BIP Europe
Biomethane Industrial Partnership

BIOMETHANE INDUSTRIAL PARTNERSHIP

ADVANCES IN CO_2 VALORISATION AND INTEGRATED HYDROGEN-BIOMETHANE PRODUCTION

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Advances in CO_2 valorisation and integrated hydrogen-biomethane production

Executive Summary

This report provides a comprehensive analysis of two key areas in the field of biomethane production: the enhancement of methanation technologies for the valorisation of biogenic CO_2 and the development of technologies for the integrated production of hydrogen and biomethane.

The report's dual scope allows for an exploration of these areas. Firstly, it assesses improved methanation technologies that enable the recycling and valorisation of biogenic CO_2. This includes the examination of catalyst development, process optimisation, and integration with renewable energy sources, all aimed at maximising the conversion of CO_2 into methane.

The report then analyses technologies that enable the integrated production of hydrogen and biomethane. It delves into the potential of the solid fraction of produced digestate for hydrogen production and the catalytic/thermochemical conversion of methane to hydrogen once biomethane has been produced.

The report highlights the ongoing research in developing more active, stable and cost-effective catalysts and optimising reaction conditions. While the potential for creating a water system that does not increase freshwater demand is recognised, particularly in regions with scarce water resources, this aspect should be assessed in future reports.

In conclusion, this report presents an examination of the current landscape of methanation and integrated hydrogen-biomethane production technologies.

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Introduction

Figure 1 is a schematic representation of the technologies that have been considered in the present report. This report has a dual scope: i) To assess improved methanation technologies to enable recycling and valorisation of biogenic CO_2; and ii) To analyse technologies to enable integrated production of hydrogen and biomethane. In the first case, (i), the focus is on biogas upgrading into biomethane (CO_2 purification), where the biogenic CO_2 generated from biogas (35% to 50%) can be used to produce additional synthetic methane through methanation.

Methanation is a process that involves converting electricity into methane molecules (CH_4) using carbon dioxide (CO_2) and hydrogen (H_2)(Rönsch et al., 2016).

"Methane synthesis", i.e. the resulting e-methane, is considered a renewable fuel of non-biological origin RFNBO (renewable fuel) if the hydrogen is renewable. The direct methanation of raw biogas can even be considered as an opportunity to avoid the CO_2 purification step. In the second case, (ii), the solid fraction of produced digestate can be processed in order to obtain hydrogen. In particular once biomethane has been produced, the methane contained therein can undergo catalytic/thermochemical conversion to hydrogen.

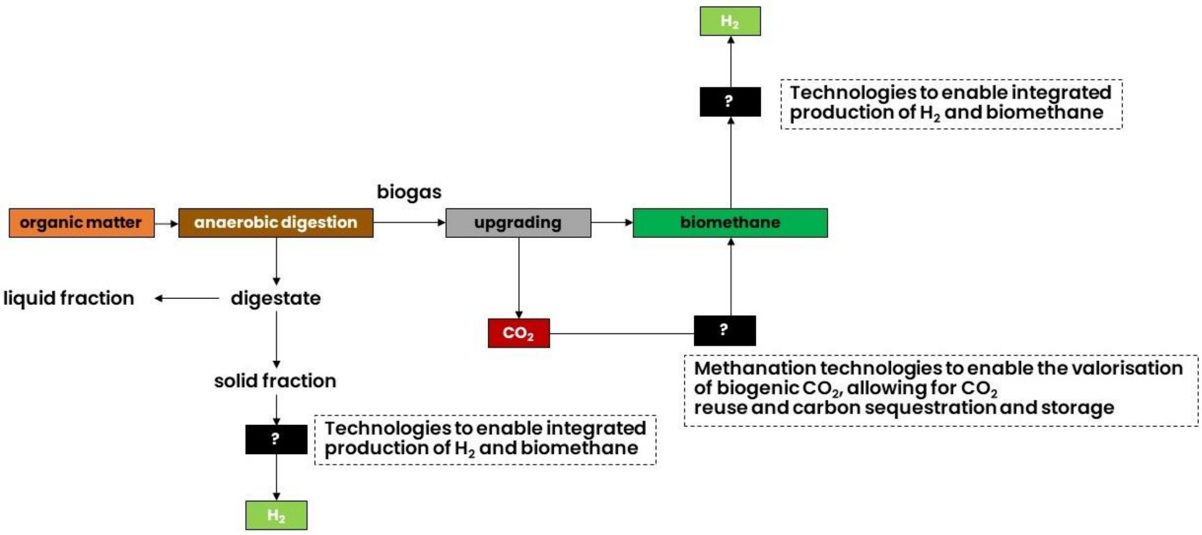

FIGURE 1 DEFINITION OF SCOPE IN THE TASK FORCE 5.3 REPORT

The process of methanation generally follows one of two major pathways: thermochemical/plasma (hereinafter referred as "catalytic") or biological (see Table 1). The valorisation of biogenic CO_2 refers to recycling CO_2 emissions derived from biological sources and used directly as the input stream for the methanation process. Biogenic CO_2 can be captured from biogas, syngas, bioethanol or from waste-to-energy plants as waste streams (Angelidaki et al., 2011). This approach helps reduce GHG emissions by capturing and utilising CO_2 that would otherwise be released into the atmosphere. Improving methanation technologies can be achieved through various methods, such as biological or chemical catalyst development, process optimisation, and integration with renewable energy sources. Catalysts play a crucial role in enhancing the reaction efficiency and selectivity of catalytic methanation (Gao et al., 2015). Researchers are continuously working on developing chemical catalysts that are more active, stable and cost-effective, and biological highly resilient catalysts including microorganisms whose metabolism is capable to produce methane at a lower cost (Chatzis et al., 2024). Optimising reaction conditions is also necessary to maximise the conversion of CO_2 into methane. Process optimisation mainly deals with the temperature, pressure and residence time for catalytic methanation, and with gas to liquid transfer for biological methanation (Rafrafi et al., 2021a; Tommasi et al., 2024). Integration with green electricity from variable renewable energy sources such as solar or wind power can provide green renewable hydrogen (e.g. via electrolysis) for the methanation process, making it a sustainable and carbon-neutral pathway. By improving methanation technologies, the goal is to enable the efficient conversion of biogenic CO_2 into e-methane, which can be used as a renewable energy source or as a feedstock for various applications. This not only contributes to reducing CO_2 emissions but also facilitates the storage and reuse of carbon in the form of methane (Asimakopoulos et al., 2021).

Table 1 shows technologies identified within the scope of sDR3. It compiles methanation technologies that enable the valorisation of biogenic CO2 and the integrated production of H2 and biomethane.

TABLE 1 METHANATION TECHNOLOGIES ASSESSED IN THE TASK FORCE 5.3 REPORT

Technologies that enable the valorisation of biogenic CO_2	Technologies that integrate the production of H_2 and biomethane
• In-situ biological methanation • Ex-situ biological methanation • Bioelectrochemical methanation route • Catalytic methanation • Plasma catalysis methanation from CO_2 and H_2	Digestate (solid fraction) to syngas • Chemical looping • Plasma catalysis steam reforming of methane

1.

Improving methanation technologies

to enable the valorisation of biogenic CO_2

1 Improving methanation technologies to enable the valorisation of biogenic CO_2, allowing for CO_2 reuse and carbon sequestration

The objective of this chapter is to provide an overview of the current state of methanation technologies, with a particular focus on those that enable the valorisation of biogenic CO_2. It aims to explore the potential of these technologies for CO_2 reuse, CO_2 emissions removal and carbon sequestration, and to identify areas for further research and development. This includes a review of the latest advances in catalysts and reactor designs, process integration and power-to-gas technologies, system optimisation approaches, and the challenges and future perspectives of these technologies.

1.1 Review of the current state of the art

Among the technologies involved in the transition to a greener energy system to meet the EU's climate objectives, advances in methanation processes hold promise in converting biogenic CO_2 into valuable synthetic methane (CH_4), a versatile energy carrier and natural gas substitute (Biomethane Industrial Partnership, 2024). This section provides an overview of the state of the art of technologies in methanation, highlighting their potential for biogenic CO_2 utilisation. It is worth noting that although the conversion of CO_2 into methane might be considered as a method for carbon sequestration, the carbon will only temporarily remain sequestrated until the methane is used further, especially in the case of combustion applications.

With regard to abiotic catalytic methanation, one key area of research focuses on improving catalysts for methanation reactions. Innovative catalyst materials such as nickel-based catalysts have shown enhanced activity and selectivity, facilitating the conversion of CO_2 and H_2 into e-methane. Catalyst optimisation also involves the design of tailored catalyst structures and compositions, promoting improved mass transfer and reaction kinetics (Frontera et al., 2017).

Biological methanation can be applied using either a mono-consortium (a single strain) or mixed consortia (a combination of various strains) (Rafrafi et al., 2021b). Impurities contained in biogas can influence the performance of microorganisms, especially in monocultures (Paniagua et al., 2022). Microorganisms are also sensitive to pH, and the carbonate/carbon dioxide equilibrium has to be subsequently monitored (Lecker et al., 2017).

Reactor design also plays a crucial role in optimising methanation processes. Advanced reactor configurations, including fixed-bed and fluidised-bed for catalytic methanation, and membrane reactors for biological and catalytic methanation, offer better control over the reaction and heat, a higher surface area for catalytic reactions, and improved heat and mass transfer for biological and catalytic reactions. These designs enable efficient conversion of CO_2 and H_2 into synthetic methane, maximising process performance and scalability.

Carbon dioxide can be obtained from various sources such as industrial emissions, biogas upgrading processes or direct air capture (Saleh & Hassan, 2023). To capitalise on biogenic CO_2

utilisation, methanation technologies are being integrated into various industrial processes. For instance, coupling methanation with biogas production facilities or power plants allows for direct utilisation of the CO_2 effluents from anaerobic digestion (AD) or gasification, enabling a circular economy approach by the valorisation of residual streams.

Power-to-methane or e-methane production involves the conversion of surplus renewable energy into hydrogen through water electrolysis. This renewable hydrogen is then combined with CO_2 in methanation processes to produce methane, which is characterised as a renewable fuel of non-biological origin (when CO_2 is biogenic, methane is also biomethane). The resulting renewable methane can be stored over longer time periods in the gas grid and used when needed, even several months after its production (Thema et al., 2019). P2G therefore offers further flexibility to the energy system.

Achieving optimal performance and economics of methanation technologies requires a holistic approach that considers the whole biogas supply chain.

While significant progress has been made in abiotic methanation technologies, challenges remain (Calbry-Muzyka & Schildhauer, 2020). Catalyst stability, catalyst poisoning and process scalability are catalytic methanation areas that necessitate further research and development. Additionally, the cost-effectiveness of these technologies needs to be improved for large-scale implementation (Morimoto et al., 2022). Cost effectiveness is driven by the hydrogen cost. Plant size is a driver, as it can generate economies of scale at electrolysis level. Looking ahead, future research on catalytic methanation should focus on developing novel catalyst materials with enhanced stability, selectivity and resistance to deactivation, whereas biological methanation improvements should relate to process intensification with mass transfer. Furthermore, the integration of methanation with other renewable energy technologies, such as solar and wind, and synergies between hydrogen and biomethane could pave the way for sustainable and carbon-neutral energy systems.

Synthetic methane has the same end-use applications as biomethane, can provide energy storage capacity and is a flexible renewable energy carrier and fuel.

Figure 2 shows the scope of the technologies described in the present section: “methanation technologies to enable the valorisation of biogenic CO_2, allowing to maximise its utilisation”.

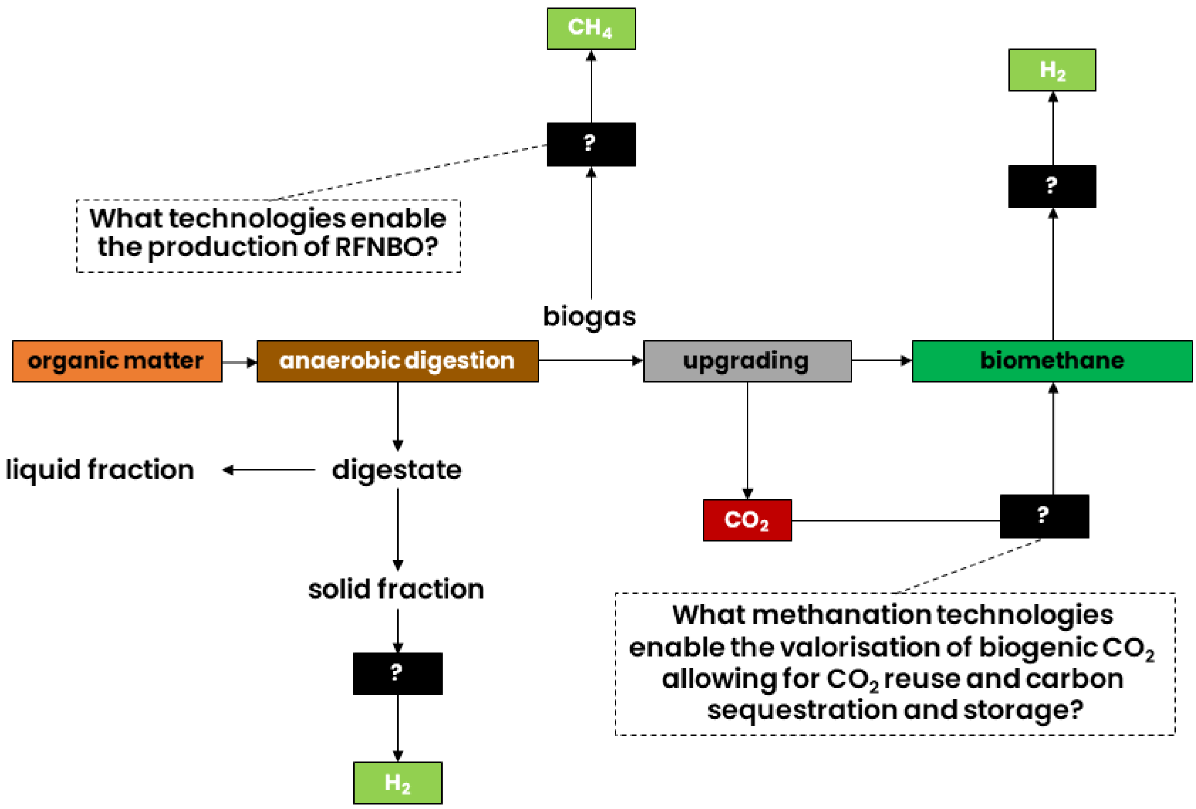

FIGURE 2 DEFINITION OF SCOPE IN THE TASK FORCE 5.3 REPORT: IMPROVING METHANATION TECHNOLOGIES AND INCREASING THE OVERALL BIOMETHANE YIELD TO ENABLE THE VALORISATION OF BIOGENIC CO_2, AND MAXIMISE UTILISATION OF CO_2 EFFLUENTS FROM BIOGAS

1.2 Identification of methanation technologies to enable the valorisation of biogenic CO_2, maximising utilisation of CO_2 effluents from biogas

This section describes the identified technologies.

Biological methanation routes

In biological methanation, CO_2 (or direct raw biogas, or syngas) and H2 are fed into a bioreactor or a bioconversion unit. The bioreactor contains specific microorganisms, methanogenic archaea, which can convert CO_2 and H2 into methane under suitable conditions. The microorganisms in the bioreactor, known as methanogens, metabolise the CO_2 and H2 through a series of biochemical reactions, resulting in the production of CH_4 and H2O. This offers the possibility of combining biomethanation easily with anaerobic digestion, as raw biogas can be directly treated without pre-treatments. This process is similar to the natural anaerobic digestion that occurs in environments such as wetlands or landfills.

In-situ biological methanation

In-situ biological methanation is a biological process whereby hydrogen is directly fed /injected into a biogas digester to facilitate the reduction of endogenously produced CO_2 into biomethane by shifting the metabolic pathway towards hydrogenotrophic methanogens (Figure 3). This conversion is driven by acetotrophic methanogenesis and hydrogenotrophic methanogenesis. Hydrogenotrophic methanogens, utilize hydrogen as an electron donor to directly convert CO_2 to biomethane. The biomethane produced qualifies as RFNBO if renewable hydrogen is used. Besides, homoacetogens utilise the injected hydrogen to convert CO_2 into acetate, which is further degraded by acetotrophic methanogens to generate CH_4.

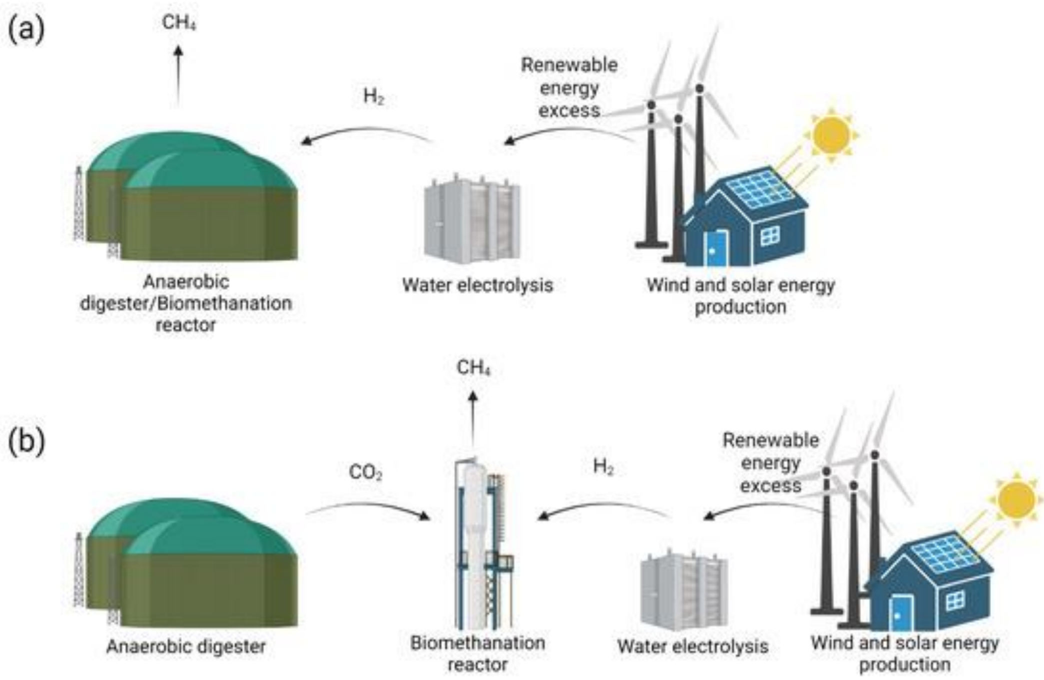

FIGURE 3 *IN SITU* (A) AND *EX SITU* (B) BIOMETHANATION TECHNOLOGIES. SOURCE: BELLINI ET AL., 2022

The technology readiness level of *in-situ* biological methanation can vary depending on the configuration of reactors and hydrogen diffusion devices used. Small-scale *in-situ* biological methanation systems such as those employed in laboratory settings tend to exhibit higher efficiency compared with larger-scale systems. Demo-scale prototypes may require additional CH_4 upgrading before injection into the gas grid. The conversion rate of CO_2 in *in-situ* biological methanation is influenced by the hydrogen gas diffusion systems and rates employed, particularly the gas-liquid mass transfer rate of H_2 (Rusmanis et al., 2019). In terms of mass quantity, the CO_2 to CH_4 conversion rate can range from 50% to 90%, resulting in varying CO_2 concentrations in the biogas, typically ranging from 25% to 3%.

Ex-situ biological methanation

In the *ex-situ* biomethanation configuration, the biological reduction of CO_2 to biomethane occurs within an *ex-situ* separate reactor unit system, where the raw biogas is directly combined with hydrogen to convert the CO_2 into biomethane via a hydrogenotrophic methanogen pathway with biomethane with a purity higher than 98% (Vo et al., 2018). Alternatively, the off-gas produced from the purification systems currently used to produce biomethane, splitting the CO_2 part contained in the raw biogas, can also be processed. As a result, ex-situ methanation systems can substitute current biogas upgrading units or complement them.

The process involves the use of specialised microorganisms that can consume H_2 and CO_2 and convert them into biomethane through microbial methanogenesis (Meslé et al., 2013).

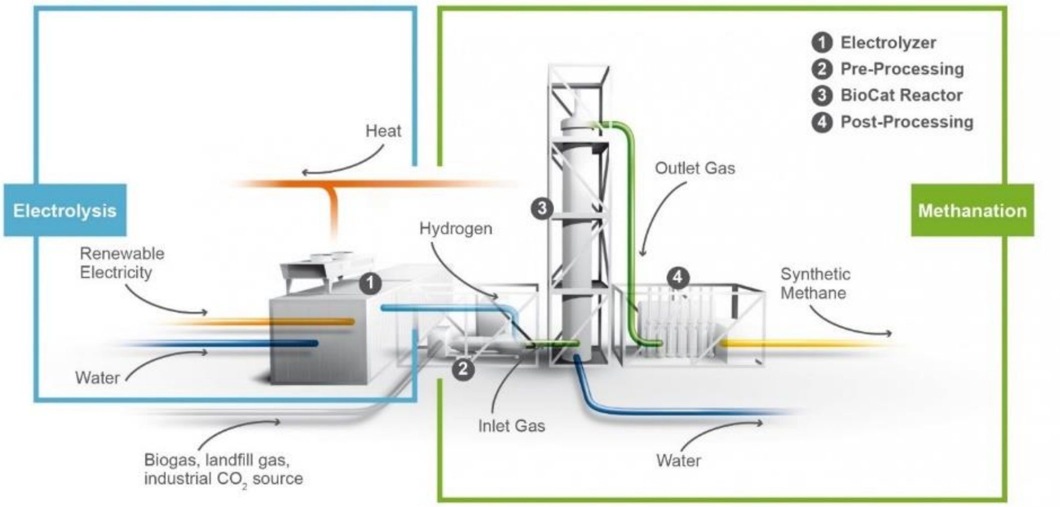

FIGURE 4 EX-SITU BIOLOGICAL METHANATION. SOURCE: ELECTROCHAEA, 2024

Ex-situ biological methanation has gained attention as a potential technology for carbon capture and utilisation (CCU) and renewable energy storage, enabling the conversion of excess renewable electricity. It offers a way to simultaneously convert carbon dioxide, which is a greenhouse gas, and store renewable electricity in renewable methane, a useful energy carrier.

It is worth noting that the ex-situ methanation technology is reaching commercial maturity, with certain suppliers and first plants at industrial scale, at least reaching TRL 8 and/or including large production facilities within the EU. On an industrial scale, biological methanation is a technology that enables the conversion of excess renewable electricity into renewable methane (CH_4) (Voelklein et al., 2019).

The application of biological methanation on an industrial scale offers a promising pathway for the conversion of renewable electricity into a storable and versatile energy carrier, contributing to the integration of renewable energy sources into existing infrastructure.

Bioelectrochemical methanation route

Electromethanogenesis is a bioelectrochemical process that enables the conversion of CO_2 into CH_4 (Cheng et al., 2009). Unlike other types of methanation process, electromethanogenesis does not rely on the direct supply of H_2 along with CO_2. Instead, it leverages the unique capabilities of archaea, which form a biofilm on the polarised cathode inside a bioreactor, to generate and utilise H_2 beneath the biofilm (De la Puente et al., 2023).

The electromethanogenesis process can be realised through various configurations of an electrochemical system. In a single-cell setup, both the anode and cathode are exposed to the microbial pool. This design allows for direct interaction between the microorganisms and the polarised electrodes. Alternatively, a double-cell configuration can be employed, wherein the anode may be abiotic, resembling a water electrolyser, or it can be fed with wastewater, facilitating the oxidation of organic compounds instead of water at a lower voltage (Palacios et al., 2024).

The potential applications of electromethanogenesis extend beyond the realm of sustainable methane production. One notable application lies in the upgrading of biogas subsequent to traditional dark fermentation (Magdalena et al., 2023). By subjecting the biogas to electromethanogenesis, the carbon dioxide content can be significantly reduced while simultaneously increasing the methane content, resulting in a higher quality fuel.

Moreover, electromethanogenesis holds promise as a viable means of energy storage and carbon utilisation. It enables the conversion of surplus electricity from renewable sources such as solar or wind power into renewable methane, a storable energy carrier. This process effectively addresses the intermittent nature of renewable energy and provides a clean and sustainable solution for energy storage.

Continued research and development efforts are focused on optimising the electromethanogenesis process, enhancing its efficiency, and exploring its wider applications. Scientists are investigating electrode materials, system configurations, and microbial communities to improve performance and establish practical implementation strategies.

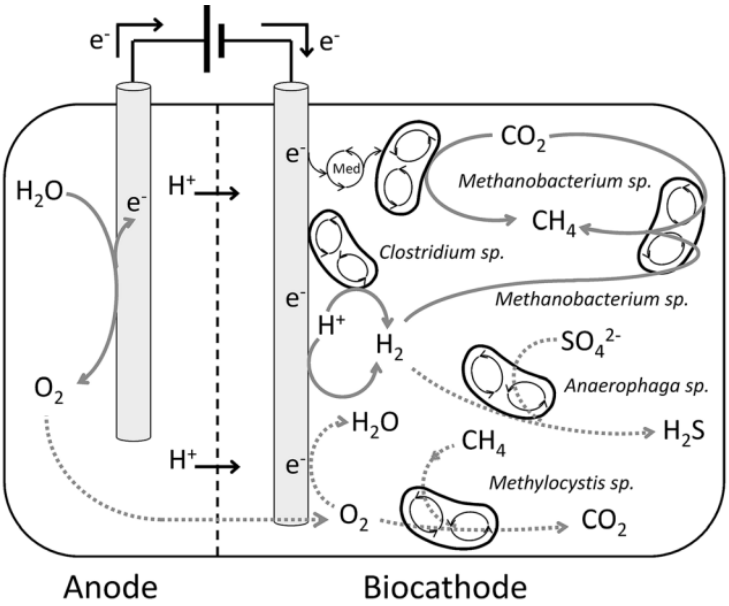

FIGURE 5 METHANE-PRODUCING (SOLID LINES) AND CROSS-OVER (DASHED LINES) REACTIONS THAT TAKE PLACE IN THE BIOCATHODE OF AN ELECTROMETHANOGENESIS REACTOR. SOURCE: BATTLE-VILANOVA ET AL., 2015

Chemical and plasma-catalysed methanation routes

Thermochemical methanation

Catalytic methanation is a chemical process that involves the conversion of CO and CO_2 into CH_4 using a catalyst (Brooks et al., 2007). It is commonly used in various industrial applications such as gas purification and the treatment of exhaust gases from coal gasification, biomass gasification, or syngas production.

The reaction typically takes place at elevated temperatures and involves the use of a catalyst, usually based on metals such as nickel (Ni) or ruthenium (Ru). The catalyst facilitates the reaction by providing active sites for the adsorption and subsequent transformation of CO and CO_2 molecules into methane. H_2 is a necessary reactant in the methanation reaction, which is added to the reactant stream to convert CO and CO_2 into CH_4.

Catalytic methanation is an important process in many energy-related industries, as it helps to remove harmful carbon monoxide and carbon dioxide emissions. It is also employed in the production of e-methane.

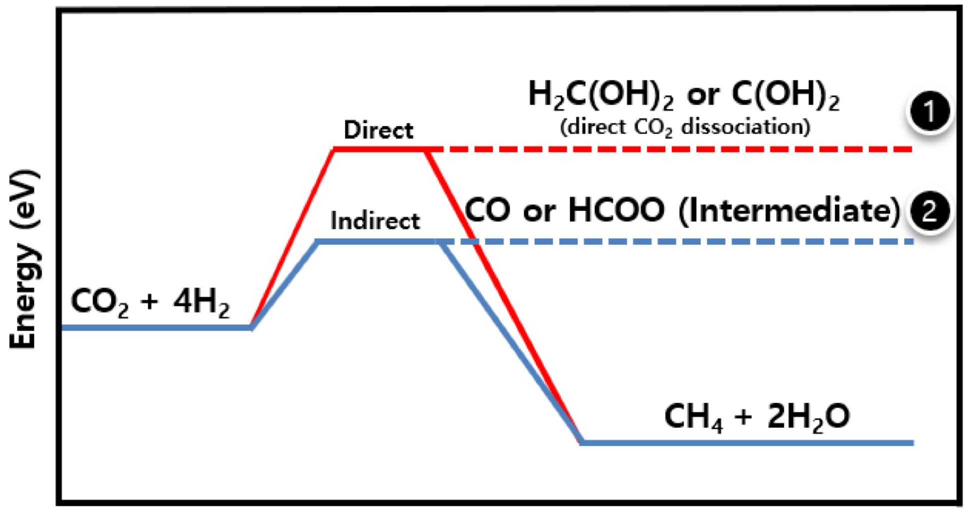

FIGURE 6 POTENTIAL REACTION PATHWAYS IN CO_2 METHANATION. SOURCE: CHO ET AL., 2020

Plasma catalysis methanation from CO_2 and H_2

Plasma catalysis is a technology that combines the use of plasma (an ionised gas) and catalysts to drive chemical reactions (Da Costa et al., 2021). In plasma catalysis methanation, plasma is used to activate the reactant gases (CO_2 and H_2), providing energy to overcome the reaction barriers. The activated gases then come into contact with a catalyst, which enhances the reaction rate and promotes the formation of methane. The process of catalytic CO_2 methanation (described above), which is already an established industrial procedure, achieves significant conversions of CO_2 to CH_4. However, the quest for optimisation of this process – reducing the reaction temperature and enhancing the catalyst's activity, selectivity, and stability – has led to the advent of plasma technology (Debek et al., 2019a).

The type of plasma generated can vary based on several factors (Debek et al., 2019b). These include the power supply used to create the plasma, the configuration of the electrodes, and the dielectric material used. The types of plasma that can be produced include direct current and alternating current glow discharges, radio frequency discharges, microwave discharges, dielectric barrier discharges, gliding arcs, plasma jets and plasma torches. Each of these plasma types has unique characteristics, making them suitable for different applications. A comparison of their characteristics with those of thermal plasma is illustrated in Figure 7.

Plasma catalysis methanation has gained attention as a potential method for CO_2 conversion and utilisation because it offers advantages such high reaction rates and the ability to control reaction selectivity (Ahmad et al., 2020). However, it is worth noting that plasma catalysis is still an area of active research, and the commercial-scale implementation of this technology is still being explored. Plasma catalysis has been recently scaled up. A strategic partnership has been formed to develop an innovative methanation technology on an industrial scale, supporting the decarbonisation of the industry. A unique process has been developed by a start-up that uses CO_2 and H_2 for conversion into methane through an innovative patented methanation process. The process relies on a cold-plasma catalytic reactor which, thanks to CO_2 captured on site and combined with hydrogen, enables the production of methane at a rate 50 times faster than a conventional catalyst. This breakthrough signifies a promising advance in the field of sustainable energy production.

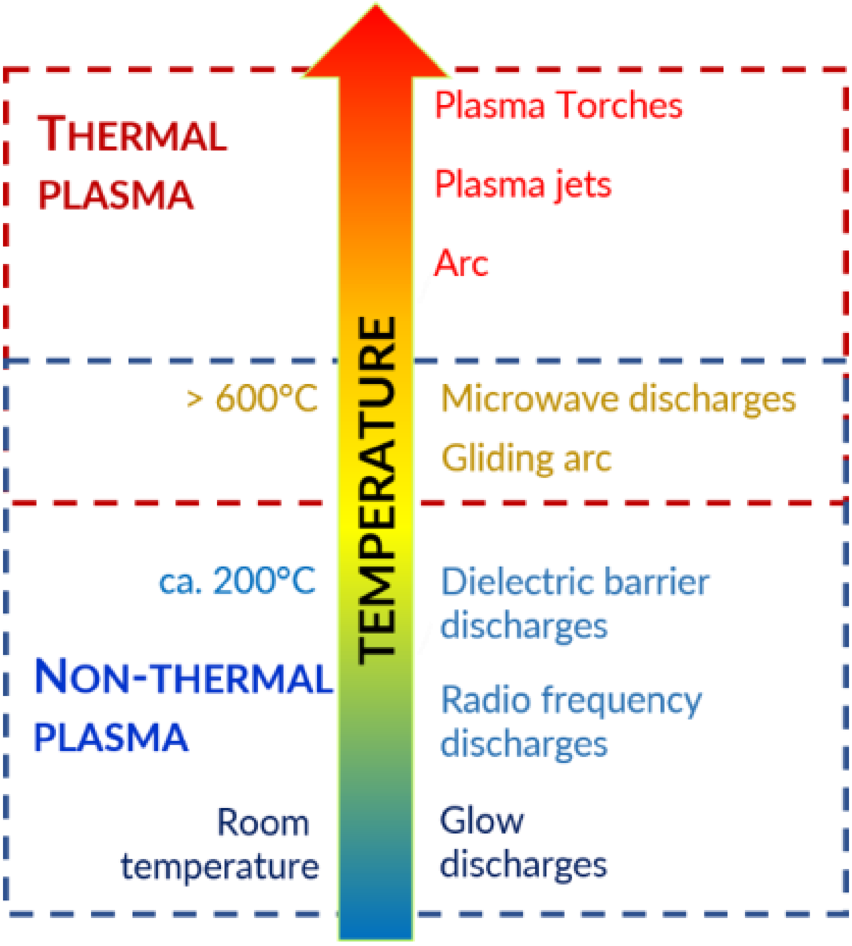

FIGURE 7 TEMPERATURE CHARACTERISTICS OF SEVERAL TYPES OF PLASMA APPLIED IN CO_2 TECHNOLOGIES. SOURCE: DEBEK ET AL., 2019B

1.3 Identification of R&D&I gaps and recommendations for improving methanation technologies for the valorisation of biogenic CO_2

Advances in methanation technologies are crucial for the effective utilisation of biogenic CO_2, enabling CO_2 reuse and carbon sequestration. However, there are several significant technological gaps that need to be addressed, along with corresponding recommendations for further transversal R&I activities (Table 2).

Table 2 Gaps and recommendations for improving methanation technologies for the valorisation of biogenic CO2

Category	Description
Catalyst development	The choice of catalyst and biocatalysts plays a vital role in the methanation process. Current catalysts, while efficient, can be expensive. There is a need for research into novel catalyst materials with improved efficiency, stability and tolerance to gas impurities.
H2 partial pressure, mass transfer and exogenous H2 addition rate	These parameters directly influence the reaction kinetics and the efficiency of CO_2 conversion. However, the optimal conditions for these parameters are not yet fully understood and require further investigation.
Optimal H_2/CO_2 ratio and microbial balance	The ratio of hydrogen to CO_2 and the balance between bacteria and CO_2-reducing methanogens are crucial in the methanation process. An imbalance could lead to suboptimal reaction conditions and lower methane yields.
Pressure management and temperature control	Both pressure and temperature affect the efficiency of syngas conversion to methane. There is a need for advanced pressure management techniques and studies to better understand catalyst degradation mechanisms at different temperatures.
Integration with diverse renewable energy sources and reactor optimisation	Methanation technologies should be compatible with various renewable energy sources. Also, reactor designs need to be optimised for improved heat and mass transfer, enhanced catalyst utilisation and higher conversion efficiencies.
Gas purity requirements and CO_2 capture and utilisation	To ensure optimal catalyst performance, it is crucial to maintain gas purity. Efficiently collecting CO_2 from the methanation process poses a technical challenge. Therefore, innovative gas purification methods and improved techniques for CO_2 capture are required.
Operational simplicity and system integration and scale-up	Methanation plants must be easy to operate. Comprehensive techno-economic and life cycle assessments are needed to evaluate the integration of methanation technologies into existing energy systems.
Collaboration and knowledge sharing	Collaboration between researchers, industry stakeholders, and policymakers is essential to accelerate the development and deployment of methanation technologies.

By addressing these gaps and implementing the recommended R&I activities, we could unlock the potential for valorising biogenic CO_2.

2.

Improving technologies

for integrated hydrogen-biomethane production

2 Improving technologies to enable integration of hydrogen production into biogas and biomethane streams

The objective of this chapter is to provide a review of the current state-of-the-art technologies that enable the integrated production of hydrogen and biomethane. We aim to explore the potential of these technologies, their applications and the challenges they face. We delve into the mechanisms of these technologies, their benefits and their limitations. The analysis focuses on how these technologies can be applied individually or in combination to achieve the integrated production of hydrogen and biomethane, depending on the specific requirements and scale of the project. Readers are referred elsewhere for an analysis of biohydrogen and the role of this renewable gas in the decarbonisation of Europe (European Biogas Association, 2024).

2.1 Review of the current state of the art

There are several technologies that can enable the integrated production of hydrogen and biomethane. One such technology involves the reforming of CH_4 in biogas, to produce H_2 and CO_2. The resulting CO_2 can be separated and captured, while the hydrogen can be utilised for various applications (European Biogas Association, 2024).

Steam methane reforming is a well-established technology that involves the reaction of biogas with steam over a catalyst to produce hydrogen and carbon monoxide (Bhat & Sadhukhan, 2009). Carbon monoxide can be further reacted with steam to produce additional hydrogen and CO_2 which can be captured for storage or other uses.

Pressure swing adsorption (PSA) is a technology used for separating hydrogen from a gas mixture (SIRCAR & GOLDEN, 2000). It utilises adsorbents that selectively adsorb certain gases while allowing others to pass through. By cycling through adsorption and desorption stages, hydrogen can be separated and purified from the biogas mixture. Biogas can be improved using PSA. In a recent study, this process was used to enhance the quality of biogas. To tackle the issue of CH_4 spillage, a green solution was proposed that converts CH_4 and some CO_2 into H_2. The system was tested in two stages and produced high-quality methane and a variety of gases (Abd et al., 2023).

Membrane separation involves the use of selective membranes that allow certain gases such as H_2 to permeate through while blocking other gases. By utilising membranes with appropriate properties, H_2 can be separated and obtained as a product.

Biogas reforming involves its thermochemical processing without separating the biomethane component. The reforming process converts the CH_4 present in biogas into H_2 and CO_2, which can be further utilised or captured.

These technologies can be applied individually or in combination to achieve the integrated production of hydrogen and biomethane, depending on the specific requirements and scale of the project. Although the above-described technologies would partially consume the CH_4 within biogas, the resultant gas could also be composed of H_2 and CO_2. Figure 8 shows the scope of the technologies described in the present section.

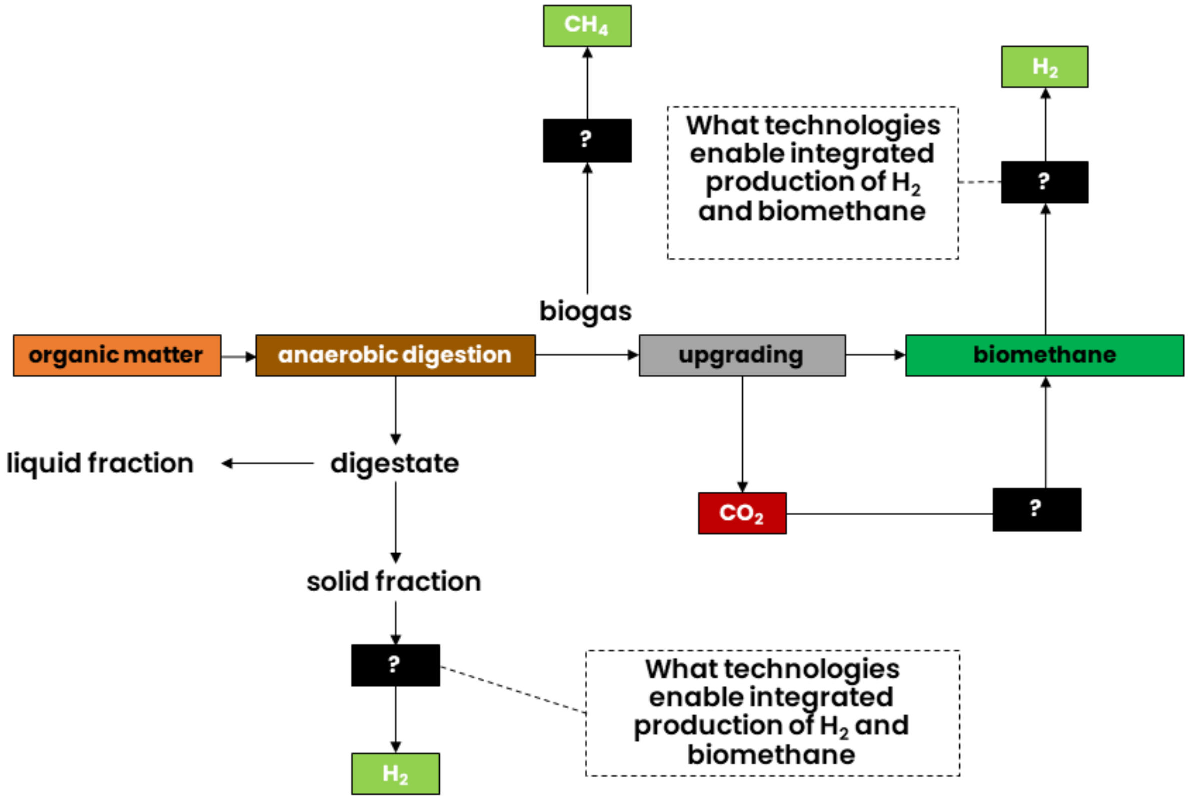

FIGURE 8 DEFINITION OF SCOPE IN THE TASK FORCE 5.3 REPORT: TECHNOLOGIES TO ENABLE INTEGRATED PRODUCTION OF HYDROGEN AND BIOMETHANE

2.2 Identification of technologies to enable integration of hydrogen production into biogas and biomethane streams

This section describes the identified technologies. It is worth noting that the technologies presented in this section produce hydrogen from methane conversion contained in biogas or hydrogen from a subproduct from the anaerobic digestion process such as digestate.

Digestate (solid fraction) to syngas

Syngas production from biodigestate involves a series of chemical reactions that transform the solid fraction of digestate. Through the gasification process, the chemical formula C + H_2O -> CO + H_2 governs the conversion. Typically, this reaction occurs at high temperatures and pressures in the presence of a gasifying agent, such as steam or oxygen. The technology readiness level of digestate gasification varies depending on the specific application and scale of the process. While gasification has been utilised for generating syngas from various feedstocks over the years, the application of digestate gasification for syngas production is still undergoing development.

The efficiency of digestate gasification relies on factors such as the quality of the digestate feedstock, the performance of the gasification reactor, and the effectiveness of the gasifying agent. The conversion rate of digestate to syngas can reach approximately 60-80% in terms of mass quantity depending on specific operational parameters employed (Giuliano et al., 2020). As described above, gasification could produce a syngas from a subproduct of anaerobic digestion, allowing for the parallel production of two different types of renewable gas molecules (methane and hydrogen).

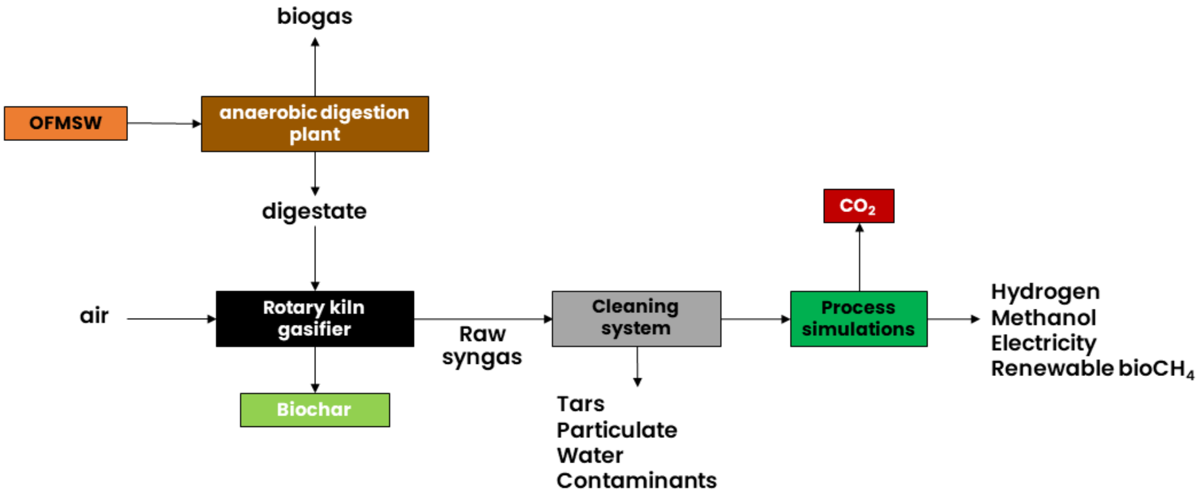

FIGURE 9 PROPOSED INTEGRATED SCHEME FOR DIGESTATE VALORISATION. FIGURE REDRAWN FROM THE ORIGINAL SOURCE (GIULIANO ET AL., 2020)

Chemical looping

Chemical looping offers an approach to convert biogas into hydrogen (H_2) (Wang et al., 2022). This technology stands out for its process intensification, as it eliminates the need for upstream biogas compression and purification, as well as downstream CO_2 removal and H_2 purification. One of the key features of chemical looping technology is its ability to incorporate CO_2 capture within the process. This means that H_2 production from biogas can potentially become carbon-negative. When it comes to energy efficiency, this technology outperforms traditional methods like steam methane reforming. It shows promise in achieving higher H_2 yields from biogas. By combining H_2 separation, purification and CO_2 capture into a single process, it could result in lower capital costs compared with conventional steam methane reforming hydrogen production processes.

The chemical looping biogas to H_2 process involves three reactors: a reducer, an oxidiser and a combustor. In the reducer, biogas undergoes complete oxidation by reacting with iron-based oxygen carrier particles. This reaction converts hematite in the oxygen carrier particles to metallic iron and iron oxide (wüstite). The reduced oxygen carrier particles then react with steam in the oxidiser to produce high-purity H_2. Simultaneously, the oxygen carrier particles are oxidised to a mixture of wüstite and magnetite. The magnetite resulting from the oxidiser reaction reacts with air in the combustor to regenerate back to hematite, restarting the redox cycle for continuous operation. The cyclic process of reduction and oxidation of the iron-based oxygen carrier particles enables the continuous conversion of biogas into H_2 without the need for separate biogas purification and CO_2 removal steps, enhancing process intensification and efficiency.

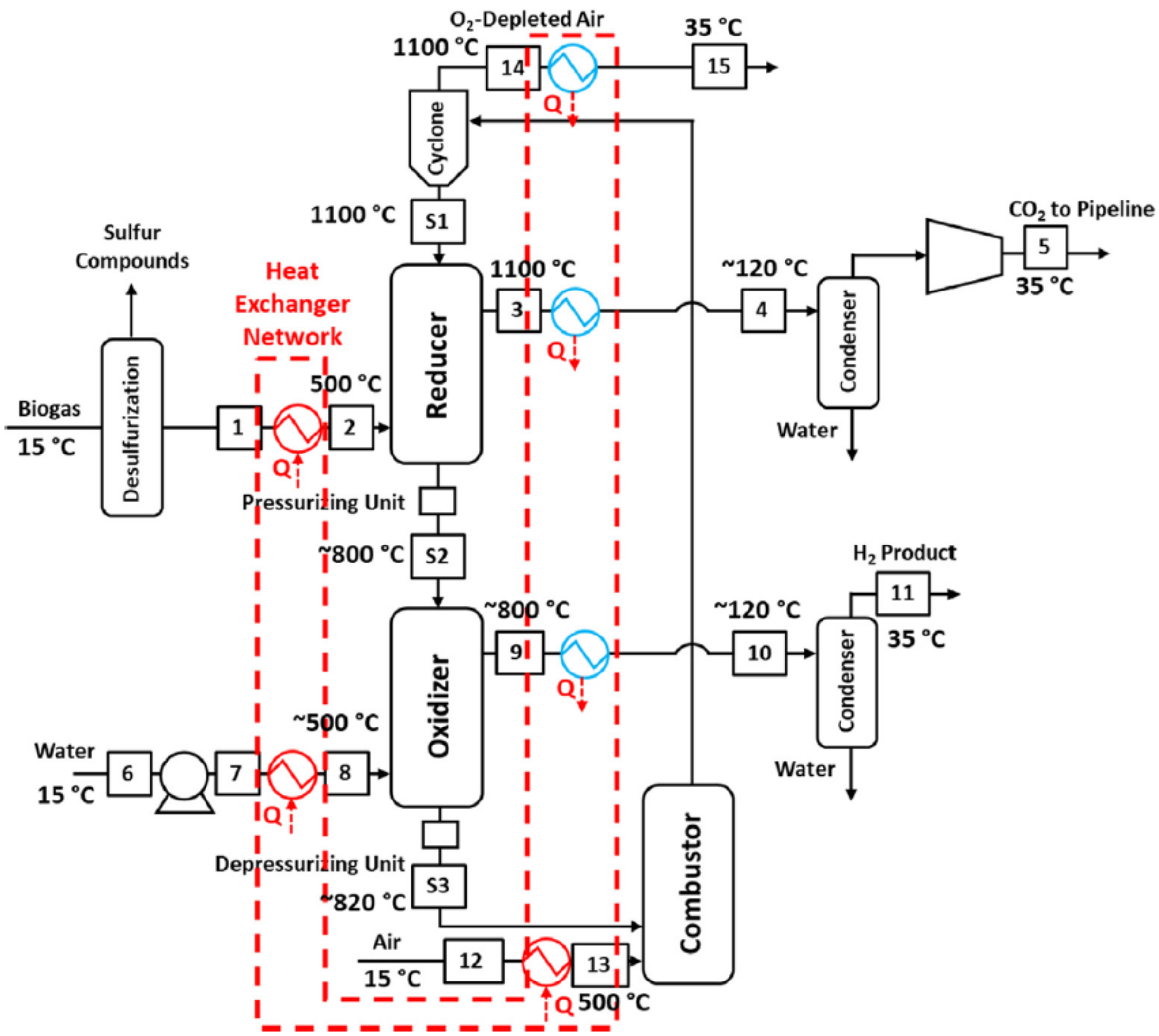

FIGURE 10 FLOW DIAGRAM OF CHEMICAL LOOPING BIOGAS TO HYDROGEN (KONG ET AL., 2020)

Plasma catalysis steam reforming of methane

A way to increase the concentration of combustible components within biogas is through thermal, catalytic and plasma methods (Dobslaw & Glocker, 2020). Ni-containing carrier catalysts are commonly used, but the reaction rate of methane and carbon dioxide is very low at temperatures below 550°C. It was found that adding hydrogen to gaseous fuels increases combustion stability and speed.

Biogas can also be processed into higher hydrocarbons, oxygenates or synthesis gas, which can be a raw feedstock for green ammonia or methanol. This requires the processing of biogas to contain H_2 and CO_2. Such reactions can be carried out in catalytic, plasma and plasma-catalytic processes.

The application of plasma-catalytic methods to enrich low methane gas diluted with CO_2 in H_2 is the subject of research in many scientific centres such as the one shown in Figure 11.

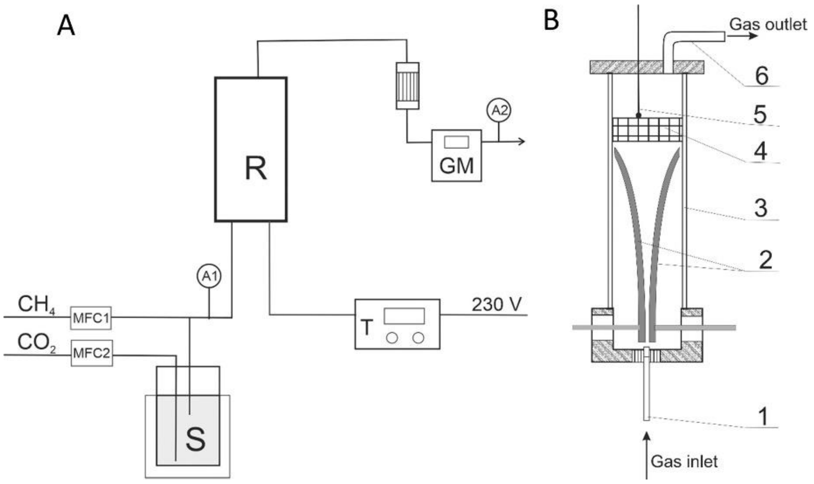

FIGURE 11 PLASMA-CATALYTIC SYSTEM WITH A TWO-ELECTRODE GLIDING DISCHARGE REACTOR. (A) EXPERIMENTAL SETUP: R—REACTOR, S—SCRUBBER WITH WATER, T—POWER SUPPLY, GM—GAS COUNTER, MFC1, MFC2—MASS FLOW CONTROLLERS FOR CH4 AND CO_2, RESPECTIVELY, AND A1 AND A2—GAS SAMPLE COLLECTION POINTS. (B) REACTOR SCHEME: 1—GAS INLET, 2—ELECTRODES, 3—QUARTZ TUBE, 4—CATALYST BED, 5—THERMOCOUPLE, AND 6—GAS OUTLET (MŁOTEK ET AL., 2021)

2.3 Identification of R&D&I gaps and recommendations for technologies to enable integration of hydrogen production into biogas and biomethane streams

The transition to a sustainable and circular economy necessitates the adoption of flexible green energy sources such as hydrogen and biomethane. However, several technological gaps need to be addressed for full integration of hydrogen production into biogas and biomethane streams. Here are the identified gaps and corresponding recommendations for further research and innovation (R&I) activities:

TABLE 3 R&D&I IDENTIFIED GAPS AND RECOMMENDATIONS FOR TECHNOLOGIES TO ENABLE INTEGRATION OF HYDROGEN PRODUCTION INTO BIOGAS AND BIOMETHANE STREAMS

Category	Description
Biomethane purification	The purification of biomethane derived from organic waste sources presents a significant challenge due to the presence of impurities. Invest in R&I to improve biomethane purification techniques, focusing on cost-effective and energy-efficient methods.
Biomethane reforming	Conventional reforming technologies require adaptations to accommodate the unique characteristics of biomethane. Advance the development of catalysts and reactor designs specifically tailored for biomethane reforming.
Hydrogen separation	Traditional separation techniques may not be optimised for the diverse gas compositions encountered in integrated hydrogen and biomethane production. Explore novel hydrogen separation technologies that can handle the complex gas compositions encountered in integrated production.
Process integration and optimisation	Achieving an efficient and cost-effective integrated production process requires optimal process integration and operation. Invest in the development of comprehensive process modelling, simulation, and optimisation tools specifically tailored to integrated hydrogen and biomethane production.
Scale-up and commercialisation	There is a need to scale up these technologies to commercial levels. Promote collaborative demonstration projects that showcase the feasibility and performance of integrated hydrogen and biomethane production at larger scales.

By prioritising these recommendations and investing in R&I activities, we can bridge the technological gaps and drive the efficient, sustainable and widespread adoption of integration of hydrogen into biogas and biomethane production streams. Such advances will contribute significantly to the global efforts of mitigating climate change and achieving a carbon-neutral future.

Conclusions

This report has provided a review of innovative technologies for the valorisation of biogenic CO_2 through improved methanation technologies and technologies for the integration of production of hydrogen into biogas and biomethane streams. Although some suppliers claim that such technologies have reached industrial maturity, the analysis conducted here has identified several significant technological gaps that need to be addressed to realise an integrated and efficient production process. These gaps span various areas, including biomethane purification, biomethane reforming, hydrogen separation, process integration and optimisation, and scale-up and commercialisation.

To bridge these gaps, the report recommends investing in research and innovation activities to improve biomethane purification techniques, advance the development of catalysts and reactor designs tailored to biomethane reforming, explore novel hydrogen separation technologies, develop comprehensive process modelling, simulation, and optimisation tools, and promote collaborative demonstration projects to showcase the feasibility and performance of integration of hydrogen production into biogas and biomethane production at larger scales.

By prioritising these recommendations, the sector could drive the efficient, sustainable and widespread adoption of these technologies. Such advances could contribute to global efforts to mitigate climate change and achieve a carbon-neutral society. The integration of hydrogen production presents a promising pathway towards a sustainable and low-carbon economy, and continued research and innovation in this field are crucial for realising its full potential.

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