Microbial Conversion of Carbon Dioxide to Biofuels: Advances and Challenges

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Abstract. This paper highlights developments in microbial electrosynthesis (MES), metabolic engineering, and photosynthetic biohybrid systems (PBSs) for biofuel production, which offer a sustainable solution to lessen dependency on fossil fuels and the emission of greenhouse gases. MES uses electroactive microbes to convert CO_2 into ethanol, methane, and other fuels using renewable electricity while integrating wastewater treatment; metabolic engineering improves CO_2 fixation by redesigning microbial pathways; and PBSs combine inorganic semiconductors with biological catalysts to improve solar energy conversion. Methane synthesis through hydrogenotrophic methanogenesis and ethanol production via acetyl-CoA pathways are examples of targeted biofuel synthesis. However, the overall energy yields remain suboptimal for large-scale deployment. Slow reaction rates, expensive hydrogen, and fluctuating CO_2 fixation efficiencies in microalgae systems are among the difficulties that are impacted by reactor design and operating factors. Process optimization and strain engineering innovations hold promise for scalability. However, further research is required due to the infrastructural requirements and economic viability of CO_2 capture and hydrogen delivery. Realizing the full potential of microbial CO_2 conversion technologies in reaching carbon neutrality will require addressing these technological and financial obstacles through interdisciplinary methods.

1 Introduction

As industrialization has become more sophisticated, the increase in fuel consumption for factory production and transport has led to a concomitant increase in the emission of greenhouse gases such as carbon dioxide [1]. Of all the many sources of CO_2 emissions, about 24% of all CO_2 emissions from burning fossil fuels come from the transportation sector [1]. Additionally, it is expected that transportation's CO_2 emissions will rise more quickly than those of other end-of-energy sectors because of the anticipated quicker future growth in demand. The rise in carbon emissions is contributing to the rapid rise in climate change and exacerbating global warming.

In order to alleviate such environmental problems, well-established biofuels (e.g., bioethanol, biodiesel) that primarily rely on plant-based biomass are seen as an important alternative to traditional fossil fuels due to their carbon-neutral nature. In contrast to

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traditional biofuel production methods that rely on algae or crops, microbial conversion of carbon dioxide to biofuels can directly utilize carbon dioxide from industrial waste gases or the atmosphere, combined with a biological pathway for efficient carbon sequestration and fuel synthesis.

As an alternative to the commodities currently obtained from fossil fuels, MES is an electrochemical technique that drives microbial metabolism for production, including the transformation of CO_2 into organic molecules with economic significance. Microbial conversion of CO_2 shows future potential due to its wide range of feedstocks like industrial exhaust, mild reaction conditions and environmental friendliness. It is possible to generate several carbon-neutral biofuels involving methane, butanol, and ethanol while at the same time combining wastewater treatment.

At the same time, this technology faces significant challenges in technical aspects due to the low reaction rate of microbial metabolism. For the economic field, the high cost of hydrogen, which is a key reducing agent for CO_2 conversion and more infrastructure investment are needed to capture and transfer CO_2 from industrial exhaust. Comparing microbial conversion to other CCU technologies or renewable energy sources, its economic viability has not yet been fully achieved. The consideration of resources and the environment is how to achieve a sustainable supply of hydrogen with the balance of carbon emission and the requirement of nutrients and water due to the large-scale microbial culture.

2 Biological Pathways for CO_2 Conversion

2.1 Microbial electrosynthesis

MES is an approach to manufacturing organic substances by converting electrical energy into chemical energy on the surface of an electrode by utilizing the microbe as a biocatalyst and facilitating electron transport between it and the electrode. Fig. 1 shows the MES mechanism scheme. Two electrodes are included in the MES system, where a membrane separates the cathode and anode. While an oxidation reaction takes place at the anode, microorganisms adhere to the cathode's surface and absorb electrons from the electrodes to convert carbon dioxide into organics like ethanol, where the decomposition of water produces protons (H^+), oxygen (O_2), and releases electrons, forming a closed circuit. In addition, electricity is used as an energy source in this system to provide energy and to regulate the CO_2 reduction electrode voltage. There are two ways for microorganisms to acquire electrons from electrodes, which are electron transfers that occur directly and indirectly. Direct transmission of electrons is when microorganisms acquire electrons by directly contacting the electrode surface through the arrival point proteins on the cell membrane, while indirect electron transfer relies on intermediate media such as hydrogen and formic acid to transfer electrons, in which microorganisms absorb hydrogen or formic acid produced by the electrode to reduce carbon dioxide (biological methanation reaction, catalyzed by hydrogenotrophic methanogen: $CO_2+4H_2 \rightarrow CH_4+2H_2O$) [2].

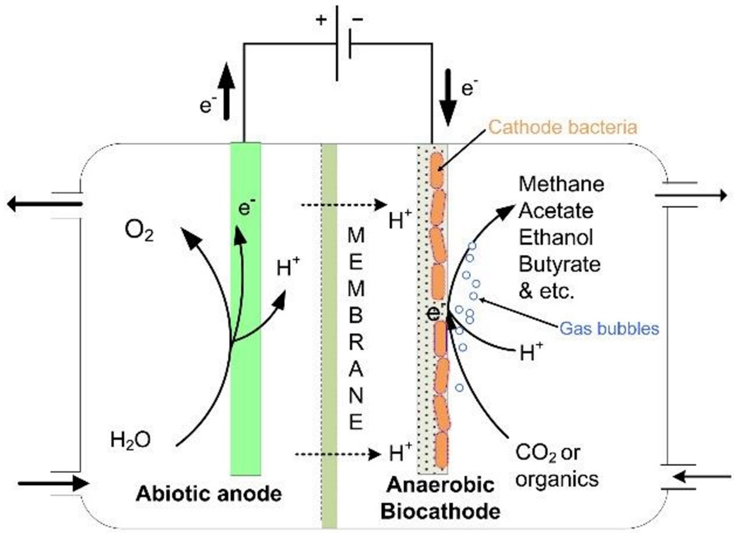

Fig. 1. Layout of MES mechanism [3].

2.2 Metabolic engineering

Metabolic engineering is a discipline that uses molecular biology (e.g., DNA recombination techniques) and thus changes the metabolic pathways of organisms to achieve the design and system optimization of cellular metabolic systems [4,5]. Both photoautotrophic and chemoautotrophic natural CO_2 fixation have been subject to genetic manipulation for a specific purpose. Using genes from one or more species, a new or improved fixer pathway is created as part of the metabolic engineering process of fixation of CO_2. One of the core technologies of metabolic engineering, which seeks to accomplish more efficient biochemical modifications, energy transmission, and synthesis of the desired products, is the analysis of altered organisms' metabolic functions. Briefly, there are five levels of metabolic engineering [6]. The first level of manipulation is to optimize existing pathways in the natural host (e.g., knockout or overexpression) to increase productivity. The second level of metabolic engineering, known as copy, paste and fine-tune, is to transfer a known (sub-)pathway from one host to another. As a result, the natural pathways of the new host are modified, leading to improved response performance. The next three levels are unnatural and novel (synthetic) pathways that are generated by known reactions (level 3, enzyme mixing and selection), new processes that employ either existing enzyme mechanisms (level 4, creative enzyme reactions) or innovative enzymes (level 5, novel enzyme chemistry).

2.3 Photosynthetic biohybrid systems

Examining the connections between inorganic nanostructures that would eventually be employed as whole-cell catalysts for bacteria and light harvesters that might reduce CO_2 was the modest beginning of the first attempts in this sector. PBSs combine the benefits of inorganic substances with biological catalysts by absorbing solar energy using semiconductor wideband light capture and then converting it into useful CO_2-derived compounds using metabolic pathways in live organisms. As opposed to the 3% of the best, inorganic semiconductor photovoltaics now frequently achieve solar-to-energy efficiencies above 20% [7].

3 Applications for Microbial CO_2 Conversion

3.1 Ethanol

Buffer characteristics regulate the MES process's pH and substrate selectivity at the cathode, which are produced by the pH fluctuations brought on through the action between HCO_3^- which acts as the substrate and acetate, which is the product. A necessary medium to facilitate the cathode's electrochemical decrease in CO_2 is hydrogen generated from water electrolysis, and the availability of hydrogen also encourages the synthesis of ethanol. Through the acetyl-CoA-dependent fermentation route, such as acetone-butanol-ethanol (ABE) fermentation, Clostridium was shown to produce higher alcohols (hydrocarbon chains longer than ethanol) through microbial synthesis [8]. Because of their high energy content and characteristics that are similar to those of gasoline, isobutanol and n-butanol were the most researched fuel targets among advanced alcohols [9].

3.2 Methanogens

Methane is created by metabolism through anaerobic respiration, commonly referred to as methanogenesis. During aerobic respiration, O_2 is reduced to H_2O, and organic molecules such as glucose undergo oxidization to CO_2. On the other hand, during hydrogenotrophic methane production, H_2 becomes oxidized to H^+ while CO_2 gets reduced to CH_4. Although methanogenesis is conceptually similar to other forms of respiration, solely methanogens—organisms capable of this particular metabolism—perform biological methane synthesis, and the energy output is exceedingly limited ($\leqslant$1 ATP per methane created). Recent discoveries have shown that methanogens are incredibly diverse, indicating that this metabolism is among the oldest on the planet [9].

4 Engineering challenges

The reduced CO_2 fixation efficiency will multiply the expense of the carbon source. Numerous parameters, such as microalgal strains, photobioreactor structures, light amount and quality, operational models, and nutrition circumstances, affect the efficiency of CO_2 fixation in microalgal production. Because photobioreactor structures impact the effectiveness of CO_2 dissolution and microalgae's consumption of CO_2, they have a significant impact on the efficiency of CO_2 fixation. Generally, supplied CO_2 is used inefficiently in open-culture systems due to the shallow levels and low CO_2 mass exchange system. Between 10% and 30% was the acceptable range of the CO_2 fixing efficiency [10-12]. According to recent studies, microalgae are often less than 50% effective at fixing CO_2 from exhaust gases. However, Chlorella sp. PY-ZU1, a species that was domesticated from Helicobacter pylori by γ-irradiation and high CO_2 levels, was used in Jun Cheng's work. Through manipulation of the CO_2 concentration (0.04%-60%), light intensity (6,000 Lux), and incubation period (7-10 days), the experimental design demonstrated how Chlorella PY-ZU1's benefit in high CO_2 environments and alterations in carbon fixation mechanisms [13]. The bioreactor's medium, brightness of light, and EBRT were all precisely calibrated to continuously bubble 15% CO_2, the level of CO_2 found in most coal-fired power plants' exhaust gases. The highest CO_2 fixation productivity increased because of this invention (85.6%) and the production of microalgal biomass, which is far more efficient than open-ended, probably 4-5 times as much [14].

5 Conclusion

With major benefits like direct integration with CO_2 isolated sources (such as manufacturing flue gases) and the ability to recycle carbon within a circular economy framework, microbial conversion of CO_2 to biofuels offers a scalable and sustainable solution to decarbonize industry. Mild operating conditions allow technologies like MES to produce biofuels (ethanol, methane) and clean wastewater synergistically while using less energy. Additionally, metabolic engineering increases adaptability by enabling customized pathways (such as the acetyl-CoA routes in *Clostridium*) to maximize yields, and PBSs surpass natural photosynthesis by achieving solar-to-energy efficiencies of over 20%. Notwithstanding these advantages, scalability is hampered by significant issues. Production rates are limited by slow microbial reaction kinetics, especially in MES and methanogenesis ($\leq$1 ATP/CH_4). Progress is further hampered by a heavy reliance on hydrogen, a costly reductant whose synthesis requires much energy, and by a lack of infrastructure for CO_2 capture and storage.

Furthermore, the CO_2 fixation efficiencies in microalgae systems continue to vary (10–85%), depending on the reactor design, the availability of light, and the dynamics of nutrients. Multidisciplinary approaches are essential for overcoming these obstacles. Improvements in enzyme and strain engineering, including metabolic rewiring based on CRISPR, may increase the specificity of pathways and the efficiency of electron transfer. Maximizing CO_2 usage can be achieved by optimizing modular photobioreactors and bioreactor designs to improve gas-liquid mass transfer. In order to encourage commercialization, governmental measures such as carbon pricing, green hydrogen subsidies, and R&D financing are crucial. PBS integration with renewable energy grids has the potential to increase economic viability and stabilize the power supply. Microbial CO_2 conversion can go from laboratory promise to industrial-scale reality by giving priority to these breakthroughs, which include infrastructure development, regulatory assistance, and technical advancements. This will hasten the process of achieving global carbon neutrality.

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