🌐 *United International Journal of Engineering and Sciences* 🌐
(UIJES – A Peer-Reviewed Journal); ISSN:2582-5887 | Impact Factor:8.075(SJIF)
📓 *Volume 5 | Special Issue 1 | 2025 Edition*
National Level Conference on "Advanced Trends in Engineering Science & Technology" – Organized by RKCE

Chemical Recycling of Carbon Dioxide to Methanol and Dimethyl Ether: Transforming Greenhouse Gas into Renewable, Carbon-Neutral Fuels and Synthetic Hydrocarbons

[1]CH. ADI LAKSHMI DEVI, [2]V. SWARUPA

[1,2] Assistant Professor, Department of Chemistry
[1,2] R K College of Engineering, Vijayawada, India
[1]*devidhayani99@gmail.com*, [2]*vaduguswarupa@gmail.com*

***ABSTRACT*: The chemical recycling of carbon dioxide (CO_2) to produce methanol and dimethyl ether (DME) offers a promising pathway to mitigate greenhouse gas emissions while generating renewable, carbon-neutral fuels and valuable synthetic hydrocarbons. This approach not only addresses the pressing issue of rising atmospheric CO_2 levels but also capitalizes on CO_2 as a sustainable feedstock for fuel synthesis. Various catalytic processes and innovative technologies are explored to optimize the conversion efficiency, selectivity, and economic feasibility of these reactions. This review highlights recent advancements, challenges, and future directions in the field, emphasizing the role of methanol and DME in sustainable energy systems and their potential as substitutes for fossil fuels.**

I.INTRODUCTION

In the pursuit of sustainable development, converting carbon dioxide (CO_2) into renewable fuels has gained substantial attention as an innovative strategy for reducing global greenhouse gas emissions. Methanol and dimethyl ether (DME) are particularly attractive targets for CO_2 utilization due to their versatility as clean-burning fuels and their role as key building blocks for synthetic hydrocarbons. Advanced catalytic systems, renewable hydrogen sources, and novel reactor technologies are at the forefront of efforts to enhance the efficiency and economic viability of CO_2-to-fuel processes. This paper delves into the technological advancements, process optimizations, and future prospects of CO_2 recycling, emphasizing its potential to revolutionize the energy sector and contribute to a sustainable, circular carbon economy.

I.I PROCESS OF COLLECTING CARBONDOXIDE FROM DIFFERENT SOURCES:

Collecting carbon dioxide (CO_2) from different sources involves various techniques designed to capture and concentrate CO_2 efficiently before it's recycled, stored, or utilized. These processes can be classified based on the sources of CO_2 emissions and the capture methods employed.

Sources of CO_2 for Collection:

1. **Industrial Sources:** Power plants, cement factories, steel manufacturing, chemical industries. These are large, stationary point sources with concentrated CO_2 emissions.

2. **Natural Sources:** Geothermal vents and natural gas fields contain high levels of CO_2.
3. **Biological Sources:** Fermentation processes in breweries and bioethanol production.
4. **Air Capture:** Capturing CO_2 directly from ambient air, typically through direct air capture (DAC) technology.

I.2 Methods of CO_2 Collection:

1. **Pre-Combustion Capture:**
   - Involves removing CO_2 before the combustion process.
   - Applied mainly in integrated gasification combined cycle (IGCC) power plants.
   - Fuel (coal, natural gas) is converted to syngas (a mix of H_2 and CO_2). The CO_2 is separated, and the H_2 is used as a clean fuel.
2. **Post-Combustion Capture:**
   - Captures CO_2 from flue gases after combustion.
   - Typically used in power plants and industrial facilities.
   - Involves chemical absorption using solvents like amines (monoethanolamine - MEA), potassium carbonate, or ionic liquids.
   - Physical adsorption techniques using zeolites, activated carbon, and metal-organic frameworks (MOFs) are also employed.
3. **Oxy-Fuel Combustion:**
   - Combustion of fossil fuels with pure oxygen instead of air, resulting in a flue gas that is mainly CO_2 and water vapor.
   - The water vapor is condensed, leaving almost pure CO_2 for capture.
4. **Chemical Looping Combustion (CLC):**
   - Utilizes metal oxides as oxygen carriers to combust fuels.
   - CO_2 is separated inherently from nitrogen, making it easier to capture.
5. **Direct Air Capture (DAC):**
   - Captures CO_2 from ambient air using sorbents or solid absorbents.
   - Requires large surface areas and significant energy input, making it cost-intensive but effective for addressing dispersed emissions.
   - Solid sorbents like metal-organic frameworks (MOFs) and liquid sorbents like potassium hydroxide (KOH) are common.

I.3 CO_2 Compression and Storage:

After capture, the collected CO_2 is compressed to a high-pressure, supercritical state for transportation via pipelines or ships. It can then be:

- **Stored in geological formations:** Depleted oil and gas reservoirs, saline aquifers, or un mineable coal seams.
- **Used in Enhanced Oil Recovery (EOR):** CO_2 is injected into oil fields to increase oil recovery while storing CO_2 underground.
- **Utilized in chemical recycling:** For producing methanol, dimethyl ether (DME), and other chemicals.

II.METHODS TO CONVERT CARBONDIOXIDE INTO METHANOL WITH DIAGRAMS:

Converting carbon dioxide (CO_2) into methanol (CH_3OH) is a promising method for recycling CO_2 and producing valuable fuels and chemicals. There are several methods for this conversion, each involving unique catalytic processes and reactor systems.

1. **Hydrogenation of CO_2 to Methanol**

Process Overview:

This is the most common and industrially viable method, where CO_2 reacts with hydrogen (H_2) over a catalyst to produce methanol.

- **Reaction:** $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$
- **Catalysts:** $Cu/ZnO/Al_2O_3$, Pd/ZnO, and In_2O_3
- **Conditions:** High pressure (50–100 bar) and moderate temperature (200–300 °C)

[CO_2] + [H_2] → [Reactor with Catalyst] → [Separator] → [Methanol + Water]
│ Catalyst: $Cu/ZnO/Al_2O_3$

2. **Electrochemical Reduction**

Process Overview:

Uses renewable electricity to convert CO_2 to methanol through an electrochemical cell.

- **Reaction:** $CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$
- **Electrodes:** Copper-based, indium oxide, and graphene-modified electrodes
- **Electrolytes:** Aqueous or ionic liquid electrolytes
- **Advantages:** Can be powered by renewable energy sources like solar or wind.

[Anode] → H_2O → $O_2 + H^+ + e^-$
[CO_2] + $H^+ + e^-$ → [Cathode] → CH_3OH

3. **Photocatalytic Conversion**

Process Overview:

Uses solar energy to drive the reduction of CO_2 to methanol using a photocatalyst.

- **Photo catalysts:** TiO_2, ZnO, CdS, and graphene-based materials

- **Light Source:** Solar or artificial UV light
- **Reaction:** $CO_2 + H_2O$ + light → $CH_3OH + O_2$

Diagram:

[CO_2] + [H_2O] + [Photocatalyst + UV Light] → $CH_3OH + O_2$

4. **Biocatalytic Conversion**

Process Overview:

Utilizes engineered microorganisms or enzymes to convert CO_2 into methanol.

- **Microorganisms:** Genetically modified cyanobacteria, yeast, and algae
- **Enzymes:** Formate dehydrogenase, formaldehyde dehydrogenase, alcohol dehydrogenase
- **Reaction:** CO_2 + NADH + ATP → CH_3OH (via multi-step enzymatic pathways)
- **Conditions:** Mild temperature and atmospheric pressure

Diagram:

[CO_2] + [Microorganisms/Enzymes] + [NADH + ATP] → $CH_3OH + H_2O$

Comparison of Methods:

Method	Catalyst/Material	Energy Source	Temperature & Pressure	Scalability	CO_2 Conversion Efficiency
Hydrogenation	$Cu/ZnO/Al_2O_3$	Thermal	200–300 °C, 50–100 bar	High	High
Electrochemical	Copper-based electrodes	Electrical	Room temperature	Medium	Moderate
Photocatalytic	TiO_2, ZnO, CdS	Solar/UV	Room temperature	Low	Low
Biocatalytic	Enzymes or engineered microbes	Biological	Mild conditions	Low	Moderate

III..METHODS TO CONVERT CARBONDIOXIDE INTO DIMETHYLETHER WITH DIAGRAMS:

Converting carbon dioxide (CO_2) into dimethyl ether (DME) is an innovative approach to recycling CO_2 while producing a clean, versatile fuel. DME can serve as a diesel substitute, LPG alternative, and a valuable chemical feedstock.

1. **Direct CO_2 Hydrogenation to DME (One-Step Process)**

Process Overview:

In this method, CO_2 is directly hydrogenated to DME in a single reactor using a bifunctional catalyst. The process combines CO_2 hydrogenation to methanol and subsequent methanol dehydration to DME.

- **Reactions:**
  - $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$ (Methanol Synthesis)
  - $2CH_3OH \rightarrow CH_3OCH_3 + H_2O$ (Dehydration to DME)
- **Catalysts:** Hybrid catalysts like $Cu/ZnO/Al_2O_3$ combined with γ-Al_2O_3 or zeolites (H-ZSM-5).
- **Conditions:** 250–300 °C, 30–80 bar

Diagram:

[CO_2] + [H_2] → [Reactor with Bifunctional Catalyst] → [Separator] → DME + H_2O

(Methanol Synthesis + Dehydration)

2. **Indirect CO_2 Hydrogenation to DME (Two-Step Process)**

Process Overview:

This method first converts CO_2 to methanol, followed by the dehydration of methanol to DME.

- **Step 1:** $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$ (Methanol synthesis)
- **Step 2:** $2CH_3OH \rightarrow CH_3OCH_3 + H_2O$ (Methanol dehydration)
- **Catalysts:**
  - Methanol synthesis: $Cu/ZnO/Al_2O_3$
  - Methanol dehydration: γ-Al_2O_3, H-ZSM-5
- **Conditions:**
  - Methanol synthesis: 200–300 °C, 50–100 bar
  - Methanol dehydration: 250–350 °C, atmospheric to moderate pressure

Diagram:

[CO_2] + [H_2] → [Reactor 1 - Methanol Synthesis] → [Separator] → CH_3OH

↓

[CH_3OH] → [Reactor 2 - Dehydration] → [Separator] → DME + H_2O

3. Electrochemical Conversion of CO_2 to DME

Process Overview:

This emerging method uses renewable electricity to drive the reduction of CO_2 to DME via an electrochemical cell.

<

- **Reactions:**
  - $CO_2 + H_2O$ + electricity $\rightarrow CH_3OCH_3 + O_2$

- **Electrocatalysts:** Copper-based, indium oxide, bismuth-based materials
- **Electrolytes:** Ionic liquids or aqueous electrolytes
- **Conditions:** Room temperature, atmospheric pressure, renewable electricity input

Diagram:

[Anode] → H_2O → $O_2 + H^+ + e^-$

[CO_2] + $H^+ + e^-$→ [Cathode] → CH_3OCH_3

4. Biocatalytic Conversion

Process Overview:

Utilizes genetically engineered microorganisms or enzymes to convert CO_2 to DME through methanol as an intermediate.

- **Microorganisms:** Engineered algae, yeast, and bacteria
- **Enzymes:** Formate dehydrogenase, formaldehyde dehydrogenase, alcohol dehydrogenase, and methanol dehydrogenase
- **Reaction Pathway:**
  - CO_2→ HCOOH → CH_2O → CH_3OH → CH_3OCH_3
- **Conditions:** Mild temperatures, atmospheric pressure, renewable feedstocks

Diagram:

[CO_2] + [Microorganisms/Enzymes] → Methanol → DME

Comparison of Methods:

Method	**Catalyst/Material**	**Energy Source**	**Temperature & Pressure**	**Scalability**	**CO_2 Conversion Efficiency**
Direct Hydrogenation	$Cu/ZnO/Al_2O_3$ + γ-Al_2O_3/Zeolites	Thermal	250–300 °C, 30–80 bar	High	High
Indirect Hydrogenation	$Cu/ZnO/Al_2O_3$, γ-Al_2O_3	Thermal	200–350 °C, moderate	High	Moderate to High
Electrochemical	Copper-based electrodes	Electrical (Renewable)	Room temperature	Low	Moderate
Biocatalytic	Engineered	Biological	Mild	Low	Moderate

Method	Catalyst/Material	Energy Source	Temperature & Pressure	Scalability	CO_2 Conversion Efficiency
	microorganisms/enzymes		conditions		

IV. Advantages of Chemical Recycling of CO_2 to Methanol and Dimethyl Ether (DME)

Converting carbon dioxide (CO_2) into methanol and DME offers numerous environmental, economic, and technological benefits. This approach not only helps mitigate the negative impacts of greenhouse gases but also creates valuable products from waste CO_2.

1. Environmental Benefits:

- **Reduction of Greenhouse Gas Emissions:**
  - This process captures and utilizes CO_2, reducing its release into the atmosphere and mitigating climate change.
- **Air Quality Improvement:**
  - Methanol and DME produce fewer harmful emissions like NO_x, SO_x, and particulate matter compared to conventional fossil fuels, contributing to cleaner air.
- **Sustainable Carbon Cycle:**
  - By recycling CO_2 into fuels and chemicals, a circular carbon economy is promoted, minimizing the carbon footprint.

2. Renewable Energy Integration:

- **Use of Renewable Hydrogen:**
  - The process can use green hydrogen produced via renewable energy (solar, wind) for CO_2 hydrogenation, enhancing sustainability.
- **Energy Storage:**
  - Methanol and DME serve as energy carriers, storing renewable energy for later use in various sectors, including power generation and transportation.

3. Economic Benefits:

- **Value Creation from Waste CO_2:**
  - CO_2, traditionally seen as a waste product, is transformed into valuable methanol and DME, adding economic value.
- **Market Potential:**
  - Growing demand for low-carbon fuels and chemicals increases the market potential for methanol and DME, creating new business opportunities.
- **Carbon Credits:**
  - Industries adopting CO_2 recycling can benefit from carbon credits, which can offset production costs and boost profitability.

4. Energy Security:

- **Reduction of Fossil Fuel Dependency:**
  - Methanol and DME provide alternatives to fossil fuels, reducing reliance on imported petroleum and enhancing energy security.
- **Diversification of Energy Sources:**
  - The production of synthetic fuels diversifies the energy portfolio, ensuring stable energy supply during fluctuations in fossil fuel markets.

5. Technological Advancements:

- **Catalyst Development:**
  - Research into efficient catalysts for CO_2 conversion drives innovation, resulting in higher efficiency, selectivity, and lower costs.
- **Scalability:**
  - The technology has the potential to scale up from pilot projects to industrial applications, making large-scale CO_2 utilization feasible.

6. Versatile Applications:

- **Fuel Versatility:**
  - Methanol and DME can be used as clean-burning fuels in transportation, power generation, and heating applications.
- **Chemical Feedstock:**
  - They are valuable raw materials for producing formaldehyde, plastics, adhesives, and synthetic hydrocarbons.
- **Hydrogen Carrier:**
  - Methanol can be reformed to produce hydrogen, making it a strategic fuel for hydrogen-based energy systems.

7. Positive Societal Impact:

- **Job Creation:**
  - Expanding CO_2 recycling industries can create new jobs in research, technology development, and manufacturing.
- **Sustainable Development:**
  - Aligns with global sustainability goals, including the United Nations' Sustainable Development Goals (SDGs) related to climate action and sustainable energy.

8. Long-Term Climate Strategy:

- **Negative Emission Technology:**
  - When combined with carbon capture and storage (CCS), this approach can achieve negative emissions, reversing CO_2 accumulation.
- **Climate Change Mitigation:**
  - Helps nations meet international climate commitments, such as the Paris Agreement, by reducing overall greenhouse gas emissions.

The chemical recycling of CO_2 to methanol and DME stands out as a multifaceted solution with far-reaching benefits, addressing environmental challenges while generating economic and technological value.

V. Applications of Chemical Recycling of CO_2 to Methanol and Dimethyl Ether (DME)

Converting carbon dioxide (CO_2) into methanol and dimethyl ether (DME) offers a wide range of practical applications across various industries. These applications not only help mitigate CO_2 emissions but also promote the use of renewable, carbon-neutral fuels and valuable chemical feedstocks. Below are the primary applications:

1. Energy and Fuel Sector:

- **Alternative Fuels:**
  - **Methanol:** Used as a direct fuel in internal combustion engines or blended with gasoline, reducing harmful emissions.
  - **DME:** A clean-burning diesel substitute with near-zero particulate emissions, ideal for transportation and industrial use.
- **Power Generation:**
  - Both methanol and DME can be used in power plants as cleaner fuels, helping reduce the carbon footprint of energy production.
- **Fuel Cells:**
  - Methanol serves as a hydrogen carrier for fuel cells, offering a renewable and portable energy source for electronic devices and vehicles.

2. Chemical Industry:

- **Feedstock for Chemicals:**
  - Methanol is a precursor for producing formaldehyde, acetic acid, and various polymers.
  - DME acts as a raw material in organic synthesis, replacing traditional, fossil-derived inputs.
- **Aerosol Propellants:**
  - DME, being non-toxic and environmentally friendly, is used as a propellant in aerosol sprays, cosmetics, and pharmaceuticals.
- **Solvents:**
  - Methanol is a widely used solvent in laboratory research, chemical processes, and pharmaceutical manufacturing.

3. Environmental Applications:

- **Carbon Capture and Utilization (CCU):**
  - Recycling CO_2 into methanol and DME helps sequester carbon, contributing to emission reduction targets.
- **Air Quality Improvement:**
  - Replacing traditional fossil fuels with methanol and DME can significantly reduce air pollutants, such as NO_x, SO_x, and particulate matter.

4. Transportation and Mobility:

- **Automotive Fuels:**
  - Methanol-blended fuels (M85, M100) and DME as a diesel alternative help in reducing vehicle emissions.
- **Marine and Aviation Fuels:**

- Methanol is considered a promising alternative marine fuel to comply with the International Maritime Organization's (IMO) emission regulations.
- Research is exploring the use of DME in aviation for lower-carbon flights.

4. Renewable Hydrogen Production:

- **Hydrogen Carrier:**
  - Methanol can be reformed to produce hydrogen, providing a cleaner, more sustainable source for hydrogen-based technologies.

5. Industrial Applications:

- **Refrigerants:**
  - DME is used as a low-global warming potential (GWP) refrigerant in refrigeration and air conditioning systems.
- **Blowing Agents:**
  - DME is used in the production of polyurethane foams as a blowing agent, reducing reliance on harmful CFCs and HFCs.

6. Economic and Energy Security:

- **Reducing Fossil Fuel Dependency:**
  - Utilizing methanol and DME as renewable fuels helps reduce dependence on fossil fuel imports, enhancing energy security.
- **Economic Opportunities:**
  - CO_2-to-fuel technologies create new economic opportunities through carbon credits, technology development, and sustainable fuel markets.

V. CONCLUSION

The chemical recycling of carbon dioxide (CO_2) into methanol and dimethyl ether (DME) represents a significant step toward sustainable energy solutions and climate change mitigation. By transforming CO_2 from an environmental liability into a valuable feedstock, this approach aligns with the principles of a circular carbon economy. The various catalytic processes and advanced technologies explored in this review demonstrate the potential for optimizing reaction efficiency, selectivity, and scalability. Despite existing challenges in catalyst development, process integration, and economic viability, continuous research and innovation are driving progress toward commercializing these technologies. As renewable, carbon-neutral fuels, methanol and DME hold promise as sustainable alternatives to fossil fuels, contributing to a cleaner, more sustainable global energy system. Achieving large-scale deployment of CO_2-to-fuel technologies will be pivotal in reducing greenhouse gas emissions and advancing a low-carbon future.

REFERENCES

1. https://pubs.acs.org/doi/abs/10.1021/jo801260f
2. https://doi.org/10.1021/bk-2024-1491.ch003
3. https://doi.org/10.1021/acsomega.4c06919

4. https://doi.org/10.1021/acs.jpca.4c01338
5. https://doi.org/10.1021/acscatal.4c02513
6. https://doi.org/10.1021/acs.chemrev.3c00148
7. https://doi.org/10.1021/acs.iecr.3c03776
8. https://doi.org/10.1021/acsomega.3c02344