CAPÍTULO 4

CONVERTING CO₂ EMISSIONS FROM BIO-BASED INDUSTRIES INTO SUSTAINABLE CHEMICALS TO MITIGATE CLIMATE CHANGE: A PRACTICAL METHODOLOGY FROM THE PERSPECTIVE OF THE R&D PROJECTS

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ABSTRACT: The transition to a low-carbon economy demands innovative approaches to mitigate the growing levels of greenhouse gases, particularly carbon dioxide (CO₂). This chapter explores the valorisation of biogenic CO₂ emissions from biobased industries, positioning it as both an environmental necessity and an economic opportunity. The accelerating climate crisis, driven by rising levels of greenhouse gases (GHGs) in the atmosphere, has intensified the global push for innovative mitigation strategies. Among these gases, CO, is the most abundant, contributing approximately 75% of global GHG emissions. Industrial activities, transportation, and fossil fuelbased energy generation are the primary sources of these emissions. However, as the world transitions toward a lowcarbon economy, bio-based industries are emerging as pivotal players in the dual role of reducing emissions and contributing renewable resources to industrial systems. Bio-based industries encompass sectors that utilize biological resources-such as biomass, agricultural residues, and organic waste—to produce energy, fuels, chemicals, and materials. As a natural consequence of these processes, they generate biogenic CO,, a renewable form of carbon dioxide derived from biological systems rather than fossil fuels. Unlike CO, emitted from fossil sources, biogenic CO, can be seamlessly integrated into circular economy frameworks, allowing for its valorisation into high-value chemicals and fuels that replace carbon-intensive products. Through advanced thermocatalytic, electrocatalytic, and biological technologies, CO, can be transformed into high-value products such as methanol, ethanol, organic acids, and polymers. These products have applications across diverse sectors, including energy, agriculture, and materials, supporting the global shift toward circular economy frameworks. The chapter also outlines a practical R&D methodology for scaling CO, valorisation technologies, emphasizing structured experimentation, data-driven optimization, and integration with renewable energy systems. Despite challenges such as infrastructure limitations, economic barriers, and the need for policy support, emerging innovations and collaborative strategies are paving the way for industrial-scale adoption. By redefining CO₂ as a resource rather than a waste product, bio-based industries can play a pivotal role in achieving climate goals and fostering sustainable industrial growth.

KEYWORDS: Biogenic CO_2 , sustainable chemicals, CO_2 conversion, gas fermentation, renewable energy integration.

1 | OVERVIEW OF BIOGENIC CO, SOURCES IN BIO-BASED INDUSTRIES

Biogenic CO_2 , a renewable form of CO_2 derived from biological processes, is emerging as a crucial resource in the transition to a sustainable, circular economy. Unlike CO_2 emissions from fossil fuels, which contribute to the accumulation of greenhouse gases in the atmosphere, biogenic CO_2 is part of the short-term carbon cycle, making its utilization inherently carbon-neutral. Bio-based industries, which focus on producing energy, fuels, and chemicals from organic and renewable resources, generate significant volumes of biogenic CO_2 as a by-product. These streams of CO_2 , often concentrated and consistent, hold immense potential for valorisation into sustainable chemicals and fuels.

Several processes within bio-based industries are particularly important for generating biogenic CO_2 . Each offers unique characteristics that determine its suitability for downstream conversion applications. The following discussion explores the primary sources of biogenic CO_2 , their advantages, and the opportunities they present for sustainable industrial processes.

Biogas and biomethane production

Biogas production through anaerobic digestion (AD) of organic materials such as agricultural residues, food waste, and wastewater is one of the most widespread methods for generating biogenic CO₂. The anaerobic digestion process breaks down organic matter to produce a mixture of methane (CH₄) and CO₂, with the latter typically constituting 30-50% of the gas composition. For biogas to be upgraded into biomethane, a purified form suitable for use as a renewable natural gas, the CO₂ must be separated, resulting in a concentrated stream (Fu *et al.*, 2019)tremendous efforts have been devoted to mitigate the CO2 accumulation in the atmosphere. Carbon capture and storage (CCS(Hou *et al.*, 2023).

The CO_2 from biogas upgrading is highly valuable due to its relatively high concentration, which reduces the costs associated with capture and purification. This CO_2 can be used in diverse applications, ranging from GHGs enrichment for agricultural productivity to conversion into methanol and other sustainable chemicals. The economic feasibility of biogas and CO_2 utilization is enhanced by its integration with existing renewable energy systems.

Fermentation processes

Fermentation is another major source of biogenic CO₂, particularly in the production of bioethanol. During fermentation, microorganisms metabolize sugars to produce ethanol, releasing CO₂ as a by-product. For example, the bioethanol industry generates nearly pure CO₂ streams as a result of yeast fermentation (Kurt *et al.*, 2023)(Gao *et al.*, 2020).

The high purity of CO_2 from fermentation processes is advantageous for direct applications, such as carbonation in beverages or as an industrial feedstock for organic acids and biopolymers. These qualities make fermentation-derived CO_2 one of the most economically viable sources of biogenic CO_2 , with minimal need for additional processing before utilization. Additionally, its consistent availability aligns with industrial production cycles, making it a reliable feedstock for scalable applications.

Biomass gasification and pyrolysis

Biomass gasification and pyrolysis are thermal processes that convert organic materials, such as forestry residues and agricultural waste, into syngas—a mixture of carbon monoxide (CO), hydrogen (H₂), and CO₂. Gasification, in particular, is gaining attention as a means of generating renewable energy and raw materials for chemical synthesis (Ning, Li and Zhang, 2023)(Wei *et al.*, 2022)

The CO₂ co-produced during gasification can be separated and valorised into chemicals like methanol or formic acid. These processes provide significant flexibility in terms of feedstock, accommodating a wide range of organic materials, and are well-suited for integration into bio-refineries. The scalability of gasification technologies makes them a promising option for centralized CO₂ utilization in industrial hubs.

Wastewater treatment and algal cultivation

Wastewater treatment facilities are increasingly recognized as sources of biogenic CO₂, as organic matter in wastewater undergoes microbial decomposition, releasing CO₂. Some facilities are now integrating algal cultivation systems that capture CO₂ while simultaneously treating wastewater. Algae not only fix CO₂ through photosynthesis but also produce valuable biomass rich in lipids, proteins, and carbohydrates, which can be processed into biofuels and biochemicals (Kajla, Kumari and Nagi, 2022)(Lee *et al.*, 2022).

Algal systems exemplify the synergy between carbon capture and resource recovery, offering dual environmental benefits. By utilizing CO₂ from fermentation or biogas processes to stimulate algal growth, these systems contribute to a circular economy model while providing sustainable feedstocks for a variety of industries.

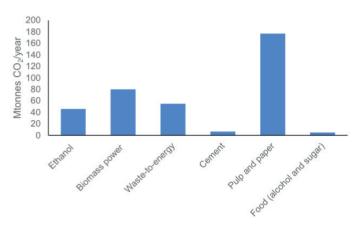


Figure 1: Biogenic CO₂ emissions across North America and Europe in 2024. Available data obtained from https://www.capturemap.no/the-biogenic-co2-breakdown/

Advantages of biogenic CO, utilization

The distinctive properties of biogenic CO₂ set it apart from fossil-derived CO₂. One of its most significant advantages is its renewability, as it is inherently part of the natural carbon cycle. Additionally, biogenic CO₂ streams from fermentation and biogas upgrading are often of higher purity, reducing the costs and complexity of downstream processing (Hou *et al.*, 2023)(Aziz, Abad and Onaizi, 2024). Economic opportunities abound for industries seeking to integrate biogenic CO₂ into their processes. By converting what would otherwise be treated as waste into valuable products, bio-based industries can create new revenue streams while reducing their overall carbon footprint. Moreover, the alignment of biogenic CO₂ utilization with renewable energy systems enables the production of truly carbonneutral or even carbon-negative products.

Challenges in utilizing biogenic CO,

Despite its potential, the utilization of biogenic CO₂ faces several barriers. The lack of infrastructure for the transport and storage of CO₂ remains a significant challenge, particularly for small-scale facilities that produce CO₂ in dispersed locations. Additionally, certain CO₂ streams, such as those from wastewater treatment, may contain impurities that require costly purification processes (Ning, Li and Zhang, 2023). Economic barriers also persist, as the high initial investment costs for capture and conversion technologies can deter widespread adoption. However, these challenges can be mitigated through policy support, such as carbon pricing mechanisms and subsidies for sustainable technologies.

As a summary, biogenic CO₂, derived from bio-based industries, represents a renewable and versatile carbon source that holds great promise for mitigating climate change. Its availability from diverse processes such as biogas production, fermentation, and

algal cultivation underscores its potential to support sustainable industrial transformation. While challenges remain in terms of infrastructure, purification, and economic feasibility, continued advancements in technology and supportive policy frameworks are paving the way for the widespread adoption of biogenic CO₂ utilization. By viewing CO₂ not as waste but as a resource, bio-based industries can play a pivotal role in shaping a circular, low-carbon future.

2 I STATE-OF-THE-ART OF THE TECHNOLOGIES FOR CO, CONVERSION

The transformation of CO₂ into sustainable chemicals and fuels represents a critical frontier in addressing climate change and fostering a circular economy. Biological, thermocatalytic, and electrocatalytic processes are leading approaches in this field, each offering distinct mechanisms and advantages. This section examines these technologies, supported by recent advancements and references to key literature.

Biological processes: Gas fermentation

Biological CO₂ conversion, particularly through gas fermentation, leverages microorganisms to transform CO₂ into high-value products such as ethanol and acetic acid. Acetogens are commonly employed in this context, using the Wood-Ljungdahl pathway (WLP) to fix CO₂ and convert it into organic compounds such as acetic acid, a precursor for biodegradable plastics and biopolymers (Fu et al., 2019) (Lee et al., 2022). Gas fermentation typically combines CO₂ with H₂ or syngas (a mixture of CO, CO₂ and H₂), enabling efficient metabolic pathways. The addition of renewable H₂ is particularly promising for enhancing process sustainability (Hou et al., 2023). The general scheme of the gas fermentation process from CO₂ as feedstock is represented in Figure 2.



Figure 2 -Scheme of gas fermentation process for the production of sustainable chemicals and fuels.

Also known as the reductive acetyl-CoA pathway, the WLP is the only linear CO₂ fixation pathway leading to acetyl-CoA and is regarded as the most efficient non-

photosynthetic mechanism for carbon fixation (Drake et al, 2008). In this linear pathway, two one-carbon units are compensated to form two-carbon building block acetyl-CoA. While these specialized energy-conservation mechanisms are widespread among acetogens, they are absent in traditional model organisms such as *Escherichia coli* or yeast.

Acetogens are ubiquitous in anaerobic environments, such as soil, animal and human guts, sediments, the deep sea, and hot springs. Several hundred acetogens have been isolated to date, spanning at least 25 different genera and including psychrophiles. mesophiles, thermophiles, and halophile (Drake et al., 2006). For biotechnological applications, mostly acetogenic clostridia are considered because many species are among the fastest-growing acetogens, already make products other than acetate, and have been used industrially. These acetogens have been studied for their potential to convert C1 feedstocks into valuable products, including Clostridium ljungdahlii, known for its ability to produce ethanol and acetate efficiently, making it a cornerstone for industrial applications (Köpke et al., 2010). Clostridium autoethanogenum, similar to Clostridium ljungdahlii, excels in ethanol production and has been extensively engineered for improved yields and expanded product portfolios (Liew et al., 2017). Clostridium carboxidivorans produces longer-chain alcohols such as n-butanol alongside acetate and ethanol, offering flexibility in the range of potential products derived from acetyl-CoA. Clostridium drakei and Clostridium scatologenes produce butyric acid, a chemical with applications in the food and chemical industries (Liou et al., 2013). Besides clostridia, a few other species, including Acetobacterium woodii, Moorella thermoacetica, and Eubacterium limosum, are also considered as good producers of added-value products for industrial use (Fakler et al., 2021). Alkalibaculum bacchi thrives in alkaline conditions, producing acetate and ethanol, which makes it useful for specific industrial setups (Liu et al., 2012). Finally, Butyribacterium methylotrophicum specializes in producing n-butanol and butyrate, further diversifying the potential outputs from gas fermentation processes (Humphreys et al., 2022).

| Microorganism | Product | Carbon conversion efficiency (%) | Operating conditions | Reference |
|----------------------------|---------------------------|--|---|--------------------------|
| Clostridium Ijungdahlii | Ethanol | 85.0 | 37°C, Anaerobic, CO ₂ /H ₂ /CO | Infantes et al., 2020 |
| Moorella thermoacetica | Acetate | 88.3 | 55°C, Anaerobic, CO ₂ /H ₂ | Harahap et al., 2023 |
| Acetobacterium woodii | Acetate, acetone, formate | 64.8 | 30°C, Anaerobic, CO ₂ /H ₂ /N ₂ | Tarraran et al., 2022 |

Table 1 Examples of microorganisms and conversion efficiencies in gas fermentation

Microbial systems are celebrated for their high specificity in producing multicarbon compounds, which are challenging to synthesize through chemical methods. For example, gas fermentation has been industrially optimized to yield significant quantities of acetic acid

and alcohols, reducing reliance on fossil-based precursors (Fu et al., 2019) (Lee et al., 2022). The versatility of acetogens lies in their ability to produce a wide range of chemicals from C1 feedstocks, with the main products including acetate, which serves as a precursor for polymers, solvents, and other chemicals, ethanol, which is extensively used in fuel, beverages, and industrial applications, and 2,3-butanediol, an intermediate for synthetic rubber, pharmaceuticals, and other materials. Other notable products include n-butanol and butyric acid, used in manufacturing solvents, plastics, and perfumes, and 1,3-butadiene, which is essential for synthetic rubber production and can now be synthesized through advanced metabolic engineering from intermediates like 2,3-butanediol.

| Compound | Titer | Yield | Productivity | Microorganism | Reference |
|----------|--------|---------------------|---------------------|-----------------------------------|----------------------------------|
| Acetate | 833 mM | n.a | 479 mmol/l/ day | A. woodii | (Straub et al., 2014) |
| Acetone | 52 mM | n.a. | 10.9 mmol/l/ day | A. woodii (GM) | (Hoffmeister et al., 2016) |
| Butanol | 6 mM | 0.074 mol/mol CO | 3.5 mmol/l/ day | C.autoethanogenum/ C. kluyveri | (Diender et al., 2016) |
| Butyrate | 220 mM | n.a. | 227 mmol/l/ day | C. ljungdahlii | (Vasudevan et al., 2014) |
| Caproate | 8.6 mM | n.a. | 14.7 mmol/l/ day | C. ljungdahlii | (Vasudevan et al., 2014) |
| Ethanol | 450 mM | 0.14 mol/mol CO | 193 mmol/l/ day | C. ljungdahlii | (Richter et al., 2013) |
| Hexanol | 4 mM | 0.05 mol/mol CO | 2 mmol/l/day | C.autoethanogenum/ C. kluyveri | (Diender et al., 2016) |

Table 2: Examples of titer, yield and volumetric productivity of some important gas fermentation target products.

Industrial initiatives have embraced the potential of acetogens, with companies like LanzaTech (https://lanzatech.com/) leading the commercialization of acetogen-based fermentation technologies to produce ethanol and other chemicals using industrial waste gases. In this sense, LanzaTech has demonstrated scalability with facilities in China, Belgium, and the USA, showcasing the ability to transform steel mill off-gases and other emissions into valuable products (Liew et al, 2016).

Despite their immense potential, challenges remain in optimizing acetogens for industrial applications. Genetic engineering for some acetogens is less advanced compared to model organisms like Escherichia coli or Saccharomyces cerevisiae, requiring further development of tools to enhance product yields and expand metabolite diversity. Mass transfer limitations in gas-to-liquid substrate delivery, such as for CO and H2, present operational challenges that need innovative reactor designs and process strategies to overcome. Energy requirements for CO₂-based pathways necessitate external energy inputs, and integrating renewable energy sources like hydrogen derived from water electrolysis

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could enhance sustainability. Efficient and cost-effective methods for product recovery and purification remain essential for the commercialization of acetogen-based processes.

As a conclusion, acetogenic microorganisms represent a transformative solution to global challenges, such as greenhouse gas emissions and resource scarcity, by converting waste gases into valuable chemicals, thus contributing to both environmental sustainability and economic opportunity. Continued research in genetic engineering, process optimization, and industrial scaling is expected to unlock the full potential of these remarkable microorganisms and their capacity to drive a sustainable bioeconomy applications (Zhou et al., 2024) (Aziz et al., 2024).

2.1 Thermocatalytic and electrocatalytic processes

Thermocatalytic and electrocatalytic processes are chemically driven approaches that offer rapid reaction rates and compatibility with industrial-scale operations. These methods rely on catalysts to transform ${\rm CO_2}$ into valuable products, ranging from fuels to polymers.

Thermocatalytic processes

Thermocatalysis involves the use of heat and catalysts to drive the reduction of CO₂. Among the most widely studied thermocatalytic pathways is CO₂ hydrogenation, where CO₂ reacts with hydrogen to produce methanol. Copper-zinc-aluminium catalysts are commonly used, achieving high efficiencies at elevated temperatures (200–300°C) and pressures (20–50 bar) (Hou *et al.*, 2023)(Wei *et al.*, 2022). Methanol synthesis is crucial for producing fuels, plastics, and solvents, making it a cornerstone of the chemical industry.

Another significant thermocatalytic pathway is Fischer-Tropsch synthesis, which first converts CO_2 into syngas through a reverse water-gas shift reaction. Syngas is then catalytically processed into hydrocarbons like diesel and kerosene using iron or cobalt catalysts. This method is gaining traction for producing sustainable aviation fuels and e-diesel.

Electrocatalytic processes

Electrocatalysis utilizes electricity, preferably from renewable sources, to reduce CO₂ in electrochemical cells. Products of this method include formic acid, methanol, and hydrocarbons such as ethylene and ethanol. Copper-based catalysts are particularly effective for producing multicarbon compounds, with advances in nanostructured designs enhancing reaction rates and product selectivity (Wu *et al.*, 2021) (Ning, Li and Zhang, 2023).

Electrocatalytic systems are well-suited for integration with renewable energy,

such as solar or wind power. Solar-driven systems, which couple photovoltaic cells with electrochemical reactors, have demonstrated potential for carbon-neutral operations. However, these systems face challenges such as competition from the hydrogen evolution reaction (HER), which reduces CO₂ reduction efficiency, and durability issues with electrode materials during prolonged operations (Gao *et al.*, 2020) (Kurt *et al.*, 2023).

Hybrid systems combining thermocatalysis and electrocatalysis are being developed to leverage the strengths of both methods. For instance, thermal activation of CO₂ followed by electrochemical reduction has shown promise in producing complex products with higher yields (Hou et al., 2023) (Aziz et al., 2024).

Emerging technologies

Emerging technologies are expanding the possibilities for CO₂ conversion, offering innovative pathways and improved efficiencies. Photoelectrochemical systems, for instance, integrate the principles of electrocatalysis and photocatalysis to harness solar energy for CO₂ reduction. These systems utilize light-absorbing semiconductor electrodes to catalyze reactions, presenting a pathway for truly sustainable operations. Plasma-assisted CO₂ conversion is another cutting-edge approach. This technology uses ionized gas (plasma) to activate CO₂ molecules, facilitating their conversion into syngas or hydrocarbons. Plasma-assisted systems are particularly suitable for decentralized applications due to their compact reactor designs and high reaction rates (Alli *et al.*, 2023).

Hybrid electrochemical-biological systems combine the strengths of electrocatalysis and microbial fermentation. In these systems, CO_2 is first converted into simple compounds like formate or acetate via electrochemical reduction, which are then metabolized by microorganisms to produce higher-value chemicals such as alcohols and biopolymers. These systems offer enhanced flexibility and efficiency, making them a promising avenue for future research and industrial implementation (Chu *et al.*, 2020).

As a conclusion, talking about CO₂ conversion we can find diverse strategies required to transform a waste product into valuable resources. Biological processes, particularly gas fermentation, are well-suited for producing complex organic compounds under energy-efficient conditions. Thermocatalytic and electrocatalytic pathways, supported by innovations in catalysts and reactor design, offer rapid conversion rates and scalability for industrial applications. Emerging technologies, such as photoelectrochemical systems and plasma-assisted conversion, further expand the scope of CO₂ valorisation. Continued advancements in these fields, coupled with supportive policies and renewable energy integration, will be critical for overcoming current limitations and achieving large-scale adoption.

3 I APPLICATIONS AND MARKET POTENTIAL OF SUSTAINABLE CHEMICALS

The conversion of CO_2 into sustainable chemicals has rapidly evolved as a pivotal strategy in addressing global climate change while creating economic opportunities. By leveraging biological, thermocatalytic, and electrocatalytic technologies, industries are unlocking new avenues for transforming CO_2 into high-value products. These products span across a variety of sectors, including energy, chemicals, and agriculture, offering a pathway to reduce dependence on fossil fuels and lower greenhouse gas emissions. This section explores the key applications and market dynamics of sustainable chemicals derived from CO_2 .

Key products derived from CO, conversion

One of the most promising applications of CO₂ conversion is the production of alcohols, such as methanol and ethanol. Methanol serves as a versatile chemical feedstock and an energy carrier. It is used in producing formaldehyde, acetic acid, and dimethyl ether (DME), which are essential for manufacturing plastics, adhesives, and fuel additives substitute for traditional fossil fuels in clean energy systems has further bolstered its market demand.

Ethanol, another is widely utilized as a biofuel and as a precursor for ethylene production, a primary building block for plastics and resins. Its sustainable production through biological and chemical pathways aligns with the global push for decarbonizing transportation and industrial processes.

In addition to alcohols and organics acids are crucial outputs of CO₂ conversion. Formic acid, often produced via electrocatalytic reduction of CO₂, finds applications in agriculture as a silage preservative and in energy storage as a hydrogen carrier. Acetic acid, synthesized through gas fermentation, can be transformed into biopolymers and other biodegradable materials by additional fermentation processes, expanding its role in sustainable packaging and consumer goods.

Polymers and olefins

The production of polymers is a transformative solution for the plastics and materials industry. Polycarbonates, produced by coupling CO_2 with epoxides, provide lightweight and durable materials for use in automotive components, electronics, and packaging. Meanwhile, the catalytic conversion of CO_2 into ethylene and propylene—key olefins—represents a significant breakthrough in reducing the carbon footprint of the polymer industry.

These CO₂-derived materials not only reduce reliance on petrochemical feedstocks but also support incorporating renewable carbon sources into industrial supply chains.

Energy and fuel applications

CO₂-derived chemicals are playing an increasingly critical role in the energy sector. Methanol and formic acid are being utilized as energy carriers in fuel cells, offering cleaner alternatives to conventional fossil fuels. Synthetic fuels, such as e-diesel and e-kerosene, produced via Fischer-Tropsch synthesis, are gaining traction in decarbonizing sectors like aviation and shipping (Suppiah, Daud and Johan, 2021).

Furthermore, the integration of CO₂ conversion technologies with renewable energy sources, such as solar and wind, has enabled the development of for instance, solar-powered electrocatalytic processes for hydrogenation. These processes are paving the way for large-scale adoption of green fuels (Quang, Milani and Abu Zahra, 2023).

Agriculture and fertilizers

In agriculture, CO₂-derived chemicals are increasingly used to enhance productivity and sustainability. Urea production, which combines ammonia and CO₂, has seen improvements in emissions intensity through advanced catalytic methods. Additionally, formic acid is employed as a preservative in animal feed, ensuring the longevity and safety of agricultural products.

Beyond fertilizers, CO₂-based innovations are also entering the realm of bio-based materials, where algae cultivation systems use CO₂ to produce biomass for biofuels, proteins, and other agricultural inputs.

Market dynamics and potential

The market for CO₂-derived chemicals is poised for rapid growth, driven by technological advancements and regulatory pressures to decarbonize industrial sectors. Methanol and ethanol markets alone are projected to grow at a compound annual growth rate (CAGR) of over 6%, supported by their adoption in clean energy systems and as sustainable feedstocks for chemical production.

Polymers and plastics derived from CO₂, including polycarbonates and olefins, are also witnessing increased demand due to the global shift toward sustainable materials. The potential for CO₂-derived polymers to replace conventional plastics in packaging and consumer goods offers substantial market opportunities.

Despite these advancements, challenges remain. The high costs of capture and conversion technologies, coupled with the need for large-scale infrastructure, pose significant barriers to widespread adoption. However, government incentives, such as carbon pricing and subsidies for renewable energy integration, are creating a more favourable environment for scaling up these solutions.

As a conclusion, CO₂ conversion technologies are unlocking a wide array of applications across chemicals, energy, and agriculture, with significant market potential

to drive sustainable industrial practices. By transforming CO_2 into alcohols, organic acids, polymers, and fuels, these innovations are not only mitigating carbon emissions but also redefining the role of CO_2 as a valuable resource. Continued advancements in catalyst design, reactor efficiency, and integration with renewable energy systems will be critical in realizing the full potential of CO_2 -derived products in global markets.

4 I PRACTICAL METHODOLOGY FOR R&D IN CO, VALORISATION

<u>Defining a practical R&D methodology: CARTIF Biotech & Sustainable Chemistry</u>

<u>Area in CARTIF Technology Centre.</u>

The successful development and scaling of CO₂ valorisation technologies rely heavily on structured R&D methodologies that integrate scientific innovation with industrial feasibility. From laboratory-scale experiments to pilot studies, practical methodologies ensure that advancements align with real-world applications. This section outlines a comprehensive framework for conducting R&D in CO₂ conversion, leveraging the expertise and infrastructure of research teams, such as the Biotechnology and Sustainable Chemistry (BQS) Area of CARTIF Technology Centre to bridge the gap between concept and implementation.

Developing successful CO₂ valorisation technologies involves multiple stages, from conceptual design and experimentation to validation and scale-up. Each stage builds upon iterative cycles of hypothesis testing, data generation, and optimization.

At the core of this methodology is the integration of three pillars:

- **1. Process understanding**: Fundamental knowledge of chemical, biological, and physical phenomena driving CO₂ conversion.
- **2. Technology development**: Experimental set-ups and protocols to evaluate catalysts, microbial strains, reactor configurations, and operating parameters.
- **3. Data-driven optimization**: Use of high-throughput experiments, advanced analytics, and computational tools to refine processes and predict performance at larger scales.

Experimental methodology: Laboratories as the nexus of innovation

Within this approach, laboratory-scale experiments form the backbone of R&D efforts in CO₂ valorisation. Advanced equipment and tailored experimental protocols enable researchers to simulate real-world operating conditions, assess performance metrics, and identify bottlenecks.

At CARTIF's BQS laboratory, we have developed capabilities to test a wide array of CO₂ valorisation processes, including gas fermentation, electrocatalytic reduction, and thermocatalytic hydrogenation. Equipped with bioreactors for microbial studies, gas diffusion cells for electrocatalysis, and analytical instruments such as gas and liquid chromatographs,

the lab supports multidisciplinary investigations.

For example, in gas fermentation processes, acetogenic bacteria such as *Moorella thermoacetica* and *Clostridium autoethanogenum* have been evaluated for their ability to convert CO₂ into acetic acid and ethanol. Under controlled conditions, we have observed conversion efficiencies exceeding 70%, highlighting the potential of these microorganisms in producing valuable biochemicals. These findings align with reported efficiencies in the literature (Ning, Li and Zhang, 2023)(Acuña López *et al.*, 2024) demonstrating the practical applicability of such systems.

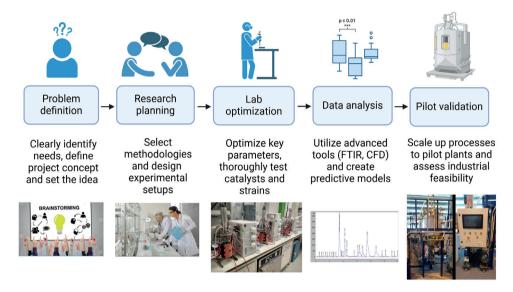


Figure 3. The R&D Workflow: A schematic showing the R&D workflow, from problem definition to pilot scale validation, integrated with BQS lab capabilities.

Integration of advanced tools. Data synthesis and visual representation

Modern R&D methodologies leverage advanced analytical and computational tools to accelerate the discovery and optimization of CO₂ conversion pathways. High-throughput experimentation, combined with machine learning algorithms, allows researchers to analyze vast datasets and identify correlations between process variables and outcomes.

For instance, at CARTIF, we utilize spectroscopic tools like FTIR and mass spectrometry to monitor reaction intermediates in real-time, providing insights into reaction kinetics and catalyst stability. Additionally, computational fluid dynamics (CFD) simulations are employed to optimize reactor designs, ensuring uniform mass and energy distribution across operating conditions. These tools enhance the predictive capability of experimental studies, reducing the time and cost associated with trial-and-error approaches.

The complexity of CO₂ valorisation technologies often necessitates clear and concise data visualization to communicate findings effectively. For example, Table 3 below

summarizes key microorganisms used in gas fermentation processes, along with their conversion efficiencies and key conditions. Such summaries provide a snapshot of the state of the art while guiding future investigations.

| Microorganism | Product | Conversion efficiency (%) | Key conditions |
|--------------------------------|---------|---------------------------|--|
| Acetobacterium woodii | Acetate | 60–65 | Anaerobic, 30°C, CO ₂ / |
| Moorella thermoacetica | Acetate | 75–80 | Anaerobic, 60°C, CO ₂ / H ₂ /CO |
| Clostridium autoethanogenum | Ethanol | 50–55 | Anaerobic, 37°C, CO ₂ / H ₂ /CO |

Table 3 Microorganisms used in gas fermentation for CO₂ conversion.

Collaborative research and scaling-up

Transitioning from laboratory-scale experiments to pilot-scale validation is a critical step in the R&D methodology. At CARTIF, we have developed collaborative research programs with industry partners to scale promising CO_2 valorisation technologies. Our pilot-scale facilities include modular bioreactors and electrocatalytic systems capable of processing multiple kilograms of CO_2 daily. These facilities allow us to evaluate the performance of technologies under industrially relevant conditions, bridging the gap between academic research and real-world implementation.

As a conclusion, we can say that by adopting a structured and iterative R&D methodology, researchers and practitioners can unlock the full potential of CO₂ valorisation technologies. At CARTIF's BQS area, we continue to leverage state-of-the-art equipment, multidisciplinary expertise, and collaborative partnerships to advance this field. These efforts not only contribute to scientific knowledge but also drive real-world solutions for mitigating climate change.

51 FUTURE CHALLENGES AND OPPORTUNITIES FOR SCALING UP \mathbf{CO}_2 CONVERSION TECHNOLOGIES

The large-scale implementation of CO₂ conversion technologies is critical for achieving climate goals and establishing a sustainable industrial model. However, significant challenges remain in scaling up these technologies to meet industrial demands while maintaining economic feasibility and environmental sustainability. This section discusses the key obstacles and potential strategies to overcome them, focusing on catalyst innovation, reactor design, integration with renewable energy, and economic considerations.

Challenges in catalyst design and efficiency

Catalyst efficiency, stability, and cost remain central challenges in scaling CO₂ conversion technologies. Current catalysts, such as those used in electrocatalysis, often suffer from deactivation during prolonged operations. For example, noble metal catalysts like platinum exhibit high activity but are economically unviable for large-scale applications due to their cost and limited availability. Stable and affordable alternatives, such as metal-organic frameworks (MOFs) and single-atom catalysts, is a promising avenue. These materials demonstrate enhanced selectivity and activity but face hurdles related to durability and reproducibility in industrial settings. Future research must tackle structures, incorporating low-cost materials, and improving resistance to deactivation under real-world conditions.

Reactor Design and Process plays a crucial role in determining the efficiency and scalability of CO₂ conversion systems. Flow electrolyzers and membrane-electrode assembly (MEA) systems have emerged as leading reactor configurations for electrocatalytic processes. However, these technologies face challenges in managing mass transfer, maintaining stability, and scaling up to industrial capacities.

Future advancements in reactor design should focus on enhancing gas diffusion layers and optimizing operating conditions such as temperature and pressure. Additionally, modular reactor designs capable of integrating multiple conversion pathways (e.g., combining electrochemical and thermocatalytic processes) hold significant potential for improving scalability and efficiency.

Integration with renewable energy sources

The reliance on renewable energy (sun, wind, etc.) is essential for the sustainability of CO₂ conversion technologies. However, the intermittency of renewable energy poses a challenge to the consistent operation of systems such as electrocatalytic reactors. Energy storage solutions, such as batteries or hydrogen, must be integrated into CO₂ conversion processes to enduring periods of low renewable energy availability.

Moreover, hybrid systems that combine renewable energy with advanced technologies, such as photoelectrochemical systems, offer opportunities to maximize energy utilization while reducing overall emissions.

Economic barriers and policy support

High capital costs and operational expenses are significant barriers to the wide dispersion of these technologies. The cost of renewable hydrogen, a critical input for many processes, remains prohibitively high for large-scale applications. Policy interventions, such as subsidies for green hydrogen production and carbon pricing mechanisms, can play a vital role in bridging this economic gap.

Additionally, to create CO₂ utilization clusters where industries collaborate to share infrastructure and resources, can reduce costs and improve the economic viability of these technologies.

Opportunities in emerging markets and research areas

Emerging markets for CO₂-derived chemicals, such as methanol, formic acid, and polymers, present significant products align with global trends toward sustainable materials and fuels, creating demand for innovative conversion technologies.

Advanced research areas, including machine learning for catalyst design and the development of hybrid biological-electrochemical systems, offer additional opportunities for innovation. These approaches ca of efficient materials and processes, ultimately enabling faster commercialization of CO₂ conversion technologies.

61 CONCLUSIONS

Scaling up CO₂ conversion technologies to industrial levels involves overcoming substantial challenges in catalyst development, reactor design, renewable energy integration, and economic feasibility. This must be balanced by significant opportunities in emerging markets, policy support, and technological advancements. By addressing these challenges through targeted research and collaborative efforts, the vision of a sustainable, CO₂-based circular economy can become a reality.

REFERENCES

Acuña López, P. et al. (2024) 'Demonstrating Pilot-Scale Gas Fermentation for Acetate Production from Biomass-Derived Syngas Streams', Fermentation, 10(6). doi: 10.3390/fermentation10060285.

Alli, Y. A. et al. (2023) 'Nanomaterials as catalysts for CO2 transformation into value-added products: A review', *Science of the Total Environment*, 868. doi: 10.1016/j.scitotenv.2023.161547.

Aziz, R., Abad, S. and Onaizi, S. A. (2024) 'Electrochemical conversion of CO2 using metalorganic frameworks-based materials: A review on recent progresses and outlooks', *Chemosphere*, 365(June), p. 143312. doi: 10.1016/j.chemosphere.2024.143312.

Chu, N. et al. (2020) 'Microbial electrochemical platform for the production of renewable fuels and chemicals', Biosensors and Bioelectronics, 150 (September 2019), p. 111922. doi: 10.1016/j.bios.2019.111922.

Drake, H. L., Gössner, A. S., and Daniel, S. L. (2008). Old acetogens, new light. Ann.N.Y. Acad. Sci. 1125, 100–128. doi: 10.1196/annals.1419.016

Drake HL, Küsel K, Matthies C, Wood HG, Ljungdahl LG. 2006. Acetogenic prokaryotes. In The Prokaryotes, ed. M Dworkin, S Falkow, E Rosenberg, K-H Schleifer, E Stackebrandt, pp. 354–420. NewYork: Springer. 3rd ed

Fackler N, Heijstra BD, Rasor BJ, Brown H, Martin J, Ni Z, Shebek KM, Rosin RR, Simpson SD, Tyo KE, Giannone RJ, Hettich RL, Tschaplinski TJ, Leang C, Brown SD, Jewett MC, Köpke M. Stepping on the Gas to a Circular Economy: Accelerating Development of Carbon-Negative Chemical Production from Gas Fermentation. Annu Rev Chem Biomol Eng. 2021 Jun 7;12:439-470

Fu, H. C. et al. (2019) 'CO2 Capture and in situ Catalytic Transformation', Frontiers in Chemistry, 7(July), pp. 1–15. doi: 10.3389/fchem.2019.00525.

Gao, P. *et al.* (2020) 'Novel heterogeneous catalysts for CO2 hydrogenation to liquid fuels', *ACS Central Science*, 6(10), pp. 1657–1670. doi: 10.1021/acscentsci.0c00976.

Hou, S. L. *et al.* (2023) 'Thermocatalytic Conversion of CO2 to Valuable Products Activated by Noble-Metal-Free Metal-Organic Frameworks', *Angewandte Chemie - International Edition*, 62(34). doi: 10.1002/anie.202305213.

Humphreys JR, Hebdon SD, Rohrer H, Magnusson L, Urban C, Chen YP, Lo J. Establishing Butyribacterium methylotrophicum as a Platform Organism for the Production of Biocommodities from Liquid C1 Metabolites. Appl Environ Microbiol. 2022 Mar 22:88(6):e0239321

Kajla, S., Kumari, R. and Nagi, G. K. (2022) 'Microbial CO2 fixation and biotechnology in reducing industrial CO2 emissions', *Archives of Microbiology*, 204(2), pp. 1–20. doi: 10.1007/s00203-021-02677-w.

Köpke M, Held C, Hujer S, Liesegang H, Wiezer A, Wollherr A, Ehrenreich A, Liebl W, Gottschalk G, Dürre P. Clostridium ljungdahlii represents a microbial production platform based on syngas. Proc Natl Acad Sci U S A. 2010 Jul 20;107(29):13087-92.

Kurt, E. *et al.* (2023) 'Perspectives for Using CO2 as a Feedstock for Biomanufacturing of Fuels and Chemicals', *Bioengineering*, 10(12), pp. 1–41. doi: 10.3390/bioengineering10121357.

Lee, H. et al. (2022) 'Engineering Acetogenic Bacteria for Efficient One-Carbon Utilization', Frontiers in Microbiology, 13(May). doi: 10.3389/fmicb.2022.865168.

Liew F, Martin ME, Tappel RC, Heijstra BD, Mihalcea C and Köpke M (2016) Gas Fermentation—A Flexible Platform for Commercial Scale Production of Low-Carbon-Fuels and Chemicals from Waste and Renewable Feedstocks. Front. Microbiol. 7:694.

Liew F, Henstra AM, Köpke M, Winzer K, Simpson SD, Minton NP. Metabolic engineering of Clostridium autoethanogenum for selective alcohol production. Metab Eng. 2017 Mar;40:104-114.

Liu K, Atiyeh HK, Tanner RS, Wilkins MR, Huhnke RL. Fermentative production of ethanol from syngas using novel moderately alkaliphilic strains of Alkalibaculum bacchi. Bioresour Technol. 2012 Jan;104:336-41.

Liou JS, Balkwill DL, Drake GR, Tanner RS. Clostridium carboxidivorans sp. nov., a solvent-producing clostridium isolated from an agricultural settling lagoon, and reclassification of the acetogen Clostridium scatologenes strain SL1 as Clostridium drakei sp. nov. Int J Syst Evol Microbiol. 2005 Sep;55(Pt 5):2085-2091.

Ning, H., Li, Y. and Zhang, C. (2023) 'Recent Progress in the Integration of CO2 Capture and Utilization', *Molecules*, 28(11), pp. 1–14. doi: 10.3390/molecules28114500.

Quang, D. V., Milani, D. and Abu Zahra, M. (2023) 'A review of potential routes to zero and negative emission technologies via the integration of renewable energies with CO2 capture processes', *International Journal of Greenhouse Gas Control*, 124(February), p. 103862. doi: 10.1016/j.iiggc.2023.103862.

Suppiah, D. D., Daud, W. M. A. W. and Johan, M. R. (2021) 'Supported metal oxide catalysts for CO2 Fischer–Tropsch conversion to liquid fuels - A review', *Energy and Fuels*, 35(21), pp. 17261–17278. doi: 10.1021/acs.energyfuels.1c02406.

Wei, K. et al. (2022) 'Recent advances in CO2 capture and reduction', Nanoscale, 14(33), pp. 11869–11891. doi: 10.1039/d2nr02894h.

Wu, L. *et al.* (2021) 'Upgrading biogas produced in anaerobic digestion: Biological removal and bioconversion of CO2 in biogas', *Renewable and Sustainable Energy Reviews*, 150(July). doi: 10.1016/j. rser.2021.111448.