogenation of CO is notably more exothermic than that of CO_2, which results in a higher demand for cooling (Alper and Yuksel Orhan 2017; Dieterich et al. 2020).

Table 1 compares the properties of some fuels. Machines such as the Otto and diesel motors can use methanol. It has a high octane number and can be mixed with gasoline, which improves combustion efficiency. Whereas methanol has relatively lower local emissions, the energy density is approximately 50% that of gasoline, and with respect to methanol, corrosion is also disadvantageous. Additionally, it does not have a lubricating impact on the motor; it can also be used either directly or with a reformer in fuel cells with high efficiency (Dieterich et al. 2020).

Some challenges and advantages of methanol as a fuel are illustrated in Fig. 3; it provides a general scheme that connects the properties of methanol to the performance of an engine.

3.1 Methanol's power density

Compared to compressed hydrogen, methanol has efficient energy storage in terms of volume and weight. Liquid hydrogen has a lower volumetric density than

Table 1 Comparison of synthetic and traditional fuels. Adapted from (Dieterich et al. 2020)

Properties	Methanol	Gasoline	DME	Diesel	LPG	FT-fuel (diesel)
Aggregate	Liquid	Liquid	Gaseous (liquid under, 5 bar)	Liquid	Gaseous (liquid under, 5–10 bar)	Liquid
Chemical formula	CH_3OH	C_5–C_{12}	CH_3OCH_3	C_{10}–C_{23}	C_3–C_4	C_{10}–C_{23}
Miscibility	In diesel and gasoline		In LPG; in diesel			In diesel
Density (g^{-1})	791	715–780	668	815–855	540 (at 10 bar)	770–860
Pollution	Oxygen content reduces local emissions		No C–C binding—almost no particle emissions	Emission of high soot and NO_X	Emissions of NO_X 80%, KW emissions 50% in comparison with gasoline	Less hydrocarbon, CO and particle emissions
LHV (MJ^{-1})	15.4–15.6	31.2–32.2	18.2–19.3	35.3–36	24.84	33.1–34.3
Boiling point at 1 atm (℃)	64.7	25 –215	–24.9	170–380	–42 to – 0.5	150–320
Degradable	Yes	No		No		Yes
Vapour pressure at 20℃ (bar)	0.37	0.45–0.9	5.3	0.01–0.1	2.1–8.3	0.01–0.1
Cetane number	5 (low)	-	55–60	45–53	-	70–80
Octane number	110–112	90–95	-	-	105–115	-

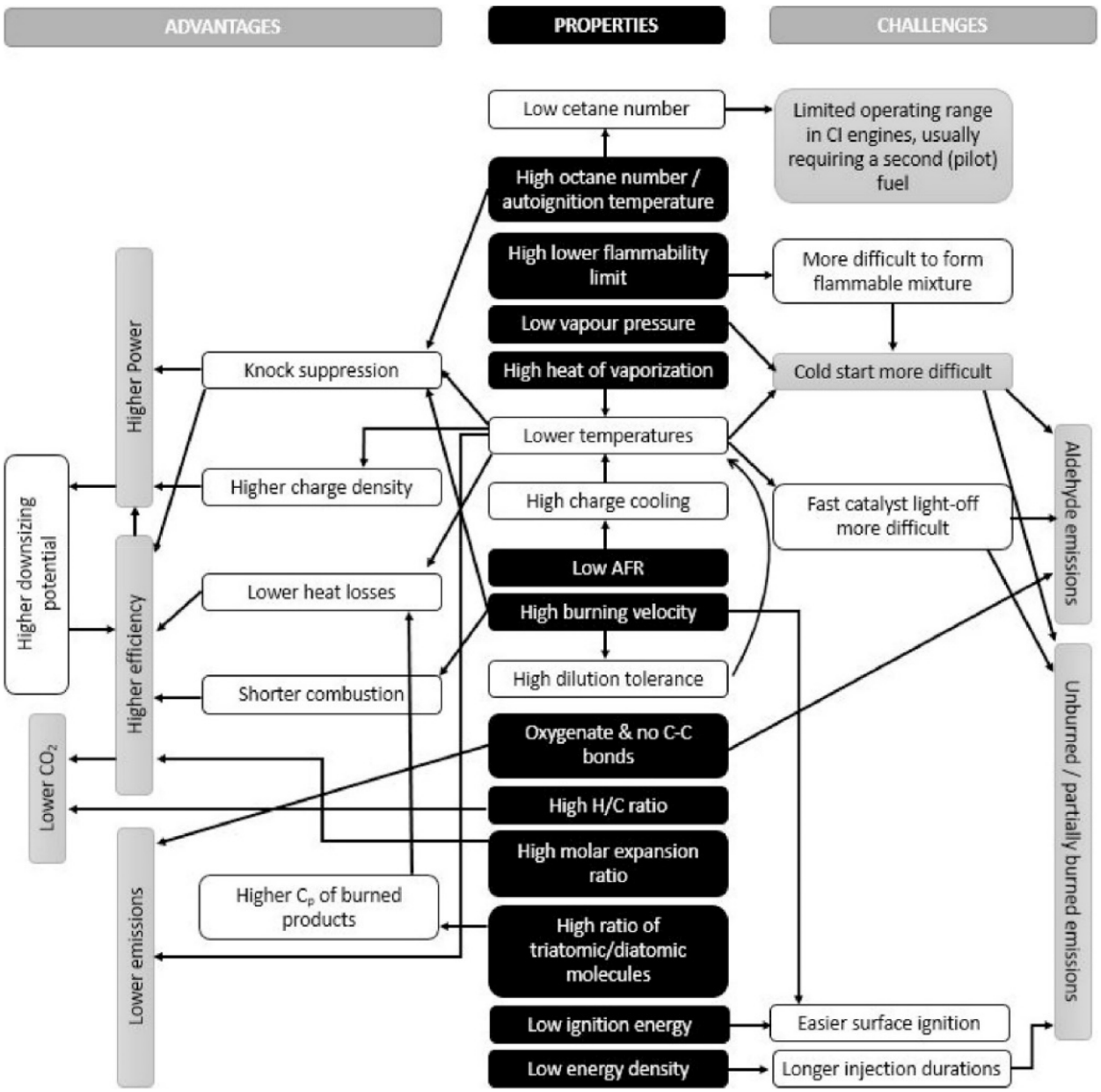


Fig. 3 The influence of the properties of methanol on the performance of an engine (Verhelst et al. 2019). Copyright 2018, Elsevier B.V. (License number: 5886441408885)

methanol; they are 99 g L^{-1} and 71 g L^{-1}, respectively, and hence do not need a cryogenic container, which requires a temperature of −253 °C (Cifre and Badr 2007; Shamsul et al. 2014; Agyekum et al. 2023). Serving as the main fuel source for FCs, the energy density of methanol is 6100 kW kg^{-1}, which increases the operative lifetime of the FC in the restricted fuel cartridge volume. Also, FCs that make use of methanol as their primary FC attain an output energy of 480 Wh within a volume of 0.6 L with a 19-h run-time; this translates into a power density of 7.4 WL^{-1} and an energy density of 289.2 Wh kg^{-1}. With 0.24 L of methanol over the course of seven hours, a mixture of methanol and water used indirectly as a polymer-electrolyte membrane fuel yields an output energy of 166 Wh, or 112.2 Wh L^{-1} of energy density and 16.9 WL^{-1} of power density (Shamsul et al. 2014).

3.2 Activation of CO_2 and methods leading to its hydrogenation into methanol

Because CO_2 molecules are thermodynamically and kinetically inert ($\Delta_f G^0 = -394.38$ kJ mol^{-1}), activation of individual molecules is difficult. Two reactive sites, carbon and oxygen, make up the linear, non-polar molecule known as CO_2. The electron shortage in carbonyl carbon suggests that carbon dioxide has a strong affinity for nucleophiles and reagents that donate electrons; the oxygen atom, however, exhibits a different behaviour (Li et al. 2014; Guil-López et al. 2019). Hence, it is required to get an effective catalyst and external energy input to convert CO_2 into methanol since its conversion is kinetically limited. A number of techniques have been created for the production of methanol using the hydrogenation of CO_2 such as (Guil-López et al. 2019):

- homogeneous catalysis
- heterogeneous catalysis
- electrochemical
- photocatalysis

3.2.1 Homogeneous catalysis

Studies on homogeneous catalysts have mostly focused on the formic acid or formaldehyde synthesis for the hydrogenation of CO_2. The complexes of ruthenium with various ligands are generally the most researched homogeneous catalysts (Huff and Sanford 2011; Cui et al. 2016; Guil-López et al. 2019). The most effective among that group has been identified to be the Ru-Triphos (Triphos = 1,1,1-tris (diphenylphosphinomethyl) ethane) (Wesselbaum et al. 2015; Guil-López et al. 2019). Kothandaraman et al. (2016) suggested utilizing the Ru catalyst (Ru-4) in pentaethylenehexamine (PEHA), whose reaction solution effectively traps CO_2, to hydrogenate CO_2 to produce methanol (Fig. 4). The study performed a CO_2 hydrogenation reaction utilizing the Ru-4 catalyst in PEHA's presence and obtained a TON of 1060 (in THF, at 7.5 MPa H_2/CO_2 (3/1) and 155 °C). It was additionally proven by using distillation that the CH_3OH/H_2O could be split from the solution following the reaction, and methanol synthesis can be obtained from the PEHA and the residual

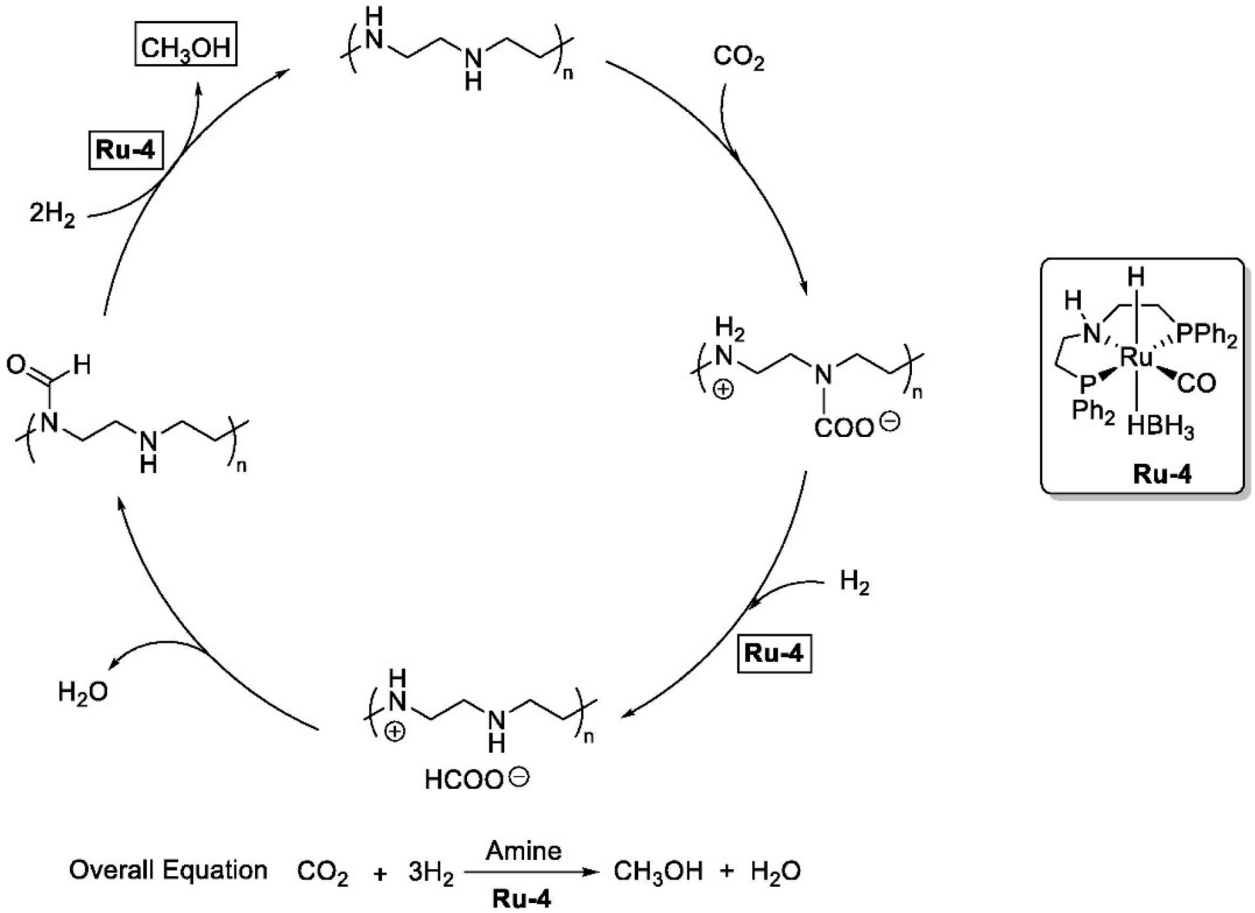


Fig. 4 Suggested procedure of the hydrogenation of carbon dioxide to methanol with PEHA (Onishi and Himeda 2022). Copyright 2022, Elsevier B.V. (License number: 5886450360157)

catalyst. Furthermore, PEHA can capture air-derived carbon dioxide (only 400 ppm in solution) and catalyze via the Ru-4 under hydrogen to methanol. It is a significant accomplishment to retrieve ruthenium catalysts (a rare metal), since there is a general difficulty in retrieving homogeneous catalysts in the carbon dioxide hydrogenation reaction (Onishi and Himeda 2022). In another study by Kar et al. (2018b), the authors proposed a biphasic 2-MTHF (2- Methyltetrahydrofuran)-water system. The carbon dioxide was initially trapped in an aqueous solution that has amines, like PEHA, and there was a hydrogenation of CO_2 to produce CH_3OH utilizing a Ru catalyst. Distillation could be used to extract the produced CH_3OH.

Most CO_2-to-methanol homogeneous catalysts that have been used so far are generally centered on noble metal complexes, especially complexes of ruthenium phosphine (Kar et al. 2018a). For this reaction, Schneidewind et al. (2017) discovered a catalyzed homogeneous system for the first non-noble metal based on cobalt (Fig. 5). Comparable to Fig. 6 Ru system, Co $(acac)_3$, $HNTf_2$, and triphos were employed as precursor catalysts (Wesselbaum et al. 2012, 2015).

3.2.2 Heterogeneous catalysis

Methanol synthesis from syngas is centered on the utilization of Cu–ZnO heterogeneous catalysts, the active phase of which is Cu, and the important promoter for the improvement of the system's activity is ZnO (Kuld et al. 2016; Guil-López et al. 2019). The traditional process for the hydrogenation of carbon dioxide exothermically into methanol (ΔH 298 K = −49.5 kJ mol^{-1}) includes the catalytic conversion under relatively low working temperatures (230–270 °C) with a number of phases as a result of the kinetic limitations (15%–25%) (Guil-López et al. 2019). Heterogeneous methanol catalysts are generally grouped into three main categories, these are Dang et al. (2019b):

- In materials that are deficient in oxygen, their vacant oxygen positions are employed as active sites. Oxide catalysts have evolved in recent years, mainly focusing on novel catalytic structures and reaction mechanisms. In a study by Martin et al. (2016), the In_2O_3-based catalysts were made, and the methanol generation mechanism was achieved. A 100% selectivity to methanol was exhibited by the In_2O_3 even at a high temperature of 300 °C under the following

Fig. 5 Cobalt-catalyzed hydrogenation of CO_2 to methanol (Kar et al. 2018a). Copyright 2017, Elsevier B.V. (License number: 5886450667058)

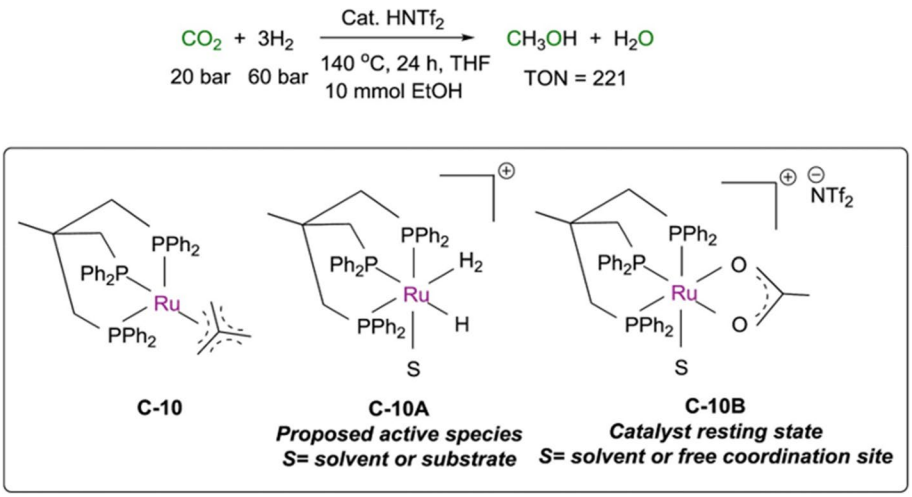


Fig. 6 CO_2 hydrogenation system (Kar et al. 2018a) Copyright 2017, Elsevier B.V. (License number: 5886450906969)

reaction conditions: $H_2/CO_2 = 4{:}1$, $P = 5.0$ MPa, and GHSV = 16,000 h^{-1} (Fig. 7).

- Similarly, in the study conducted by Rui et al. (2017), through a combination of In_2O_3 powder and Pd/peptide composite, a Pd/In_2O_3 catalyst was prepared. The results of their investigation suggest that the catalytic hydrogenation of carbon dioxide to methanol is dependent on the interfacial sites and the oxygen vacancy. The catalyst that was obtained showed a higher performance with carbon dioxide conversion over 20%, a selectivity for methanol beyond 70%, and a space-time yield up to 0.89 gMeOH h^{-1} $gcat^{-1}$ at 5.0 MPa and 300 °C. The TEM and SEM images for the Pd/In_2O_3 catalysts and Pd-P composite are presented in Fig. 8. The outcome of their study showed a strong

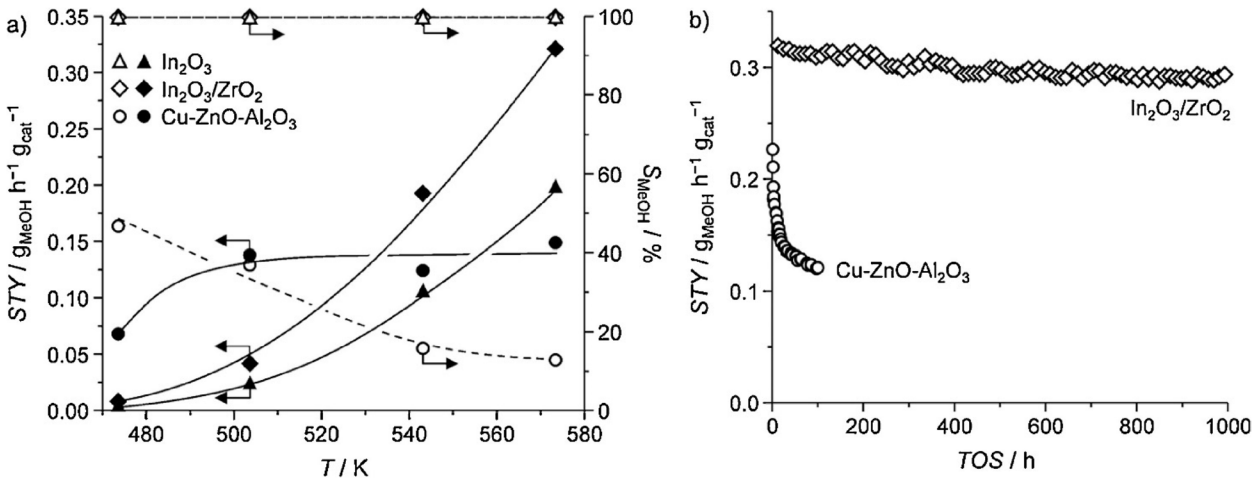


Fig. 7 **a** Methanol selectivity and STY for carbon dioxide hydrogenation over large In_2O_3, In_2O_3/ZrO_2 (9 wt% In), and the standard $Cu/ZnO/Al_2O_3$ catalyst for different temperatures. **b** the progression of the STY of methanol with time on stream over In_2O_3/ZrO_2 and $Cu/ZnO/Al_2O_3$ (Martin et al. 2016). Copyright 2016, John Wiley and Sons. (License number: 5913140924227)

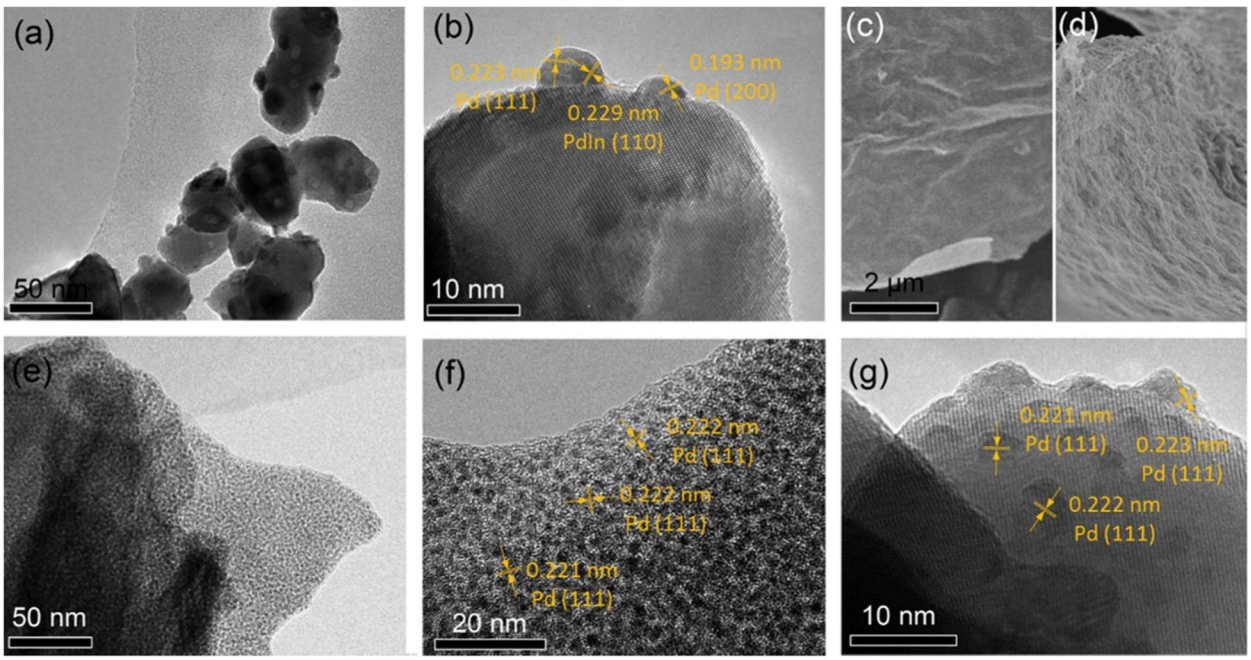


Fig. 8 Transmission electron microscopy diagrams of (**a**) and (**b**) Pd-I/In_2O_3, SEM images of (**c**) and (**d**) Pd-P composite, TEM images of (**e**) and (**f**) Pd-P composite, (**g**) Pd-P/In_2O_3 (Rui et al. 2017). Copyright 2017, Elsevier B.V. (License number: 5886460183900)

interaction between the In_2O_3 and the Pd in the prepared catalysts by utilizing the traditional method.

- Catalysts that are metal-based are mostly modified catalysts for hydrogenation of CO, with Cu species being the key active component, like Pd, Ag, Au, and Pt, which are noble metals. It is extensively known that the active phase for the synthesis through carbon dioxide hydrogenation is metallic Cu. The processes that lead to methanol from the CO_2 hydrogenation over the Cu-based catalysts were suggested by several scholars via means of density functional theory (DFT) estimations and experiments. The reaction routes for CO_2 hydrogenation over Cu are illustrated in Fig. 9. The first route corresponds to the formate (*HCOO) intermediate, which occurs through the reaction of CO_2 with a surface atomic H through either the Langmuir–Hinshelwood (LH) mechanism or the Eley–Rideal (ER) mechanism (Zhao et al. 2011; Dang et al. 2019b). The hydrogenation of *HCOO is then subsequently done to obtain dioxymethylene (*HCOOH). This is followed by another hydrogenation to $^*H_2COOH$, cleaved to ($^*H_2CO$) formaldehyde and (*OH) hydroxyl. Further hydrogenation of the adsorbed $^*H_2CO$ occurs to obtain methylenoxy ($^*H_2COH$) or methoxy ($^*H_3CO$) as well as methanol ($^*H_3COH$), which is the final product (termed as the formate pathway).
- The other catalytic system is made up of a unique catalytic structure. This has a different reaction mechanism compared to the earlier catalytic systems presented above. The hydrogenation of CO_2 into methanol has been catalyzed by frustrated Lewis pairs (FLPs). The formation of UiO-66-P-BX was done through the grafting of some potential LP functional groups, P-BX_2, on the organic ligand terephthalic acid of UiO-66. They also attached the Lewis

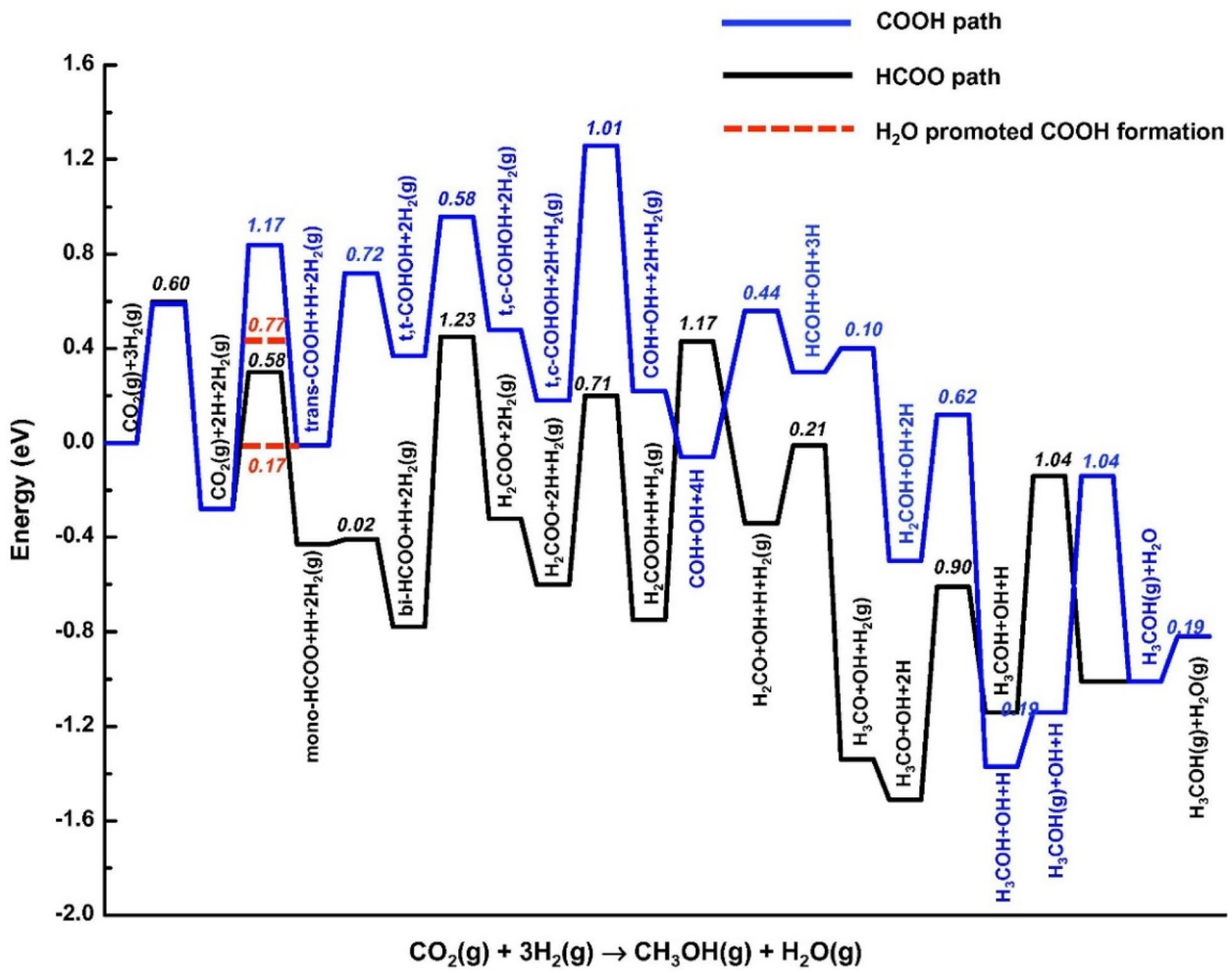


Fig. 9 Possible energy surfaces for the carbon dioxide hydrogenation to methanol on Cu(1 1 1) through the mechanisms of formate and hydrocarboxyl (Zhao et al. 2011). Copyright 2011, Elsevier B.V. (License number: 5886460431650)

pair -BX_2 on 4,4'-biphenyldicarboxylate (BPDC) (i.e., the organic linker) in the UiO-67 via fixing the BX_2 moiety at carbon C_2 and substituting C_3 with N; this led to the formation of UiO-67-NBX_2 (X = CH_3, F, CN, CF_3, or NO_2). These novel catalysts helped in the heterolytic dissociation of H_2 to produce hydridic and protic H atoms, which bind to the Lewis acid and base sites, respectively. This accelerates a chain of concurrent transfers of two hydrogens for methanol production (Dang et al. 2019b).

3.2.3 Photocatalysis

Photocatalytic reduction of CO_2 is identified as a favorable route for the conversion of CO_2 to useful chemicals and fuels through the use of solar energy. Several forms of photocatalysts for the reduction of CO_2 are presented in the literature; these include mixed-metal oxide (MMO)-based, metal–organic framework (MOF)-based, plasmonic-based, and TiO_2-based photocatalysts (Shinde et al. 2022).

The MOF is an organic–inorganic hybrid crystalline porous material comprising metal ions enveloped by organic linkers. The MOF's internal surface area is remarkably large as a result of the internal hollow structure. This is because the metal ions act as nodes to connect the linker arms into one (Su et al. 2017; Shinde et al. 2022). The MOF demonstrates unparalleled structural diversity and atomic structural uniformity compared to other porous materials; it also has tunable porosity, uniform pore structures, and flexibility in network topology. The following MOF-based photocatalyst types, i.e., MOF-derived, MOF-based, MOF composites, single-site MOFs, and MOFs as support, are used for CO_2 reduction (Shinde et al. 2022).

Traditional TiO_2-based nanoparticle photocatalysts supported on reduced graphene oxide surfaces were utilized as photocatalysts with high activity for the synthesis of methanol from the reduction of CO_2 with a methanol yield of 2330 μmol $gcat^{-1}$ h^{-1} (Olowoyo et al. 2019). The limited amount of ultraviolet radiation in the entire spectra makes the photoactivity of TiO_2 under solar illumination low. However, the band gap of TiO_2 can be reduced as a result of the nanocomposite TiO_2-reduced graphene because of the influence of the reduced graphene oxide. The additional tested photocatalysts for this procedure are dependent on the cupric and cuprous oxides (CuO as well as Cu_2O) reinforced on the reduced graphene oxide surface (Guil-López et al. 2019; Liu et al. 2019).

MMOs that have two or more forms of metal and oxygen are largely utilized as photocatalysts for the reduction of CO_2. The semi-conducting nature of their aqueous suspensions, which are visible light-irradiated, has been a major area of study. MMO forms an important photocatalyst that is different from normal oxides in situations like redox, acid–base, and surface area. They are extensively studied as a result of their tremendous chemical and thermal stability compared to single oxides (Gawande et al. 2012; Thompson et al. 2019; Shinde et al. 2022; Ng et al. 2022).

In recent times, the efficiency of photocatalysis has improved as a result of plasmonic photocatalysis for the reduction of carbon dioxide under irradiation with visible light. It uses precious metal nanoparticles spread on photocatalysts that are semiconductors; it possesses excellent characteristics like localized plasmonic surface resonance (LSPR), which performs a significant role in visible light absorption as well as active charge carrier excitation. The LSPR helps in the plasmonic photocatalysts' performance since it supports excellent light absorption within an extensive range of wavelengths simultaneously, thereby accelerating an efficient transfer of energy to semiconductors (Vu et al. 2020).

3.2.4 Electrochemical

Various products can be made from the direct electrochemical CO_2 reduction; this, however, is dependent on the reaction medium and the catalyst material. CO_2 electrochemical reduction can mostly proceed through 2, 4, 6, and 8 electron reduction routes in non-aqueous phases, aqueous, and gaseous phases at varying cell and electrode configurations. Methane (CH_4), oxalic acid ($H_2C_2O_4$) or oxalate ($C_2O_4^{2-}$) in basic solution, CO, formaldehyde (CH_2O), ethylene (CH_2CH_2) or ethanol (CH_3CH_2OH), formate ($HCOO^-$) or formic acid (HCOOH) in basic solution, and methanol (CH_3OH) are the principal products of the reduction (Albo et al. 2015). CO_2 electrochemical activation via electrocatalysts permits hydrogenation to methanol under mild circumstances. Metals such as Pd, Pt, and Ru have all been considered as possible catalysts for CO_2 electrochemical activation, generally supported on K- or Na-modified β-alumina, to be able to enhance the ceramic β-alumina's conductivity and the chemisorption of H_2 and CO_2 over the active sites of the metal. Other studies are also assessing some less-costly metals, like Ni supported on YS zeolite or Cu supported on K-β-alumina (Guil-López et al. 2019).

4 Methanol production methods, economics, and its applications in the industry

An assessment of methanol as an alternative sustainable fuel for marine use indicates that methanol from conventional NG has a higher global warming potential (almost five times) compared to biomass-produced methanol. Although technologies for renewable methanol have

shown lower carbon intensities compared to those of fossil fuel alternatives, methanol generation from renewable feedstocks has some deficiencies, such as higher costs and lower energy efficiency. Novel methods for synthesizing methanol in a renewable way with a relatively lower carbon footprint have been proposed in various studies. In addition to processes such as carbon capture units, other studies have also proposed the modification of upstream processes, including the design of methods or ways using renewable feedstocks that have an inherent, intrinsically lower carbon footprint (Harris et al. 2021). Biofuels are fuels gotten from biomass; they may be liquid or gas; they can be derived from different biomass sources; hence, they can be produced virtually at most places (Verma et al. 2012). Different types of chemicals and biofuels, such as bioethanol, bio methanol, formaldehyde, acetic acid, synthetic liquid hydrocarbons and biodiesel, can be obtained from biomass, and most of these products are accessible on the market currently (Gautam et al. 2020).

The production of methanol can be said to be green or renewable if the source of the carbon is a waste product, the source of energy originates from renewable sources, and the produced hydrogen is not from fossil fuels (Olah 2005). Bio-methanol is a methanol manufactured from biogas, which is obtained from municipal solid waste feedstock or biomass and is also categorized as renewable methanol (Roode-Gutzmer et al. 2019). Using CO_2 as a chemical feedstock is increasing in methanol production, as indicated early in this paper, as a result of rising interest in carbon capture and use. Some commonly referenced methods in literature that are usually used are catalytic carbon dioxide hydrogenation with renewable H_2 to methanol (Leonzio et al. 2019; Bos et al. 2020; Lee et al. 2020). Currently, the technology's large scale and commercial development are being championed by Carbon Recycling International (CRI 2023). Three different renewable methods for the synthesis of methanol are presented in Fig. 10.

4.1 Biomass-to-methanol

All sources of biomass can be gasified to generate methanol; however, the most suitable materials for such purposes are those with low moisture, as they provide efficiencies that can go up to 55%. Similarly, black liquor obtained from the manufacturing of paper is a potential feed for gasification and the production of methanol. This could, however, be more effective in small countries such as Sweden and Finland, where they have widespread paper mills. It has been stated that such economies can produce up to 50% of their fuel demand for their motors in this fashion (Bozzano and Manenti 2016). The way in which methanol can be produced from biomass while preventing an increase in the concentration of CO_2 in the atmosphere is presented in Fig. 11.

Researchers have investigated the process of turning biomass into methanol in detail and it has occasionally been carried out commercially. *Gasification* is a crucial thermochemical conversion process for biomass. Biomass is transformed into a multi-functional gaseous mixture when a gasifying agent (GA) is present, mostly known as synthesis gas or syngas. A solid residue is further obtained after the conversion of the biomass (char) (Asadullah 2014; Molino et al. 2018). The syngas is made up of a combination of CH_4, CO_2, H_2, CO (main components), and NH_3, H_2O, tar, and H_2S, as well as other trace species (secondary components), with a structure contingent on the nature of feedstock, gasification technology, and the operating conditions (i.e., bed material type, pressure and temperature of the gasifier, and the GA) (Ahmad et al. 2016; Molino et al. 2018). The process of gasification can be divided into four phases: reduction (endothermic), oxidation (exothermic), pyrolysis (endothermic), and drying (endothermic). Tar-reforming is another process that can be used to turn big tar molecules into light hydrocarbons (Sikarwar et al. 2017). Gasification is made up of various overlapping sub-processes, as mentioned earlier, and as such, involves complex combinations of various reactions, as presented in Table 2**.** The feedstock's drying occurs until a temperature of 120 °C; species that are volatile are produced below 500 °C. Char gasification can start at 350 °C. By using exothermic combustion reactions, the heat can be produced internally; it can also be sourced from external sources. An equation showing a basic gasification reaction is presented in Eq. (4) (Lange 2007; Sikarwar et al. 2017).

$$\begin{aligned} Biomass \rightarrow CO_{(g)} + H_{2(g)} + CH_{4(g)} + Tar_{(l)} + H_2O_{(l)} \\ + H_2S_{(g)} + NH_{3(g)} + C_{(s)} + tracespecies \end{aligned} \quad (4)$$

The gasification of biomass is done by utilizing various forms of gasifiers, i.e., fluidized beds, fixed beds, and entrained flow reactors. The conversion process is thermochemical, and it includes complicated reactions, mass transfer, and heat transfer processes. Gasifying agents like oxygen, air, and steam are needed for the gasification process to help transform carbonaceous feedstocks into gaseous fuels (Gupta et al. 2022). Recent literature studies that looked at biomass gasification include different aspects applied to produce methanol. Piazzi et al. (2022) assessed the exergy and energy efficiencies of various combined biomass gasification coupled to Fischer–Tropsch synthesis (IGFT) designs. They developed four different models, i.e., air-based gasification, hot gas cleaning (HGC), FT synthesis; air-based gasification, cold gas cleaning (CGC), FT synthesis; steam-based gasification, HGC, FT synthesis; and air-based gasification, cold

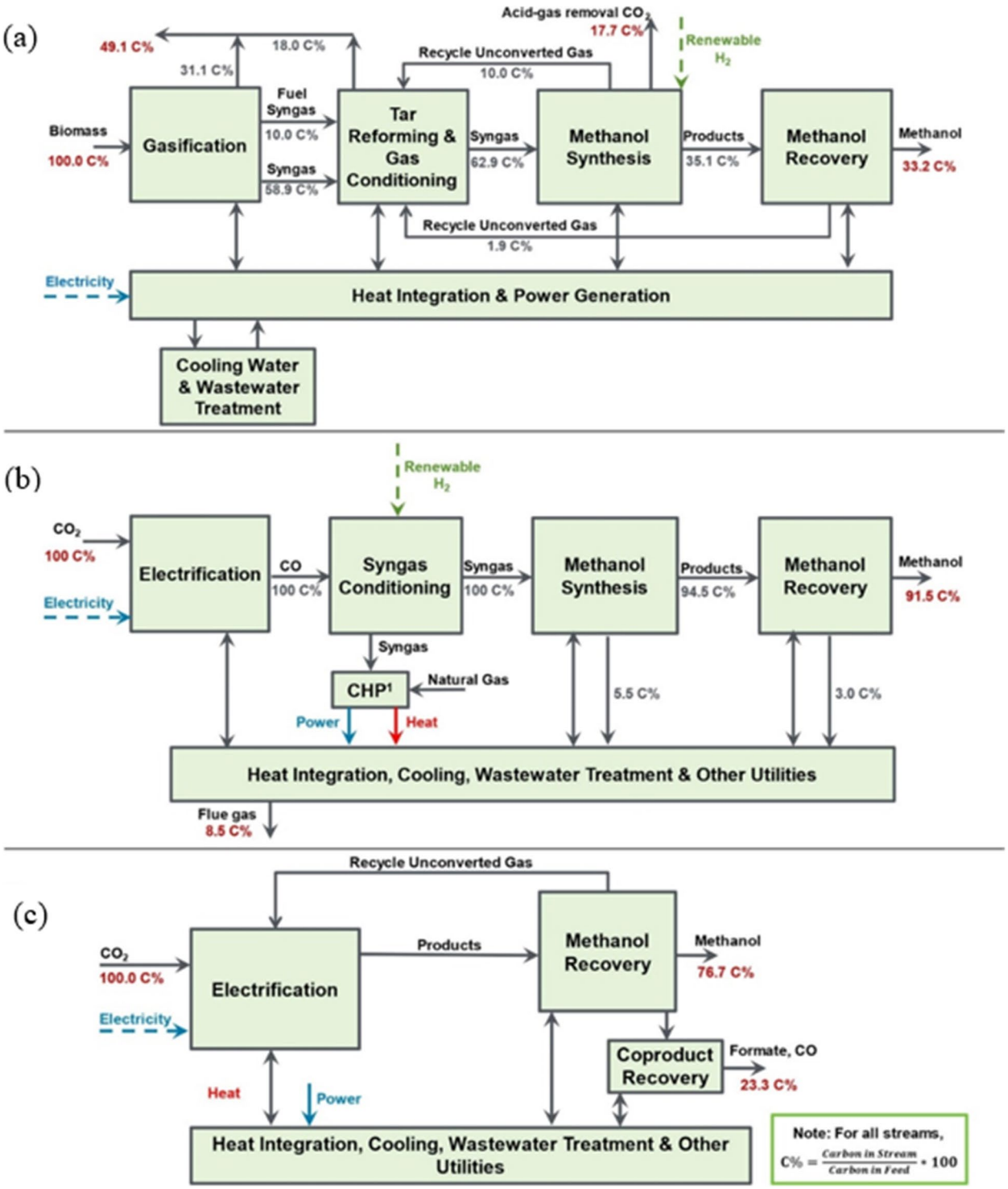


Fig. 10 Flow chart of the processes of the three renewable methanol production methods: (**a**) conversion of biomass to methanol, (**b**) joined electrolysis of CO_2 and H_2O oxidation for the conversion of syngas to methanol (indirect electrolysis), and (**c**) direct electrolysis of CO_2 to methanol (Harris et al. 2021). Copyright 2021, Elsevier B.V. (License number: 5886460704332). CHP represent combined heat and power. The percentages indicate the baseline carbon flows for external (red) streams and the internal (grey) streams which are normalized by the quantity of carbon in the feedstock

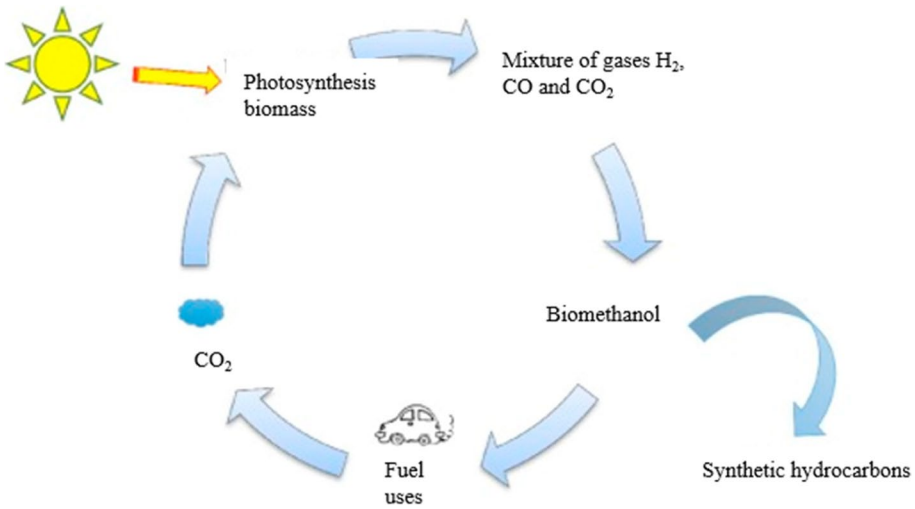


Fig. 11 Bio-methanol's carbon cycle (Bozzano and Manenti 2016). Copyright 2016, Elsevier B.V. (License number: 5886461048850)

Table 2 Chemical reactions that take place in the gasification of biomass with steam as gasifying agent. Adapted from (Sikarwar et al. 2017). CC BY-NC

Name of reaction	$\Delta G^0_{r(298)}(kJ/mol)$	$\Delta H^0_{r(298)}(kJ/mol)$	Chemical equation
Hydrogenating gasification	168.6	123.7	$C + 2H_2 \leftrightarrow CH_4$
Boudouard equilibrium	140.1	205.3	$C + CO_2 \leftrightarrow 2CO$
Water gas shift (WGS)	−28.5	−41.47	$CO + H_2O \leftrightarrow CO_2 + H_2$
Heterogeneous WGS	89.8	130.4	$C + H_2O \leftrightarrow CO + H_2$
Steam reforming of methane	118.4	172.6	$CH_4 + H_2O \leftrightarrow CO + 3H_2$
Dry reforming of methane	−50.3	−74.9	$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$
Ethylene	−111.6	−104.3	$2CO + 4H_2 \leftrightarrow C_2H_4 + 2H_2O$
Ethane	−212.7	−172.7	$2CO + 5H_2 \leftrightarrow C_2H_6 + 2H_2O$
Propane	−293.2	−165.1	$3CO + 7H_2 \leftrightarrow C_3H_8 + 3H_2O$
Butane	−376.7	−161.9	$4CO + 9H_2 \leftrightarrow C_4H_{10} + 4H_2O$
Pentane	−457.9	−159.7	$5CO + 11H_2 \leftrightarrow C_5H_{12} + 5H_2O$
Hexane	−539.6	−158.3	$6CO + 13H_2 \leftrightarrow C_6H_{14} + 6H_2O$

gas cleaning (CGC), FT synthesis. According to their findings, high energy efficiency and exergy were obtained for designs that utilized a hot gas cleaning system or steam as an agent of gasification. The maximum exergy irreversibility occurred at the gasification part of the process, both in terms of exergy loss and destruction, as a result of the degradation of large chemical exergy. Studies by Sues et al. (2010), Cruz et al. (2017), Samavati et al. (2018), and Ostadi Mohammad et al. (2019) conducted an exergy analysis of biomass gasification, most of which used the integrated gasification Fischer–Tropsch configuration. A promising method for producing synthetic biofuels is the gasification of lignocellulosic biomass followed by FT synthesis. They have the option to be integrated with other systems for co-production of electrical power (i.e., combined-cycle power plants) (Zhang 2010a; Kalinci et al. 2012; Cruz et al. 2017).

Conventional *pyrolysis* was basically developed for charcoal production, with the by-product being methanol. In the current pyrolytic process, a thermo-chemical path is taken in which a more innovative thermal treatment is used to transform biomass into gases and bio-oil under an inert atmosphere (Raheem et al. 2015). The conditions under which pyrolysis operates are classified into two distinct phases, i.e., slow and fast pyrolysis as presented in Fig. 12. Close to 19%−57% of biomass is produced as bio-oil (as final product) and char under the fast pyrolysis (Haiduc et al. 2009). However, according to a study by Grierson et al. (2009), a slow pyrolysis of some six different species of micro-algae could result

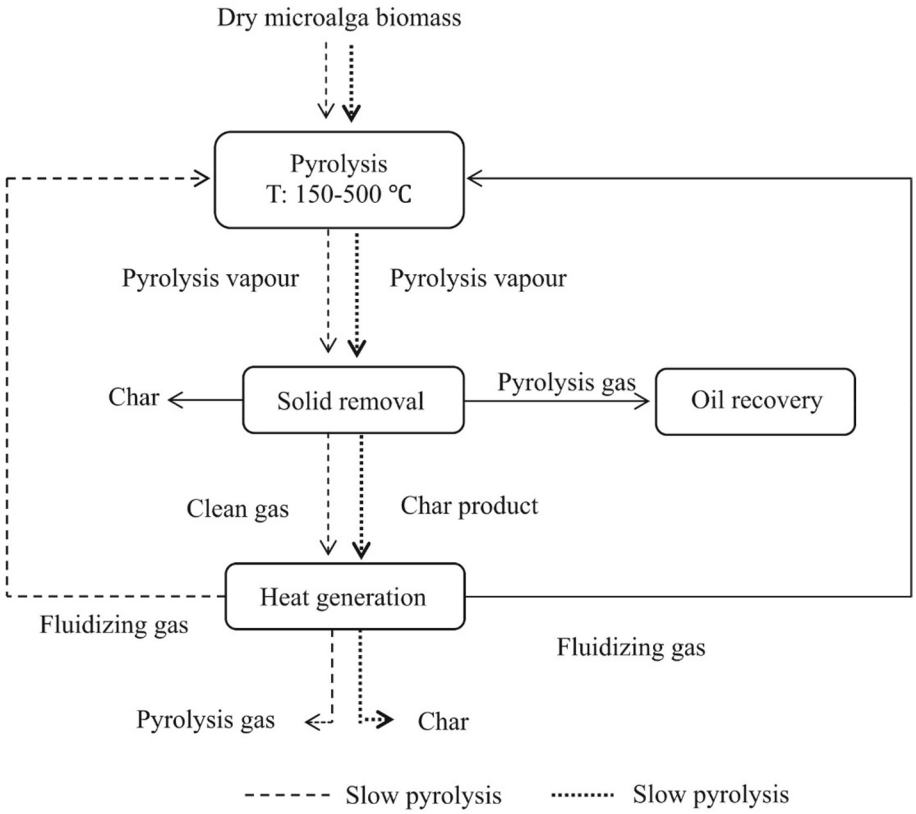


Fig. 12 A description of the process and the formation of products from pyrolysis (Suali and Sarbatly 2012). Copyright 2012, Elsevier B.V. (License number: 5886470773196)

in 30%–63% char, 24%–43% bio-oils, and 13%–25% gas production for the different micro-algal biomass. The first step in all processes of thermochemical conversion is pyrolysis. It is a complex route that includes de-polymerization, aromatization, isomerization, dehydration, and charring (Collard and Blin 2014; Gautam et al. 2020). The pyrolysis of biomass starts with moisture loss, and then reactions occur in two phases where the initial processes are described via the formation of char, fragmentation, and depolymerization, as well as minor reactions such as the cracking of oil and re-polymerization.

Wet biomass is transformed into liquid fuels through *liquefaction* in the presence of catalysts under the following conditions: high pressure (5 bar–20 bar) and low temperature (200 °C–500 °C). The processes involved in pyrolysis are quite similar to those of thermal liquefaction and are a mixture of different reactions such as decarboxylation, dehydrogenation, dehydration, and deoxygenation (Mohanty et al. 2022). However, it changes in the requirements of pressure and temperature conditions, the catalyst type, and it also produces liquid, mostly compared to that of pyrolysis (Gautam et al. 2020). Liquefaction can be classified into two categories, i.e., direct or indirect. Direct liquefaction, also referred to as hydrothermal liquefaction (HTL), involves the transformation of biomass into liquid fuels using thermochemical processes. It is processed at a high temperature in a pressurized water setting within a time period to allow the breaking down of the solid biopolymeric structure into largely liquid components. Requirements like pressure and temperature are high for the HTL mechanism in order to keep the water in either a supercritical or liquid state. Utilizing water as a solvent eliminates the necessity of drying the biomass (Elliott et al. 2015; Ibarra-Gonzalez and Rong 2019). Liquid tar, bio-oil, as well as condensable organic vapor are the products formed in this process (Ye et al. 2013; Mohanty et al. 2022). Indirect liquefaction through syngas formation produces oil; it involves two stages, and therefore it is used for methanol production (partial CO hydrogenation). The raw materials used in this mechanism determine the characteristics of the products (Fahmy et al. 2020; Mohanty et al. 2022). Table 3 shows a contrast of the benefits and drawbacks of the various thermochemical conversion technologies used to generate bio-oil.

Table 3 Bio-oil production and a comparison of the key thermochemical method. Adapted from (Ibarra-Gonzalez and Rong 2019).Copyright 2018, Elsevier B.V. (License number: 5886520833991)

Technology	Operation requirements	Process description and reaction mechanism	Merits	Demerits
Gasification	Occurs at about 600–1000 ℃ in an environment of a regulated quantity of oxidizing agent; atmospheric pressure; drying necessary; residence time of 3–4 s	Production of syngas comprising of mostly H_2, and CO. Production of fuels through gasification demands the generation of syngas, followed by the clean-up of syngas, WGSR and FT synthesis	This technology is matured and already commercialized in terms of power and heat generation	The process demands higher temperatures. Generates 80 wt% gas and 20 wt% oil, hence it needs FT reaction to enhance the production of oil
Fast pyrolysis	Comparatively high temperature i.e., 450–500 ℃; non-availability of oxygen; atmospheric pressure; a brief residence time (~ 1 s); drying necessary	Light, small molecules are transformed into oily products by fast condensation and uniform reactions in the gas phase	The produced oil is high up to 80 wt% on dry feed; relatively low capital cost	The fuel acquired has poor quality
Hydrothermal liquefaction	Long residence time (0.2–1.0 h.); drying unnecessary; temperature is lower (300–400 C); high pressure (5– 20 MPa)	Takes place in a medium that is aqueous, which includes complicated order of reactions (dehydration, decarboxylation, and hydrogenation of functional groups, etc.)	The obtained bio-oil is of high quality (low moisture content and high heating value)	The oil yield is comparatively (20 wt%–60 wt%); require high pressure equipment, hence higher capital cost

In essence, the reaction between H_2 and CO produces methanol, and the presence of CO_2 intensifies that reaction. The goal is to create two-phase catalytic reactors that can use catalysts such as carbon, alumina, silica, or graphene, which can be supported on a large surface area or unsupported at the nanoscale (Jackson and Mahajan 2004). Moreover, methods based on plasma have been developed to turn biomass waste into alcohol. One significant drawback of these procedures is their high cost, which results from the requirement for costly metal catalysts and the necessary pressure and temperature ranges of 5–20 MPa and 200–900 ℃ (Riaz et al. 2013; Gautam et al. 2020). It is therefore important to explore different methanol production methods where cost is significantly minimized. One of the promising pathways is the biochemical approach, whose feedstock will be methane for the methanotrophic bacteria, which will transform it into methanol at ambient temperature and pressure (Gautam et al. 2020). A review of recent studies on biomass-methanol production is presented in Table 4.

4.1.1 Some challenges linked to biomass-methanol production

The produced syngas from the processes of gasification is found to be suitable for the generation of bio-methanol. Large quantities of biomass are, however, required for large-scale production. The biomass resources used for its production are therefore expected to not be edible in order to avoid competition with food crops (Shamsul et al. 2014). The small bulk density of biomass means it requires a high number of truck movements to be done, making logistic operations a challenge. Furthermore, some properties, such as its seasonality (making availability dependent on time) and geographic distribution, make its collection, transportation, and storage costly and difficult. Hence, it demands extensive infrastructure in terms of logistics (Akbarian et al. 2022). It is for this reason that Caputo et al. (2005) assessed the effect of logistical factors like specific purchased biomass cost, vehicle capacity, distribution density, and specific vehicle transport cost to understand the extent to which they affect the viability of bioenergy production. Furthermore, products of biowaste commonly contain sulfur compounds (i.e., carbonyl sulfide, thiophene, and hydrogen sulfide). Such chemicals have the capacity to negatively affect the gasification catalysts even when their quantities are not much (less than 10 ppm) (Watson et al. 2018; Akbarian et al. 2022). Although syngas from biomass is green, it may have, for example, soot, which is made of microparticles of submicron size. Energy efficiency can therefore be reduced and cause breakdowns by triggering obstructions in pipes, hot-gas filters, heat exchangers, and toxic catalysts. It is therefore important to regulate the concentration of soot in syngas because it is important for the commercialization of biomass gasification, stability, and scale-up. Some of the approaches that can be used to control the quantity of soot are through the reduction of benzene and C_2 hydrocarbons. Also, pretreatment for raw biomass can be used to reduce the level of soot (He et al. 2021).

4.2 CO_2 electrolysis to methanol

A technique used to reduce the amount of CO_2 released into the atmosphere as a result of burning fossil fuels is called CO_2 capture and storage, or CCS. However, a number of technical and financial obstacles, including an unknown rate of CO_2 leakage, a lack of capital investment, and geological incapacity in some areas, face the CCS technology. For the technology to advance toward widespread development, these obstacles must be removed. Due to its capacity to transform waste CO_2 into valuable products like methanol and other significant chemicals, carbon capture utilization, or CCU, has attracted a lot of attention recently. A few advantages of using carbon dioxide are that it is non-toxic, renewable, and less expensive (Li and Tsang 2018).

4.2.1 Direct CO_2 electrolysis to methanol

The electrolysis of CO_2 offers effective, on-site production of a chemical, provided there exist catalyst and reactor combinations with appropriate selectivity, overpotential, stability, and ability to withstand commercially germane current densities (Burdyny and Smith 2019; Sarp et al. 2021). If the electrolysis of CO_2 goes in the way of the electrolysis of water for production, then the latter, which currently reaches total thermal efficiencies of more than 70% in modular systems (Ayers 2019), could realize this potential. Cathodic reduction of carbon dioxide to saturated-chain alcohols such as n-propanol, ethanol, and methanol needs six electrons and six protons, which are offered by the oxidation of water; this is presented in Eq. (4). For methanol production ($n=1$), some major hurdles still exist in the areas of CO_2 electro-reduction research, as presented supra. In order to resolve these hurdles, it will be important to develop a catalyst that binds CO stably to its surface but maintains the ability for the initiation of four protons and four electrons reduction to methanol (Sarp et al. 2021).

$$nCO_2 + (6n)H^+ + (6n)e^- \rightarrow C_nH_{2n+1}OH + (2n-1)H_2O \quad (4)$$

Even though the reaction is viable thermodynamically, the linear CO_2 molecule's inert nature as well as the multiple proton and electron transfers make the general reaction slow kinetically. To facilitate such reactions, active catalytic materials will be required, and an appreciation

Table 4 Review of recent literature on Biomass-Methanol production

No	Study	Objective	Method and tool used	Key findings
1	(Sun and Aziz 2021)	Green and sustainable methanol production	Direct chemical looping: (1) biomass chemical looping gasification (B-CLG); (2) biomass chemical looping hydrogen production (B-CLHP)	B-CLG and B-CLHP recorded exergy efficiencies of 75.61% and 71.59%, respectively. B-CLHP was found to be more economically viable, it recorded a levelized cost of methanol of 383.59 USD/t
2	(Yang et al. 2018)	Conceptual design and modelling process for an efficient biomass-to-methanol (BTM)	Gasification by dual-stage entrained flow	An exergy efficiency of about 70% was attained via energy integration. The cost of production of the BTM is around CNY 2056–2284 per ton methanol (i.e., 302–336 USD/t) representing roughly 20% more than coal-to-methanol and close to NG-to methanol
3	(Adil and Rao 2022)	Optimization of methanol production response system	Kinetics by Vanden Bussche and Graaf's. Projection and the optimization of the studied responses was done using the prepared surrogate model	The following enhanced figures were recorded for the conversion of carbon (46.97%), methanol yield (46.95%), and methanol production (1.21 mol h^{-1})
4	(Li et al. 2023c)	To improve the primary operating parameters and reveal how biomass affects the operation process	Simulated using the Aspen Plus software	The simulated outcome indicated that if the proportion of biomass to coal is 1:1, water steam is gasification agent, SR = 0.36, CR = 0.8, the net produced methanol can get to a maximum of 7022.32 kg h^{-1}, 241.51% greater than just utilizing coal, generating 37.68% less carbon dioxide than just using coal
5	(Zhang et al. 2021b)	A model was created, validated, and used to calculate the bio-methanol yield in order to investigate the feasibility of producing biofuels from a variety of feedstocks. These feedstocks included biomass, biochar, and pyrolysis oil	Simulated using the Aspen Plus software	The initial results for the economic evaluation showed that the production of bio-methanol from biochar can be an appealing alternative
6	(Zhang et al. 2023b)	Efficiency enhancement of conventional biomass conversion to methanol	A recently created cogeneration system that combines an electrolytic water subsystem, an s-CO_2 cycle, and a conventional biomass to methanol system	For instance, a biomass that has a 2.78 kgs^{-1} mass flow rate could record a 19.89% energy efficiency improvement for their new process
7	(Cuezzo et al. 2023)	To simulate and assess how the sugarcane industry's methanol production from biogenic CO_2 affects the environment	Methanol production at the industrial level using direct hydrogenation of carbon dioxide from the sugar alcohol industry	The outcome of the investigation show that the green methanol production is a fine alternative for industrial decarbonization. A sustainable agriculture will determine the viability of the whole process since it forms the foundation of the biorefinery
8	(Santasnachok et al. 2020)	To examine an analytical model for the generation of methanol from the gasification of algae biomass applying the process of biomass gasification (air–steam)	Simulated using the Aspen Plus software	The investigation found an increase in the syngas yield due to higher gasifier temperature and steam to algae ratio
9	(Zhu et al. 2022c)	To assess the thermo-economics of the generation of methanol via RE source of biogas	Aspen HYSYS software was employed for simulation	Exergy efficiency of 54.11% was obtained for their proposed process, where the combination of the steam cycle had a key part. It was also found that the overall rate of destruction in terms of exergy was 90,527.02 kW, and the reformer and burner with 29% and 51%, respectively, possess the maximum percentage in exergy destruction
10	(Poluzzi et al. 2022)	To evaluate biomass to methanol plant, employing a low temperature electrolysis technology	A sorption-enhanced gasification technology was used	The enhanced reactor design was identified to be desirable from the perspective of the techno-economics. It recorded a 20% lower cost of the e-MeOH (30.80 €/ GJ_{LHV} vs. 37.76 €/ GJ_{LHV})

of the complex reaction pathways is essential for the design of the materials (Zhang et al. 2021a). Even though much work has been made towards the development of flow reactors for the electro-reduction of CO_2, the development of reactor design still needs to be relooked at in terms of the optimization of efficiency at the system level and mass transport (Angulo et al. 2020; Sarp et al. 2021). Methanol possesses a unique characteristic that could help in enhancing system-level efficiency compared to other room-temperature liquids that can be obtained through the reduction of CO_2. Methanol's boiling point at atmospheric pressure (65 °C) is beyond room temperature; however, it is similar to the polymer electrolyte membrane (PEM) electrolyzer's operational temperatures. This offers an opportunity for an effective integration process, as presented in Fig. 13, where methanol is produced at the gas phase while water is eliminated as a liquid. It allows methanol separation from gas and liquid recycle streams through an unsophisticated glycol-cooled condenser and gas–liquid separator, which minimizes the requirement for expensive distillation (Sarp et al. 2021).

4.2.2 CO_2 hydrogenation to produce methanol

The major products for carbon dioxide activation and transformation are methanol, methane, hydrocarbons (LPG, olefins, aromatics, and gasoline), and DME (Centi et al. 2013). There has been much attention given to the use of excess power from sustainable resources like wind and solar, the "power-to-fuel" strategy, and CO_2 hydrogenation, which is central to this technology when combined with the capture of CO_2 and the production of renewable H_2 from electrolysis. Hence, for CO_2 hydrogenation, several studies, such as Landau et al. (2014), Ruiz et al. (2016), Zhang et al. (2018b), Chen et al. (2019a), and Nezam et al. (2021) assessed the various methods to manufacture different chemicals as fuels or feeds in other methods.

CO_2 conversion to methanol by hydrogenation reaction (Eq. (1)) requires a substantial supply of energy; thus, it is required to provide an adequate catalytic system. Looking at the importance of CO_2 hydrogenation, Li et al. (2018b) in their recent study provided some opportunities and challenges for its production. The traditional process is generally performed at a temperature of 200 ℃, and pressure of 35–55 bar, with the highest selective and active catalysts based on $Cu/ZnO/Al_2ONiu_3$ (Dalena et al. 2018a).

In theory, two key paths (except catalyst enhancements) can be followed to improve the production of methanol in conventional reactors, i.e., unconverted synthesis gas recycling after the separation of products via condensation and removal of in situ reaction products. CO_2 catalytic hydrogenation via renewable energy-produced hydrogen gas (H_2) is, however, regarded as a potential route for methanol's sustainable production, as well as formic acid, lower olefins, and higher alcohols and hydrocarbons (Dalena et al. 2018a).

The catalyst used for the hydrogenation of CO_2 is usually the same as that utilized in the hydrogenation of CO for the production of methanol. Several studies have indicated that the type of catalyst, reactor configuration, and operating conditions have a significant influence on the CO_2 hydrogenation to methanol. Several metal-based catalysts, as presented in earlier sections, have been assessed for methanol synthesis, and the most active catalytic element has been found to be copper (Cu), employing various promoters like Si, B, Zn, Cr, Ag, Ce, Ti, Ga, Zr, V, Al, etc. (Arena et al. 2007; García-Trenco et al. 2017; Tada et al. 2017; Lam et al. 2018; Tang et al. 2019; Saeidi et al. 2021). Even though there is much reported literature on Cu-based catalysts, their sintering, deactivation, and phase segregation in the hydrogenation of CO_2 processes have given more reasons to study novel materials. Indium oxide (In_2O_3) has therefore been found as a developing material in the synthesis of methanol by CO_2 hydrogenation as a result of its stability and high selectivity (Martin et al. 2016; Tsoukalou et al. 2019; Frei et al. 2020).

It is important to get catalysts that are more water-tolerant and can offer an extended lifespan for the plant. An attempt has been made to use Pd as a catalyst for the production of methanol from $CO_2 + H_2$ even though it is not environmentally benign or economically viable. Pd is expected to be a poor catalyst for methanol production, which has been proven by (Bahruji et al. 2016) This is because it favorably catalyzes the RWGS reaction to generate CO, but it also produces an insignificant quantity of methane. However, the selectivity of Pd could be improved when it is alloyed with other metals. Maybe a case of this will be when Pd is supported on ZnO, a reduction in the high temperature ($> \sim 300$ °C) will result in the creation of a 1:1 PdZn alloy (Bahruji et al. 2016, 2017; Bowker 2019). This demonstrates excellent selectivity to methanol (Xu et al. 2016). There are several ways to synthesize such catalysts, and with other assistance, like the $ZnAl_2O_3$, for its performance enhancement, which can compete with that of the traditional CZA catalysts. It can similarly function with Pd levels as low as 1% and remain effective; however, it is costly (Bowker 2019).

The combination of ZrO_2 and Cu results in a very active, stable, and selective catalyst. Yet, a recent study by Stangeland et al. (2021) showed that Cu/ZnO still outshines Cu/ZrO_2 in terms of performance, particularly at low temperatures. Similarly, the selectivity and activity of mono-metallic Cu catalysts can be improved with CeO_2 in the hydrogenation of CO_2 to methanol (Zhu et al. 2020b).

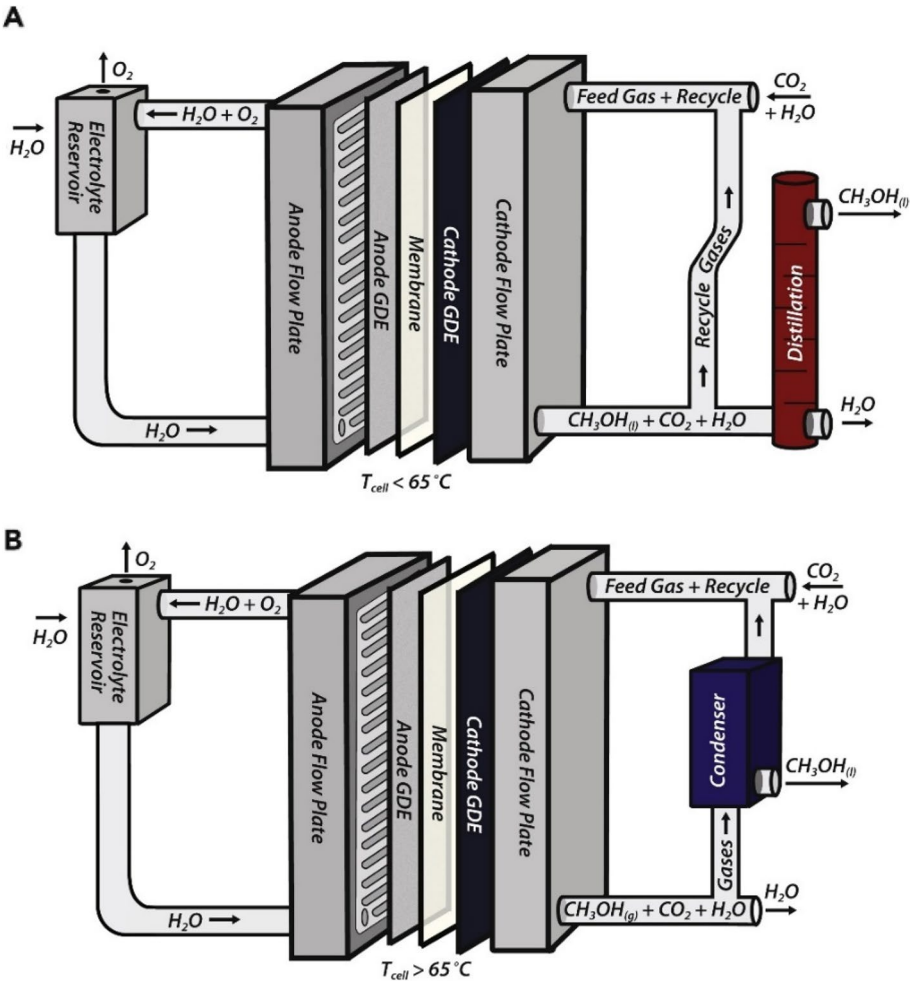


Fig. 13 Configurations of a two Zero-Gap System for electrolysis of CO_2 to Methanol (Sarp et al. 2021). Copyright 2020, Cell Press. (License number: 5886521131077)

However, the applicability of CeO_2 is limited due to its low stability in the presence of water (Wang et al. 2020; Schwiderowski et al. 2022). Cu/MgO, which demonstrated a high rate of formation of methanol in the hydrogenation of CO to methanol (Fig. 14), is not appropriate for the use of CO_2-containing feed gases since it is poisoned via the creation of very stable carbonates and bicarbonates on the surface of the catalyst (Nielsen et al. 2020; Schwiderowski et al. 2022).

Researchers such as Ye et al. (2014) and Rui et al. (2017) have reported that In-based catalysts exhibit similar performance in bifunctional catalysts like Pd-In, and composite In-based oxides/zeolite (Gao et al. 2018; Dang et al. 2019a), and Zr-In (Chen et al. 2019c). Furthermore, flame spray pyrolysis (FSP) was found to be an efficient approach to preparing effective catalysts for the purpose of hydrogenating CO_2 to produce methanol (Niu et al. 2022). The FSP method was utilized by Zhu et al. (2021a) for the preparation of the catalysts of Cu/ZnO-CeO_2, Cu/CeO_2 and Cu/ZnO as shown in Fig. 15b. The study identified that the inclusion of CeO_2 improves the dispersion of Cu compared to that of the ZnO due to its stronger Cu-CeO_2 interactions. The high selectivity of the CH_3OH can also be ascribed to the synergistic interactions of Cu-CeO_2 and Cu–ZnO.

A study by Chen et al. (2019b) as presented in Fig. 16, indicated that the formate route was better over the Cu-LaO_x interface in comparison to the hydrocarboxyl path. The LaO_x improved the Cu dispersion, which then enhanced the adsorption of CO_2. The approach resulted in 81.2% selectivity for methanol at a CO_2 conversion rate of 6% within a period of 100 h. In the study of Wang et al. (2019), the authors also suggested the application of visible light irradiation to excite electrons over Cu–ZnO. They showed that there was an easier activation of the reaction intermediates. This resulted in a reduction

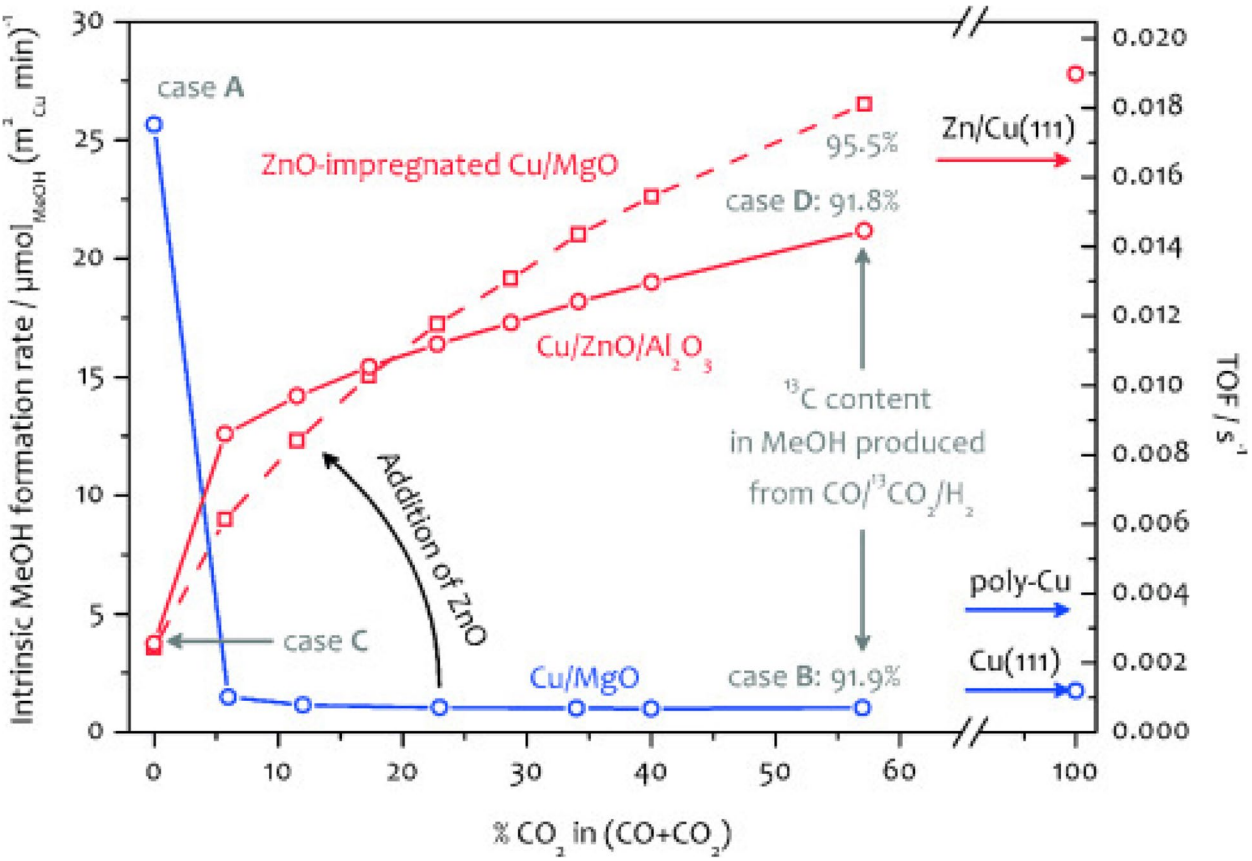


Fig. 14 Rate of intrinsic methanol-formation of a Cu/MgO (blue), a Cu/ZnO/Al_2O_3 (red), and a Cu/MgO/ZnO catalyst (red dashed), acquired through the impregnation of ZnO onto Cu/MgO, as a function of the CO_2 concentration in the feed gas [(CO_2+ CO)/H_2/inert = 14:59:27] at a pressure of 30 bar and temperature of 503 K (Studt et al. 2015). Copyright 2015, Wiley-VCH Verlag GmbH& Co. KGaA, Weinheim. (License number: 5913150015947)

of 40% in terms of activation energy, which was accompanied by a 54% increase in the production of methanol. Photo-mediated catalysis was cited as the cause through the formate pathway. Some current research on the transformation of CO_2 to methanol is reviewed and depicted in Table 5.

4.3 Techno-economic analysis and industrial application of methanol

Techno-economic analysis was conducted by researchers mainly using simulations, employing modeling-based analysis techniques to study the production and utilization of methanol. Battaglia et al. (2021) investigated the decarbonization of the chemical process industry through the use of "green" methanol produced from renewable electricity. A process model was created to use water electrolysis to transform CO_2 from a coal-fired power plant into methanol. According to the study, a network of recovery heat exchangers could increase plant efficiency from 26.74% to 37.22%, save 4.59 MW of energy, and lower the demand for heating and cooling by 81% and 47%. The price of methanol was in line with future market prices, ranging from 2624–2706 €t^{-1} to 565–647 €t^{-1}. Similarly, the Aspen Plus® and the TEPET tool for techno-economic analysis were used by Rahmat et al. (2023) to simulate the e-MeOH plant. The plant can achieve energetic and exergetic Power-to-Fuel (PtF) efficiency of 52.4% and 56.4%, respectively. The study states that the production of e-MeOH is possible at net present value of 1129–1481 €t^{-1} or 57–74 €GJ^{-1}, which could be doubled if the plant in Germany runs solely on solar and wind power. Additionally, Zhang et al. (2019a) investigated the solid-oxide electrolysis process's techno-economic optimization of CO_2 hydrogenation for the production of green methanol. To assess the process and its tradeoff between production cost and energy efficiency, a case study was carried out. The research produced 150 kton of CO_2 utilization and 100 kton of pure methanol, which translates to an annual renewable energy storage capacity of 800 GWh. With a 13-year payback period, the cost of producing methanol at 560 \$ton^{-1} was not economically feasible at an electricity

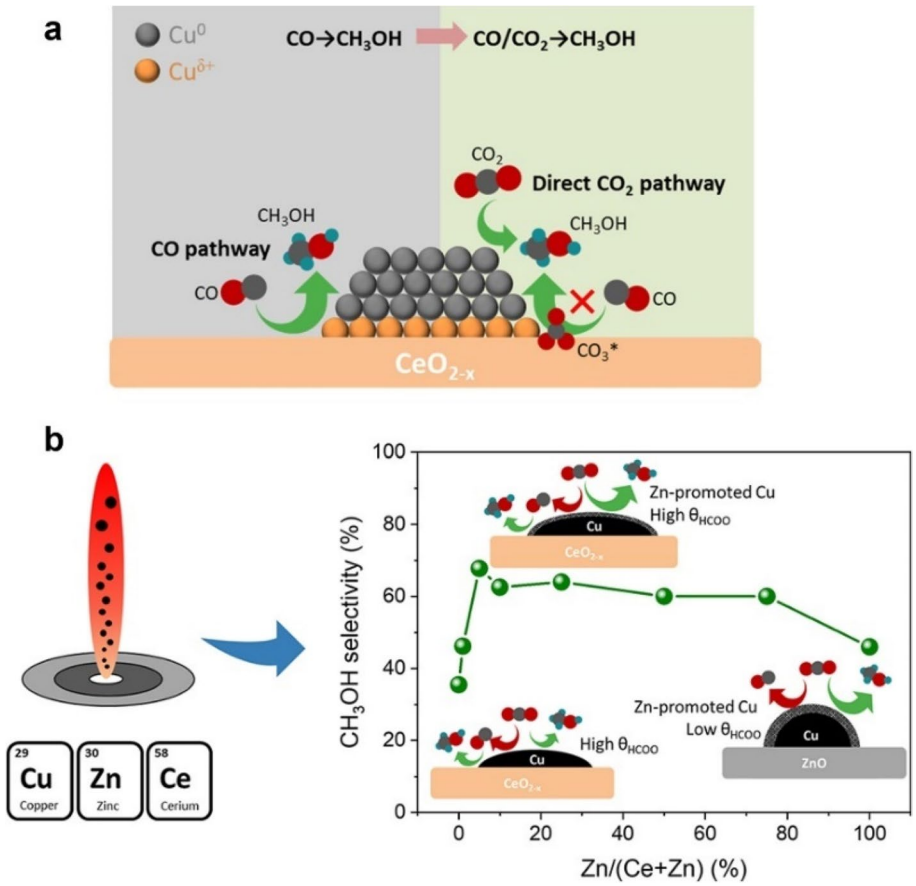


Fig. 15 **a** Suggested approach for the methanol production process using CO/CO_2 over Cu/CeO_2 (Zhu et al. 2020a). Copyright 2020, American Chemical Society. CC-BY-NC-ND (**b**) Synergistic metal-support interactions support the selectivity of CH_3OH in the hydrogenation of CO_2 based on $Cu/ZnO\text{-}CeO_2$catalysts (Zhu et al. 2021b). Copyright 2020, American Chemical Society. CC-BY-NC-ND

price of 73.16 $\$MWh^{-1}$. Using an Aspen Plus simulation model, Xiao et al. (2009) evaluated the life cycle of the production of biomethanol. With 42.7% energy efficiency, they discovered a methanol yield of 0.308 kg per (kg rice straw). 387 $USDt^{-1}$ was the total cost of production; 338.35 $USDt^{-1}$ represented the economic cost, and 38.65 $USDt^{-1}$ represented the environmental cost. Utilizing rice straw has been found to be an advantageous material for improving the environment and using agricultural waste. Chiou et al. (2023) investigated six different schemes based on adiabatic and non-adiabatic fixed-bed reactors as means of converting CO_2 to methanol. With an average market price of 378 $USDton^{-1}$ and a methanol minimum required selling price of 998 $USDton^{-1}$, Scheme 5's two-reactor system offered the best decarbonization potential and the lowest production cost. The hydrogen produced from SMR with carbon capture on both flue gas and syngas leads to net decarbonization, as evidenced by the finding that the highest amount of CO_2 that can be produced when using hydrogen is 6.554 ton-CO_2 per ton-H_2. In two scenarios—photovoltaic electrolysis with a battery and without a battery, using grid electricity—the efficiency of integrated methanol synthesis and hydrogen production using a heat exchanger network (HEN) was examined in the study by (Nizami et al. 2022). The cost per tonne of methane produced was 1040.17 and 1669.56 $ per tonne-MeOH, respectively. The total emissions of CO_2 equivalent were 0.244 and –0.016 kg-CO_2-eq per MJ-MeOH, respectively.

Methanol is a commonly utilized chemical in industries and common in our daily lives. It is mostly used as fuel in factories and for the generation of electricity due to its high efficiency as an energy carrier (Jadhav et al. 2014; Schorn et al. 2021). Some other applications for methanol are as follows:

Antifreeze–the chemical property of methanol enables it to reduce the freezing point of a liquid (water-based) and raise the boiling point. It is because of these properties that it is appropriate for methanol to be utilized in windshield washer fluids as an antifreeze to avoid freezing the cleaning fluid. Methanol is also introduced in NG pipelines to help reduce water's freezing point in the

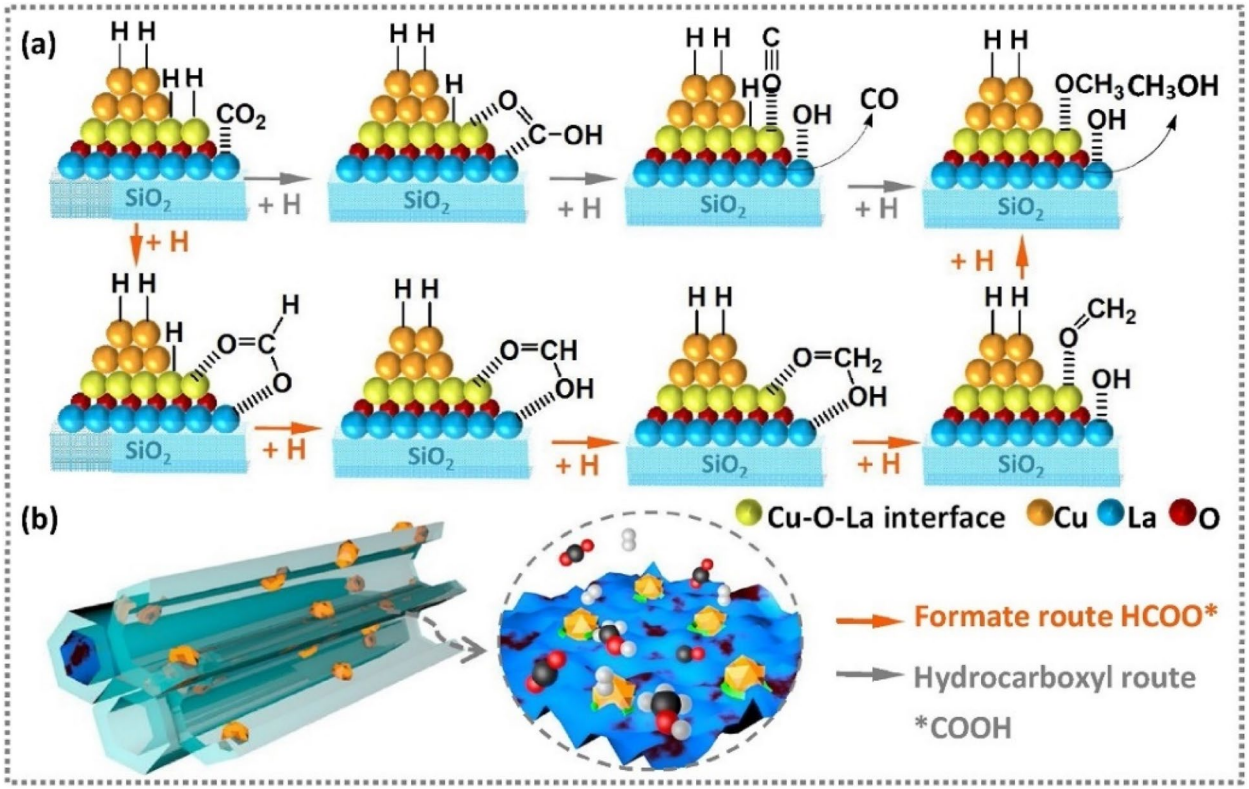


Fig. 16 Suggested mechanism of reaction for the hydrogenation of CO_2 over $Cu_1La_{0.2}$/SBA-15 catalyst (Chen et al. 2019b). Copyright 2019, Elsevier B.V (License number: 5886540390309)

course of the transportation of oil and gas (Haschek et al. 2010; Garg and Ketha 2020; Xu et al. 2020).

Solvent–it is also used as a solvent in industry to help in the creation of resins, inks, dyes, and adhesives. Methanol is also employed in the manufacturing of important products in the pharmaceutical industry, some of which are streptomycin, cholesterol, hormones, and vitamins (Haschek et al. 2010; Garg and Ketha 2020; Xu et al. 2020).

Methanol to DiMethylEther–in the petrochemical industry, methanol is used as a C1 building block, and a greater portion of it is produced and utilized as a substitute fuel in the DME industry. Properties of DME, i.e., ignition temperature and octane number close to those of diesel fuel, result in less engine noise, less smoke, and lower NO_x emissions compared to those of conventional diesel engines (Hosseininejad et al. 2012). The performance of DME fuel blend with diesel fuel has been presented in various analyses. For example, Taghavifar et al. (2019) explored the application of varying fuel blends of D50M30DME20, D60M10DME30, D70M20DME10, and D80M20 with different ratios of exhaust gas recirculation. Blending 20% of DME (D50M30DME20) and 30% methanol with diesel at 1400 rpm produced high pressure and accrued heat with 35% mechanical efficiency. However, a blend of D80M20 at 2000 rpm with a 20% exhaust gas recirculation produced a relatively inferior efficiency for the engine with defective combustive performance.

Methanol Fuel Cells–the need for external power supplies for charging various electrical gadgets is growing globally. Chemical energy is converted to electrical energy by PEM fuel cells. An example of the PEMFC is the DMFC (direct methanol FC), whose fuel is methanol solutions or methanol and operates at ambient temperature. It is comparable to the electrolysis of a methanol–water solution system. The typical reaction for the method is as presented in Eq. (5) (Dalena et al. 2018b).

$$CH_3OH + 1.5O_2 \rightarrow CO_2 + 2H_2O \quad (5)$$

The DMFC structure is made up of two porous electrocatalytic electrodes that are at both ends of a solid polymer electrolyte membrane. The overall cell reaction's thermodynamic reversible potential is estimated to be 1.214 V (Mallick et al. 2016; Dalena et al. 2018b). Electrons and protons are released through the oxidation of methanol and water in the anode catalyst layer (ACL) as indicated in Eq. (6). The protons get to the cathode

Table 5 Review of recent research on the production of methanol from CO_2

No	Study	Objective	Method and tool used	Key findings
1	(Chein et al. 2021)	To systematically analyze the influence of operating conditions, geometry of the reactor, unreacted syngas recycles and syngas composition on the performance of methanol synthesis	Both thermodynamic equilibrium and kinetic models were used	They found that the yield of methanol can be improved through raising residence time from increased diameter of the reactor. The residence time can be increased by a longer reactor however a large drop in pressure resulted in a reduction in methanol production. As a result of the nature of the exothermic reaction, the produced methanol is lower from an adiabatic reactor compared to the isothermal reactor because of the increase in temperature. The result of the CO_2 hydrogenating indicates that eliminating water can increase the yield of methanol
2	(Jiang et al. 2023)	To look into how various formic acid concentrations affect the selectivity, structural characteristics, and CO_2 conversion of methanol catalysts	It was an experimental study. The study employed the formic acid-assisted synthesis of Cu–ZnO-Al_2O_3 catalyst to catalyse the CO_2 hydrogenation for the production of methanol	As per their findings, the application of formic acid altered the Cu^+/Cu^0 ratio, resulting in an increase in the quantity of medium-strong base sites within the catalyst and an improvement in the selectivity of methanol
3	(Salomone et al. 2023)	To create catalysts that will convert CO_2 into methanol. Additionally, in an effort to reduce CO emissions and boost methanol yield, the effectiveness of co-precipitated In_2O_3-CeO_2 and In_2O_3-ZrO_2 binary oxide catalysts for methanol synthesis was investigated	It was an experimental study	The findings indicated that the greater specific activity ($168\ mg_{CH_3OH} g_{In_2O_3}^{-1} h^{-1}$ at temperature of 300 ℃ and pressure of 2.5 MPa of $In_{40}Zr_{60}$) was attributable to the electronic promotion of Zr. The addition of CeO_2, however, had no positive effect on the activity
4	(Zhou et al. 2023)	To estimate the influence of varying technologies of CO_2 capture on the operations of the entire process of the production of methanol	A steady-state modelling and simulation of the four different technologies of CO_2 capture (phase-change separation (PCS), monoethanolamine (MEA), gas membrane separation (GMS) and dimethyl carbonate (DMC)) were used for the analysis	According to the outcome of study, the GMS recorded the highest energy efficiency of 68.4%, the PCS followed with 66.2%, DMC recorded 64.3%, and that of the MEA was 61.3%
5	(Zhang et al. 2022a)	To evaluate high selective methanol production from the hydrogenation of CO_2 over Mo-Co–C-N catalyst	The experimental study utilized porous carbon, a ZIF-67 template, and a Mo-Co catalyst in a fixed-bed CO_2 hydrogenation reaction to enhance methanol selectivity, while altering the calcination temperature and Mo to Co ratio	The maximum space–time yield of 3.3 $mmol/g_{cat}/h$ was attained at a temperature of 275 °C
6	(Yusuf and Almomani 2023)	To improve the operating conditions for viable catalytic CO_2 hydrogenation to methanol utilizing Cu/ZnO/Al_2O_3 catalyst operated the following conditions: 210 °C and 70 bar	The Aspen Plus software was employed for the analysis	The study revealed that an adiabatic reactor with a 1:7 CO_2/H_2 ratio produced methanol with a yield of 99.84% and a CO_2 conversion of 95.66%

Table 5 (continued)

No	Study	Objective	Method and tool used	Key findings
7	(Yousaf et al. 2022)	To analyze the techno-economics of combined methanol and hydrogen production process by CO_2 hydrogenation	A high temperature SOE as a hydrogen generation (12.16 ton/hr) source from steam is combined with the process of the hydrogenation of CO_2 to reduce methanol production cost	The combination of solid oxide electrolyzer (SOE) with the production process of methanol occasioned a 22.3% reduction in hydrogen cost relative to that of alkaline water electrolyzer. Therefore, there was a reduction in the cost of 63.5 ton/hr, it moved from 1063 $/ton to 701.5 $/ton, for the generation of methanol
8	(Borisut and Nuchitprasittichai 2019)	The aim of the research was to reduce the cost of synthesizing methanol per ton	Use of response surface methodology (RSM) for methanol production optimization through the process of CO_2 hydrogenation	The minimum cost obtained for the produced methanol was 565.54$/t of produced methanol
9	(Do and Kim 2019)	To propose and assess a novel process for methanol production by combining thermochemical splitting and CO_2 hydrogenation technologies	The study utilized PSE-centric methods like simulation and optimization to create a comprehensive model for the proposed AS2M frameworks	Their suggested method attained a maximum energy efficiency of 15.5%, and a least selling cost of 0.94 $/kg for methanol was obtained
10	(Choi et al. 2019)	To investigate the influence of particle size for Ni NPs supported on β-Ga_2O_3 for the hydrogenation of CO_2 to methanol at a pressure of 0.5 MPa	The model Ni nanoparticles having a range between 3.3 and 10.2 nm were produced by means of the hot injection approach through regulation of the reaction time and temperature	Methanol's activation energies with Ni NPs rose from 6.0 to 18.4 kcal mol^{-1} when there was an increase in the size of the nanoparticle

by passing through the electrolyte membrane, while the electrons move through an external circuit to the cathode (Dalena et al. 2018b).

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad (6)$$

5 Bibliometric analysis

A brief bibliometric analysis was conducted along the study objectives to understand the study trend and evolution of methanol production between the periods of 2013 and 2023 using the Scopus database. A total of 232 documents were retrieved from the database using keywords such as "methanol production methods" OR "biomass to methanol production" OR "carbon dioxide to methanol" OR "green methanol production", which were then fed into the VOSviewer and the Biblioshiny package in the R software for analysis and visualization. The overall information for the documents evaluated is presented in Fig. 17. Research in the area of study recorded an annual growth rate of 3.63% with a total authorship of 867.

The co-occurrence, fractional counting, and author keywords were used for the analysis. The results as presented in Figs. 18 and 19 show major networks between the production of methanol and certain particular keywords related to the different production methods, some of which are CO_2 reduction, bio-methanol, biofuels, biomass-to-methanol, CO_2-to-methanol, gasification, optimization, hydrogenation, etc. A total of 7 clusters and 135 links were identified. The places with dense clusters indicate that those words are more connected, and such words are more relevant to the production of methanol. The thicker and bigger circles represent the frequency of usage of the word or phrase in published literature.

Most of the keywords are words that are related to CO_2 conversion to methanol; according to the network, they have a strong link to the production of methanol. Keywords like carbon dioxide emissions, CO_2-methanol, and carbon dioxide fixation are terms that fall closely to the dense cluster of methanol production. This implies that for the last 10 years, most studies on methanol production have focused on the use of CO_2 conversion to methanol, especially due to the increasing need to reduce CO_2 pollution and the abundant nature of that resource for methanol production.

The ways in which the different themes have developed for the study period was divided into three different time periods, i.e., 2013–2017, 2018–2020, and 2021–2023. As demonstrated in Fig. 20, there has been a considerable evolution in the areas of research on the research topic over the years. Studies within the first 4 years (i.e., 2013–2017) were mainly limited in terms of scope; topics such as biodiesel, gasification, methanol, CO_2 reduction, and methanol synthesis were the main areas of focus. During the second period of the analysis (i.e., 2018–2020), this, however, evolved to include topics such as electrocatalysis, carbon dioxide utilization, bio-methanol, and biomass gasification. This suggests that researchers expanded their studies beyond just the production of methanol and CO_2 reduction in the first four years to cover its uses in different areas of life. The last stage of the evolution covers the period between 2021 and 2023, where topics like life cycle assessment (LCA), process simulation, methanol synthesis, etc., were investigated by researchers. During the period, researchers such as Hoppe et al. (2018), Li et al. (2018a); Eggemann et al. (2020), Adnan and Kibria (2020), and Zang et al. (2021) conducted LCA analysis on the methanol synthesis. The thematic map for the various author keywords used by various researchers is presented in Fig. 21. The thematic map is produced

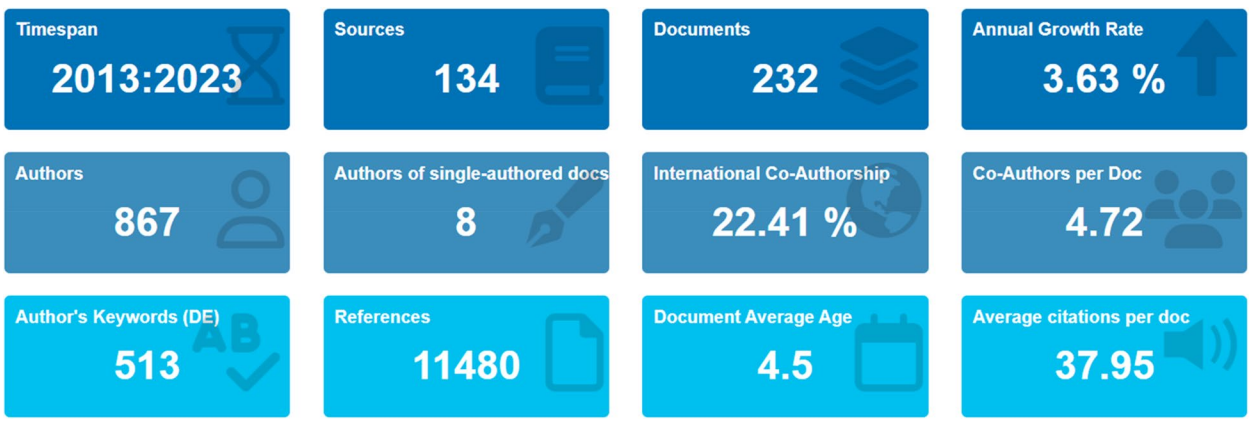


Fig. 17 Overview of the main information for the study period

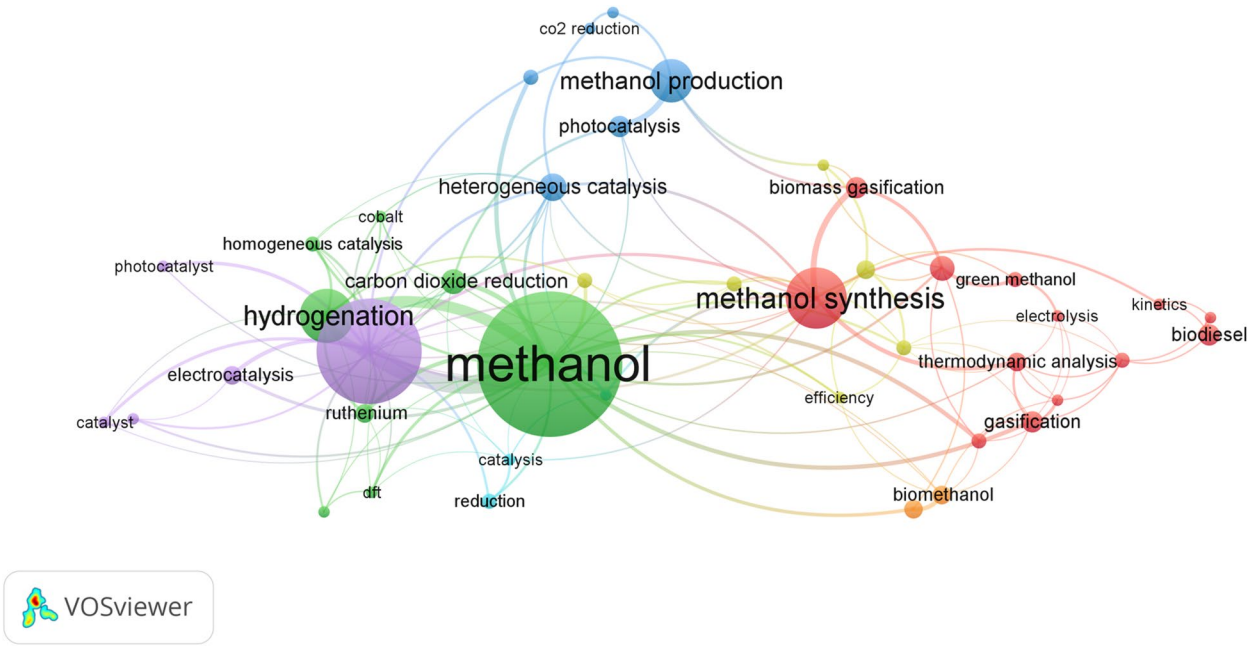


Fig. 18 Research network visualization for the production of methanol

based on the centrality and density of the keywords used by the authors over the years. It has four topological regions. It is generated using the semi-automatic algorithm in the Biblioshiny package and reviews the various titles of the documents assessed in the study. The clusters presented in the graph show the topics or areas of the research, whereas the cluster size highlights the proportion to the number of author keywords. The graph has four quadrants, i.e., the motor themes, niche themes, emerging/declining, and basic themes.

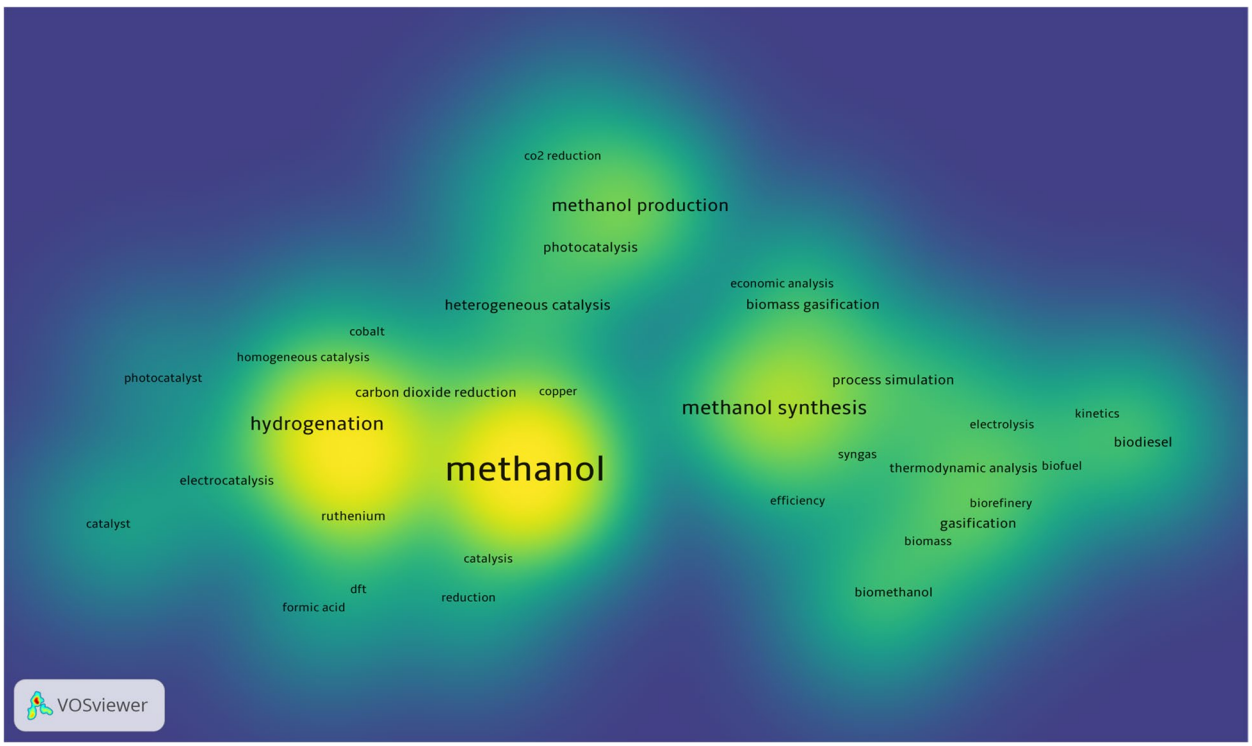


Fig. 19 Density visualization for the production of methanol research

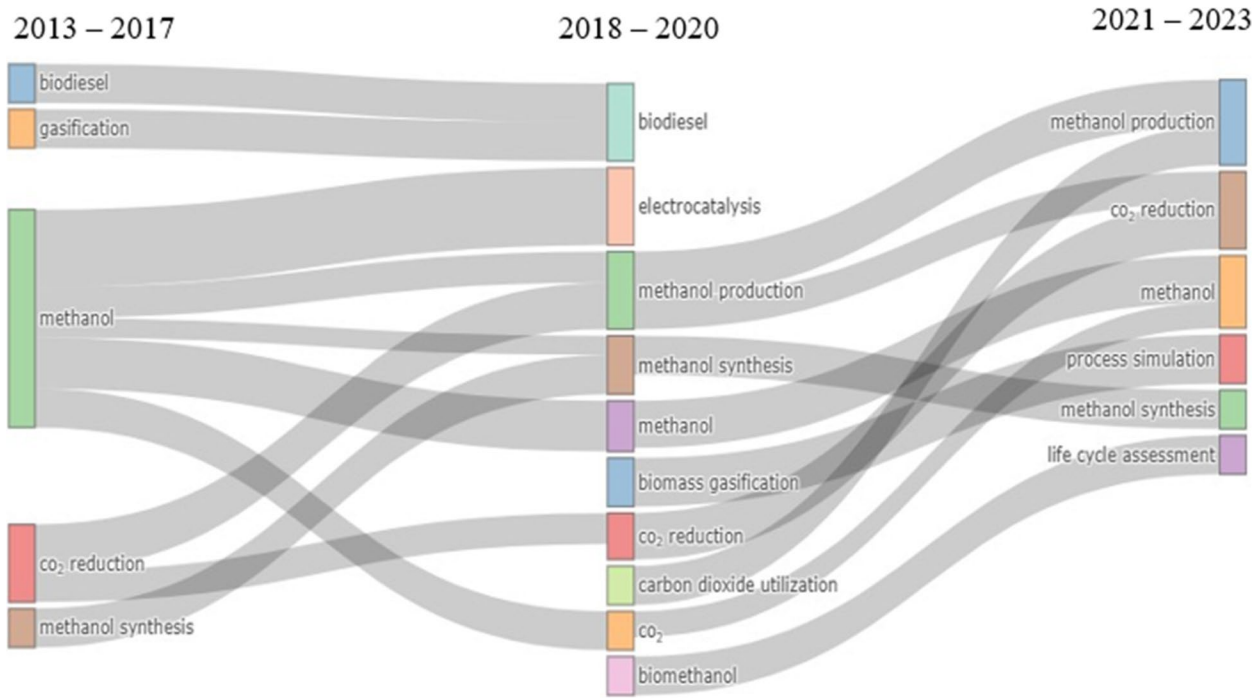


Fig. 20 Evolution of themes within the past decade in the study area

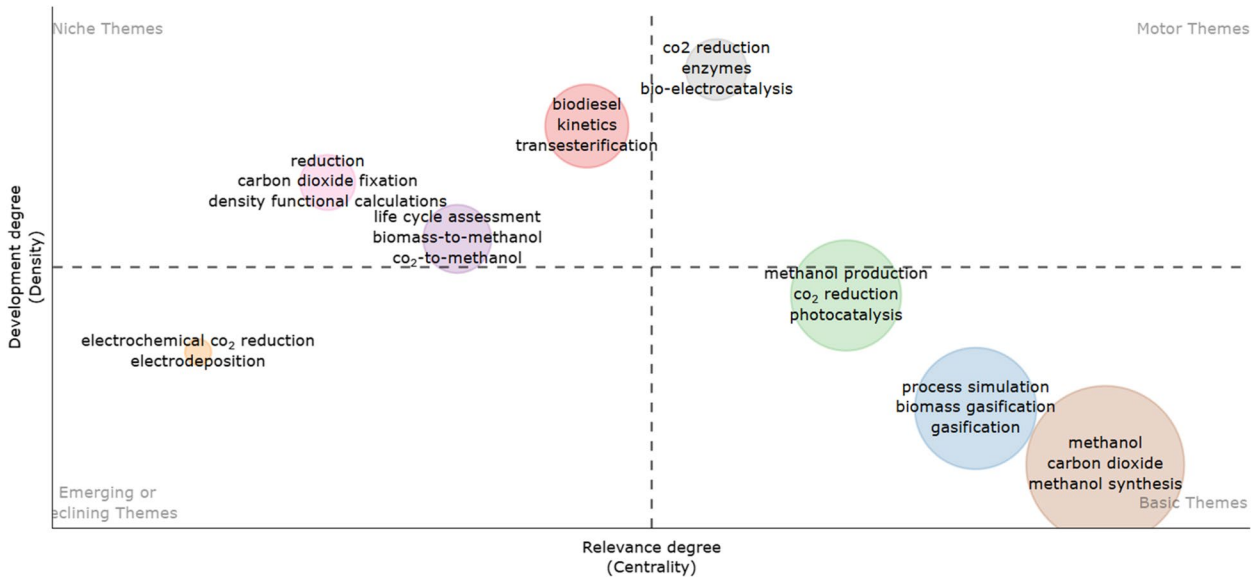


Fig. 21 Thematic map for the author keywords

The motor themes quadrant refers to themes that are well-developed and important in the area of research; the niche themes correspond to topics that are isolated and highly developed. The emerging or declining themes appear in the third quadrant. The fourth quadrant has the basic themes, which are topics that are transversal, general, and basic in the research field (Cobo et al. 2011; Agyekum and Odoi-Yorke 2024). The motor themes have topics such as CO_2 reduction, enzymes, and bio-electrocatalysis; these themes are well developed in the area of

research. Studies by Zeng et al. (2014), Liang et al. (2015), Gallo et al. (2020), Ma et al. (2022), and Garcia-Baldovi et al. (2023) assessed various aspects of CO_2 reduction to methanol; similarly, other studies by Zhang et al. (2021c), Weliwatte and Minteer (2021), Katagiri et al. (2022), and Luan et al. (2023) also investigated recent advances in the use of bio-electrocatalysts for CO_2 reduction. The niche themes recorded three different clusters; themes such as biodiesel, kinetics, and transesterification fall within the first and highly dense cluster; such themes are mostly interlinked and studied together by researchers. The second cluster in the niche themes consists of themes like reduction, carbon dioxide fixation, and density functional calculations. The density functional theory has been used by researchers like Sun et al. (2015), Kumari et al. (2015), Liu et al. (2018), and Kopač et al. (2019) to investigate the methods for CO_2 reduction to methanol. One cluster appeared in the declining or emerging themes; it has topics such as electrodeposition and electrochemical CO_2 reduction. The electrodeposition technique is a long-standing process that has been used to coat thin layers of one metal on top of another to help in the alteration of its surface characteristics through the donation of electrons to the ions in a solution. In recent years, the electrodeposition technique has gained much recognition in the area of methanol production (Abraham and Chetty 2021; Traipop et al. 2021). The topics in the emerging/declining themes can best be described as emerging instead of declining since these are new topics being researched by scientists in the area of methanol production. The last quadrant, i.e., the basic themes, has three clusters with topics that are basic in the research field, all of which have already been discussed in earlier sections.

The factorial analysis presents the conceptual framework for the topic of research (Fig. 22). The clustering of the author keywords was done using the K-means approach. This allows researchers to find documents or topics that are common in concept. The outcome as presented in the graph can be explained through the use of the individual points' locations and how they are distributed across the dimensions. Words that are close have a similar distribution structure (Aria and Cuccurullo 2017). According to the outcome of the algorithm as presented in the graph, during the study period, the majority of the author keywords exhibited a similar distribution and strong correlation.

The geographical collaboration map indicating co-authored documents among countries around the world is shown in Fig. 23. The Biblioshiny software was used in the visualization of the research collaborations in the study area. It demonstrates the social structure of the scientific community in the area of biomass and CO_2 conversion to methanol. The intensity of the blue color is an indication of the number of publications in that country; on the other hand, the level of collaboration among the academics in the various countries is represented by the red lines. A total of nine clusters with 279 links were observed. A total of 61 documents were recorded for China; the United States followed with 28 documents; India, Italy, Spain, and Malaysia followed with 15, 12, 11, and 10 documents, respectively. Other countries followed with single-digit figures under the various clusters. China comes first globally in terms of research on methanol production and consumption; hence, many resources are invested in its studies. The highest collaboration occurred between China and the United States of America, which recorded a frequency of six. The next highest collaborations with frequencies of two each occurred between China–Denmark, China–Germany, India–France, India–Malaysia, Italy–Iran, Italy–Netherlands, Italy–Switzerland, Malaysia–Bangladesh, Malaysia–Pakistan, and the United States–Korea. It is worth indicating that a country like China, which is leading in green methanol production research, is intensifying its methanol vehicle development to reduce pollution in the environment and also secure the supply of energy (Li et al. 2023b, 2023a).

6 The way forward for the production of renewable methanol.

The cost of production is a key hindrance to renewable methanol adoption; just like other sustainable alternate fuels and feedstocks, the cost differential between renewable methanol and fossil-based alternatives may continue for some time to come. Compared to methanol obtained from natural gas and coal-based production, which have costs of production ranging between 100 $\$t^{-1}$ and 120 $\$t^{-1}$, and 150 $\$t^{-1}$ and 250 $\$t^{-1}$, respectively, that of renewable methanol is assessed to be higher. On the European market, for instance, the cost of methanol fluctuates in the range of 200 $\$t^{-1}$–400$\$t^{-1}$ when adjusted for inflation. It therefore suggests that fossil fuel-based methanol is already competitive with several fuels produced from petroleum, such as diesel, gasoline, heating oil, and jet fuel (IRENA 2021). The production cost for bio-methanol, and e-methanol (from hydrogen and CO_2) are estimated to be 327 $\$t^{-1}$–764 $\$t^{-1}$, and 800 $\$t^{-1}$–1600 $\$t^{-1}$, respectively, making them very expensive (IRENA 2021). Hence, the right policies ought to be put in place to stimulate and sustain renewable methanol's production and utilization on a large scale. More research is needed to determine how CO_2 to methanol technologies affect the environment. Future studies may concentrate on evaluating the effects of the entire life cycle, i.e., life cycle assessment, contrasting various approaches, and streamlining the procedure to cause the least amount of environmental destruction.

Renewable methanol production methods ought to be at a technology readiness level (TRL) that is high enough

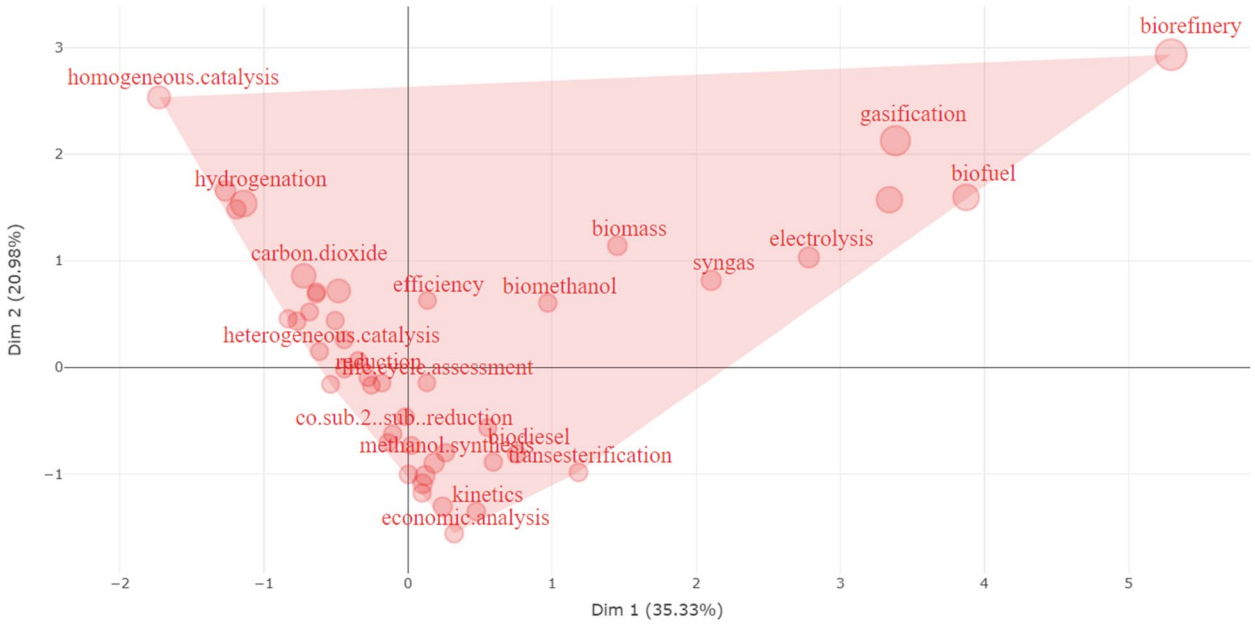


Fig. 22 Factorial analysis for the author keywords

to be deployed at scale; this will enable them to compete with traditional methanol production methods in the near future. According to a study by Harris et al. (2021), biomass-methanol is the only production route that can be potentially implemented at scale in the near term. In terms of cost, biomass gasification to methanol at a cost of 0.39 $\$kg^{-1}$ could compete with conventional methanol production's economic performance. Additionally, the use of commercialized methanol production pathways from biomass offers the opportunity to incorporate them with existing traditional methanol plants, which will result in a reduction in cost and transition time. Factors such as established infrastructure and high productivity are some of the advantages of the thermochemical conversion of biomass waste. Although it has a high rate of productivity in terms of the quantity of methanol produced, there is still little information in the literature on the technical drawbacks, proper conditioning of appropriate raw materials, cheaper catalysts depending on the feedstock of the biomass, as well as some process parameters such as residence time, particle size, temperature, and yield (Gautam et al. 2020). All of these factors have to be looked at

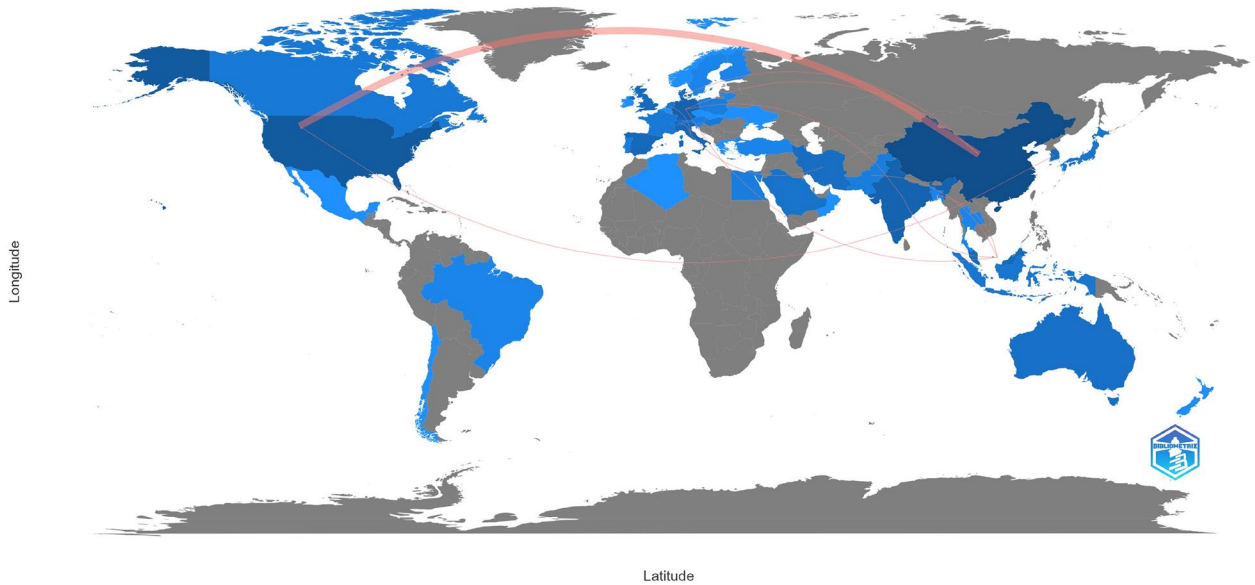


Fig. 23 Country research collaboration map

prior to its large-scale implementation for the production of methanol. Effective CO_2 capture is critical to the conversion process, and cutting-edge capture technologies, such as direct air capture (DAC), including innovative materials, membrane separation, and liquid absorption techniques, are necessary to make CO_2–based methanol economically viable (Sodiq et al. 2023; García-Bordejé and González-Olmos 2024). A closed-loop system that transforms captured CO_2 into methanol for use as a fuel or chemical feedstock might be created by integrating CO_2 capture combined with utilization (CCU) procedures into the current carbon capture and storage infrastructure (Pérez-Fortes et al. 2016; Djettene et al. 2024).

A look into the reviewed literature suggests that Cu-based catalysts are the most commonly used for CO_2 hydrogenation to methanol, particularly Cu–Zn based catalysts, as a result of their excellent activity. Cu-based catalysts are, however, found to have low selectivity when subjected to low H_2/CO_2 conditions or low pressure. It is therefore important for future studies to focus on developing other forms of catalysts that do not depend on Cu. Such catalysts must have characteristics such as high stability, high performance, and cheapness in terms of cost. Going forward, it is vital to construct durable and efficient catalysts. There has been some positivity in the use of new ligands with functional groups that improve activity via metal-ligand cooperation. Such ligands include proton- and electron-responsive ligands, which have the potential to lose some protons or electrons, respectively. Energy footprints could be greatly reduced by solar-assisted CO_2 reduction processes, which use solar energy to power catalytic reactions (Dey et al. 2004; Adekoya et al. 2019). High efficiency and stability for direct CO_2 conversion to methanol should be the main goals of research into photocatalysts such as TiO_2, CdS, or copper-based materials.

Furthermore, the production of renewable hydrogen via water electrolysis is essential for CO_2-to-methanol conversion processes (Barbato et al. 2013; Sollai et al. 2023). The economics of producing CO_2 to methanol will be greatly impacted by lowering the cost of producing hydrogen. Also, reactor configurations should be optimized for CO_2 to methanol conversion; this can lower energy consumption and increase yield. For catalytic reactors to transfer heat and mass more efficiently, research on flow chemistry and creative reactor designs is essential.

In terms of policy, biomass can be employed for the generation of bio-methanol or e-methanol in the industrial and transport sectors. There may be varying paths to carbon neutrality for each sector; hence, there should be a public policy by various governments and institutions across the globe that creates an equal playing field to expand the opportunities therein and not rather limit them. Furthermore, robust policies and programs will be required to remove the hindrances linked to the development and introduction of renewable methanol. Government mandates for incentives for renewable fuels, fuel blending quotas, and carbon taxes could influence the willingness of the energy market to pay a premium for clean methanol (IRENA 2021).

7 Conclusions

Producing methanol from renewable sources is gaining traction in the world's quest to reduce its GHG emissions. Its production can be done by either using conventional sources or renewable sources, and it is projected to be a possible solution to the world's clean energy needs in the near future. This study reviewed recent developments in the production of clean methanol from biomass and CO_2 sources. The challenges associated with the generation of methanol from the two sources were also highlighted. The study combined bibliometric and traditional review methods to assess the recent trends and evolution of methanol production and use. The study revealed that the immature nature of the technologies used for the production of clean methanol continues to serve as a hindrance to the product's mass production. For instance, methanol production via the process of biochemical conversion remains at the laboratory level, even though it has proven to be a promising production option. Cu-based catalysts are the most used for CO_2 hydrogenation to methanol, particularly Cu–Zn based catalysts, because of their excellent activity. Cu-based catalysts are, however, found to have low selectivity when subjected to low H_2/CO_2 conditions or low pressure. It is therefore important for future studies to focus on developing other forms of catalysts that do not depend on Cu. Such catalysts must have characteristics such as high stability, high performance, and cheapness in terms of cost. It is also important to get catalysts that are more water-tolerant, which can extend the life of the plant. An effort has been made to use Pd as a catalyst for the synthesis of methanol from $CO_2 + H_2$, even though it is not environmentally benign or economically viable. The trend in research as identified through the bibliometric analysis indicates that the research in the last decade has developed from just the process of producing methanol to its application in industrial settings. It indicates that a total of 867 authors were involved in research on the topic. Major networks between methanol production techniques and particular keywords were found through analysis employing co-occurrence, fractional counting, and author keywords. A total of 135 links and 7 clusters were found. The factorial analysis revealed that the majority of the author keywords used during the study period have a similar distribution and are strongly connected, suggesting a shared concept. The study concluded with potential future research directions.

Authors' contributions
All authors contributed to the study conception and design. Conceptualization, material preparation, funding, data collection, writing of original draft, reviewing and editing, and analysis were performed by Ephraim Bonah Agyekum. Reviewing and editing, materials preparation, resources, and funding were performed by Paul C. Okonkwo and Farhan Lafta Rashid, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Data availability
Data used in the current study are available from the corresponding author on reasonable requests.

Declarations

Ethics approval and consent to participate
This article does not contain any studies with human participants or animals performed by any of the authors.

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Competing interests
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Author details
[1]Department of Nuclear and Renewable Energy, Ural Federal University Named After the First President of Russia Boris Yeltsin, 19 Mira Street, Ekaterinburg 620002, Russia. [2]Western Caspian University, 31, Istiglaliyyat Street, Baku AZ1001, Azerbaijan. [3]Applied Science Research Center, Applied Science Private University, Amman, Jordan. [4]Jadara University Research Center, Jadara University, Irbid, Jordan. [5]Tashkent State University of Economics, Islam Karimov Street 49, Tashkent City 100066, Uzbekistan. [6]Mechanical & Mechatronics Engineering Department, College of Engineering, Dhofar University, Salalah, Oman. [7]Petroleum Engineering Department, College of Engineering, University of Kerbala, Karbala 56001, Iraq.

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