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REVIEW ARTICLE

Biocatalysts for biomethanol production: Advancements and future prospects

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ABSTRACT

Biomethanol, a renewable and sustainable alternative to traditional fossil-fuel-derived methanol, has garnered considerable attention as a potential solution to mitigate greenhouse gas emissions and dependence on non-renewable resources. The utilization of biocatalysts in biomethanol production offers a promising avenue to achieve environmentally friendly and economically viable processes. Paper highlights the biocatalytic pathways involved in biomethanol synthesis. Particular emphasis is placed on microbial biocatalysts, such as methanogenic archaea and certain bacteria, which possess the unique capability of converting carbon dioxide and hydrogen into methanol through a series of enzymatic reactions. Additionally, enzyme-based systems derived from various microorganisms and genetically engineered organisms are also discussed as potential biocatalysts for biomethanol synthesis. Paper also delves into the current challenges and limitations faced in harnessing biocatalysts for biomethanol production. These challenges include substrate availability, low conversion rates, enzyme stability, and process scalability. Several strategies to address these issues are highlighted, including metabolic engineering, synthetic biology, and bioprocess optimization techniques. The advantages of utilizing biocatalysts for biomethanol production are outlined. Biocatalytic routes offer the advantage of operating under mild conditions, which reduces energy consumption and minimizes the production of unwanted by-products. Furthermore, the utilization of renewable feedstocks, such as carbon dioxide captured from industrial emissions or waste streams, enhances the sustainability of the process. The final section discusses future prospects and potential research directions in the field of biocatalytic biomethanol production. Advances in biotechnology, omics technologies, and computational modeling are poised to accelerate the discovery and optimization of novel biocatalysts, thereby unlocking the full potential of biomethanol as a sustainable fuel and chemical precursor. The use of biocatalysts for biomethanol production offers an attractive approach to establish a green and circular economy. With ongoing research and technological advancements, the field holds significant promise for reducing carbon emissions and transitioning towards a more sustainable energy landscape. However, to fully realize the potential of biocatalytic biomethanol production, interdisciplinary collaboration and concerted efforts are required to address existing challenges.

Keywords: biomethanol; biological conversion; methanotrophs; methane; renewable energy; biocatalysts

1. Introduction

There are several ways of methanol production, reported and discussed and these processes use the different feedstock like agrowastes, forestry residues/wastes and also food/organic wastes derived biogases[1,2]. These are converted by different biological processes with contribution of methanotrophs microbes. Methanotroph microbes are different species of bacteria and can function at high temperature conditions[3]. In

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natural ways in landfills and sewage sites, different nature of organic wastes are degraded to different forms of simple monomers and also different acid, alcohol and also gasses. Then the contribution of methanogen bacteria converts into biogases containing a major fraction of methane[3,4]. Due to high demand for biomethanol, now people are involved in e-Methanol production tasks with better facilities and this was first discussed by European energy with first installation plants in Kasso, Aabenraa, and Southern Denmark. In this European energy innovators claimed green energy development with sustainable fuel solutions[5].

These can be found as strong track records in entire Europe with with various institutions claiming for wind energy and photovoltaic (PV) as renewable energy facilities/plants. In Europe, people are showing their interest in development with the engagement/entering of companies into e-Methanol markets with claims to apply many renewable energy technologies[6]. These can support e-Methanol development with production plants at the worldwide level. Several challenges have been reported in development of e-Methanol production plants with the sources of renewable energy to power plant processes[5,6]. This can be an opportunity for finding viable off-take based on final product prices with little higher than traditional methanol process. Still, there is no final partner availability that can be encouraged with sufficient knowledge to make the e-Methanol production projects successful[7,8]. Some effort in e-Methanol production is reported with capturing of carbon dioxides from renewable sources. Few methods are explored with production of renewable methanol production in more expensive ways than the traditional methanol synthesis/production. Traditional ways of methanol are discussed for brown and gray nature via utilization of coal and natural gasses as non-renewable feedstock[8,9].

Various analyses were done on cost of fossil fuel based methanol production and is reported in ranges of $100–$250 per metric-tonnes (mt) that was given by IREA (International Renewable Energy Agency) with partnership to Methanol production Institutes. Earlier methanol cost was estimated to $770/mt[10]. Due to the promotion of renewable fuels context, current period methanol production of biomethanol was found to double compared to past few decades. Prediction: In 2050, total biomethanol production can reach 500 million mt/year with effort to reduce the production cost[11]. In the last few years, production capacity of methanol production with installation of several plants was reported in Europe. In this regard, nearly 20 MW electrolysis and synthesis plants were reported for hydrogen and methanol production. It is collaborating with the Linde industry with European Unions (EUs) preliminary selection stage for funding. In this effort, nearly 0.2 million mt/year of renewable methanol production is reported[10,11]. Local governments in Europe are also provided with promotion and investment opportunities. Till this period, there is limited support from current governments that support and involve in renewable methanol production and it is a big struggle to achieve traction in the global markets. IMO 2030 (international maritime organization) prediction, there are no details shown for uses of biomethanol and also no legislation recommendation on its use[12,13].

In context to traditional/conventional mode derived methanol, reduction in carbon dioxide emission can be only found to 15% while compared to conventional marine fuels. But it can be stored at ambient temperatures[12]. Renewable methanol usage in transportation vehicles is shown with multiple advantages like reduction in carbon dioxide (CO_2) emission up to 65%–95% that was claimed by joint IRENA and also methanol production agencies. Some challenges are found as lack of fueling infrastructure and it can hold back the fuel's emergence as an alternative bunker feedstock in S&P global Platts[10,13]. In Europe, the current period is discussed for development of methanol bunkering infrastructure. In this context, double-fuel engines can be utilized for methanol-based fuels/very low sulphur (S) fuel oils in current vehicle services. Further effort was shown in methanol consumption with showing competitiveness in Emission control area (ECA) zone[14]. This shows the recent increase in prices of conventional bunker fuels. In the current period, biomethanol production costs are found to \$400/mt and it was compared to the cost of traditional modes of synthesized methanol. Efforts for double fuel engine vessels are found with the opportunity to utilize the methanol fuels and it can bridge the gap between traditional fuels and renewable fuels[15].

Renewable methanol fuel showed multiple advantages like low flammability, high performance and low carbon emission. Many reports are shown for biomethanol use in fuel cell-powered vehicles with capacity to degrade it into carbon dioxide and water (in steam form)[14,15]. In the case of M85 fuel composition, it is a mixture of 85% methanol and 15% gasoline and then it can be used in existing vehicles without any technical modification. Further biomethanol production is achieved via application of gasification and also pyrolysis process[16,17]. In the current period, the gasification process is utilized for higher amounts of biomethanol compared to the pyrolysis process. In the renewable mode of biomethanol production process, several types of waste biomasses from forage grasses, tree and crop residues are used[18]. Different biomasses are screened in this context to high biomethanol yield (55%) that was achieved from uses of rice bran. In methanol production processes efforts, high-temperature conversion of reused-derived fuels is reported with a very promising process[15–18]. Now in recent improvement in temperature conversion process and also uses of multiples production is reported. It shows good alignment of the on-stream time for the plant's capacity (8400 h operation/year). Next analysis was done on energy efficiency of various natures including biomethanol and then methanol efficiency is found to be lower than natural gas-based plants with limited batteries[19].

Next studies were done on impact on energy cost and greenhouse gas (GHG) emission. And it is associated with extraction and distribution of fuels including natural gas. Natural gas is shown to be better for extraction and distribution processes[20]. Efforts are shown in estimation of CO_2 emission in biomethanol and it is found to be half compared to CO_2 emission from waste-to-energy application[19,21]. This can be found to be 45% or less compared to methanol from natural gas. Big challenge in the biomethanol commercialization process is relatively high capital costs. Some reports discussed the key factors that affect the economics of RDF disposal. Final suggestions were on recommendations for establishing the policy framework with credits to environmental advantages on biobased methanol or other biobased materials[22]. Policy makers insights is discussed for methanol uses and production and then biomethanol showed as the most important and versatile platform chemical for chemical industry[21,22]. Efforts are also shown for other chemicals like additives for gasoline, solvents and antifreeze agents and these can be utilized in the biodiesel production process[20,22]. This review explores biomass wastes sources, processes for biomethanol production and also catalysts role in conversion of biomass into biomethanol with impact to environment.

2. Production of biomethanol

Several efforts for methanol synthesis are discussed and in context to fuels development efforts, renewable-power assisted CO_2 capturing process and utilization is explored in detail for methanol production. This study for methanol synthesis is shown with increased attention in the current period[11,22]. This is a study for assessment on the techno-economics of methanol synthesis via capturing the carbon dioxide with hydrogenation process that can result in renewable hydrogen production with uses of photovoltaic (PV) based electrolysis. This process can use CO_2 that originated from natural gas field processing. In this study, there was a report on two scenarios such as PV electrolysis with/without a battery with uses of grid electricity[11,12]. This study was started with a proposed process system and then it simulated using Aspen HYSYS. v11. In this proposal, a proton exchange membrane (PEM) electrolyzer was applied for the electrolysis process[23,24]. **Figure 1** shows the coal conversion into methanol.

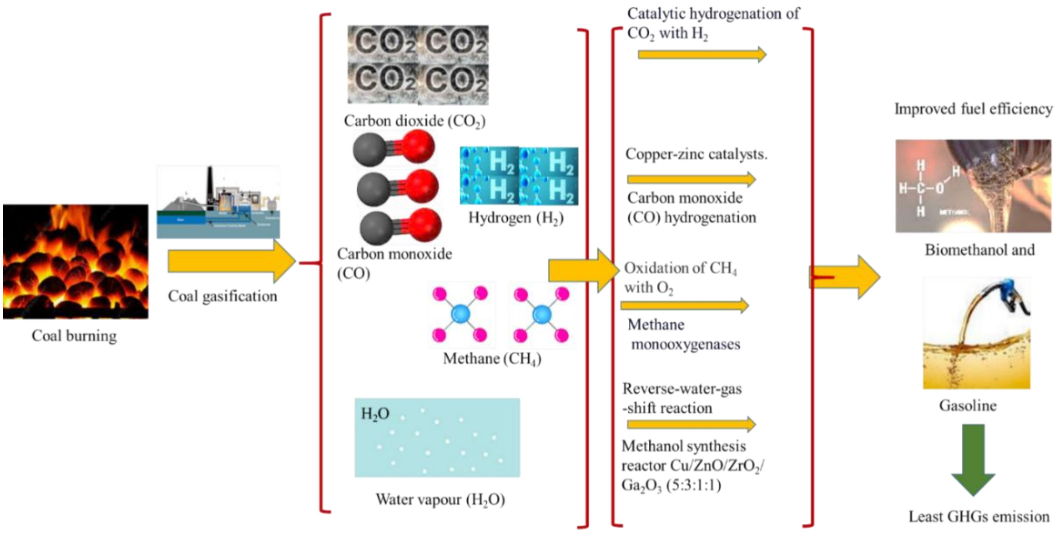

Figure 1. Methanol synthesis from coal carbon sources that are converted by different conversion process for different waste matters.

Methanol synthesis was achieved via the CO_2 hydrogenation process that was later modelled using the kinetic model with consideration of carbon monoxide and carbon dioxide as carbon sources[25]. Later efforts were done on economic analysis via uses of levelized cost process and also environmental assessment of CO_2-eq emission performance. From performed experiments, results were shown on overall energy efficiency of integrated hydrogen production and also methanol before (with value of 48.4%) and after (with value of 55.2%) the heat integration process. It was done by using a heat exchanger network (HEN)[26,27]. Further efforts were made on the economic perspective on methanol production and it was found nearly $1040.2 and $1669.6/mt tonnes methanol for PV-grid and also PV-battery respectively. Further study was shown on environmental perspectives of the process of CO_2-eq emission from the whole process of methanol synthesis and then it was shown two different values (like 0.244 kg-CO_2-eq/MJ-methanol) for PV-grid and PV-battery system respectively[28,29].

In recent research efforts, it was focused on methanol based transportation fuel production development. This was done after conversion to fuel (like dimethyl ethers) and plastics. Current global methanol production trend is found to be 45 million tonnes/ year and it is normally the same nature to fossil fuels, mainly natural gas[30]. Reports are shown on methanol production from other carbon containing feedstock like biogas, biogas, waste streams and CO_2. Biomethanol/renewable methanol production occurs from several feedstock and also processes[31]. Biomethanol is chemically similar to conventional methanol and is discussed for several advantages like reduced GHGs emission and also fossil fuel uses. It was compared with conventional methanol production. Biomethanol (synthesis by pyrolysis) can be converted into several products/renewable feedstock[31,32].

Studies were done on biomethanol production cost with estimation of 1.5 to 4 times higher than the cost of natural gas-based methanol. Current fossil fuel prices were found in the range of $100 to $200/t. Biomethanol production costs were mainly dependent on feedstock prices, plant set-up and also local conditions[33]. Recent effort was found on biomethanol demonstration projects function and operation. And it was focused on used waste biomass and byproducts that come from industrial processes like feedstock with the provision of best economic efficiency[34]. It was discussed for glycine by-products (and it produced from biodiesel production) and also black liquor (from pulp and paper industry). These are considered as basic feedstock for biomethanol synthesis[33,34]. This feedstock can be produced from commercial scale plants in the Netherlands and it was utilized there for production of biomethanol in their synthesis plant operation. In Iceland, renewable methanol production occurs by combination of hydrogen and carbon dioxide[35]. Reports are also shown on other potential feedstocks like biogas from landfill sites or solid organic wastes from sewage and also bagasse (come from milled sugarcane fiber)[36].

Some recent projects were demonstrated with many benefits with favorable conditions like low feedstock prices (for glycerine), strong integration with conventional industrial processes (like pulp and paper industry) and also inexpensive renewable electricity. Further effort was found on kind local conditions and also niche opportunities that promote the biomethanol production with integration to bioethanol from sugarcane waste matter[37,38]. Other was found on co-feeding biomass feedstock and also fossil fuels, Next effort was done on co-production of heat, electricity and other chemicals with value-added natures. The emphasis was shown on utilization of locally grown plant biomass for biomethanol production and it can make the country less dependent on fossil fuels imports with help in reduction of GHG emission[39,40]. It compared methanol uses (come from fossil fuel) with stimulation to local economic and employment. Co-feeding of renewable feedstock in natural gas or coal based methanol production is explored with better facilities. It can be applied in gradual manners with introduction of biomethanol production that helps in reduction in environmental impact compared to conventional mode methanol production. In recent years, effort was shown on uses of biomass feedstock for biomethanol production[40]. It can compete with uses of biomass for other products and commodities synthesis. Use of biofuels is found for transportation tasks, electricity and heat generation and it can come from plant biomass and also other biomass. Other biomass based products are biogas, chemical and plastics as reported from biological processes[37,41,42].

Discussion showed the availability of biomass feedstock at optimal conditions for biomethanol production. And promotion in optimal uses of biomass can provide the full credits to environmental advantages like end uses of feedstock with help of entire life cycle study[43]. A number of policy options are discussed for eco-labelling, incentives, carbon tax and informal campaigns and these can help to promote the optimal use of biomass resources for biomethanol synthesis[44]. Other approaches for methanol production are discussed and it can utilize the different concentrated carbon sources like natural gas, coal, biomass, byproducts streams, carbon dioxide (from flue gasses)[43,44]. Methanol production is reported to complete in many steps and it discusses the plant biomass configuration for biomethanol production with strong similarity to coal-based methanol production (by gasification process)[45]. Two different approaches for biomethanol production are discussed such as uses of biogas for biomethanol (very similar to methanol production from natural gas) and also carbon dioxide uses for biomethanol[45,46].

Several conventional plants are discussed including gasification, gas cleaning and also reforming of high hydrocarbons. Further water-gas shift, hydrogen addition and/or CO_2 removal is also discussed as conventional approaches for methanol synthesis with effort to purification tasks from plants[47,48]. Several feedstocks of primary biomass are discussed with a pretreatment process as raw material. It needs chipping and drying the woody biomass with purification of liquid feedstock. In methanol production in the gasification process, first feedstock is required to gasify into synthesis of gas (syngas), a mixture of CO, CO_2, H_2 and hydrocarbon[49,50].

This process needs a limited amount of oxygen during feedstock heating (above 700 °C temperature). It can improve the formation of CO, and H_2 with help in reduction of unwanted CO_2, H_2O. It has been found for uses of sources of oxygen, inert gasses (like nitrogen for increased gas flow via gasifier) and downstream equipment[51]. These can result in costly processes due to high cost of equipment/investment. Uses of pure oxygen can be found to be too expensive for methanol production. Economic optimal conditions can be found between oxygen purity and production cost, electricity prices and equipment cost[51,52].

From different approaches of methanol production, the initial syngas composition can depend on the carbon sources and gasification technique. The concentration of CO, and H_2 can be changed in various ways. In this process, first unprocessed syngas can contain a small fraction of CH_4 and also other light weight hydrocarbons with high energy content[53,54]. These are gone for the reformation process to convert into CO, and H_2 by application of high temperature catalytic steam reforming or by autothermal reforming (ATR) process. These reform processes can help to lead to the carbonaceous residues formation with reduction in the performance of catalysts[55]. Still today, there is no option of cost-effective mode of reforming process. In another technique, the initial hydrogen concentration in the syngas is used to very less amounts for optimal methanol synthesis[56]. Next, it can reduce the share of CO, but increase the H_2 share in the water gas-shift reaction conversion process. This can convert the CO and H_2O into CO_2, H_2. And CO_2 can be removed directly by using the chemical absorption process by amines[56,57].

Researchers have discussed the different approaches of carbon dioxide removals like adsorption into liquids, cryogenic permeation (via membrane) and separation with advanced development. But it needed more time for practical application[58]. Normally hydrogen production can be done separately and then it is added to syngas. Industrial hydrogen can be produced by two techniques like steam reforming of methane and also electrolysis of water. Electrolysis process is costly[58,59]. This can offer important synergies due to production of oxygen during the electrolysis process for partial oxidation in the gasification process step. Later, it can be replaced by air separation techniques[60]. Efficiency of electrolysis can be detected by the use/availability of renewable electricity. This approach can provide the precise process in presence of enough oxygen for the gasification process and it can be associated with hydrogen production in low concentration to meet the optimal stoichiometry in the syngas[59,60].

3. Biocatalysts/catalysts in biomethanol production

3.1. Catalysts in biomethanol synthesis

Earlier efforts on methanol production were reported to convert the syngas into methanol and it requires a catalytic process based on copper oxide, chromium oxide and zinc oxide catalyst. In this approach of methanol production, distillation is applied for removal of water from methanol during its synthesis process[61]. And it was found to depend on important input and outputs with uses of electrolysis process. Several techniques were discussed for methanol production like coal gasification process (cost-competitive) from long times onward. Now application of biomass gasification is discussed that is not proven as a cost-competitive process[62]. Efforts are shown by different researchers for production of biomethanol. Normally, any carbon source can be converted into syngas but recent projects are only focused on the biomethanol production that utilized the byproducts from many industrial operations[61,62].

But it provides several advantages. In this context, integration of biomethanol synthesis was shown with other facilities with effort to make the process simple including feedstock supply and logistics with sharing of associated cost[63]. Several analyses were done on the overall economy of an integrated plant and it was found to be less sensitive to price fluctuation of one of its products[64]. Several waste matters like black liquor (from pulp processing), bagasse (from sugarcane mills) glycerine (from biodiesel production plant), and municipal solid waste are utilized as potential feedstock for biomethanol production[63,64]. Biomethanol production can be achieved by application of thermochemical pathways with or without catalysts and it is also discussed for utilization of biological conversion techniques. The feedstock for biomethanol production can sometimes depend on concentrated carbonaceous material like biomass, solid wastes, CO_2 and also coals[65,66]. **Figure 2** shows the different feedstock for methanol conversion.

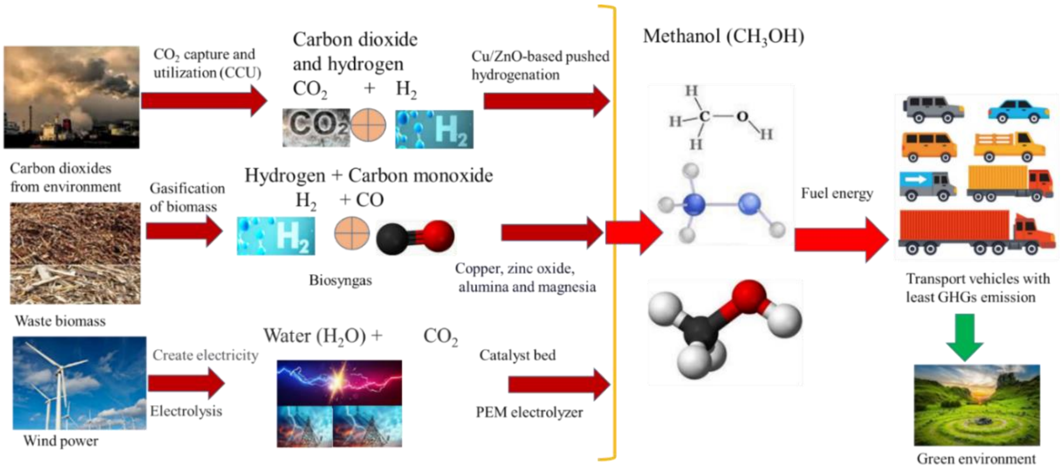

Figure 2. Methanol synthesis from different carbon sources that are captured by different conversion process.

Biomethanol production can occur at lab-scale reactors but it needs the requirement of high temperature. This can show low conversion efficiency with the requirement of a large amount of biomass. This can prevent a wide range of applications as technology at industrial scale[67]. Number of efforts were done on thermochemical pathway application for biomethanol production that needed a catalyst or no need for a catalyst. But biological conversion approaches can be applied for biomethanol production[68,69]. At industrial scales, several types of agricultural based biofuels production are reported and these are biodiesel, biomethanol, methane, bio-oil and bioethanol. In effort to biomethanol synthesis from the biomass conversion process, it requires several steps like biomass drying, biosyngas sweeting, gasification, methanol synthesis and purification step[69]. In methanol synthesis process pure oxygen can prefer to prevent costly nitrogen application before synthesis. It contained several key parameters of lignocellulosic biomass gasification like temperature at 600 K, gasifier height (20 m), gasifier diameter (2 m) and oxygen ratio (10%) with steam ratio (10%)[70]. At unbalanced S ratio, it requires the reverse water-gas shift operation and it can adjust the composition before starting methanol synthesis in the reactor. It is not worth the water-gas shift reaction. It can be active on the Cu-Zn based catalyst in industrial synthesis. It needs another operation that combines with the sweetening to clean the biosyngas before methanol production[71]. Main task is the removal of particulates by means of filter and cyclones and then tar reforming is applied for conversion of tar species into additional (with high S ratio) syngas, removal of water and also biosyngas compression task. Methanol can be purified to market grade[71,72]. **Table 1** shows the methanol production by several catalytic reaction.

Table 1. Biomethanol synthesis by catalysts involvements and also thermochemical reactions with promotion to waste mitigation.

Biomethanol	Catalysts	Process conditions	References
Renewable-power-assisted CO2 capture and utilization (CCU) for methanol	Cu/ZnO-based	CO_2 hydrogenation using renewable hydrogen from photovoltaic (PV)-based electrolysis and CO_2 originating from natural gas field processing	[6]
Hydrogenation of carbon dioxide is reported methanol and other products	Photocatalytic based reaction in isothermal or adiabatic reactor used	Carbon capture and utilization systems are found for hydrogenation of carbon dioxide that produced biomethanol	[11]
A methanol (MeOH) synthesis route based on CO_2 utilization is reported	$Cu/ZnO/Al_2O_3$ is used with at 76 bar and 210 °C.	This methanol synthesis is integrated with enhanced gas recovery (EGR) and geo-sequestration.	[12]

Table 1. (*Continued*).

Biomethanol	Catalysts	Process conditions	References
A methanol production from syngas with kinetic model study was reported	Cu catalysts is used	Methanol yield (47%), carbon conversion (47%) and methanol production (1.21 mol h−1) are reported with reactor at 220 °C and 50 bars	[15]
Direct bio-syngas to methanol generation process is reported	$Cu/ZnO/Al_2O_3$ is commercial catalyst	This process used a high-pressure microreactor, and a commercial catalyst was used for the methanol generation process	[16]
Methanol production from pure CO_2 and H_2 mixture hydrogenation is reported	$Cu/ZnO/Al_2O_3$ catalyst is used	Reactor containing recycle mood has ensured a higher efficiency up to 65% methanol yield at the range of (200–250 °C) and 50 bar.	[20]
Flexible methanol and hydrogen production from biomass gasification	Gasification technology is reported with with $Cu/ZnO/Al_2O_3$ catalyst (CZA) pellets	Economic impact of multi-product plants can flexibly produce methanol (26 and 55%) and hydrogen (64 and 90%) and it is carried out with higher CO_2 capture efficiency.	[21]
A 100 MW stand-alone wind power to methanol process is reported	Spraying $CuO/ZnO/Al_2O_3/V_2O_3$ slurry on SS-plate is reported	Integration of utilities for CO_2 air capture, hydrogen production from co-harvested water and methanol synthesis is incorporated with capital costs	[24]
The individual synthesis of methanol and ethane from methane is reported	Sub-10 nm Pt and Fe particles as catalyst at anode with 150–200 °C.	In the electrolysis of humidified methane, methanol was produced through the formation of active oxygen intermediates from water vapor	[28]
Novel methanol production process developed by integrating CO_2	Hydrogenation and thermo-chemical splitting technologies is reported with photocatalyst.	Solar field for CO_2 and H_2O splitting using concentrated solar thermal energy is integrated to methanol production by hydrogenation of CO_2 and CO.	[29]
Selective partial oxidation of methane to methanol is reported	Fixation of AuPd alloy nano particles within aluminosilicate zeolite crystals	Heterogeneous catalyst system for enhanced methanol productivity in methane oxidation at mild temperature (70 °C) is reported	[30]
Converting methane in a direct and mild manner for methanol.	Exploring advanced low-temperature C–H activation catalysts and reaction systems	Reaction processes operated at low-temperature thermocatalysis systems or driven in electro- and photocatalysis systems can achieve efficient methane conversion. Then it was converted to methanol.	[32]
Synthesis of methanol and methanol derivatives from methane	Direct catalytic synthesis of methanol	Use of multicomponent catalysts to stabilize methanol is discussed with superior performance of systems which produce methanol derivatives	[33]
Conversion of biomass-derived polyols and sugars into methanol and syngas ($CO + H_2$)	Catalysts is reported with Cu dispersed on titanium oxide nanorod (TNR)	UV light irradiation under room temperature is effective for the selective C−C bond cleavage to methanol	[40]

3.2. Biocatalysts role in methanol production

In context to biocatalysts’ role in methanol production, methanotrophs can be applied to convert methane from the environment or biomass bio based methane. In this context, researcher interests have been increased in recent years and this organism showed their potential for transformation of methane into valuable bioproducts like methanol[73]. Methane availability in natural gas and also its low cost/prices have shown to help to promote the biomethanol synthesis. Some of bioproducts like methane derived products are methanol, polyhydroxyalkanoates and single cell protein[74]. Many challenges are needed to overcome to achieve commercialization of biologically manufactured methane to products like methanol. To take a holistic view, the production process can lead the future bioeconomy with methane as the primary feedstock[73,74]. Methane is found in natural and shale gas but it can be converted into methanol via a bioprocess by methanotrophs. It can be used as a valuable chemical feedstock for the value-added chemicals. Novel methanotroph *Methylomonas* species DH-1 is applied for conversion of methane to methanol under an effective biochemical process[73,75]. This microbial strain was isolated from activated sludge from brewery plants and it can be characterized by phylogenetic analysis, electron microscopy and chemotaxonomic analysis. *Methylomonas* species DH-1 is aerobic, gram (-ve) rod-shaped and non-motile bacteria and it comes under type-1 methanotroph and growth condition and bioconversion in batch mode is done for methane to methanol[76].

Bioprocess parameters are methane concentration, pH, biocatalyst loading, MDH inhibitors, and concentration of formate. These parameters were analysed and optimized. Methane was used for production of methanol titer (~1.34 g/L^{-1}), volumetric conversion rate (0.332 g/L^{-1} h^{-1}) and specific methanol rate (0.0752 g/g^{-1} $cell/h^{-1}$). Next promising characteristic of *Methylomonas* species DH-1 can be found for best producer of methanol up to tolerance of concentration of 7% v/v. Further these microbes showed more advantage of high-titer methanol[73,76]. For methanol production/synthesis, methane needs to convert at atmospheric temperature and pressure. Further it needs the application of methane monooxygenase (MMO)/complete cell of methane oxidizing bacteria as a biocatalyst. Recently, methanol production has been reported using the methane-oxidizing bacteria and then it is more promising than the isolated enzymes that showed many disadvantages like high costs and also the unstable nature of MMO[77].

This enzyme instability is due to come from outside the bacterial cell. Several reports have discussed the methanol production by the use of methane oxidizing bacteria. Further studies were done on extracellular accumulation of methanol by methane-oxidizing bacteria[78]. This is done with help of various reaction conditions with need to optimal level. In this context, researchers have applied the inhibitors for methanol dehydrogenase that can minimize the conversion of methanol to formaldehyde[77,78]. This task was done with determination of this conversion (methanol to formaldehyde). Normally, methanol hydrogenase application is needed after the completion of oxidation of methane to methanol with help of MMO enzyme. Methanol hydrogenase enzyme inhibition is very important and its activity can occur in shortage of nicotinamide adenine dinucleotide (NADH)[79].

This shortage can be fulfilled by cellular energy that can come from various organic compounds, required for metabolic reaction, replication of bacteria and also hydroxylation of methane[80]. So, it needs methanol oxidation inhibitors and also optimum electron donors that can help to supply energy to bacterial cells. It needs in addition to use the methane-oxidizing bacteria as a biocatalyst with culturing in active form that can be used for methane conversion to start to methanol. It needs a good understanding of the bacterial methane metabolism process and it is crucial to develop at a practical level for methanol production. Then it can be found best whole cell biocatalysts for methanol production[77,80]. **Figure 3** shows the biomethanol production by different species of methanotrophs.

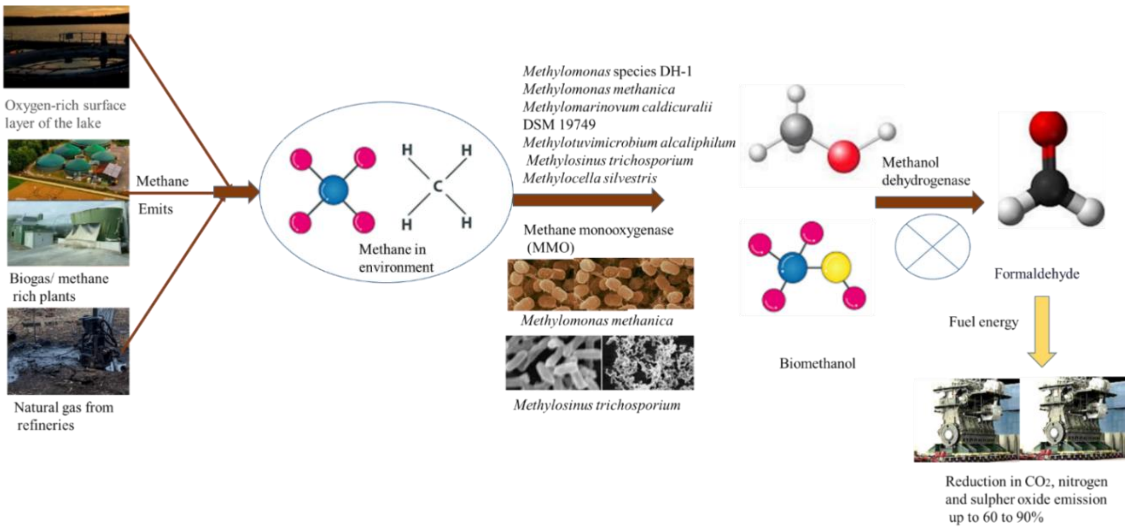

Figure 3. Biological bioprocesses for methanol synthesis by different species of methanotroph that good sources of MMO that convert to methane to methanol.

Methylomarinovum caldicuralii DSM 19749 is reported in the new family Methylothermaceae and order Methylococcaceae. It is gram positive bacteria. It is different from general Methanothermus and Methylhalobius. The consistent and also distinctive physiological traits, *Methanothermus* (includes the most thermophilic species) and *Methylohalonius* (includes the most halophilic species[81]. These genus can include the *pmo*A gene that codes the pMMO enzyme and it can be detected in geothermal areas and also deep sea hydrothermal vents fields[80,81]. Methane conversion into methanol is reported using several approaches and then methanol can be converted into several value-added products/chemicals by chemical conversion processes and techniques. MMO is a key enzyme that uses oxygen and methane to convert into methanol[82]. Methanotrophic bacteria can also transform methane into methanol but it needs the inhibition of methanol dehydrogenase to avoid its degradation. Recent process on biocatalytics conversion of methane to methanol is a crucial step in the methane based refinery system. Further it needs to explore the future prospective for methanol production[81,82]. There are several species of methanotrophs and these are *Methylotuvimicrobium alcaliphilum, Methylomonas methanica, Methylosinus trichosporium and Methylocella silvestris.* These species were validated by different researchers for methanol tolerance and production on pure methane and also biogas with the contribution of enzyme activities that involve in methane utilization task[83].

Among these selected methanotrophs *M. alcaliphilum* showed the maximum tolerance capability of 6% v/v and it showed the maximum methanol production of 308 mg/L and 247.4 mg/L on pure methane and biogas as substrates respectively. Further it was detected for activities of methane monooxygenase and formate dehydrogenase enzymes in *M. alcaliphilum.* This *M. alcaliphilum* is reported to contain high concentration of cells (98.40 mmol/min/mg cells) and enzyme/protein (0.87 U/mg protein) respectively[84]. Biotransformation trials for 14 L fermentor were reported for increased methanol production (418 and 331.2 mg/L) and yield coefficient (0.83 and 0.71 mg methanol/mg) for pure methane and biogas respectively as substrates. And systematic selection of methanotroph can result in the best haloalkaline strain *M. alcaliphilum* for biomethanol production[83,84].

In context to biomethanol production, microbial consortia of methanotrophs are shown to possess the efficient biological process than single isolates. And then it was designed and also evaluated for a synthetic microbial consortium that can contain the methanotroph *Methylocystis* sp. M6 and its helper *Hyphomicrobium* sp. NM3[85]. Later these were used to develop a novel methanotrophic process with utilization of dialysis membranes. Further, study on this consortium was done for increased methane-oxidation rate (MOR) in *Hyphomicrobium* sp. It showed increased biomass and stability at the suitable dilution rate (0.067 day^{-1}) in fed-batch co-culture vessels[86]. For the *Methylocystis* sp. M6 strain qRT-PCR study was done with gradual increase in population with time and then in case of *Hyphomicrobium* sp population, it remained stable despite cell washing condition[85,86].

Other properties like synergistic interaction of this microbe's population was reported. At 0.1 day (dilution rate), spiking of *Hyphomicrobium* sp. is reported to increase with increased methanotrophic activity and then later *Hyphomicrobium* sp. population decreases with time, confirming the optimal consortium at less than 0.1 day[87]. Later effort was put on *Hyphomicrobium* sp cultivation on dialysis membrane with the bioreactor then MOR was found to increase in linear way up to 155.1 m.mol/liter/day at 0.067, 0.1 and 0.4 day-1 with highest value for a methanotrophic reactor[85,88]. And **Table 2** shown the biocatalysts sources from different methanotroph that helped in biomethanol production.

Table 2. Biomethanol synthesis from different methanotroph with effective sources of biocatalysts.

Biomethanol	**Biocatalysts**	**Bioprocess conditions**	**References**
Metabolic engineering to methanotrophs and its application to bio-methanol synthesis	Engineered methanotrophs	OMICS studies on several model methanotrophs have been conducted to provide strategies to engineered methanotrophs	[5]
Methane converted to biomethanol	Recent progress on biocatalytic conversion is reported with uses of methanotrophs	Methanotrophic bacteria can transform methane to methanol by inhibiting methanol dehydrogenase	[7]
Biological Methanol Production is reported	*Methylocystis bryophila* is good sources of biocatalyst	Maximum methanol (4.63 mM) production at pH 6.8, 30 °C, 175 rpm, 100 mM phosphate buffer, 50 mM $MgCl_2$ with methanol dehydrogenase inhibitor, CH_4 concentration (50%) and 24 h	[9]
Methanol production from biogas	Thermotolerant methanotrophic consortium	It is evaluated for cell growth and methanol production (33 g/L of methanol at 47 °C) with biogas with cell yields (0.22–0.40 g of cells/g of methane) at temperatures from 30 to 55 °C and pH from 5.5 to 7.5	[48]
Methane (CH_4) cycle for atmospheric CH_4 to convert into methanol	Methane-oxidizing bacteria (MOB) like *Methylocystis*, *Methlylocystis-Methylosinus* and JR2 and JR3.	Higher CH_4 oxidation potential (MOP) (ng CH4 g−1 h−1 dws) was observed in winter (14.12) compared with rainy and summer coinciding high methanotrophic diversity/abundance induced methanol synthesis	[52]
Rice field soil for bioconversion of methane to methanol reported	Potential of microbial consortium enriched from rice field soil reported	Methanol production (without MDH inhibitors) revealed (~130 mM/4.16 g/L) from enriched consortium. It closes to 132.5 mM (4.24 g/L) methanol production by pure strain of *Methylococcus capsulatus*	[74]
PHB is used as intracellular reducing power for methanol production	Methanotrophic strain i.e. *Methylo cystis hirsute* as biocatalsts sources	PHB accumulating methanotrophic strain i.e. *Methylocystis hirsuta* was investigated with coupling PHB consumption (higher methane conversion efficiency (~69%) with methanol production (399 mg/L).	[76]
Catalyse methane to methanol conversion under mild conditions	Methane monooxygenases from methanotrophs are enzymes	*Thermosynechococcus elongatus* BP-1 into the membrane fraction containing particulate methane monooxygenase (pMMO) from *Methylosinus trichosporium* OB3b. It pushes methanol production.	[78]
Methanol production from CO_2 by resting cells	Using resting cells of *Methylosinus trichosporium* IMV 3011 as biocatalysts	Catabolism of stored Poly-β-Hydroxybutyrate (PHB~38.6%) can provide intracellular reducing equivalents to improve the intrinsic methanol production capacity	[79]
Repeated batch methanol production from a simulated biogas mixture	By using immobilized *Methylocystis bryophila*	Maximum methanol concentrations of 4.88 mmol L^{-1}, 7.47 mmol L^{-1}, and 7.02 mmol L^{-1} are achieved using the gas mixtures like CH_4:CO_2 (2:1 ratio), CH_4:hydrogen (4:1 ratio), and CH_4:CO_2:H_2 (6:3:2 ratio) respectively	[84]
CO_2 conversion by enzymatically reduction into methanol in a cascade reaction	Co-immobilizing the three dehydrogenases in siliceous mesostructured cellular foams (MCF)	It observed a 4.5-fold higher methanol yield in comparison to enzymes free in solution. Enzymes were immobilized in order of size and with a loading of 50 mgenzymes $gsupport^{-1}$	[89]

3.3. Development of novel biocatalyst

Reduction of carbon dioxide into methanol is occurred by enzyme mediated reactions in cascade mode and its three enzymes like formate (FateDH), formaldehyde (FatdDH) and alcohol hydrogen (ADH). In these conversion reactions, improvement in the yield of methanol from these reactions are reported by co-immobilizing three dehydrogenases (DH) in siliceous mesostructured cellular foams (MCF)[89]. The siliceous MCF material consists of large mesopores and it is suitable for the co-immobilization of these large enzymes compared to other enzymes. Further improvement in interaction between the enzymes and support can occur due to host silica material. This silica material can be functionalized with mercaptopropyl groups (MCF-MP)[90]. Next, enzymes were fluorescently labelled in an independent way and then it can be easily monitored for their uptake and spatial distribution into the particle. For co-mobilization tasks, three dehydrogenases were combined to co-immobilize by using two sequential techniques[89,90]. In the first approach, the enzymes were immobilized based on reaction order (FateDH$\rightarrow$FateH$\rightarrow$ADH) and in the second approach, order of enzymes was kept based on their size (FateDH$\rightarrow$ADH$\rightarrow$FatdDH)[91]. For better understanding of protein loading, some tests were done with two different weight values like 50 and 150 mg. enzyme/g. support. And then it was observed for 4.5 fold high methanol yield compared to free enzymes in solution forms. Another study was done on enzyme activity that was immobilized based on order of size with loading of 50 mg. enzyme/g. support[89,91].

In another report, studies were done on abundance of hydrogen (H adatoms) and this generation is found due to oxygen vacancy creation on the indium oxide (In_2O_3) surface. Due to enhanced surface oxygen vacancies, it can lead further for improved carbon dioxide conversions into methanol or other products. From this conversion result, an effective synergy between the active Ni sites and surface oxygen vacancies on the In_2O_3 surface. Then it can cause a superior catalytic performance on carbon dioxide hydrogenation with high methanol selectivity[92]. From this conversion reaction, CO (carbon monoxide) generation is reported as product only. And it is also detected for ignoring the formation of methane at a lower temperature (225 ℃) of reaction. This condition can push for high selectivity of methanol (100%) synthesis in this conversion[93]. Further, the observation was found for temperature value change (in range between 225 and 275 ℃) on methanol synthesis (higher than 64%). Finally, methanol selectivity can be still higher than 54%) at 300 ℃ of temperature with a carbon dioxide conversion of 18.5% and then methanol yield is found to be 0.55 g MeOH/g.cat/h at 5 MPa. It has been found that activities of Ni/In_2O_3 are higher than most of the reported In_2O_3 based catalysts[92,93].

Some efforts were done on orange peel-based biocatalyst and it was developed from different acid protonation and then it can be used as a metal free catalyst for production of hydrogen from sodium borohydride ($NaBH_4$). This hydrogen can be utilized for methanol production from the CO_2 conversion process[94]. To make the orange peel-based biocatalysts with higher catalytic activity, some experiments on pure orange peel were done by researchers. It was done with different acid molar concentration and calcination temperatures. Next, the physical morphology, chemical interaction and surface texture analysis was done by different analytical techniques such as TGA (thermogravimetric analysis), BET (Brunauer-Emmett-Teller), XRD (X-ray diffraction) FTIR (Fourier transform infra-red) and Raman spectroscopy[95]. From experimental results, it was determined that high concentration acid-treated biocatalysts (40% H_3PO_4, 40% H_2SO_4 and 40% HCl) and calcined (at 450 ℃) for 1 h period were shown to keep higher catalytic activity. And then biohydrogen production at 35 ℃ and 70 ℃ is reported to involve a methanol breakdown process with 3% NaBH4[93,95].

This reaction was shown to mediate with catalytic activity by a mixture of acid-treated catalysts with values of 46, 213 and 63,842 ml/min/g at 35 ℃ and 70 ℃ respectively. Further observation was found for increase of molar concentration of biocatalyst with 40% individual acid in prolonged sample is shown. HGR rate was not found satisfactory compared to 40% of mixture of the acid-treated catalyst and it is due to less number of active sites[94,95]. Commercial scale methanol synthesis is shown to occur by catalyst mediated reaction and this conversion reaction is offered a poor efficiency in carbon dioxide feedstock and also it is due to low conversion of CO_2 and its deactivation process. This is the result of high water production during this process[96]. To solve this issue/barriers, an efficient process is reported to consist of three stage heat exchangers.

It is proposed for the carbon dioxide hydrogenation process. In this process, catalyst volume in the methanol reactor was divided into three sections to load the reactors[97]. Then the product stream of each reactor was conveyed to a flask drum to remove methanol and water from unreacted gasses like CO, CO_2 and H_2. And then a gaseous stream can enter to the top of the next reactor as the inlet feed[95,96].

In this reactor, novel configuration can increase the CO_2 conversion nearly two times compared to one stage reactor. Further benefit was found to reduce the water production that occurred due to uses or assisted of water permselective membrane in each reactor and it can remove the water from reactor side[95,97]. The proposed process was compared with a one stage reactor from coal and natural gas. Methanol production was reported to occur at nearly 288, 305, 586 and 569 ton/day in CR, one stage, three stage and three-stage membrane reactor respectively[98]. Report is shown for methanol production rate in three-stage MR and it showed slightly lower yield than three-stage reactors. The produced water can cause the catalyst poisoning and it is reduced in MR configuration reactors. Results from the proposed process are found to be a strongly feasible way to produce the methanol competitive with traditional synthesis processes[97,98].

Some results show that the proposed process is a strongly feasible way to produce methanol that can be competitive compared with a traditional synthesis process. Conversion of carbon dioxide and also methanol production rate is reported to increase nearly 50% and 103% compared to one stage reactor respectively[99]. Further observation was shown for high amounts of water that can cause the catalyst poisoning, occurring in the CO_2 hydrogenation process. Next impacts of H-SOD membranes were shown while assisted in all three reactors of three-stage configuration[98,99]. It is also reported for application of water perm-selective membrane impacts. And it helps to minimize the water concentration (that is an undesirable product in this process) in all the three reactors. This process was compared with the conventional methanol synthesis routes/process (that is used to produce methanol from coal and natural gas)[96,98]. And this approach is shown to produce methanol at an increased rate (in 281 tons/day) in three-stage membrane reactors. Many works related to methanol production are still theoretical in nature without any economic assessment. But recently some works claimed some potential for wide application with good starting points for future research[95,99].

Recently several efforts have been made for creating multiple mutations via performing the experiment approach and also in a simultaneous way, limiting choices can be made by application of statistical approaches. In this context, nearly 10,000 variants were gone for testing via experimental set-up strategies. Still not much information is available for those mutations that can lead to enhanced enzyme proficiency[100]. In a recent review, a brief description of available computation techniques/approaches was done to explore the molecular basis of improved catalysis and discussed to achieve by direct evolution (DE)/Darwinian evolution. In this technique, an overview of the strength and weakness of current computational methods/approaches were explored[101]. These techniques were explored by taking some recent representative examples. Computational technique helps in better understanding of enzyme power and it can help provide the highly active variants for future development of methanol or any other product. Now some robust computational techniques can predict the amino acids changes that are needed for enzymatic activity[100,101].

Computational techniques can provide the attractive alternatives/options to understand, model and rational way of constructing novel enzymes mediated catalysis at a reduced cost. The development of robust computational techniques is capable of improving an enzymatic catalysis process[102,103]. DE is discussed in the current period as one of the most challenging and exciting roads/ platforms in the biocatalysts process. In recent years, various computational techniques have been applied in a wide range and it has helped to enhance the promiscuous/achievable activities of natural enzymes[103,104]. These approaches have helped to explore the multiple sequence, and also structure alignment. This has helped to simultaneously design the entire protein backbone structures and also amino acid sequences[102,105]. Efforts were made on redesigning active sites of natural enzymes. This task can normally be achieved by mutation of a subset of the active site residue via maintaining the rigid backbone[104,105]. Some scientists like Mayo and Hellinga have discussed in laboratory media that pioneered automated computation design and this design was able to create an array of redesigned binding protein and enzymes[106,107]. In computational techniques, thioredoxin conversion into a primitive esterase is reported with the help of Origami-Rotor-Based Imaging and Tracking (ORBIT) programme. This programme explores the conformational and sequence space to generate the new variants[108–110].

Most successful strategy is computational inside-out methodology and it can combine the structure prediction utilities in the Rosetta software. Some of these software are RosettaMatch, RosettaDesign, Quantum Mechanics (QM~ theozyme)[106,108]. Further efforts were shown in proof of concept for the inside-out protocol and it was successfully designed for novel enzyme catalysts for Kemp elimination. Further it was used for Retro-aldol and Diels-Alder reactions also[109]. Some extensive reviews of the inside-out protocol and designed variants was reported. An alternative to RosettaMatch was discussed that was done to redesign natural protein and it already presents the desired catalytic machinery. These alternatives are the SABER program and Scaffold-Selection. Other strategies/methods were applied to match the theozyme into a protein active site. These are OptGraft and PRODA_MATCH[111,112]. Molecular dynamic (MD) simulations are applied to find the key to rank and also identify the best enzyme mutants. Further effort was shown on development of CASCO (CAtalytic selectivity by Computational design) framework[113]. And this framework can involve high-through MD to engineer enzyme stereo-selectivity. And this enzyme testing can help to replace most of the experimental screening assay[113,114].

4. Biomethanol for reducing carbon emissions

Methane is reported as next-generation carbon feedstock and it is found as vast reserves of natural and shale gas. Methane conversion into methanol is reported by various approaches and in turn it can be utilized for conversion into starting materials/chemicals. This conversion can help to production of many valuable chemicals/products with help of existing chemical conversion approaches[115]. In this context, MMO is found as a key enzyme with catalysis capabilities with addition of oxygen to methane. And methanotrophic bacteria can show the transformation capability of methane to methanol which can be inhibited by methane dehydrogenase enzyme[116,117]. Some recent review emphasized the progress on biocatalytic conversion of methane into methanol as a key step and it can be applied to achieve the methane-based refinery with future perspective of this conversion technology[117,118].

Several approaches have been discussed for production of methanol from methane and it has achieved a high rate of conversion by using the high density of cells of *Methylosinus trichosporium* QB3b in biological processes. Further impact is shown for high concentration of phosphate buffer in this process[119]. This biological process is reported to have a nearly good amount/concentration of methanol (1.1 g/L) and it occurred in reaction media at optimal reaction conditions. These reaction parameters are 17 g dry cell/L and 400 mmol/L phosphate and 10 mmol/L of $MgCl_2$ with also 20 mmol/L sodium formate. From this process/approach, conversion of methane was reported to more than 60% and then 0.95 g/L methanol production was found in the biotransformation process[120]. This conversion reaction was done in a membrane aerated reactor that was introduced with methane and oxygen with two separate dense silicone tubing. From this conversion result, it was claimed as an efficient technique with promising processes with capacity to high rate of conversion of methane to methanol[119,120].

Researchers have put efforts to achieve the economical and sustainable mode of methane reduction and it is done with application of various methanotrophs microbial strain and it can utilize the natural methane as feedstock (**Figure 4**). By exploiting *Methylosinus sporium* strain, it is possible to utilize the synthetic gas and also methane for methanol production[121]. Some studies were done on methanol production by *Methylosinus sporium* strain that utilized methane and synthetic gas and in this process, optimal pH (6.8), substrate concentration (50%), phosphate buffer concentration (100 mM), temperature (30 °C), incubation period (24 h), reaction volume to headspace ratio (1:5) were taken with 20 mM $MgCl_2$; and 100mM methanol dehydrogenase inhibitor[122]. Further studies were done on optimal production and process conditions that resulted in the improved methanol production from 0.086 mM to 5.8 mM. In this process, covalent immobilization of *Methylosinus sporium* on chitosan support material with high stability and reusability for six cycles under batch culture conditions[121,122]. The immobilized cells were utilized for the mixture of synthetic gas containing methane, carbon dioxide and also hydrogen in a ratio of 6:3:1[123]. This was found more effective than free cell activity and then it showed the maximum production of 6.12 mM. This work was claimed as the first report on high methanol production by *M. sporium* stain and it was covalently immobilized on a solid support from a synthetic mixture[121,123].

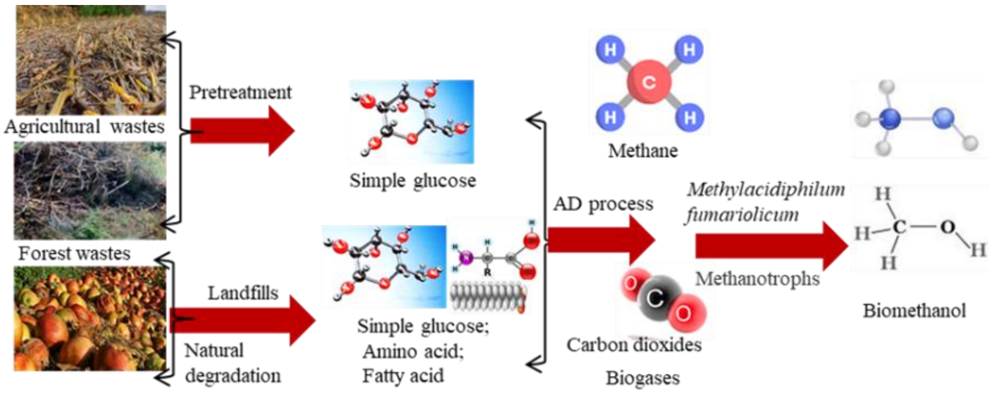

Figure 4. Processes for conversion of waste biomass to biomethanol.

In recent periods, methanol is used for energy storage and it can be used for a wide range of products synthesis. Methanol production can be achieved by plant biomass uses in numerous countries. And these countries can be reported as good producers of biomethanol. Some reviews explored the methanol production with contribution in techno-economy and environmental variability possibility[124]. In this context lignocellulosic biomass has good sources of cellulose and hemicellulose and it is highly suitable for gasification-based biomethanol production[125]. These methanol was compared to fossil fuels impacts and then biomass-based biomethanol is shown to reduce the nitrogen oxide emission (by 80%) CO_2 (by 95%) and also sulfur oxide reduction to some extent[126]. The cost and yield of biomethanol was also dependent on feedstock characteristics, initial investment and plant location. Now use of biomethanol is found as commentary fuel with diesel, natural gas and dimethyl ether with a lot of benefits in terms of fuel economy, thermal efficiency and reduction in GHGs (greenhouse gasses) emission[124–126].

Discussion is shown for biomethanol utility as energy sources with numerous benefits like high octane value (87–110), low flammability, high performance and low emission of carbon matter. It is totally different from fossil-based methanol and it can be fully miscible with water, conventional methanol and different organic compounds. Biomethanol showed several usefulness such as substitute fuel to gasoline in internal combustion engines[127]. Next, it can be used as a replacement to diesel via biodiesel or dimethyl ether production. Biomethanol can be utilized in methanol-fuelled vehicles or hybrid automobiles and also it can be used for electricity generation via gas turbine or fuel cell and it can be used as a power house[128]. Various reports are shown on improvement in fuel economy and reducing particle number emission with validation via experimental investigation on a methanol gasoline dual-fuel spark engine. In this study, an intake port was used to inject methanol into the engine and then it was checked for reduction in particle numbers emission via enhancing the fuel economy[127,128].

Next, researchers have gone to find the stoichiometric air-fuel ratio and then it was maintained throughout the experiment period. Based on results from their experiment, an increase in methanol addition in gasoline can improve the fuel economy by reducing the brake-specific fuel consumption[129]. And then the total particle number of the engine was found to reduce up to a minimum level of 5×10^4 N/ml with a 99.6% reduction compared to the baseline. A methanol engine can be shown to have 25% more brake thermal efficiency than using the single spark ignition system at 0.11–0.29 MPa[130]. And brake mean effective pressure is 0.11–0.29 MPa with an engine speed of 1600 rpm. A study was done of diesel-methanol dual-fuel engine operation and it showed many advantages compared to pure diesel based engine operation[129,130]. Further testing operation was also done on the intercooled heavy-duty turbocharged diesel engine. This engine was six cylinders at fixed load and also 1500 rpm of engine speed. In diesel-methanol dual fuel engine operation, reduction in intake air temperature is reported and it can make the exhaust gas thermal efficiency and temperature to be reduced value[131]. Further impact was shown on increased amount of methanol addition in the fuel blend, it showed a decrease in nitrogen oxide, nitric oxide and also smoke emission. But formaldehyde, nitrogen dioxide, total hydrocarbon, carbon monoxide and also methanol emission to be higher values[127,131].

5. Challenges and limitations in harnessing biocatalysts for biomethanol

Reports are shown on many challenges and also limitations on different approaches of production of biomethanol. First limitation of biomethanol is to achieve environmental and techno-economic performance and benefits. Three approaches of methanol product are reported like the baseline case approach is found for methanol synthesis that coal uses[132]. And second approach (case-1) is the conversion of coal to methanol and it is found from solar energy integration and third approach (case-2) is discussed as a hybrid solar-biomass route of methanol production that occurred from the carbon dioxide hydrogenation process. 45.7% and 57.5% lower environmental effects were found for the second and third approach once it compared with the baseline route of methanol uses[133]. Reports are shown on production cost of methanol by case-2 and case-1 approaches and these are found to be five times and three more compared to baseline case cost (229. 7 US$/ton). Some analytical study was done on the impact of techno-economic performance of the bio-based integrated coal gasification combined cycle (BIGCC) process[132,133]. BIGCC is used to produce the heat energy. This BIGCC can be affected by different biomass feedstock and then it can be utilized for deployment in climate change mitigation situations. The BIGCC technology can demand a high amount of biomass raw material that affects the land-use sector depending on condition and constraints on the land-use side[133,134].

Effort was done on CO_2 capture BIGCC system for case 2 and then negative GHGs emission (−1092.1 kg CO_2 eq) was reported compared to case-1 CO_2 emission (927.8 kg CO_2 eq) and Baseline case (3607 kg CO_2 eq)[135]. Further study was done on the case-1 route as an economically feasible process with average carbon tax level (72.08 US$/ton CO_2 eq). And methanol as fuel was used in a power chain integrated model that can assess the economic viability in the Caribbean region. The estimation was done on reduction up to 0.10 US$/KWh power and this can save the nearly 6000 MW annual power production via methanol uses[136,137].

In biomethanol synthesis, various nature of thermo-chemical and biochemical routes have been exploited and they pushed to achieve this methanol synthesis from waste biomass. In this context, advantages and limitations for both the processes/routes are discussed with their basic principles and also issues (to be addressed) by technological modes of up-gradation process[138]. Further, these need to exploit the future energy demand. In biochemical routes, it finds the utility of different microbes as biocatalysts for biomethanol production at normal pressure and temperature conditions. But the reports have discussed the various process parameters impacts on microbial modes of biomethanol production. Several efforts have been made to make the process cost-effective with better improvements that can show the capacity to utilize the biogases in place of natural gas for biomethanol synthesis[139]. And it is found in the development of methane utilizing microbial systems engineered via genetic engineering tools. This effort can bridge some gaps in existing processes with facilitation to technology development for large/commercial scale biomethanol synthesis. Further it needs to exploit the economical rate of biomethanol production with capability to meet the future demand[138,139]. In thermochemical route and biochemical conversion process, different nature of biomass can be utilized. And thermochemical processes, gasification, pyrolysis and liquefaction processes are applied for biomethanol synthesis. And in biochemical routes, utilization of methanotrophs are reported to produce the methanol with help of MMO enzyme[140].

Further, discussion shows methanol production reaction and it is an exothermic reaction with the need of a catalyst combined with high pressure (at 300 bar) and temperature (200–400 °C). Application of high temperature and pressure is one economic issue/challenge for methanol production[141]. But these parameters are needed to utilize as appropriate operating conditions that can maintain catalytic activity. Normally reactions in thermodynamically mode are preferred for low temperature and high pressure conditions for the high rate of methanol production and it is due to the exothermic nature of these reactions[140,141]. Next, a study was shown on high temperature needs that can lead to enhanced activity of catalysts but the specificity of reaction is found to reduce that results in high amount/concentration of side products with decreased yield of methanol product[142,143].

In methanol production, carbon dioxide requirement needs to be removed with increasing selectivity and also yield of methanol. In this task, the gas ratio requirement can make it mandatory to modulate the syngas composition before the exothermic gas-phase catalytic reactor for methanol production[144,145]. During the methanol production, syngas need to undergo a water-gas shift reaction with utility to maintain the hydrogen/carbon monoxide ratio (more than 2:1). This can favor the kinetic and control the byproducts formation[138,146].

Challenges are reported to global scale biomethanol production (nearly 45 million tons/year) and for this target, fossil fuels like natural coal were used. It is concerned with climatic change and also depletion of fossil/non-renewable fuel with sparking of natural gas prices. So, recommendations are given for the utilization of renewable feedstock for biomethanol production[147]. Further, biomethanol production can occur from virgin or waste biomass, non-biogenic waste streams or also CO_2 from flue gasses. This feedstock conversion is achieved by a gasification process that converts it into syngas[148,149]. Then it is gone to several steps in sequential ways via attaining the optimal composition and process parameters that can push methanol synthesis. Some examples are done by removing the CO_2 and also by adding hydrogen. This approach can decrease the environmental impact by promoting biomethanol production[150].

In this context, some proposals were reported with use of renewable electricity and also hydrogen needs via electrolysis process. And this approach, biomethanol synthesis, was identical in chemical nature to conventional modes of synthesized methanol[151]. Till time only 200 thousand tonnes of biomethanol is produced every year and this capacity needs to increase via establishing of many synthesis plants that can achieve the more than 1 million tonnes methanol/year[151,152]. Efforts were put into assessing the environmental performance of biomethanol and some technologies are involved. This performance is highly dependent on the plant set-up, the feedstock applied, and co-products formation quantities. Some scientific studies were done to model the biomethanol production with a wide range of assumptions[152,153].

6. Conclusion

This paper discusses the different nature of the methanol synthesis process. This paper focussed mainly two approaches like thermochemical based routes with catalysts application and also biochemical routes for biomethanol synthesis. Thermochemical routes of methanol synthesis are applied to utilize the waste biomass and gasification, pyrolysis and liquefaction processes are discussed with their advantages and limitations. In the biochemical route of biomethanol synthesis, methanotrophs microbial systems are used that are good sources of biocatalysts. This paper also discusses the novelty of biocatalysts that push the biomethanol synthesis at lower temperature and pressure. Methane monooxygenase (MMO) and methanol dehydrogenase are main biocatalysts that decide the methanol synthesis in biological processes. Further this review explores the different nature of feedstock like waste biomass, CO_2, sewage nutrients, methane (from natural gas), coal, and biogas. This feedstock helps to minimize the biomethanol production by thermochemical routes. Different properties of methanotroph have been explored to possess the MMO and Methanol dehydrogenase enzymes and then conditions were optimized for best activity in methanol yield and production. Methanol as fuel used in transport systems is the best alternative option to minimize the carbon dioxide or other toxic gasses emission with minimization of greenhouse effect and climatic change.

Conflict of interest

The authors declare no conflict of interest.

Abbreviations

ADH	Alcohol hydrogenase
ATR	Autothermal reforming
BET	Brunauer-emmett-teller
BIGCC	Bio-based integrated coal gasification combined cycle
CASCO	CAtalytic selectivity by computational design
CO	Carbon monoxide
CO_2	Carbon dioxide
Cu-Zn	Copper zinc
DE	Direct evolution
ECA	Emission control area
EUs	European Unions
FatdDH	Formaldehyde dehydrogenase
FateDH	Formate dehydrogenase
FTIR	Fourier transform infra-red
GHG	Greenhouse gas
H_2	Hydrogen
HEN	Heat exchanger network
IMO	International maritime organization
In_2O_3	Indium oxide
IREA	International renewable energy agency
MCF	Mesostructured cellular foams
MCF-MP	Mercaptopropyl groups
MD	Molecular dynamic
MJ	Mega joule
MMO	Methane monooxygenase
MOR	Methane-oxidation rate
Mt	Metric-tonnes
$NaBH_4$	Sodium borohydride
NADH	Nicotinamide adenine dinucleotide
ORBIT	Origami-rotor-based imaging and tracking
PEM	Proton exchange membrane
pMMO	Particulate methane monooxygenase
PV	Photovoltaic
qRT-PCR	Quantitative reverse transcriptase-Polymerase chain reaction

S	sulphur
TGA	Thermogravimetric analysis
XRD	X-ray diffraction

References

1. Nair LG, Agrawal K, Verma P. An overview of sustainable approaches for bioenergy production from agro-industrial wastes. Energy Nexus 2022; 6: 100086. doi: 10. 1016/j.nexus.2022.100086
2. Sarkar O, Butti SK, Mohan SV. Acidogenic biorefinery: Food waste valorization to biogas and platform chemicals. In: Bhaskar T, Pandey A, Mohan SV, et al. (editors). Waste Biorefinery. Elsevier; 2018. pp. 203–218.
3. Tsegaye B, Jaiswal S, Jaiswal AK. Food waste biorefinery: Pathway towards circular bioeconomy. Foods 2021; 10(6): 1174. doi: 10.3390/foods10061174
4. Oh SH, Hwang IY, Lee OK, et al. Development and optimization of the biological conversion of ethane to ethanol using whole-cell methanotrophs possessing methane monooxygenase. Molecules 2019; 24(3): 591. doi: 10.3390/molecules24030591
5. Lee OK, Hur DH, Nguyen DTN, Lee EY. Metabolic engineering of methanotrophs and its application to production of chemicals and biofuels from methane. Biofuels Bioproduct and Biorefinery 2016; 10(6): 848–863. doi: 10.1002/bbb.1678
6. Nizami M, Slamet, Purwanto WW, Solar PV based power-to-methanol via direct CO_2 hydrogenation and H_2O electrolysis: Techno-economic and environmental assessment. Journal of CO_2 Utilization 2022; 65: 102253. doi: 10.1016/j.jcou.2022.102253
7. Hwang IY, Lee SH, Choi YS, et al. Biocatalytic conversion of methane to methanol as a key step for development of methane-based biorefineries. Journal Microbiology and Biotechnology 2014; 24(12): 1597–1605. doi: 10.4014/jmb.1407.07070
8. Shoji O, Watanabe Y, Monooxygenation of non-native substrates catalysed by bacterial cytochrome P450s facilitated by decoy molecules. Chemistry Letters 2016; 46(3): 278–288. doi: 10.1246/cl.160963
9. Patel SKS, Mardina P, Kim SY, et al. Biological methanol production by a type II methanotroph methylocystis bryophila. Journal Microbiology and Biotechnology 2016; 26(4): 717–724. doi: 10.4014/jmb.1601.01013
10. Schakel W, Oreggioni G, Singh B, Strømman A, Ramírez A. Assessing the techno-environmental performance of CO_2 utilization via dry reforming of methane for the production of dimethyl ether. Journal of CO_2 Utilization 2016; 16: 138–149. doi: 10.1016/j.jcou.2016.06.005
11. Leonzio G. State of art and perspectives about the production of methanol, dimethyl ether and syngas by carbon dioxide hydrogenation. Journal of CO_2 Utilization 2018; 27: 326–354. doi: 10.1016/j.jcou.2018.08.005
12. Luu MT, Milani D, AbbasA. Analysis of CO_2 utilization for methanol synthesis integrated with enhanced gas recovery. Journal of Cleaner Production 2016; 112: 3540–3554. doi: 10.1016/j.jclepro.2015.10.119
13. Moioli E, Wötzel A, Schildhauer T. Feasibility assessment of small-scale methanol production via power-to-X. Journal of Cleaner Production 2022; 359: 132071. doi: 10.1016/j.jclepro.2022.132071
14. Nash M, Mullett G, Ma X, et al. Methanol as a marine bunker fuel. Available online: https://chemicalmarketanalytics.com/blog/methanol-market-outlook-2/ (accessed on 6 November 2023).
15. Adil A, Rao L. Methanol production from biomass: Analysis and optimization. Materials Today: Proceedings 2022; 57: 1770–1775. doi: 10.1016/j. matpr.2021.12.450
16. Adil A, Prasad B, Rao L. Methanol generation from bio-syngas: Experimental analysis and modeling studies. Environmental, Development and Sustainability 2023. doi: 10.1007/s10668-023-03541-1
17. Shamsul NS, Kamarudin SK, Rahman NA, Kofli NT. An overview on the production of bio-methanol as potential renewable energy. Renewable and Sustainable Energy Reviews 2014; 33: 578–588. doi: 10.1016/j.rser.2014.02.024
18. Sandeep K, Dasappa S. Oxy-steam gasification of biomass for hydrogen rich syngas production using downdraft reactor configuration. International Journal of Energy Research 2014; 38(2): 174–188. doi: 10.1002/er.3019
19. Arnaiz del Pozo C, Cloete S, Jiménez Álvaro Á. Carbon-negative hydrogen: Exploring the techno-economic potential of biomass co-gasification with CO_2 capture. Energy Conversion and Management 2021; 247: 114712. doi: 10.1016/j.enconman.2021.114712
20. Samiee L, GhasemiKafrudi E. Assessment of different kinetic models of carbon dioxide transformation to methanol via hydrogenation, over a Cu/Zno/Al_2O_3 catalyst. Reaction Kinetics Mechanisms and Catalysis 2021; 133(2): 801–823. doi: 10.1007/s11144-021-02045-1
21. Poluzzi A, Guandalini G, Romano MC. Flexible methanol and hydrogen production from biomass gasification with negative emissions. Sustainable Energy & Fuels 2022; 6(16): 3830–3851. doi: 10.1039/d2se00661h
22. Mota N, Guil-Lopez R, Pawelec BG, et al. Highly active Cu/Zno–Al catalyst for methanol synthesis: Effect of aging on its structure and activity. RSC Advances 2018; 8(37): 20619–20629. doi: 10.1039/c8ra03291b
23. Kumar SS, Himabindu V. Hydrogen production by PEM water electrolysis—A review. Materials Science for Energy Technologies 2019; 2(3): 442–454. doi: 10.1016/j.mset.2019.03.002

24. Bos MJ, Kersten SRA, Brilman DWF. Wind power to methanol: Renewable methanol production using electricity, electrolysis of water and CO_2 air capture. Applied Energy 2020; 264: 114672. doi: 10.1016/j.apenergy.2020.114672
25. Mujeebu MA. Hydrogen and syngas production by superadiabatic combustion—A review. Applied Energy 2016; 173: 210–224. doi: 10.1016/j.apenergy.2016.04.018
26. Ju H, Giddey S, Badwal SPS. The role of nanosized SnO_2 in Pt-based electrocatalysts for hydrogen production in methanol assisted water electrolysis. Electrochimica Acta 2017; 229: 39–47. doi: 10.1016/j.electacta.2017.01.106
27. Palanisamy G, Oh TH, Thangarasu S. Modified cellulose proton-exchange membranes for direct methanol fuel cells. Polymers 2023; 15(3): 659. doi: 10.3390/poly m15030659
28. Hibino T, Kobayashi K, Nagao M, et al. Alternating current electrolysis for individual synthesis of methanol and ethane from methane in a thermo-electrochemical cell. ACS Catalysis 2023; 13(13): 8890–8901. doi: 10.1021/acscatal.3c01333
29. Do TN, Kim J. Process development and techno-economic evaluation of methanol production by direct CO_2 hydrogenation using solar-thermal energy. Journal of CO_2 Utilization 2019; 33: 461–472. doi: 10.1016/j.jcou.2019.07.003
30. Jin Z, Wang L, Zuidema E, et al. Hydrophobic zeolite modification for in situ peroxide formation in methane oxidation to methanol. Science 2020; 367: 193–197. doi: 10.1126/scien ce.aaw1108
31. Bjorck EC, Dobson DP, Pandhal J. Biotechnological conversion of methane to methanol: Evaluation of progress and potential. AIMS Bioengineering 2018; 5(1): 1–38. doi: 10.3934/bioeng.2018.1.1
32. Meng X, Cui X, Rajan NP, et al. Direct methane conversion under mild condition by thermo-, electro-, or photocatalysis. Chemistry 2019; 5(9): 2296–2325. doi: 10.1016/j.chempr.2019.05.008
33. Ravi M, Ranocchiari M, van Bokhoven JA. The direct catalytic oxidation of methane to methanol—A critical assessment. Angewandte Chemie International Edition 2017; 56(52): 16464–16483. doi: 10.1002/anie.201702550
34. de Souza RFB, Florio DZ, Antolini E, Neto AO. Partial methane oxidation in fuel cell-type reactors for co-generation of energy and chemicals: A short review. Catalysts 2022; 12(2): 217. doi: 10.3390/catal12020217
35. Hibino T, Kobayashi K, Ito M, et al. Direct electrolysis of waste newspaper for sustainable hydrogen production: An oxygen-functionalized porous carbon anode. Applied Catalysis 2018; 231: 191–199. doi: 10.1016/j.apcatb.2018.03.021
36. Xu N, Coco CA, Wang Y, et al. Electro-conversion of methane to alcohols on “capsule-like” binary metal oxide catalysts. Applied Catalysis 2021; 282: 119572. doi: 10.1016/j.apcatb.2020.119572
37. Haider MH, Dummer NF, Knight DW, et al. Efficient green methanol synthesis from glycerol. Nature Chemistry 2015; 7(12): 1028–1032. doi: 10.1038/nchem.2345
38. Wu CT, Yu KMK, Liao F, et al. A non-syn-gas catalytic route to methanol production. Nature Communication 2012; 3(1): 1050. doi: 10.1038/ncomms2053
39. Braden DJ, Henao CA, Heltzel J, et al. Production of liquid hydrocarbon fuels by catalytic conversion of biomass-derived levulinic acid. Green Chemistry 2011; 13(7): 1755–1765. doi: 10.1039/c1gc15047b
40. Wang M, Liu M, Lu J, Wang F. Photo splitting of bio-polyols and sugars to methanol and syngas. Nature Communication 2020; 11(1): 1083. doi: 10.1038/s41467-020-14915-8
41. Shen K, Kumari S, Huang YC, et al. Electrochemical oxidation of methane to methanol on electrodeposited transition metal oxides. Journal of the American Chemical Society 2023; 145(12): 6927–6943. doi: 10.1021/jacs.3c00441
42. Arnarson L, Schmidt PS, Pandey M, et al. Fundamental limitation of electrocatalytic methane conversion to methanol. Physical Chemistry Chemical Physics 2018; 20(16): 11152–11159. doi: 10.1039/C8CP01476K
43. Gautam P, Neha, Upadhyay SN, Dubey SK. Bio-methanol as a renewable fuel from waste biomass: Current trends and future perspective. Fuel 2020; 273: 117783. doi: 10.1016/j.fuel.2020.117783
44. Sikarwar VS, Zhao M, Fennell PS, et al. Progress in biofuel production from gasification. Progress in Energy and Combustion Science 2017; 61: 189–248. doi: 10.1016/j.pecs.2017.04.001
45. Kumabe K, Fujimoto S, Yanagida T, Ogata M, Fukuda T, Yabe A, et al. Environmental and economic analysis of methanol production process via biomass gasification. Fuel 2008; 87(7): 1422–1427. doi: 10.1016/j.fuel.2007.06.008
46. Sun H, Wang W, Koo KP. The practical implementation of methanol as a clean and efficient alternative fuel for automotive vehicles. International Journal of Engine Research 2019; 20(3): 350–358. doi: 10.1177/1468087417752951
47. Raheem A, Wan Azlina WAKG, Taufiq-Yap YH, et al. Thermochemical conversion of microalgal biomass for biofuel production. Renewable and Sustainable Energy Review 2015; 49: 990–999. doi: 10.1016/j.rser.2015.04.186
48. Su Z, Ge X, Zhang W, et al. Methanol production from biogas with a thermotolerant methanotrophic consortium isolated from an anaerobic digestion system. Energy and Fuels 2017; 31(3): 2970–2975. doi: 10.1021/acs.energyfuels.6b03471
49. Patinvoh RJ, Osadolor OA, Chandolias K, et al. Innovative pretreatment strategies for biogas production. Bioresource Technology 2017; 224: 13–24. doi: 10.1016/j.biortech.2016.11.083

50. Muñoz R, Meier L, Diaz I, Jeison D. A review on the state-of-the-art of physical/chemical and biological technologies for biogas upgrading. Reviews in Environmental Science and Bio/Technology 2015; 14(4): 727–759. doi: 10.1007/s11157-015-9379-1
51. Su YC, Sathyamoorthy S, Chandran K. Bioaugmented methanol production using ammonia oxidizing bacteria in a continuous flow process. Bioresource Technology 2019; 279: 101–107. doi: 10.1016/j.biortech.2019.01.092
52. Bhardwaj Y, Reddy B, Dubey SK. Temporal shift in methanotrophic community and methane oxidation potential in forest soil of dry tropics: High throughput metagenomic approach. Biology and Fertility of Soils 2020; 56(6): 859–867. doi: 10.1007/s00374-020-01444-1
53. Lattner JR, Harold MP. Autothermal reforming of methanol: Experiments and modelling. Catalysis Today 2007; 120(1): 78–89. doi: 10.1016/j.cattod.2006.07.005
54. Gao F, Zhan H, Zeng ZY, A methanol autothermal reforming system for the enhanced hydrogen production: Process simulation and thermodynamic optimization. International Journal of Hydrogen Energy 2023; 48(5): 1758–1772. doi: 10.1016/j.ijhydene. 2022.10.067
55. Herdem MS, Sinaki MY, Farhad S, Hamdullahpur F. An overview of the methanol reforming process: comparison of fuels, catalysts, reformers, and systems. International Journal Energy Research 2019; 43(10): 5076–5105. doi: 10.1002/er.4440
56. Chen WH, Su YQ, Lin BJ, et al. Hydrogen production from partial oxidation and autothermal reforming of methanol from a cold start in sprays. Fuel 2021; 287: 119638. doi: 10.1016/j.fuel.2020.119638
57. Iruretagoyena D, Hellgardt K, Chadwick D. Towards autothermal hydrogen production by sorption-enhanced water gas shift and methanol reforming: A thermodynamic analysis. Journal of Hydrogen Energy 2018; 43(9): 4211–4222. doi: 10.1016/j.ijhydene.2018.01.043
58. Marlin DS, Sarron E, Sigurbjörnsson Ó. Process advantages of direct CO2 to methanol synthesis. Frontier Chemistry 2018; 6: 446. doi: 10.3389/fchem.2018.00446.
59. Kiss AA, Landaeta FSJ, Ferreira ICA. Towards energy efficient distillation technologies–making the right choice. Energy 2012; 47: 531–542. doi: 10.1016/j.energy.2012.09.038
60. Rahman FA, Aziz MMA, Saidur R, et al. Pollution to solution: Capture and sequestration of carbon dioxide (CO_2) and its utilization as a renewable energy source for a sustainable future. Renewable and Sustainable Energy Review 2017; 71: 112–126. doi: 10.1016/j.rser.2017.01.011
61. Ay S, Ozdemir M, Melikoglu M. Effects of metal promotion on the performance, catalytic activity, selectivity and deactivation rates of $Cu/ZnO/Al_2O_3$ catalysts for methanol synthesis. Chemical Engineering Research and Design 2021; 175: 146–160. doi: 10.1016/j.cherd.2021.08.039
62. Behrens M. Coprecipitation: An excellent tool for the synthesis of supported metal catalysts. From the understanding of the well-known recipes to new materials. Catalysis Today 2015; 246: 46–54. doi: 10.1016/j.cattod.2014.07.050
63. Bhardwaj A, Ahluwalia AS, Pant KK, Upadhyayula S. A principal component analysis assisted machine learning modeling and validation of methanol formation over Cu-based catalysts in direct CO_2 hydrogenation. Separation and Purification Technology 2023; 324: 124576. doi: 10.1016/j.seppur.2023.124576
64. Etim UJ, Song Y, Zhong Z. Improving the Cu/ZnO-based catalysts for carbon dioxide hydrogenation to methanol, and the use of methanol as a renewable energy storage media. Frontiers in Energy Research 2020; 8: 545431. doi: 10.3389/fenrg.2020.545431
65. Zheng H, Narkhede N, Han L, et al. Methanol synthesis from CO_2: A DFT investigation on Zn-promoted Cu catalyst. Research on Chemical Intermediates 2020; 46(3): 1749–1769. doi: 10.1007/s11164-019-04061-2
66. Simanungkalit SP, Jones I, Okoye CO, et al. A preliminary attempt of direct methanol synthesis from biomass pyrolysis syngas over $Cu/ZnO/Al_2O_3$ catalysts. Biomass and Bioenergy 2023; 174: 106850. doi: 10.1016/j.biombioe.2023.106850
67. Zhang F, Zhang Y, Yuan L, et al. Synthesis of Cu/Zn/Al/Mg catalysts on methanol production by different precipitation methods. Molecular Catalysis 2017; 441: 190–198. doi: 10.1016/j.mcat.2017.08.015
68. Yang B, Liu C, Halder A, et al. Copper cluster size effect in methanol synthesis from CO_2. Journal of Physical Chemistry C 2017; 121(19): 10406–10412. doi: 10.1021/acs.jpcc.7b01835
69. Wang G, Chen L, Sun Y, et al. Carbon dioxide hydrogenation to methanol over Cu/ZrO2/CNTs: Effect of carbon surface chemistry. RSC Advances 2015; 5(56): 45320–45330. doi: 10.1039/c5ra04774a
70. Studt F, Behrens M, Kunkes EL, et al. The mechanism of CO and CO_2 hydrogenation to methanol over Cu-based catalysts. ChemCatChem 2015; 7(7): 1105–1111. doi: 10.1002/cctc.201500123
71. e Silva MPG da C, Miranda JC de C. Energy efficiency of thermochemical syngas-to-ethanol production plants. SN Applied Sciences 2021; 3(5): 534. doi: 10.1007/s42452-021-04526-3
72. Fózer D, Tóth AJ, Varbanov PS, et al. Sustainability assessment of biomethanol production via hydrothermal gasification supported by artificial neural network. Journal of Cleaner Production 2021; 318: 128606. doi: 10.1016/j.jc lepro.2021.128606
73. Hur DH, Na J, Lee EY. Highly efficient bioconversion of methane to methanol using a novel type I Methylomonas sp. DH-1 newly isolated from brewery waste sludge. Chemical Technology & Biotechnology 2017; 92(2): 311–318. doi: 10.1002/jctb.5007

74. Priyadarsini A, Singh R, Barbora L, et al. Methanotroph detection and bioconversion of methane to methanol by enriched microbial consortium from rice field soil. Bioresource Technology Reports 2023; 22: 101410. doi: 10.1016/j.biteb.2023.101410
75. Bak SY, Kang SG, Choi KH, et al. Phase-transfer biocatalytic methane-to-methanol conversion using the spontaneous phase-separable membrane μCSTR. Journal of Industrial and Engineering Chemistry 2022; 111: 389–397. doi: 10.1016/j.jiec.2022.04.021
76. Fergala A, AlSayed A, Eldyasti A. Utilization of Polyhydroxybutyrate (PHB) as intracellular reducing power for methanol production to alleviate the reliance on external energy sources by Methylocystis hirsute. Journal of Environmental Chemical Engineering 2021; 9(4): 105314. doi: 10.1016/j.jece.2021.105314
77. Baba T, Miyaji A. Application of biocatalysts for the production of methanol from methane. Catalysis and the Mechanism of Methane Conversion to Chemicals. Springer; 2020.
78. Ito H, Kondo R, Yoshimori K, Kamachi T. Methane hydroxylation with water as an electron donor under light irradiation in the presence of reconstituted membranes containing both photosystem II and a methane monooxygenase. ChemBioChem 2018; 19(20): 2152–2155. doi: 10.1002/cbic.201800324
79. Xin JY, Zhang YX, Zhang S, et al. Methanol production from CO_2 by resting cells of the methanotrophic bacterium Methylosinus trichosporium IMV 3011. Journal of Basic Microbiology 2007; 47(5): 426–435. doi: 10.1002/jobm.200710313
80. Hirayama H, Suzuki Y, Abe M, et al. Methylothermus subterraneus sp. nov., a moderately thermophilic methanotroph isolated from a terrestrial subsurface hot aquifer. International Journal of Systematic and Evolutionary Microbiology 2011; 61(11): 2646–2653. doi: 10.1099/ijs.0.028092-0
81. Hirayama H, Abe M, Miyazaki M, et al. Methylomarinovum caldicuralii gen. nov., sp. nov., a moderately thermophilic methanotroph isolated from a shallow submarine hydrothermal system, and proposal of the family Methylothermaceae fam. nov. International Journal of Systematic and Evolutionary Microbiology 2014; 64(Pt 3): 989–999. doi: 10.1099/ijs.0.058172-0
82. Han JS, Ahn CM, Mahanty B, Kim CG. Partial oxidative conversion of methane to methanol through selective inhibition of methanol dehydrogenase in methanotrophic consortium from landfill cover soil. Applied Biochemistry and Biotechnology 2013; 171(6): 1487–1499. doi: 10.1007/s12010-013-0410-0
83. Kulkarni PP, Khonde VK, Deshpande MS, et al. Selection of methanotrophic platform for methanol production using methane and biogas. Journal of Bioscience and Bioengineering 2021; 5(5): 460–468. doi: 10.1016/j.jbiosc.2021.07.007
84. Patel SKS, Kondaveeti S, Otari SV, et al. Repeated batch methanol production from a simulated biogas mixture using immobilized methylocystis bryophila. Energy 2018; 145: 477–485. doi: 10.1016/j.energy.2017.12.142
85. Jeong SY, Kim TG. Development of a novel methanotrophic process with the helper micro-organism Hyphomicrobium sp. NM3. Journal Applied Microbiology 2019; 126(2): 534–544. doi: 10.1111/jam.14140
86. Barros-Rodríguez A, García-Gálvez C, Pacheco P, et al. Isolation of methane enriched bacterial communities and application as wheat biofertilizer under drought conditions: An environmental contribution. Plants 2023; 12(13): 2487. doi: 10.3390/plants12132487
87. Zhou Y, Zhang R, Tian K, et al. Characteristics of the methanotroph used in coalbed methane emission reduction: Methane oxidation efficiency and coal wettability. Fuel 2023; 349: 128596. doi: 10.1016/j.fuel.2023.128596
88. Jeong SY, Kim TG. Determination of methanogenesis by nutrient availability via regulating the relative fitness of methanogens in anaerobic digestion. Science of the Total Environment 2022; 838: 156002. doi: 10.1016/j.scitotenv.2022.156002
89. do Valle Gomes MZ, Masdeu G, Eiring P, et al. Improved biocatalytic cascade conversion of CO_2 to methanol by enzymes Co-immobilized in tailored siliceous mesostructured cellular foams. Catalysis Science & Technology 2021; 11(21): 6952–6959. doi: 10.1039/d1cy01354h
90. Pani A, Shirkole SS, Mujumdar AS. Importance of renewable energy in the fight against global climate change. Drying Technology 2022; 40(13): 2581–2582. doi: 10.1080/07373937.2022.2119324
91. Akpahou R, Odoi-Yorke F. A multicriteria decision-making approach for prioritizing renewable energy resources for sustainable electricity generation in Benin. Cogent Engineering 2023; 10(1): 2204553. doi: 10.1080/23311916.2023.2204553
92. Jia X, Sun K, Wang J, et al. Selective hydrogenation of CO_2 to methanol over Ni/In_2O_3 catalyst. Journal of Energy Chemistry 2020; 50: 409–415. doi: 10.1016/j.jechem.2020.03.083
93. Ye J, Ge Q, Liu C. Effect of PdIn bimetallic particle formation on CO_2 reduction over the $Pd–In/SiO_2$ catalyst. Chemical Engineering Science 2015; 135: 193–201. doi: 10.1016/j.ces.2015.04.034
94. Panda D, Sharma S, Gangawane KM. Synthesis of novel biocatalyst from organic waste protonated with acid treatment for hydrogen production. International Journal of Hydrogen Energy 2023; 48(63): 24242–24254. doi: 10.1016/j.ijhydene.2023.03.117
95. Saka C. Efficient and durable H_2 production from $NaBH_4$ methanolysis using N doped hybrid $g\text{-}C_3N_4\text{-}SiO_2$ composites with ammonia as a nitrogen source. Fuel 2022; 324: 124594. doi: 10.1016/j.fuel.2022.124594
96. Tada S, Watanabe F, Kiyota K, et al. Ag addition to $CuO\text{-}ZrO_2$ catalysts promotes methanol synthesis via CO_2 hydrogenation. Journal Catalysis 2017; 351: 107–118. doi: 10.1016/j.jcat.2017.04.021

97. Meyer JJ, Tan P, Apfelbacher A, et al. Modeling of a methanol synthesis reactor for storage of renewable energy and conversion of CO_2—Comparison of two kinetic models. Chemical Engineering and Technology 2016; 39(2): 233–245. doi: 10.1002/ceat.201500084
98. Xu X, Shuai K, Xu B. Review on copper and palladium based catalysts for methanol steam reforming to produce hydrogen. Catalysts 2017; 7(6): 183. doi: 10.3390/catal7060183
99. Samimi F, Rahimpour MR, Shariati A. Development of an efficient methanol production process for direct CO_2 hydrogenation over a $Cu/ZnO/Al_2O_3$ catalyst. Catalysts 2017; 7(11): 332. doi: 10.3390/catal7110332
100. Romero-Rivera A, Garcia-Borràs M, Osuna S. Computational tools for the evaluation of laboratory-engineered biocatalysts. Chemical Communications 2017; 53(2): 284–297. doi: 10.1039/c6cc06055b
101. Lovelock SL, Crawshaw R, Basler S, et al. The road to fully programmable protein catalysis. Nature 2022; 606(7912): 49–58. doi: 10.1038/s41586-022-04456-z
102. Zhang Z, Long M, Zheng N, et al. Inside out computational redesign of cavities for improving thermostability and catalytic activity of Rhizomucor Miehei lipase. Applied and Environmental Microbiology 2023; 89(3): e0217222. doi: 10.1128/aem.02172-22
103. Delgado-Arciniega E, Wijma HJ, Hummel C, Janssen DB. Computationally supported inversion of ketoreductase stereoselectivity. ChemBioChem 2023; 24(9): e202300032. doi: 10.1002/cbi c.202300032
104. Cui Y, Sun J, Wu B, Computational enzyme redesign: Large jumps in function. Trends in Chemistry 2022; 4(5): 409–419. doi: 10.1016/j.trechm.2022.03.001
105. Doble MV, Obrecht L, Joosten HJ, et al. Engineering thermostability in artificial metalloenzymes to increase catalytic activity. ACS Catalysis 2021; 11(6): 3620–3627. doi: 10.1021/acscatal.0c05413
106. Dahiyat BI, Mayo SL. Protein design automation. Protein Science 1996; 5(5): 895–903. doi: 10.1002/pro.5560050511
107. Hellinga HW, Richards FM. Construction of new ligand binding sites in proteins of known structure. I. Computer-aided modeling of sites with pre-defined geometry. Journal of Molecular Biology 1991; 222(3): 763–785. doi: 10.1016/0022-2836(91)90510-d
108. Dahiyat BI, Mayo SL. De novo protein design: Fully automated sequence selection. Science 1997; 278(5335): 82–87. doi: 10.1126/science.278.5335.82
109. Kosuri P, Altheimer BD, Dai M, et al. Rotation tracking of genome-processing enzymes using DNA origami rotors. Nature 2019; 572(7767): 136–140. doi: 10.1038/s41586-019-1397-7
110. Leman JK, Künze G. Recent advances in NMR protein structure prediction with ROSETTA. International Journal of Molecular Sciences 2023; 24(9): 7835. doi: 10.3390/ijms24097835
111. Richter F, Leaver-Fay A, Khare SD, et al. De novo enzyme design using Rosetta3. PLoS One 2011; 6(5): e19230. doi: 10.1371/journal.pone.0019230
112. Kiss G, Röthlisberger D, Baker D, Houk KN. Evaluation and ranking of enzyme designs. Protein Science 2010; 19(9): 1760–1773. doi: 10.1002/pro.462
113. Ashworth MA, Bombino E, de Jong RM, et al. Computation-aided engineering of cytochrome P450 for the production of pravastatin. ACS Catalysis 2022; 12(24): 15028–15044. doi: 10.1021/acscatal.2c03974
114. Öner A, Çelebi-Ölçüm N. Rapid computational evaluation of small-molecule hydrolase mimics for preorganized H-bond networks. International Journal of Quantum Chemistry 2020; 121(2). doi: 10.1002/qua.26423
115. Pen N, Soussan L, Belleville MP, et al. Methane hydroxylation by Methylosinus trichosporium OB3b: Monitoring the biocatalyst activity for methanol production optimization in an innovative membrane bioreactor. Biotechnology and Bioprocess E 2016; 21(2): 283–293. doi: 10.1007/s12257-015-0762-0
116. Singh R, Ryu J, Kim SW. Microbial consortia including methanotrophs: Some benefits of living together. Journal of Microbiology 2019; 57(11): 939–952. doi: 10.1007/s12275-019-9328-8
117. Bodelier PLE, Pérez G, Veraart AJ, Krause SMB. Methanotroph ecology, environmental distribution and functioning. In: Lee EY (editors). Methanotrophs. Springer; 2019. pp. 1–38.
118. Balasubramanian R, Rosenzweig AC. Structural and mechanistic insights into methane oxidation by particulate methane monooxygenase. Accounts of Chemical Research 2007; 40(7): 573–580. doi: 10.1021/ar700004s
119. Duan C, Luo M, Xing X. High-rate conversion of methane to methanol by Methylosinus trichosporium OB3b. Bioresource Technology 2011; 102(15): 7349–7353. doi: 10.1016/j.biortech.2011.04.096
120. Sahoo KK, Datta S, Goswami G, Das D. Two-stage integrated process for bio-methanol production coupled with methane and carbon dioxide sequestration: Kinetic modelling and experimental validation. Journal of Environmental Management 2022; 301: 113927. doi: 10.1016/j.jenvman.2021.113927
121. Patel SKS, Selvaraj C, Mardina P, et al. Enhancement of methanol production from synthetic gas mixture by Methylosinus sporium through covalent immobilization. Applied Energy 2016; 171: 383–391. doi: 10.1016/j.apenergy.2016.03.022
122. Hou R, Zhang N, Yang C, et al. A novel structure of natural gas, electricity, and methanol production using a combined reforming cycle: Integration of biogas upgrading, liquefied natural gas re-gasification, power plant, and methanol synthesis unit. Energy 2023; 270: 126842. doi: 10.1016/j.energy.2023.126842
123. Bi W, Tang Y, Li X, et al. One-step direct conversion of methane to methanol with water in non-thermal plasma. Communication Chemistry 2022; 5(1): 124. doi: 10.1038/s42004-022-00735-y

124. Deka TJ, Osman AI, Baruah DC, Rooney DW. Methanol fuel production, utilization, and techno-economy: A review. Environmental Chemistry Letter 2022; 20(6): 3525–3554. doi: 10.1007/s10311-022-01485-y
125. Arteaga-Pérez LE, Gómez-Cápiro O, Karelovic A, Jiménez R. A modelling approach to the techno-economics of Biomass-to-SNG/Methanol systems: Standalone vs Integrated topologies. Chemical Engineering Journal 2016; 286: 663–678. doi: 10.1016/j.cej.2015.11.005
126. Akhoondi A, Osman AI, Eslami AA. Direct catalytic production of dimethyl ether from CO and CO_2: A review. Synthesis and Sintering 2021; 1(2): 105–120. doi: 10.53063/synsint.2021.1229
127. Kim H, Byun M, Lee B, Lim H. Carbon-neutral methanol synthesis as carbon dioxide utilization at different scales: Economic and environmental perspectives. Energy Conversion and Management 2022; 252: 115119.
128. Zhang Q, Chen H, Li B, et al. A novel system integrating water electrolysis and supercritical CO_2 cycle for biomass to methanol. Applied Thermal Engineering 2023; 225: 120234. doi: 10.1016/j.applthermaleng.2023.120234
129. Fózer D, Volanti M, Passarini F, et al. Bioenergy with carbon emissions capture and utilisation towards GHG neutrality: Power-to-Gas storage via hydrothermal gasification. Applied Energy 2020; 280: 115923. doi: 10.1016/j.apenergy.2020.115923
130. Chen Q, Gu Y, Tang Z, Sun Y. Comparative environmental and economic performance of solar energy integrated methanol production systems in China. Energy Conversion and. Management 2019; 187: 63–75. doi: 10.1016/j.enconman.2019.03.013
131. Hennig M, Haase M. Techno-economic analysis of hydrogen enhanced methanol to gasoline process from biomass-derived synthesis gas. Fuel Processes and Technology 2021; 216: 106776. doi: 10.1016/j.fuproc.2021.106776
132. Woolf D, Lehmann J, Lee DR. Optimal bioenergy power generation for climate change mitigation with or without carbon sequestration. Nature Communications 2016; 7: 13160. doi: 10.1038/ncomms13160
133. Klein D, Bauer N, Bodirsky B, et al. Bio-IGCC with CCS as a long-term mitigation option in a coupled energy-system and land-use model. Energy Procedia 2011; 4: 2933–2940. doi: 10.1016/j.egypro.2011.02.201
134. Bai Z, Liu Q, Gong L, Lei J. Investigation of a solar-biomass gasification system with the production of methanol and electricity: Thermodynamic, economic and off-design operation. Applied Energy 2019; 243: 91–101. doi: 10.1016/j.apenergy.2019.03.132
135. Adekoya D, Tahir M, Amin NAS. Recent trends in photocatalytic materials for reduction of carbon dioxide to methanol. Renewable and Sustainable Energy Reviews 2019; 116: 109389. doi: 10.1016/j.rser.2019.109389
136. AlNouss A, McKay G, Al-Ansari T. A techno-economic-environmental study evaluating the potential of oxygen-steam biomass gasification for the generation of value-added products. Energy Conversion and Management 2019; 196: 664–676. doi: 10.1016/j.enconman.2019.06.019
137. Yao Z, You S, Ge T, Wang CH. Biomass gasification for syngas and biochar co-production: Energy application and economic evaluation. Applied Energy 2018; 209: 43–55. doi: 10.1016/j.apenergy.2017.10.077
138. Gautam P, Neha, Upadhyay SN, Dubey SK. Bio-methanol as a renewable fuel from waste biomass: Current trends and future perspective. Fuel 2020; 273: 117783. doi: 10.1016/j.fuel.2020.117783
139. Sheets JP, Lawson K, Ge X, et al. Development and evaluation of a trickle bed bioreactor for enhanced mass transfer and methanol production from biogas. Biochemical Engineering Journal 2017; 122: 103–114. doi: 10.1016/j.bej.2017.03.006
140. Sheets JP, Ge X, Li YF, et al. Biological conversion of biogas to methanol using methanotrophs isolated from solid-state anaerobic digestate. Bioresource Technology 2016; 201: 50–57. doi: 10.1016/j.biortech.2015.11.035
141. Kumar N, Chauhan NS. Nano-biocatalysts: Potential biotechnological applications. Indian Journal Microbiology 2021; 61(4): 441–448. doi: 10.1007/s12088-021-00975-x
142. Zdarta J, Meyer AS, Jesionowski T, Pinelo M. A general overview of support materials for enzyme immobilization: Characteristics, properties, practical utility. Catalysts 2018; 8(2): 92. doi: 10.3390/catal8020092
143. Zdarta J, Norman M, Smułek W, et al. Spongin-based scaffolds from Hippospongia communis demosponge as an effective support for lipase immobilization. Catalysts 2017; 7(5): 147. doi: 10.3390/catal7050147
144. Kucharska K, Rybarczyk P, Hołowacz I, et al. Pretreatment of lignocellulosic materials as substrates for fermentation processes. Molecules 2018; 23(11): 2937. doi: 10.3390/molecules23112937
145. Valverde-Pérez B, Xing W, Zachariae AA, et al. Cultivation of methanotrophic bacteria in a novel bubble-free membrane bioreactor for microbial protein production. Bioresource Technology 2020; 310: 123388. doi: 10.1016/j.biortech.2020.123388
146. Sahoo KK, Goswami G, Das D. Biotransformation of methane and carbon dioxide into high-value products by methanotrophs: Current state of art and future prospects. Frontier Microbiology 2021; 12: 636486. doi: 10.3389/fmicb.2021.636486
147. Cucaita A, Piochon M, Villemur R. Co-culturing Hyphomicrobium nitrativorans strain NL23 and Methylophaga nitratireducenticrescens strain JAM1 allows sustainable denitrifying activities under marine conditions. Peer J 2021; 9: e12424. doi: 10.7717/peerj.12424
148. Takeuchi M, Yoshioka H. Acetate excretion by a methanotroph, Methylocaldum marinum S8, under aerobic conditions. Bioscience, Biotechnology, and Biochemistry 2021; 85(11): 2326–2333. doi: 10.1093/bbb/zbab150

149. Ruiz-Ruiz P, Gómez-Borraz TL, Revah S, Morales M. Methanotroph-microalgae co-culture for greenhouse gas mitigation: Effect of initial biomass ratio and methane concentration. Chemosphere 2020; 259: 127418. doi: 10.1016/j.chemosphere.2020.127418
150. Le HTQ, Lee EY. Methanotrophs: Metabolic versatility from utilization of methane to multi-carbon sources and perspectives on current and future applications. Bioresource Technology 2023; 384: 129296. doi: 10.1016/j.biortech.2023.129296
151. Zhang C, Ottenheim C, Weingarten M, Ji L. Microbial utilization of next-generation feedstocks for the biomanufacturing of value-added chemicals and food ingredients. Frontiers in Bioengineering and Biotechnology 2022; 10: 874612. doi: 10.3389/fbioe.2022.874612
152. Pham DN, Nguyen AD, Lee EY. Outlook on engineering methylotrophs for one-carbon-based industrial biotechnology. Chemical Engineering Journal 2022; 449: 137769. doi: 10.1016/j.cej.2022.137769
153. Kang CK, Jeong SW, Jo JH, et al. High-level squalene production from methane using a metabolically engineered Methylomonas sp. DH-1 strain. ACS Sustainable Chemistry & Engineering 2021; 9(48): 16485–16493. doi: 10.1021/acssuschemeng.1c06776