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Advances in Solar-Driven CO_2 Conversion to Methanol by Bio-Inspired Multienzyme Cascade Systems: A Mini Review

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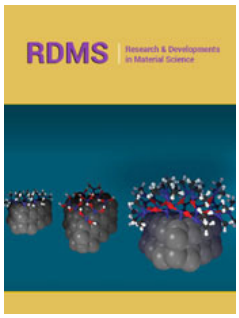

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Abstract

The increasing concentration of carbon dioxide (CO_2) in the atmosphere, surpassing critical safety thresholds, alongside rising global energy demands driven by population growth, underscores the urgent need for sustainable energy solutions. This review explores various techniques-thermal, photochemical, electrochemical, and enzymatic-aimed at converting CO_2 into valuable hydrocarbons and other products. Enzymatic approaches, utilizing proteins and microorganism-based enzymes for CO_2 reduction via redox reactions, are highlighted for their environmental friendliness, reduced toxicity, and efficiency in transforming CO_2 into hydrocarbon fuels. Strategies integrating enzymatic systems with polymers, transition metals, and semiconductors to enhance CO_2 reduction applications are discussed, emphasizing the critical role of enzyme immobilization. Additionally, the review explores the integration of enzyme systems with photo catalysts in semi-artificial photosynthesis systems resembling natural photosystem. Solar fuel generation through photocatalytic CO_2 conversion emerges as a promising approach, harnessing sunlight to efficiently produce methanol (MeOH), ethanol, and formic acid. While metal-based photocatalysts encounter challenges such as poor dispersion and toxicity, bio-inspired alternatives utilizing redox enzymes offer sustainable solutions. The review concludes by addressing emerging challenges and innovative approaches in enzymatic CO_2 reduction, with a focus on optimizing methanol production through multienzyme systems and membrane-based strategies to advance sustainable energy technologies.

Keywords: Biocatalysis; CO_2 conversion; Methanol; Enzymatic catalysis; Microbial metabolism; Sustainable chemistry

Introduction

Climate change is a global issue of paramount concern, demanding attention from policymakers, academic researchers in environmental sciences, and various stakeholders. The rapid increase in greenhouse gas emissions, notably carbon dioxide (CO_2), poses significant environmental challenges such as global warming, environmental degradation, and various social, financial, and technological complications [1]. The concentration of CO_2 in the atmosphere has risen sharply, driven primarily by anthropogenic activities like fossil fuel combustion and industrial processes. CO_2, a major greenhouse gas, is intricately linked to climate change, prompting global initiatives and targets for emission reduction, including substantial targets set by the Intergovernmental Panel on Climate Change (IPCC) [2]. Efforts to curb CO_2 emissions are crucial to mitigate its adverse impacts on climate and weather patterns, such as disrupting monsoons and exacerbating climate-related risks. In response to these challenges, solar fuel generation emerges as a promising solution, particularly through photocatalytic conversion of CO_2 into valuable hydrocarbon fuels like methanol (MeOH) [3] (Figure 1). This approach harnesses sunlight efficiently and cost-effectively to drive chemical reactions that convert CO_2 into useful products. While traditional metal-based photocatalysts exhibit high performance, they are limited by issues such as poor dispersion, toxicity, and

high production costs. In contrast, bio-inspired photocatalysts, which mimic natural photosynthesis using enzymatic processes, offer a sustainable alternative. Enzyme-based systems have gained attention for their efficiency and compatibility with natural processes, showcasing advancements in designing multienzyme systems integrated into membranes [4]. These systems optimize catalytic efficiency by carefully controlling enzyme composition, assembly, and immobilization techniques. Such innovations aim to maximize methanol production while minimizing energy consumption and environmental impact, positioning enzyme-based photocatalysis as a key technology for industrial CO_2 capture and renewable fuel production [5].

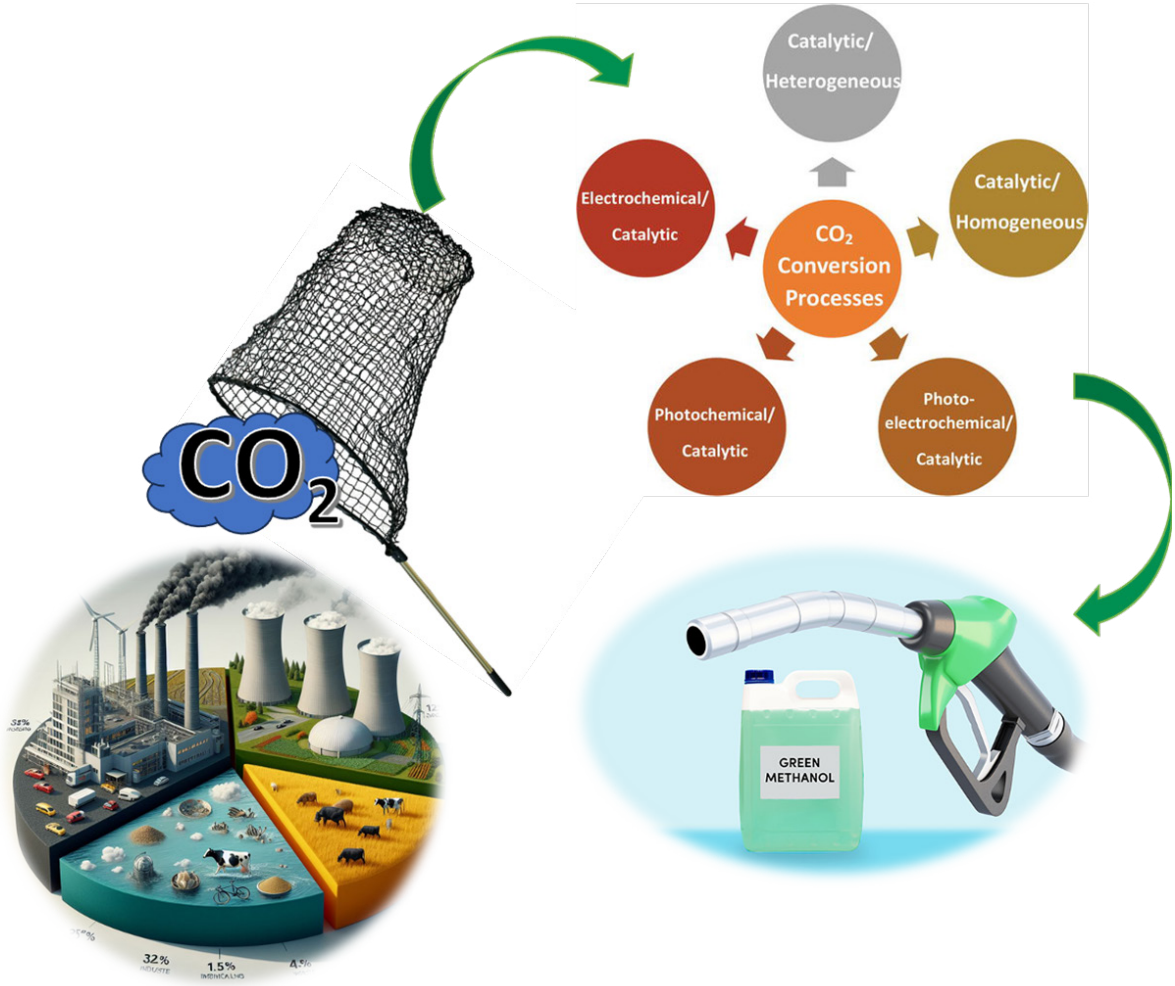

Figure 1: Graphical representation of CO_2 to methanol production.

Recent research has focused on enhancing enzyme stability and performance through innovative immobilization methods, such as incorporating enzymes into membranes or entrapping them within membrane pores using advanced filtration techniques. Promising results include sustained methanol production over multiple cycles, demonstrating the potential of enzyme-based systems in achieving sustainable CO_2 utilization and contributing to a greener, more efficient future.

Role and advantages of biocatalyst

Autotrophic organisms convert atmospheric CO_2 into organic molecules through six main pathways: the Calvin-Benson-Bassham cycle, reductive citric acid cycle, reductive acetyl-CoA pathway, 3-hydroxypropionate cycle, 3-hydroxypropionate/4-hydroxybutyrate cycle, and dicarboxylate/4-hydroxybutyrate cycle [6]. The Calvin-Benson-Bassham cycle is the most dominant, handling over 90% of natural CO_2 fixation. This process relies on carboxylase enzymes to incorporate CO_2 into organic substrates, but they face challenges like inefficient energy use, slow productivity, and high-water consumption, limiting their application in biofuel production. Biotechnological and synthetic biology approaches aim to enhance the efficiency of these processes. Formate dehydrogenases (FDHs) have been studied for their ability to reduce CO_2 to methanol using NAD(P)H [7]. Biocatalysts, including enzymes and microorganisms, are valuable for CO_2 reduction due to their high selectivity and efficiency under mild conditions. Enzymes are advantageous as they do not require complex growth conditions, unlike microorganisms which need specific environmental conditions. Challenges for enzymes include lower activity in aqueous solutions, which can be mitigated by

immobilization techniques to improve stability, reusability, and prevent contamination. Current research focuses on optimizing biocatalysts for CO_2 reduction, including using multiple enzymes for better product selectivity and developing optimal enzyme immobilization conditions.

Enzymatic CO_2 reduction

Dehydrogenase enzymes, part of the oxidoreductase family, are essential for transferring electrons from oxidant to reductant species. Acting as catalysts in oxygen-independent reactions, function as oxidizing agents that transfer electrons or hydrogens. They are widely used in CO_2 reduction, with catalytic sites that convert CO_2 into specific intermediates. Dehydrogenases typically require cofactors such as Nicotinamide adenine dinucleotide (NADH), Nicotinamide adenine dinucleotide phosphate (NADPH), or Methyl Viologen to facilitate electron and hydrogen donation, which is crucial for reducing CO_2 into various products. These cofactors possess a catalytic binding domain and a coenzyme/NAD+ binding domain, arranged into a super-secondary structure composed of three polypeptide chains, including β sheets and α-helices oriented in a specific way. The NAD+ binding domain features a Rossmann fold with mononucleotide binding subdomains, which are crucial for recognizing and binding NAD+/NADH during catalysis. Although the function of the NAD+ binding domain is consistent across all dehydrogenase enzymes, each enzyme has a distinct catalytic domain suited to its specific role.

Mechanism of photocatalytic CO_2 reduction

There are three crucial steps in the mechanism of the photocatalytic reaction (Figure 2) [8]:

1. Light that has enough energy to be absorbed in order to create electron-hole pairs;

2. The movement and separation of electron-hole pairs: Upon light absorption, an electron leaves behind a positive hole when it migrates from the valence band to the conduction band. This hole can then be filled by another electron from the valence band, resulting in the creation of a new hole. Holes may travel in this manner throughout the semiconductor surface.

3. Through the process of desorption, surface species interact with electron-hole pairs to generate the end products.

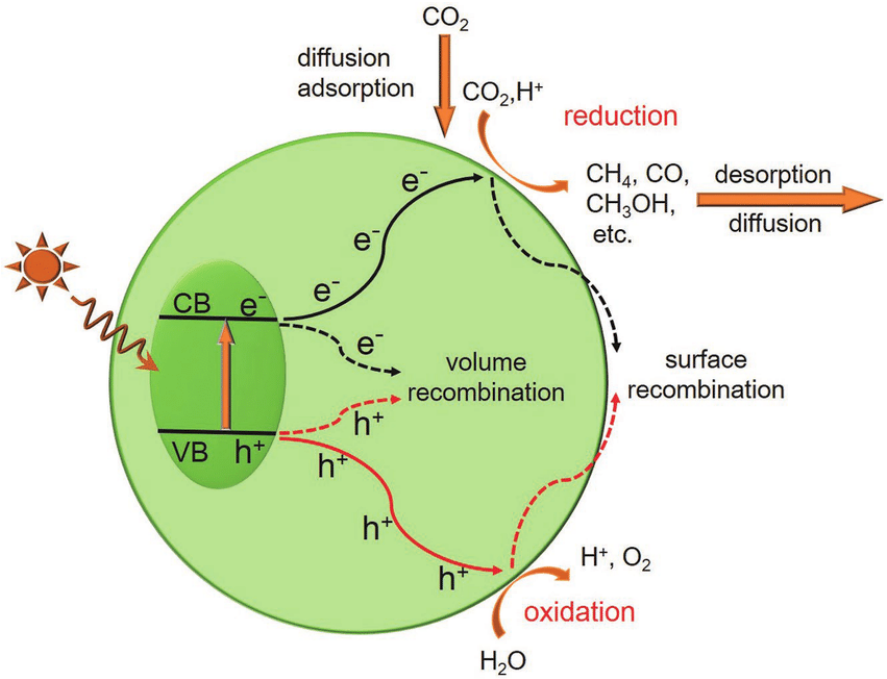

Figure 2: Photocatalytic CO_2 reduction mechanism [8].

Multienzyme system

Nanoparticle based multienzyme system: Kuwabata et al. [9] used formate dehydrogenase from Pseudomonas Oxalaticus and methanol dehydrogenase from Methylolophilus Methylophus to create a multienzyme system strategy for CO_2 reduction. In an H-type two-compartment cell, they used Methyl Viologen as a co-factor. They saw that at greater enzyme concentrations, a mixture of formaldehyde and methanol was produced, whereas at lower concentrations, formaldehyde was the only product produced. Using titanium nanoparticles, Sun et al. [10] created an environmentally friendly and effective encapsulation technique that converts CO_2 to methanol. Using a biomimetic mineralization technique, they contained Formate dehydrogenase, Formaldehyde dehydrogenase, and Alcohol Dehydrogenase within Titania nanoparticles templated with protamine. The immobilized enzymes used NADH as an electron donor to convert CO_2 successively into methanol, formaldehyde, and formic acid (HCOOH). This co-immobilized multienzyme system was more efficient than free enzyme systems, producing high-productivity products over a larger pH and temperature range.

Polymer based multienzyme system: Using formate dehydrogenase, formaldehyde dehydrogenase, and alcohol dehydrogenase immobilized in a silica sol-gel matrix, Obert et al. [11] showed an efficient polymer-based multienzyme system for converting CO_2 into methanol. In the presence of NADH, this method converted CO_2 step-by-step to formate, formaldehyde, and methanol, resulting in methanol concentrations ranging from 0.001 to 0.05M, which are noticeably greater than those obtained with free enzyme systems. Building on these findings, Wu et al. [12] suggested a sophisticated multienzyme system that makes use of a Silica Sol-Gel matrix that has been modified with polyethylene glycol (SC-PEG). They changed the size of the silica pore to increase the effectiveness of Alcohol Dehydrogenase by encasing Formate dehydrogenase, Formaldehyde dehydrogenase, and Alcohol Dehydrogenase in SC-PEG. Increased yields of methanol synthesis resulted from this change.

By employing three dehydrogenase enzymes, Lu et al. [13] successfully converted CO_2 to methanol in a unique biochemical method. They contrasted enzyme systems in free form with enzymes immobilized in pure alginate gel and an alginate gel that has been silica oxide hybridized (ALG-SiO2). With a methanol production yield of 98.1%, the hybrid gel system outperformed the systems with free enzyme and pure alginate gel.

Jiang et al. [14] created a Capsule-a-bed scaffold with guest dehydrogenase microcapsules made using Layer-by-Layer assembly and bio-mineralization techniques in order to improve methanol production even more. Compared to conventional Co-immobilization techniques, this hybrid microcapsule system produced higher methanol yields by spatially dividing microcapsules within the scaffold utilizing Co-encapsulation technology. By using a p-type indium phosphide semiconductor photoelectrode modified with Metal-dependent Formate dehydrogenase from Pseudomonas oxalaticus, Parkinson et al. [15] pioneered a novel method of CO_2 reduction to formate and 80-93% of formate was produced as a result.

Multienzyme system with cofactor regenerating system: El-Zaheb et al. [16] suggested a unique method for recovering NADH that makes use of glutamate dehydrogenase, an extra enzyme, for cofactor regeneration. Four enzymes were encapsulated within polystyrene particles using a co-immobilization technique: glutamate dehydrogenase, alcohol dehydrogenase, formaldehyde dehydrogenase, and formate dehydrogenase. This process made it possible for CO_2 to be converted to methanol one after the other through effective cofactor-enzyme interactions. After 11 reuse cycles, they reported an approximately 80% retention of enzyme productivity and a methanol production rate of 0.02μmol/h/g enzyme. Zhang et al. [17] also created a Glutamate Dehydrogenase (GDH)-based cofactor regeneration system for CO_2 reduction to methanol. Their method involved using NADH as the cofactor and encasing the four enzymes in hollow nanofibers made by coaxial electrospinning. To improve CO_2 absorption, carbonic anhydrase was added to the hollow nanofiber's exterior surface. A noteworthy accomplishment in methanol production efficiency was made possible by the nanofiber, which was made of Polyurethane A85E (PU) with dissolved Cationic polyelectrolyte (PAH, poly (allylamine hydrochloride)), as demonstrated in. The nanofiber enabled a methanol yield of roughly 103.2%. In order to replace glutamate dehydrogenase (GDH) with phosphote dehydrogenase (PTDH) for cofactor replenishment during the conversion of CO2 to methanol, Cazzels et al. [18] looked into this possibility. Three regeneration systems were compared: PTDH, Glycol Dehydrogenase (GlyDH), and a photosystem that was isolated and mimicked natural chloroplasts. Three regeneration systems that were integrated with NADH and encapsulated within silica nanoparticles utilizing phospholipids were compared: PTDH, Glycol Dehydrogenase (GlyDH), and a Photosystem that mimicked natural chloroplasts isolated from spinach leaves. According to the study's findings, the PTDH-based system performed better than the others, showing a 55-fold increase in methanol production efficiency over free enzyme systems.

A unique photochemical enzymatic regeneration system based on a synthetic carbon nitride array material was presented by Liu et al. [19]. This system included NADH and three dehydrogenase enzymes into the carbon nitride array, which served as a template for cofactor renewal and enzyme immobilization. With TEOS acting as an electron donor and a rhodium complex acting as a photosensitizer, they were able to produce methanol with a yield of 0.21 mmol MeOH-1 Genzyme-1 when exposed to visible light.

Conclusions, Future Aspects and Challenges

Climate change remains a critical global challenge, necessitating concerted efforts from policymakers, researchers, and industry stakeholders to mitigate its effects. The escalating levels of CO_2, primarily from anthropogenic activities, have intensified the urgency to develop effective solutions for greenhouse gas emissions. The photocatalytic conversion of CO_2 into valuable hydrocarbon fuels like methanol offers a promising pathway for sustainable energy production. Bio-inspired photocatalysts, which emulate natural photosynthesis, present a sustainable and efficient alternative to traditional metal-based systems. Recent advancements in enzyme-based systems, particularly through innovative immobilization techniques, have shown great potential in enhancing catalytic efficiency and stability. By optimizing enzyme composition, assembly, and immobilization, these systems can maximize methanol production while minimizing environmental impact. Furthermore, the role of oxidoreductase enzymes in CO_2 reduction, despite facing challenges such as sensitivity and degradation, has been pivotal in advancing this field. Immobilization techniques have improved enzyme stability and promoted reusability, making industrial-scale applications viable through the use of bioreactors and other innovative methods.

Future research should focus on overcoming the challenges associated with enzymatic CO_2 conversion, such as the sensitivity and potential degradation of dehydrogenases under sunlight and high temperatures. Developing more robust and stable enzyme systems through advanced immobilization techniques and exploring alternative approaches like natural photosystem II, semi-artificial photosynthesis, and de novo catalysts customized

with metal ions can enhance the efficiency and scalability of CO_2 reduction processes. Additionally, integrating computational methods and molecular simulations can provide deeper insights into the active sites of enzymes, leading to further improvements in catalytic performance. Addressing these challenges will be crucial for achieving efficient and sustainable CO_2 utilization, ultimately contributing to a greener and more sustainable future. Continued interdisciplinary collaboration and innovation will be key to advancing these technologies and realizing their full potential in combating climate change.

References

1. Lee ZH, Sethupathi S, Lee KT, Bhatia S, Mohamed AR (2013) An overview on global warming in Southeast Asia: CO_2 emission status, efforts done, and barriers. Renewable and Sustainable Energy Reviews 28: 71-81.
2. IPCC (2018) Summary for Policymakers.
3. Gusain R, Kumar P, Sharma OP, Jain SL, Khatri OP (2016) Reduced graphene oxide-CuO nanocomposites for photocatalytic conversion of CO_2 into methanol under visible light irradiation. Applied Catalysis B: Environmental 181: 352-362.
4. Pragya S, Rohit S (2021) Utilization of bio-inspired catalyst for CO_2 reduction into green fuels: Recent advancement and future perspectives. Journal of CO_2 Utilization 53: 101748.
5. Liu J, Cazelles R, Chen ZP, Zhou H, Galarneau A, Antonietti M (2014) The bioinspired construction of an ordered carbon nitride array for photocatalytic mediated enzymatic reduction. Physical Chemistry Chemical Physics 16: 14699-14705.
6. Feng J, Ma D, Gao S, Liao Y, Feng J, et al. (2023) Recent advances in engineering heterotrophic microorganisms for reinforcing CO_2 fixation based on calvin-benson-bassham cycle. ACS Sustainable Chemistry & Engineering 11(26): 9509-9522.
7. Calzadiaz-Ramirez L, Meyer AS (2022) Formate dehydrogenases for CO_2 utilization. Current Opinion in Biotechnology 73: 95-100.
8. Jinghua W, Yang H, Wen Y, Yanguang L (2017) CO_2 reduction: From the electrochemical to photochemical approach. Advanced Science 4(11): 1700194.
9. Kuwabata S, Tsuda R, Hiroshi Y (1994) Electrochemical conversion of carbon dioxide to methanol with the assistance of formate dehydrogenase and methanol dehydrogenase as biocatalysts. Journal of The American Chemical Society 116(12): 5437-5443.
10. Sun Q, Jiang Y, Jiang Z, Zhang L, Sun X, Li J (2009) Green and efficient conversion of CO_2 to methanol by biomimetic coimmobilization of three dehydrogenases in protamine-templated titania. Industrial and Engineering Chemistry Research 48(9): 4210-4215.
11. Obert R, Dave BC (1999) Enzymatic conversion of carbon dioxide to methanol: enhanced methanol production in silica sol - gel matrices. Journal of the American Chemical Society 121(51): 12192-12193.
12. Wu H, Huang S, Jiang Z (2004) Effects of modification of silica gel and ADH on enzyme activity for enzymatic conversion of CO_2 to methanol. Catalysis Today 98: 545-552.
13. Lu Y, Jiang Z, Xu S, Wu H (2006) Efficient conversion of CO_2 to formic acid by formate dehydrogenase immobilized in a novel alginate - silica hybrid gel. Catalysis Today 115: 263-268.
14. Jiang Y, Sun Q, Jiang Z (2009) Capsules-in-bead scaffold: a rational architecture for spatially separated multienzyme cascade system. Journal of Material Chemistry 19: 9068-9074.
15. Parkinson AB, Weaver PF (1984) Photoelectrochemical pumping of enzymatic CO2 reduction. Nature 309: 148-149.
16. El-Zahab B, Dustin D, Ping W (2007) Particle-tethered NADH for production of methanol from CO_2 catalyzed by coimmobilized enzymes. Analytical Science 99(3): 508-514.
17. Zhang Z, Zhang X, Xiaoyan J (2022) Developing and regenerating cofactors for sustainable enzymatic CO_2 conversion. Processes 10(2): 230.
18. Cazelles R, Drone J, Fajula F, Ersen O, Moldovan S, et al. (2013) Reduction of CO_2 to methanol by a polyenzymatic system encapsulated in phospholipids-silica nanocapsules. New Journal of Chemistry 37: 3721-3730.
19. Liu J, Cazelles R, Chen ZP, Zhou H, Galarneau A, et al. (2014) The bioinspired construction of an ordered carbon nitride array for photocatalytic mediated enzymatic reduction. Physical Chemistry Chemical Physics 16: 14699-14705.