

Review

Biological Hydrogen Methanation with Carbon Dioxide Utilization: Methanation Acting as Mediator in the Hydrogen Economy

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Abstract: Hydrogen is one of the main energy carriers playing a prominent role in the future decarbonization of the economy. However, several aspects regarding the transport and storage of this gas are challenging. The intermediary conversion of hydrogen into high-density energy molecules may be a crucial step until technological conditions are ready to attain a significant reduction in fossil fuel use in transport and the industrial sector. The process of transforming hydrogen into methane by anaerobic digestion is reviewed, showing that this technology is a feasible option for facilitating hydrogen storage and transport. The manuscript focuses on the role of anaerobic digestion as a technology driver capable of fast adaptation to current energy needs. The use of thermophilic systems and reactors capable of increasing the contact between the H₂-fuel and liquid phase demonstrated outstanding capabilities, attaining higher conversion rates and increasing methane productivity. Pressure is a relevant factor of the process, allowing for better hydrogen solubility and setting the basis for considering feasible underground hydrogen storage concomitant with biological methanation. This feature may allow the integration of sequestered carbon dioxide as a relevant substrate.

Keywords: anaerobic digestion; energy storage; reactor productivity; hydrogen conversion; high-pressure fermentation; biomethane; carbon dioxide



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1. Introduction

The current energy crisis associated initially with a higher energy demand after the removal of the pandemic restrictions and further aggravated by the Russian invasion of Ukrainian territory has set the focus of governments and society on the vulnerability of energy production and distribution systems. Centralized systems are characterized by high efficiency thanks to the benefits of lower installation costs which are greatly reduced with the increase in scale. Electricity generation is still mainly produced worldwide from fossil energy sources (4.4 TW), although renewables have increased their share in recent years. However, the energy demand has kept increasing almost linearly since 1990, except for the 2008 economic crisis and the 2019–2020 pandemic [1,2]. Given this context, a continuous increase in energy demand is expected in years to come, despite the extensive efforts to increase efficiency in energy use.

Renewable energies are considered an alternative for reducing CO₂ global emissions, presenting great advantages when considering decentralized energy production because of their lower transmission costs and lower exposure to cascading failures [3]. This feature

seems a significant advantage given the high vulnerability of centralized systems in a war scenario. Additionally, the application of decentralized production in developing countries is an interesting solution for increasing the energy access of rural populations located far away from production centers and lacking a good transmission network [4,5]. However, in developed countries where the energy market is dominated by centralized systems with a well-developed transmission network, decentralization does not seem reasonable in many cases unless electricity prices drive the market to increase off-grid energy systems.

One of the main disadvantages of wind and solar technologies is their intermittent nature, which makes them unavailable at some specific moments, becoming a serious problem in cases of standalone energy production systems [6], needing a backup to cover up for periods of null production. This feature leads to an over-dimension of installations needed to ensure complete coverage of the energy demand. Energy storage may come into play as a reliable solution. However, many storage systems are costly and still present a low energy density if compared with fuels. Lead acid batteries have a storage capacity of 30–50 Wh/kg, translating into an equivalent mass of methane of 5.6–9.5 g when considering the efficiency of 38% in electricity conversion. Li-ion batteries with higher energy density (90–190 Wh/kg) [7] show an energy storage capacity in terms of methane equivalent to 17–36 g. Although efforts are being made to increase the energy density of storage, as is the case of aqueous zinc batteries (410 Wh/kg) [8], long-term energy storage is dominated by technologies capable of accumulating a high amount of energy per unit volume.

Potential hydro-storage and compressed-air storage systems are examples of long-term energy storage [9]. The first one is characterized by having a large scale (1000–1500 MW) with high capital costs and highly site limited. In contrast, the latter requires the availability of high-volume underground reservoirs unless liquefied air is stored in high-pressure vessels. However, accumulation in underground reservoirs or abandoned mines, if available, is preferable because it aids in reducing installation costs [10–12]. A recent innovative way for storing energy at a large scale was developed by Advanced Rail Energy Storage (ARES) LLC, California. The patented system stores energy by raising a mass against gravity force when it is at the accumulating energy stage and returning it to its initial lower position when releasing energy [13]. The use of rails and wagons similar to those of train transportation gives the name to the system. The GravityLine™ storage system consists of multiple 5 MW tracks using a chain driver instead of a cable [14].

Another way of storing energy is by its conversion into hydrogen. If the process is carried out using electricity, it is denoted as electrochemical conversion. Currently, hydrogen is mainly produced from natural gas reforming and coal gasification, thus being referred to as “grey hydrogen” in the first case and “brown” in the second. However, hydrogen is designated as “blue” if carbon storage is attained. When this gas is produced using renewable energy, it is called “green hydrogen”. The use of this same classification when hydrogen is obtained from low-carbon emission energy sources (nuclear power) is still the subject of debate [15]. Carbon capture and storage technologies can serve as a transition technology to reach the objective of producing “green hydrogen” until this latter can become cost-competitive. However, there is a risk of delaying this transition due to the high cost associated with carbon capture technologies [16].

Because of the intermittent nature of some renewable energies, coupling these systems into a hydrogen production chain is an efficient way to store surplus energy and recover it during high electricity demand. This way eliminates the disadvantage of wind and solar systems that only produce energy when climatic and daily conditions are favorable, but not when energy is needed [17]. The conversion of excess electricity into an energetic gas enables the integration of electric and gas networks. Thus, surplus electric power can produce hydrogen using water electrolyzers and store/transform this gas or distribute it in the natural gas network [18] or an independent specialized gas network.

The hydrogen economy concept is not new and has recently awakened renewed interest in politics and society. The wide use of hydrogen in industry and transport sector is being reconsidered as an alternative for reducing greenhouse gas emissions.

Using hydrogen as fuel and/or energy carrier presents the main advantage of zero carbon emission release at the point where energy is used, thus aiding in eliminating dispersed CO₂ emission when applied to transport systems or as fuel in industrial equipment. CO₂ storage can be attained in central facilities where hydrogen is obtained from fossil fuels, taking advantage of the economy of scale since the high costs of carbon capture and storage highly influence the final cost of blue hydrogen thus produced [19]. The tremendous amount of hydrogen needed to act as an economic driver still makes the production of this valuable gas from fossil sources necessary. The technology is mature enough with several companies offering the combined technology of hydrogen production and carbon storage, as is the case of Honeywell (Charlotte, NC, USA), Linde/BASF Technology (Munich, Germany), and Thyssenkrupp AG (Essen, Germany) [20–23].

Efforts are being made to produce hydrogen from different renewable sources, but high capital investment costs and small production scale are still important barriers. Currently, a great amount of hydrogen is needed in industrial processes, being mainly produced from steam reforming of fossil fuels, and recently the majority of projects deal with methane steam reforming [24,25]. Figure 1 shows a schematization of different technologies available for producing hydrogen.

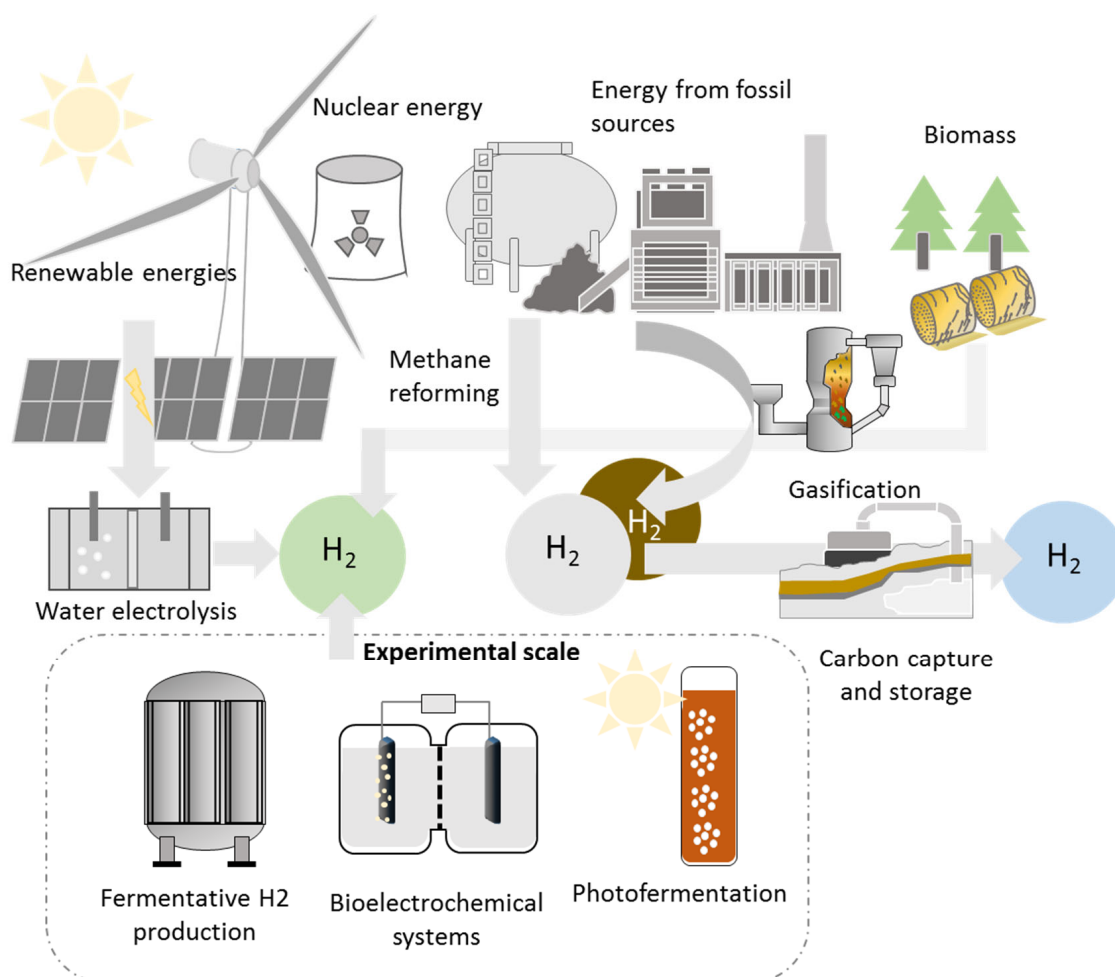


Figure 1. Schematization of processes available for hydrogen production.

Biological processes are still underdeveloped, with fermentative hydrogen production probably being the one closer to reaching commercial status. Bioelectrochemical systems (BES) and photo-fermentation processes are still costly. The volumetric production of photo-fermentation under batch condition was 1.6 L H₂/L_{reactor}, as reported by Das and Basak [26], or expressed as yield, with a value of 66.03 mL H₂/g TS, reported by Zhang

et al. [27]. For BES, yields obtained by De Gioannis et al. [28] were between 75.5–78.8 mL H₂/g TOC or expressed as a productivity rate, 0.3 L H₂/L_{reactor} d by Rosenbaum et al. [29]. The fact is that after several years of research work, the experimental scale is still small, and many of these experiments are performed with synthetic substrates. Dark fermentation presents similar yields (56.7–81.3 mL H₂/g TS [30–32]), but the advantage of a simplified reactor configuration plays in favor. The main constraints that prevent the increase in scale for BES and photo-fermentation are associated with the area/volume ratio needed for the reactor, complexity of the configuration, stability of the process, and difficulties experienced under long-term operation. Sterilization is a requirement that should be avoided; therefore, keeping a stable population is challenging due to the risk of the predominance of undesirable microorganisms with higher growth rates. This phenomenon is known as microbial shifts, and it is a severe drawback of the process.

The great amount of hydrogen that will be needed in the industrial and transport sector requires solutions capable of attaining high efficiency and easy and fast scale-up. Current research works and resources should focus on practical aspects regarding the way hydrogen can be integrated into the economic cycle. Solutions are needed regarding the logistics associated with hydrogen production, transport, and storage. Future work should deal with the expected increase in electricity demand associated with decarbonization and the way this energy will be obtained, considering that the use of fossil fuels should be greatly reduced, water scarcity will need to be confronted, and social rejection is a phenomenon that is emerging linked to the increased demand of land for installing windmills and solar panels.

2. Hydrogen Storage

Among the important factors that make the expansion of hydrogen as an energy carrier difficult are the low volumetric energy density and safety issues, making the transport and storage of this light gas complex. These two aspects impair serious constraints if a fast introduction into the market is desirable. Hydrogen has a lower heating value (LHV) of 120 MJ/kg. However, when translated into volumetric units, this value falls to 10.8 MJ/m³, a much lower value than that of methane (35.8 MJ/m³) at the same standard conditions. If compared with liquefied natural gas (with a value of 21–24 MJ/L) or gasoline (32 MJ/L), the volumetric energy density of hydrogen is disappointing, with a value of only 3.1 MJ/L at 350 bars, or 5.0 MJ/L at 700 bars [33]. The transport and storage of hydrogen present serious challenges starting with the amount of energy needed for increasing its volumetric density to reach storing conditions at high pressure and/or low temperature and the lack of feasible solutions for attaining storage in a compact and lightweight manner [34] capable of reaching energy densities comparable with that of conventional fuels. Figure 2 shows a schematization of different technologies available for hydrogen storage.

Different storage tanks are available in the market with pressure ranging between 250 and 700 bars. There are several advancements regarding the use of different materials. Metal hydrides, nanostructured carbon-based clusters, activated carbon, metal–organic frameworks (MOFs), and liquid organic hydrogen carriers (LOHCs) [35–39] are the examples of materials and ways for storing hydrogen. Cho et al. [40] reviewed different hydrogenation and dehydrogenation reactions using different types of LOHCs and catalysts. Formic acid/formaldehyde/ammonia, homocyclic compounds, and nitrogen and oxygen-containing compounds are considered in their review as feasible organics for developing a technology pathway. The full development and economic feasibility of this alternative are still under research, with several pilot-scale and large-scale projects being implemented. The LHyTS project is an example. The project aims to demonstrate the feasibility of exporting hydrogen from Scotland to Rotterdam using methylcyclohexane (MCH) as a hydrogen carrier [41]. Another example is the SherLOHCk project aimed at developing suitable catalysis to optimize the loading and unloading stage of LOHCs and determine the economic feasibility of the process [42]. These different options involve the use of organics. Nevertheless, the technology would be more interesting if carbon recycling could

be integrated into the process, as would be the case of using previously sequestered and stored carbon dioxide. Other large scale-projects involve the construction of a long-distance transport system using pipelines to create an H_2 gas network or developing national H_2 gas grids using current natural gas infrastructure, as is the case of the Get H_2 Nukleus project, where a gas grid of about 130 km would connect green hydrogen production centers and industrial consumers from Lingen to Geselkirchen [43].

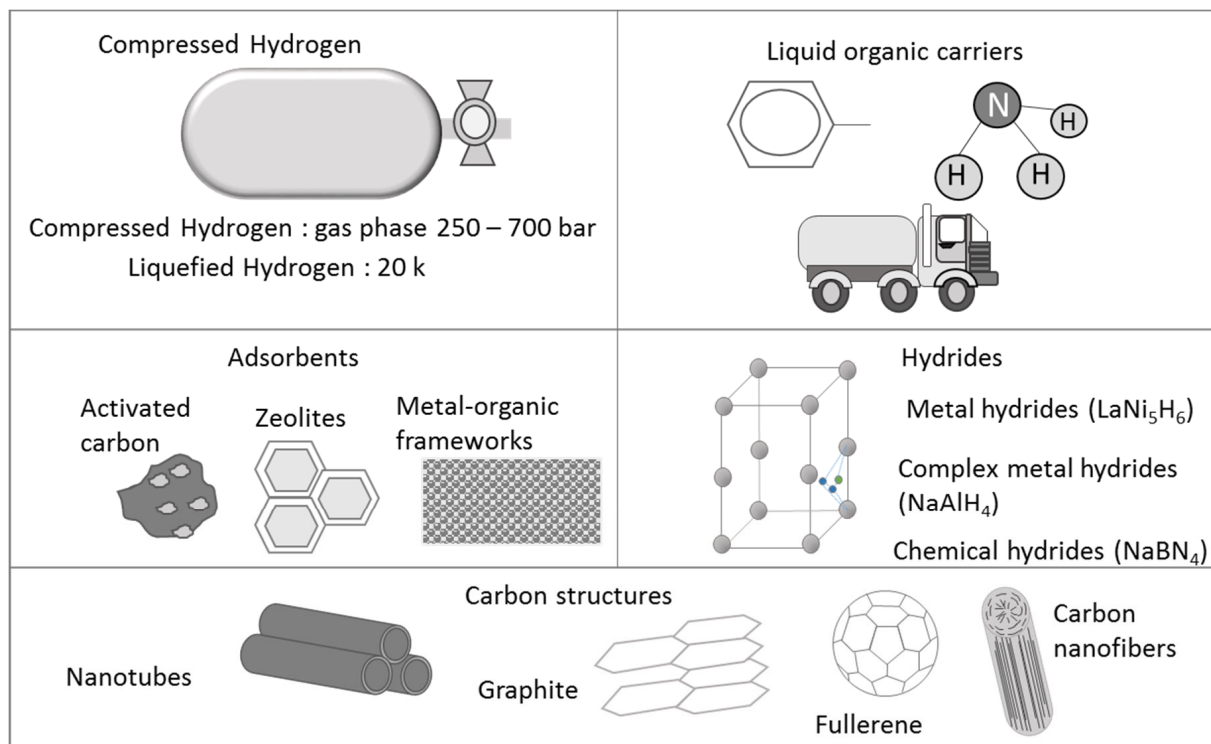


Figure 2. Technologies currently available for hydrogen storage.

Hydrogen storage under cryogenic conditions has been employed in rocket applications and aerospace missions. Although experience has been gained, the technology is full of challenges if an expansion is to be envisioned for commercial aviation, road transport, and other industrial sectors. The liquefaction attains a density of $70.9 \text{ kg H}_2/\text{m}^3$, which is much higher than the density obtained by other methods, such as hydrides, adsorption-based systems, or transformation into other chemical compounds [44]. High-pressure vessels or vessels capable of withstanding a temperature of 20 K at lower pressures are needed. Materials capable of resisting such conditions safely are scarce since diffusion of hydrogen into the metal structure causes embrittlement and fracture of the recipient [45,46]. Most storing vessels are made of stainless steel and aluminum alloys. Composite materials offer the advantage of a lighter weight, but hydrogen permeation is still a problematic issue [46]. Additionally, the amount of energy needed for liquefaction is about 35–45% of the lower heating value of hydrogen. Other limitations include gas losses during storage, transportation, and handling, which may be as high as 45% of the initial volume acquired [47–49].

Another way for storing hydrogen is by transforming it into small molecules to increase its energetic density, as it is the conversion into methane or ammonia. This strategy allows for reducing constraints associated with gas storage. It also takes advantage of the use of well-developed technology at a large scale and the availability of existing infrastructure without summing up additional restrictions [50], thus favoring a fast technology transition. Ammonia can serve as a suitable mediator since this gas has a high density as a hydrogen carrier (17.7 wt %), being liquefied at 8.58 bars. Therefore, carbon steel tanks can be used

for storage. In addition, a vast network of pipelines is already available, offering a much lower transport cost than that estimated for compressed H₂ [51].

Ammonia can be used directly as a substitute for fossil fuels, although having a lower heating value (18.6 MJ/kg) and lower flame speed than gasoline [52] (Kobayashi et al., 2019). However, these disadvantages can be compensated by applying a higher compression ratio and by the fact that it can be used in both spark ignition engines and compression-ignition engines [53]. Ammonia is currently being considered a feasible alternative fuel for decarbonizing deep-sea vessels [54] or as a sustainable fuel for aircraft [55]. However, in this latter case, due to engine constraints, the implementation would be more challenging regarding NO_x control and corrosive behavior [56]. In addition, several barriers must be overcome, such as production costs, availability close to ports and airports, safety considerations, and toxicity effects on humans and the environment [57].

The feasibility of reverting the process to release hydrogen from ammonia at a relatively low temperature (400 °C) was demonstrated by Zhang et al. [58] using Ruthenium catalysts. However, the use of this high-cost metal and its low abundance keep pressure on developing new bimetallic catalyst systems with similar capabilities to those based on noble metals [59]. Ammonia borane (NH₃BH₃) is another interesting candidate for storing hydrogen thanks to its high H₂ density (19.6% hydrogen). Çelik Kazici et al. [60] reported on the feasibility of releasing hydrogen from ammonia borane using PdCoAg/AC nanoparticles at temperatures between 20 and 50 °C. Similarly, Xu et al. [61] developed an Ag@Pd core-shell catalyst for releasing hydrogen from this same compound.

Methane is the other small molecule produced from the catalyzed conversion of hydrogen, but in this case, the Sabatier process is used, which is currently experiencing a renaissance [62]. This strategy is known as Power-to-Gas (PtG) technology, or specifically Power-to-Methane (PtM), where the excess electricity, mainly from renewable sources, is used to produce hydrogen by water electrolysis and then transform it into methane [63]. Hydrogen and CO₂ react at relatively high temperatures (200–350 °C) with the aid of a catalyst. The reaction has an exothermic behavior; thus, temperature control is needed to avoid catalyst sintering problems [64]. The result is methane and water formation, with a maximum conversion efficiency of 83% [65,66]. The process is well developed, and if high-activity catalysts are available at a lower cost, then the process would attain a status close to industrial commercialization in a short time. An industrial plant was built in 2013 by ETOGAS GmbH (now acquired by Hitachi Zosen Inova) in a project owned 100% by Audi [67–69].

Hydrogen may also be transformed into methane by biological means. The conventional anaerobic digestion process can serve as a technology for storing energy in line with the PtG concept, having a similar global warming potential as that of the Sabatier process, as reported by De Roeck et al. [70] from results of the life cycle assessment of the two processes. The amount of raw energy stored at 60–180 bar as methane is about 2.1–6.3 MJ/L, whereas this value falls to 0.6–1.9 MJ/L when hydrogen is considered under equivalent conditions. Farghali et al. [71] proposed the integration of anaerobic digestion and pyrolysis systems along with the conversion of hydrogen into biogas, thus upgrading its quality and storing carbon as biochar after the thermal processing of digestate. Several technologies can be integrated into the PtG concept, which would aid in increasing the circularity of the economic model and, at the same time, help reduce fossil fuel use. However, many of these approaches deal with thermal technologies that, at present, are not widely extended due to their low economic feasibility. Therefore, pyrolysis, gasification, and hydrothermal conversion of biomass are technologies that may seem a valuable ally in the integral transformation of biomass, but high installations costs prevent this approach from becoming a reality, although their coupling with digestion processes demonstrated higher energetic efficiency [72–75]. Table 1 summarizes the energy density of different chemical compounds.

Table 1. Energy density of gases and fuels commonly used for energy storage. The value of energy volumetric density for lithium-ion batteries was added for the sake of comparison.

Compound	Energy Density (MJ/L)	References
H ₂ (STP)	1.08×10^{-4}	
CH ₄ (STP)	3.58×10^{-4}	
LNG	21–24	
Gasoline	32	
Compressed H ₂ at 350 bar	3.1	[33]
Compressed H ₂ at 700 bar	5.0	[33]
Liquefied H ₂	8.5	[44]
Ammonia at −33 °C	12.7	[76]
MCH when used as hydrogen transport ¹	2.8	[49]
Li-ion batteries	0.97–2.7	[77]

STP: standard temperature and pressure conditions, LNG: liquefied natural gas. MCH: Methylcyclohexane, Li-ion: lithium-ion. ¹ Value estimated using a density of 769 kg/m³ for MCH and an atomic hydrogen content of 6.16% (*w/w*). LHV of hydrogen was 120 MJ/kg.

Biological methanation is a naturally occurring process that takes place in the later stages of digestion. The reactions of this conversion route are hydrogenotrophic methanogenesis and homoacetogenesis. In the first case, organisms use H₂ and CO₂ as sole energy and carbon sources, and in the latter, H₂ is converted into acetate and subsequently oxidized into methane by acetoclastic methanogens [78]. Using existing anaerobic digesters to either upgrade biogas or as conversion units for storing extra energy derived from renewables to reduce the mismatch between production and demand is a technological option with great potential for success. This strategy is based on using existing infrastructure, allowing energy storage and aiding in increasing the decentralized production of the energy since many digestion plants already count with combined heat and power operating units or biogas upgrading units, thus accelerating the transition into the hydrogen economy.

Biomethanation aids in generating local energy sources capable of substituting natural gas in a decentralized manner, thus reducing transportation costs. Tauber et al. [79] assessed the biomethanation conversion potential in Austria and estimated a conversion capacity of about 2.9–4.4% of the country's yearly renewable electricity production under the PtG concept. In the case of Spain, the energy mix is characterized by a high share of renewables, causing the system to be over-dimensioned. The total installed power is 107,505 MW, with 58.4% associated with renewables (wind accounting for 25.7% and solar for 22.8%). However, on the day of maximum energy demand (41,483 MWh on 8 January 2021), only 33% of wind energy and 16.2% of solar energy out of the installed capacity was available to cover the demand [80], thus requiring import energy from other countries and needing for nuclear energy to serve as a reliable back-up system.

Valle-Falcones et al. [81] studied the feasibility of producing hydrogen from wind energy surplus and its further storage in an underground salt dome. The surplus wind energy reported for only one Spanish community (Castilla y León) was estimated to be 503 GWh for a 9-month period in 2020. However, some other aspects also result crucial to guarantee the feasibility of the PtG concept, as demonstrated by Bekkering et al. [82]. The efficiency of the electrolyzer, investment costs, and electricity price are the most sensitive factors remarked by these authors as having the main influence on the economic viability of the process. Thus, if biological conversion is to be run only with surplus electricity as a way to favor the economic balance, a detailed analysis regarding the effect of intermittency in the biological reactor should also be assessed.

Hydrogen transport and storage are full of challenges. Given the flammability limits of this gas and explosive behavior, it seems reasonable to wonder if the proper route should be the centralized production and subsequent transport in pipelines which may be subject to climatic stress and high maintenance costs. The high diffusivity of hydrogen also creates concerns regarding hydrogen losses during handling operations and associated safety issues. Economic and risk assessments are needed as part of future research work that may

help decide if decentralized hydrogen production or storage and transport of hydrogen in a more stable form should be the best option. The quality of water and scarcity of this resource are other factors that should be carefully evaluated. How would society react to using water for hydrogen production under a scenario of extreme drought? This is a question needing an answer.

3. Biological Conversion of Hydrogen to Methane in Reactors with Mixed Substrates

The anaerobic digestion of wastes into methane is a process with a wide application at large scale, although having great complexity with a diverse group of microorganisms involved and different stages taking place in a sequential manner, starting with the transformation of high molecular weight species into smaller intermediaries (mainly short chain fatty acids) to finally give rise to the production of methane [83–85]. Attaining stable performance involves controlling biological parameters and reactor conditions [86], which makes challenging the daily operation of these units against seasonal modifications of the feed and climatic conditions. However, experience is vast, and the technology has been perfectly developed with several large-scale digesters treating sewage sludge in wastewater treatment plants (WWTP), manures in livestock farms, or a mixture of different wastes and agronomic substrates in centralized units. Efforts are still being made to increase the conversion efficiency, as it is temperature-phased digestion systems, high-rate configuration reactors, high-solid digestion, and the enhancement of methanogenesis by adding supplements such as nano-additive, adsorbents, or carbon conductive materials [87–94].

The final stage of the digestion process is the one having a particular repercussion in the methanation of hydrogen. From here, a new line of research has been developed, thus opening new technical opportunities for reducing biogas upgrading costs and increasing waste treatment centers' versatility by using digesters as H_2/CO_2 conversion units. The main organisms responsible for attaining hydrogen conversion are homoacetogenic bacteria and hydrogenotrophic methanogens. Homoacetogenic bacteria catalyze the formation of acetate from C1 carbon sources; thus, in the case of using CO_2 , hydrogen serves as an electron donor [95], but these bacteria are also capable of using CO. Thanks to the presence of acetyl-CoA synthase and by following the Wood–Ljungdahl pathway, gaseous mixtures $CO_2/CO/H_2$ can be transformed into acetate [96].

Hydrogenotrophic methanogens are the other organisms responsible for transforming H_2/CO_2 . These organisms are present in almost all methanogenic orders except the Methanomassiliicoccales [97]. At mesophilic conditions, a consortium formed by various bacteria and archaea forms a complex biological pathway involving homoacetogenesis–acetoclastic methanogenesis and hydrogenotrophic methanogenesis. However, at thermophilic conditions, the pathway is dominated by these latter organisms [98], with *Methanothermobacter* genus dominating the archaea population at temperatures between 55 and 70 °C [99,100].

The interest in using these organisms is not new. Barik et al. [101] demonstrated their high capability in growing in conjunction with methanogens to valorize the low-calorific gas derived from gasification, known as syngas. This gas contains H_2 , CO, and CO_2 as main components and smaller amounts of methane and short-chain hydrocarbons [102,103]. Several reports are found in the scientific literature regarding syngas conversion using pure and mixed microflora [104–106], along with specially selected mixtures of organisms for attaining the conversion of CO to methane [107–109]. The interest has further increased to develop technologies based on valorizing steel mill waste gases. The Steelanol project is an example at the industrial level. A European-funded project where ArcelorMittal inaugurated a carbon utilization plant for producing ethanol in its Steel plant in Ghent (Belgium) in 2022, with the technology of LanzaTech [110,111]. Nutrient-limited conditions applied to the microflora allow shifting metabolism to produce ethanol instead of acetate [112].

The conversion of syngas derived from biomass gasification may be another option for transforming $H_2/CO/CO_2$ mixtures into methane and increasing its volumetric energy content. The thermal process can be integrated into the same biomass valorization

chain, thus treating digestate by thermal methods, reducing the mass of material needing final disposal after anaerobic digestion, and transforming the gas mixture obtained from gasification into methane in the same digester. Reports of Andreides et al. [113] indicated that acclimation of the anaerobic microflora to the gaseous substrate is unnecessary. Westman et al. [114] demonstrated the high conversion capacity of anaerobic microflora in transforming the gaseous mixture using a reverse membrane bioreactor, attaining high cell density, and reducing gas transfer limitations. Robazza et al. [115] tested the ability of mixed microflora to ferment syngas derived from pyrolysis and pyrolysis aqueous condensate (PAC), a residual stream obtained from the pyrolysis process having difficult treatment. These authors reported on substantial detoxification of PAC independently of the rates of syngas metabolism. PAC detoxification was performed by anaerobic mixed microflora in a first fermentation stage producing acetate, and further transformation into L-malate was carried out in a second fermentation stage. Although these approaches may seem promising, syngas derived from biomass contains some toxic compounds, such as hydrogen cyanide and tars, which endanger fermentation development. Efforts are being made at a quasi-commercial scale to solve these inhibitory problems to efficiently remove toxic organics, although alternatives currently available are expensive [116–118].

3.1. Process Configuration

Hydrogen methanation can be carried out in the same digester treating the organic waste, in this case serving hydrogen as an additional co-substrate to enhance methane productivity, or it can be carried out exclusively in a reactor specially operated to attain the conversion into methane, thus needing an additional source of CO₂ and nutrients. In the first case, it is cataloged as in situ methanation, whereas in the latter, it is called ex situ methanation [78,100]. This conversion process can be understood as a reliable substitute for biogas upgrading technologies. Biogas contains water vapor, hydrogen sulfide, ammonia, and large quantities of CO₂ that need to be removed if gas network requirements are to be met.

Biogas is usually valorized in situ for producing electricity using combined heat and power (CHP) units or heat in boilers or is upgraded to meet standards similar to those of natural gas. The first two cases require minimum cleaning operations associated with H₂S and water vapor removal [119]. Biogas valorization requires upgrading to increase its quality close to that of natural gas so that it can become a gaseous substitute [120,121]. Most biogas upgrading plants are based on expensive and high energy-demanding technologies such as chemical/water scrubbing, membrane separation, and pressure swing adsorption [122,123]. The use of the same biological process already working in the plant for attaining an increase in methane concentration allows for improving methane productivity, and it may aid in reducing plant operating costs. Studies evaluating the energy demand of the different upgrading technologies are necessary to assess real savings when intending their replacement for biological H₂/CO₂ conversion, given the significant investment and maintenance costs associated with electrolyzers. Figure 3 shows a schematization of in situ and ex situ methanation processes.

The main disadvantage of direct hydrogen addition into the digester (in situ methanation) may be associated with the increase in hydrogen partial pressure, which may cause disturbances in the sequential conversion of organics, inhibiting acetogenesis by creating thermodynamically unfavorable conditions causing the accumulation of volatile fatty acids [124,125], causing pH reduction if alkalinity available in the reactor liquor is not enough to compensate its effect or cause microbial inhibition.

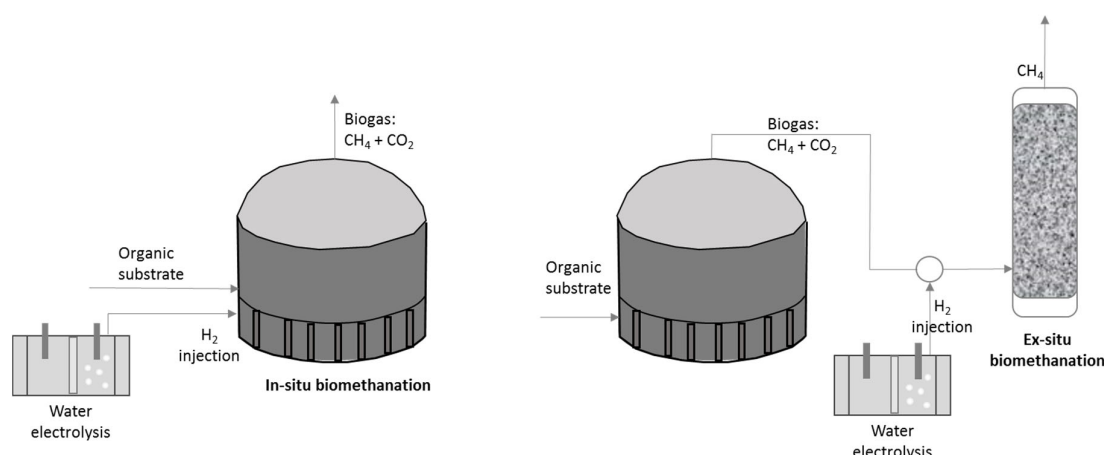


Figure 3. Schematization of hydrogen biological conversion into methane under the in situ and ex situ methanation configurations.

Illi et al. [126] tested a hydrogen methanation reactor under mesophilic conditions with an injection rate of 0.031 and 0.063 $\text{m}^3 \text{H}_2/\text{m}^3_{\text{reactor}} \text{h}$ in concomitance with the treatment of maize hydrolyzate. Hydrogen addition did not cause any disruption in acid conversion, thus leading to an increase in methane productivity from 0.91 to 1.2 $\text{m}^3/\text{m}^3_{\text{reactor}} \text{d}$ (32% increase) when comparing the operation with and without hydrogen addition. However, the higher injection rate decreased the conversion of hydrogen into methane, at approximately 62%, against 75.5%, which was attained at the lower injection level. Additionally, the authors did not report any significant changes in the methane content of biogas since its concentration was similar for all conditions tested. Previous results obtained by Martínez et al. [127] were in consonance, in this case studying the addition of hydrogen to a digester treating sewage sludge under mesophilic conditions, obtaining a 13% increase in biogas production, without evidencing changes in biogas composition. The conversion of hydrogen, following the indirect route of producing acetate and, subsequently, methane, also leads to a global reduction in CO_2 content. The concomitant transformation of an organic substrate and hydrogen, as in the previous experiments, may result in small changes in CO_2 levels, which were probably not detected by the measurement techniques.

Okoro-Shekwaga et al. [128] studied the effect of the hydrogen injection point on the sequence of the digestion process. For this purpose, batch assays were evaluated using an in situ configuration with food waste used as substrate. The authors used a reactor containing only inoculum, another one containing the mixture of inoculum and food wastes, and a third system used to add H_2 gas to the mixture of inoculum and food wastes. This configuration allows obtaining data from inoculum background production, methane production from food wastes, and analyzing the effect of adding H_2 to the food waste digestion system. The gas addition was carried out prior to acidification, during acidification, and at the end of volatile fatty acid (VFA) assimilation.

The authors indicated that the best strategy for avoiding VFA accumulation was the injection, either at the initial stage of the fermentation or after acids derived from the co-substrate were assimilated. In the first case, fast assimilation and conversion of hydrogen were observed with a significant reduction in CO_2 content, but without evidencing pH changes. However, when hydrogen was added in the subsequent stages, the presence of excess VFA resulted in the lack of biomethanation enhancement. In contrast, when performed at the final stage, an increase in pH was registered, but a lower improvement in methane production rate and methane concentration was obtained. These findings may be interesting when reactors are operating under plug flow configuration since, in this case, the length of the reactor will be associated with a particular stage of the fermentation. Thus, the hydrogen injection point should be located close to the entrance of the feed. However,

under a continuously stirred tank reactor (CSTR) configuration, the reactor liqueur is at the final digestion stage due to the operating characteristic of this type of reactor, where the reaction rates run under deprived substrate conditions. Adding hydrogen to the digester would be equivalent to adding the gaseous substrate at the final stage of digestion, hence causing a pH rise, as already found by Luo et al. [129] and Wahid et al. [130].

3.2. Mass Transfer Limitations

Mass transfer limitations are the main explanation for low conversion rates. Hydrogen solubility in water is low, with a value of 1.6 mg H₂/kg water at 273 K [131]. Therefore, the access of microorganisms to the substrate will be conditioned by the concentration gradient and the ability to transfer hydrogen from the gas to the liquid phase. This transport phenomenon is restricted by its diffusion coefficient and the superficial area available. That is, mass transport is dominated by diffusion of the solute across the liquid-side boundary layer, a process described by Fick's law in terms of a coefficient that accounts for diffusion, the layer thickness (KL), and the interfacial area (a), leading to a unique parameter describing the process (KLa) [132]. In this way, a better distribution of gas bubbles with smaller sizes will favor mass transfer, thanks to the increase in the overall surface area, but also because of the higher time bubbles would spend inside the digester due to the lower buoyancy force and lower rising speed [133]. The experiences performed by Liu et al. [134] demonstrated that introducing hydrogen in the form of nano-bubbles allowed for higher methane production rates than those obtained from micro-bubbles. However, the higher energy requirement to produce such small bubbles may eliminate any benefit associated with a higher methane production rate.

Another critical factor worth mentioning is that applying direct hydrogen injection to large-scale digestion systems would benefit from the higher pressure existing in these reactors due to the height of the liquid column and the higher drag force experienced by gas bubbles because of the greater sludge viscosity. Therefore, higher KLa values are to be expected for the mass transfer phenomenon, and better conversion rates are to be obtained with increasing reactor scale. Several research works are available in the literature describing small-scale experiments under batch conditions. However, there is an urgent need for testing units with larger scale and specific equipment capable of handling biogas and hydrogen mixtures and analyzing energy demand. Herkowiak et al. [135] tested a hybrid pumping system for introducing hydrogen, which can operate as a gas dispersion unit and provide mixing, generating small bubbles when needed with low energy demand. More experimental work regarding large-scale reactors is needed to verify the real benefits of hydrogen injection and the energy demand of the auxiliary equipment associated with this strategy. Special requirements regarding the safe handling of this gas are needed, along with working protocol modifications in WWTP if digesters are to be used as hydrogen conversion units. Hydrogen has a wide range of flammability limits, much higher flame speed than gaseous hydrocarbons, and lower energy requirements for ignition. These properties make of this gas very exigent in safety measures for handling and daily operating activities.

3.3. Effect of Temperature

The temperature increase is another strategy for increasing microbial reaction rates, but gas solubility may be adversely affected. However, in methanation studies found in the literature, thermophilic conditions tested proved to be superior. Tang et al. [136] studied the ex situ conversion process reporting that organisms responsible for hydrogen conversion were mainly *Methanobacterium* and *Methanoculleus* (hydrogenotrophic methanogens). After the upgrading process, these authors attained a methane content in biogas of 91.4%. In a different study, Bassani et al. [137] reported similar upgrading results when testing mesophilic and thermophilic conditions but obtaining higher conversion efficiencies for the latter. Both reactors experienced enrichment in hydrogenotrophic methanogens with a concomitant decrease in acetoclastic methanogens. The source of inoculum seems to be

irrelevant, with organisms being easily adapted to new temperature conditions, as shown by Figeac et al. [138], who tested mesophilic and thermophilic inoculum, reporting a fast acclimation to the temperature increase and also reported higher methane production rates for thermophilic systems. However, the process became more unstable with the increment in temperature beyond 55 °C. This feature can be considered a disadvantage since stable long-term reactor operation is critical for attaining industrial application. The microflora diversity is relevant when testing ex situ biomethanation since these cultures can degrade acetate whenever a process perturbation is observed. Logroño et al. [139] corroborated these findings when testing the behavior of a mesophilic reactor for an extended period, using different inoculum sources. These authors reported that highly diverse cultures showed better performance because acetoclastic methanogenesis was active throughout the whole experimental period, reducing the tendency to acetate accumulation. These results seem contradictory, but they are really consistent with the adaptation of microflora to reactor conditions. A mixed microflora can be easily adapted to specific temperature and loading rate conditions, but these operating conditions, in turn, will create, as a consequence, a preferential proliferation of some specific microbial biomass. Thus, the long-term operation under a thermophilic regimen will cause the washout of acetoclastic methanogens.

In general, applying thermophilic conditions tends to enrich the culture of hydrogenotrophic methanogens. Homoacetogens cannot compete with hydrogenotrophic methanogens for the H_2/CO_2 substrate, changing even their metabolism, using acetate as substrate and producing back hydrogen and CO_2 , which causes a greater increment in H_2 -consuming species [140]. Increasing fermentation temperature affects gas solubility, but the decrease in this parameter seems to be compensated by the higher assimilation rate demonstrated by the performance of thermophilic microorganisms [141], thus keeping a strong gradient active, which translates into better conversions and higher methane production at higher temperatures [142,143]. Considering that the main limitation of this process is attaining a good transfer between the gas and the liquid phase along with retaining the cellular biomass responsible for hydrogen conversion, injecting hydrogen into typical AD reactors does not seem an efficient and practical way for the conversion of hydrogen into methane as the results clearly indicate. Testing different reactors' configurations capable of attaining these goals is the logical sequence of experimentation. Table 2 shows a list of small-scale experiments with reactors mainly operated under batch conditions. The next section will review different reactor configurations studied to enhance methane productivity.

Table 2. Small-scale experiments found in the scientific literature regarding biological conversion of hydrogen into methane. CSTR stands for continuously stirred tank reactor.

Operating Conditions	Regimen	Main Results	References
Fed-Batch system. Substrate: Cattle manure H_2 injection into the head space	Mesophilic (39 °C) Working volume: 5 L	31% increase in CH_4 production with 400 mL H_2 injected. No significant increase in CH_4 concentration No effect reported regarding $H_2:CO_2$ molar ratio	[144]
H_2 injection at 4:1 $H_2:CO_2$ molar ratio H_2 loading rate: 2 L/ L_{reactor} d	Mesophilic CSTR working volume: 3.6 L Thermophilic CSTR working volume: 4.5 L	Better thermophilic performance but needing longer adaptation time to achieved maximum efficiency. 84% of CO_2 conversion efficiency with a methane production ¹ of 0.084 L CH_4 / L_{reactor} d	[142]

Table 2. Cont.

Operating Conditions	Regimen	Main Results	References
Batch ² Substrate: glucose, and diluted manure to provide nutrients. Intermittent H ₂ injection	Mesophilic (37 °C) Working volume: 0.5 L 4:1 (H ₂ :CO ₂) molar ratio considered as optimum	Increase in CH ₄ content from 67 to 94%. High residual H ₂ levels caused VFA accumulation. pH increase observed with the increase in CO ₂ conversion Methanobacterium increased in abundance	[130]
Batch Substrate: Maize leaf Hydrogen injection of 507 mL/L _{reactor d}	Thermophilic (52 °C) Working volume: 20 mL	Excess H ₂ addition caused VFA accumulation and CO ₂ depletion, along with stimuli for homoacetogens to convert CO ₂ and H ₂ into acetate. pH control needed to avoid excessive increase. Enrichment of Methanobacterium	[145]
Acclimation of mixed cultures. Testing shear rate and media composition	Mesophilic (37–38 °C) Working volume: 50 mL and 500 mL	Enrichment attained using a mixed culture. 97% CH ₄ content obtained. Predominating methanogens were Methanobacterium and Methanoculleus genus	[146]
Testing different H ₂ :CO ₂ ratios 24 h gas residence time	Mesophilic (37 °C) Thermophilic (55 °C) Working volume: 50 mL	The maximum CH ₄ concentration was obtained at thermophilic condition (81%) with a 4:1 H ₂ :CO ₂ molar ratio Average H ₂ utilization efficiency of 92%, with a conversion yield of 0.23 L CH ₄ /L H ₂	[143]
H ₂ injection 4:1 H ₂ :CO ₂ molar ratio Gas loading rate: 6 L/L _{reactor d} (4.8 L H ₂ /L _{reactor d})	Mesophilic (37 °C) Working volume: 4.5 L Packed bed reactor testing glass pipe tubes and ceramic balls as filling material	Average methane production rate between 4 and 5 L CH ₄ /L _{reactor d} , with glass pipe filling showing better performance ³ .	[147]

¹ Estimated from data reported. Specific methane production for thermophilic system of 0.014 L CH₄/g VSS d. Biomass measured as grams of volatiles suspended solids (VSS). Biomass concentration in reactor of 4 g VSS/L.

² Catalogued as Batch by the authors, although reactors were fed with glucose and hydrogen was intermittently added, evaluating the different operating cycles. ³ Value reported is not congruent with theoretical methane yield derived from the reaction. An amount of 0.25 mol of CH₄ are to be expected for each mole of H₂ added.

4. Biological Conversion of Hydrogen to Methane with CO₂ as Substrate in Specialized Reactors

The main limitation of the H₂/CO₂ conversion process is dictated by the low transport of gases into the liquid phase. Increasing mass transfer area by modifying bubble size would lead to an increase in the energy demand when operating under a CSTR configuration either under in situ or ex situ modalities, as already described in previous sections. Increasing agitation speed also favors the mass transfer process leading to an increase in KLa values [148], but also brings as a disadvantage an increase in energy demand, which is a crucial aspect when reactor dimensions are in the order of thousands of cubic meters. The increment in the available biomass to transform a determined substrate also aids in increasing gas conversion rates. However, it may also adversely affect the energy demand of mixers due to increased liquid viscosity. Therefore, cell biomass immobilization has been proposed to increase cell density and facilitate interphase contact. Other biomass retention methods are using membranes, recycling of cells after sedimentation or centrifugation, or operating as a sequencing batch reaction system, allowing for biomass sedimentation inside the reactor.

Jee et al. [149] tested a packed bed system using ceramic material (bed volume: 0.8 L), reporting a methane production rate of 6 L CH₄/L_{bed} h (144 L CH₄/L_{bed} d). Another configuration tested was hybrid systems, thus denoted because cellular biomass is present in the reactor forming granules, whereas the primary substrate is the gas injected into the reactor. This type of configuration has been tested for the conversion of H₂:CO₂ mixtures by Daglioglu et al. [150], reporting a methane production rate of 19 L/L_{reactor} d with an H₂ injection rate of 19.2 L/L_{reactor} d (gas injection rate of 24 L gas/L_{reactor} d at an H₂:CO₂ ratio of 4:1), resulting in a methane yield higher than the theoretical value of 0.25 L CH₄/L H₂. Microbial analysis indicated that in addition to hydrogenotrophic species, acetoclastic species were also observed in the system, although the feeding substrate was exclusively conformed by the H₂:CO₂ mixture [151].

Dupnock and Deshusses [152] evaluated a trickling bed reactor using polyurethane foam (PUF) under mesophilic conditions. These authors reported maximum methane productivity of 38 L CH₄/L_{reactor} d with a yield equivalent to the theoretical one. However, other reports regarding this type of configuration were unable to reach such high production rates, ranging between 1.2–2.5 L CH₄/L_{reactor} d [153–155]. Other types of immobilized reactors were studied by Dağlıoğlu et al. [156] using as carriers plastic material and glass beads at a gas injection rate of 6 L gas/L_{reactor} d at 4:1 molar ratio (H₂:CO₂) under mesophilic conditions achieving methane production rates between 4.8 and 5.14 L CH₄/L_{reactor} d. Even though the expected yield should have been lower considering the limits imposed by the chemical reaction. Gas retention time in these reactors was estimated to be about 2 and 2.58 h, obtaining a methane concentration of around 80% in the exiting gas. This low methane content was explained by the use of a mixed inoculum, reporting also the presence of ethanol and butanol in the liquid phase. Figure 4 shows different configurations of reactors commonly used for evaluating the biological conversion of hydrogen into methane.

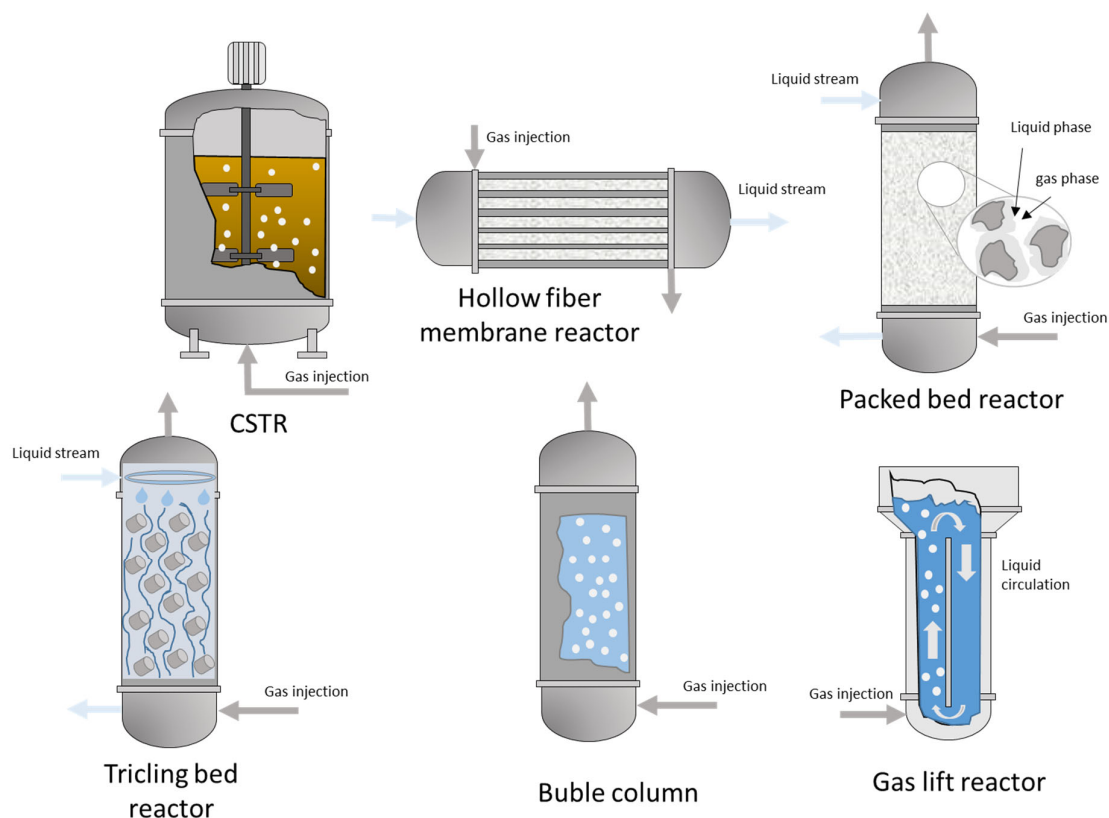


Figure 4. Schematization of different reactor configurations used for assessing performance of hydrogen biological conversion into methane.

The use of liquid flow modulation in trickling bed reactors was proposed by Ullrich and Lemmer [157] for increasing the superficial area available for hydrogen transport to the liquid phase; this way, the continuous irrigation of liquid is avoided, giving time for increasing the contact between the gas up-flowing phase and the liquid static layer covering the biofilm. The intermittent sparkling of the packed bed avoids dehydration of biofilm and improves conversion performance [158]. However, in the experiment of Ullrich and Lemmer [157], only a 10% increase in methane content was observed, thanks to liquid modulation when running the reactor at 5-bar pressure. From information reported in the scientific literature, trickle bed reactors constitute a practical and efficient method of reacting H_2 and CO_2 to generate bio-methane, given the high ability to increase gas–liquid contact and biomass retention.

Membrane reactors are another type of configuration suitable for retaining cell biomass and promoting interphase contact. Ju et al. [159] tested a hollow-fiber membrane reactor at mesophilic conditions, operating as a gas–liquid heterogeneous system, with the gas being introduced in the inner side of the hollow-fiber from where it diffuses through the liquid contained in the carcass section. A mixture of $H_2:CO_2$ at a 4:1 molar ratio was fed as a gaseous substrate. The authors tested the system under acidic and neutral conditions, reporting a greater methane evolution at this latter condition with a significant content of acetic acid in the liquid phase whenever pH was kept close to neutral conditions. However, no data were reported to allow estimating methane yields. Table 3 shows a list of results reported in the literature under different reactor configurations designed to retain cell biomass and increase gas–liquid contact.

Table 3. Biological methanation experiments found in the literature using non-conventional reactors.

Reactor Configuration	Operating Conditions and Working Volume	Methane Production Rate (MPR) ($L\ CH_4/L_{\text{reactor}}\ d$)—Main Results	References
Biotrickling filter Packing material: PUF (Temperature: 52 °C)	H_2 injection rate: 11 $L/L_{\text{reactor}}\ d$ Reactor volume: 0.291 L	MPR: 3.03 (Methane concentration: 98%) Reactor inoculated from a mixed anaerobic culture extracted from a biogas plant digester. Methanobacterium and Methanothermobacter represented $62.3 \pm 1.5\%$ and $31.1 \pm 1.0\%$ of the total archaea respectively	[160]
Bubble column (Temperature: 54 °C)	Gas injection rate: 3 $L/L_{\text{reactor}}\ d$ (gas composition: $CH_4:H_2:CO_2$ of 23:62:15 (%)) Reactor volume: 1.2 L	84% conversion of H_2 injected Accumulation of acetate at the end of the experiment Methane content output gas: 97–98% Reactor inoculation with thermophilic digestate. Methanothermobacter thermautotrophicus was the most abundant methanogen.	[161]
Pressurized CSTR (Pressure: 122 KPa Temperature: 60 °C)	0.5 L/min Reactor volume: 3 L Gas injection rate: 240 $L/L_{\text{reactor}}\ d$ $H_2:CO_2$ ratio: 4:1	MPR: 65.6, for pressurized system 92% increase when compared with atmospheric control system Pure culture of Methanothermobacter thermautotrophicus	[162]

Table 3. Cont.

Reactor Configuration	Operating Conditions and Working Volume	Methane Production Rate (MPR) (L CH ₄ /L _{reactor} d)—Main Results	References
CSTR reactor with H ₂ supplemented using submerged membranes Temperature: 35 °C	H ₂ injection rate: 0.87 L/L _{reactor} d Gas recirculation rate: 200 L/L _{reactor} d Reactor volume: 20 L	MPR: 0.54 Value obtained from combined digestion of sewage sludge and H ₂ addition. (42% increase in MPR when compared with sewage sludge digestion). <i>Methanoculleus</i> sp., <i>Methanospirillum</i> sp., <i>Methanolinea</i> sp., and <i>Methanobacterium</i> sp. were the hydrogenotrophic archaea dominating in the reactor	[163]
Thermophilic anaerobic sludge blanket reactor Temperature: 55 °C	H ₂ injection rate: 16 L H ₂ /L _{reactor} d Gas composition: CH ₄ :H ₂ :CO ₂ of 23:62:15 (%) Reactor volume: 6.3 L	MPR: 3.9 96% H ₂ conversion. Optimum gas recycle rate: 200 L/L _{reactor} d Testing mesophilic and thermophilic system founding better performance at higher temperature <i>Methanothermococcus thermolithotrophicus</i> was the dominant species under thermophilic conditions	[164]
Anaerobic trickling bed at high pressure Mesophilic: 40–41 °C	H ₂ injection rate: 10.87–10.98 L H ₂ /L _{reactor} d Reactor trickling bed volume: 13 L + fixed bed volume: 1.5 L	MPR ¹ : 4.09 at 1.5 bar, 4.29 at 5.0 bar. Increasing pressure to 9 bar did not lead to significant increase in MPR. Methane concentration in biogas increased with pressure, from 64.13% to 86.51% with pressure increasing from 1.5 to 9 bar	[165]
Two-phase fixed bed reactor Temperature: 53–55 °C	H ₂ injection rate: 25.2 L H ₂ /L _{reactor} d Effective volume of the two-reactor (serial) system: 4.0 L	MPR: 6.35 (maximum value) Average H ₂ conversion rate: 97.1% Average MPR at optimal stage: 1.73	[166]

PUF: Polyurethane foam. CSTR: Continuously stirred tank reactor. ¹ MPR reported is higher than theoretical one.

Taking into account that gas solubility and mass transfer issues are the main limitations of heterogeneous reactions, operating at higher pressure conditions seems a feasible solution for increasing reactor volumetric efficiency. Organisms capable of standing high pressures are referred to as piezophiles, having limits close to 100 MPa, and are represented by a wide variety of eubacterial and archaeal populations [167,168]. Experimental evidence regarding the use of methanogens under high pressure was reported by Takai et al. [169] describing culture media conditions for a hyperthermophilic methanogen (120 °C and 20 MPa) and by Mayumi et al. [170] regarding methanogenesis at 55 °C and 5 MPa, evidencing changes in the conversion pathways associated with the applied pressure. Thus, the authors stated that pressure increase would lead to the dominance of acetoclastic methanogenesis. In a different study, Mauerhofer et al. [171], evaluating the performance of high-pressure methanogens, reported that the marked increase in hydrogen solubility attained with pressure increase was not equivalently correlated to methane productivity. Thus, in their study, increasing pressure from atmospheric conditions to 10 and 50 bar led to an increase in 5 and 25-times higher hydrogen solubility, but methane productivity only reached a two and three-fold increase, respectively. Probably, a higher biomass density would have led to higher methane conversion rates, but under the conditions tested, the system was found to be limited by an additional factor. The best performance reported by Mauerhofer et al. [171] was obtained for hyperthermophilic methanococci *Methanotorris*

igneus and *Methanocaldococcus jannaschii*, with maximum methane evolution rate values of 15.1 ± 0.4 and 6.14 ± 0.12 mmol/L h, respectively. These experiments demonstrated the feasibility of a fast turnover of hydrogen into methane.

Other reactor configurations, which may benefit from improved gas-liquid transfer area, are gas lift reactors. These reactors may be easily adapted to an ex situ methanation configuration and may aid in improving hydrogen assimilation due to their high capability of retaining the gaseous phase. A specific process dynamic can be obtained due to the different settling characteristics of microbial granules. Gas-lift reactors allow high gas residence time, thanks to the possibility of recycling the gaseous stream by modifying the velocities of the riser and downcomer section and establishing a desired geometry for the top clearance section. Gas-lift configuration has been tested for biological desulfurization of sulfate-rich effluents using hydrogen and CO₂ as energy and carbon sources [172–174].

Weijma et al. [175] tested this configuration by injecting a mixture of H₂/CO₂ along with sulfate. In their study, the authors reported the predominance of sulfate reduction/homoacetogenesis over methanogenesis when the expected theoretical behavior should have been the other way around. In this case, the strategy proposed was to remove sulfate anions from the incoming liquid stream, but the configuration could be easily adapted to allow methanation at a high rate. Thus, this configuration may seem suitable for using these same gaseous streams but, in this case, for producing extra methane.

Underground Reservoirs as Large-Scale Bioreactors

Recent studies are focusing on the use of underground reservoirs initially thought for the storage of CO₂, but with new findings regarding the use of this gas as a partner molecule in the turnover of hydrogen into methane. The simple storage of CO₂ is giving rise to a new alternative where underground reservoirs are transformed into large-scale biological reactors. Tyne et al. [176] reported the conversion of CO₂ into methane in an underground reservoir for carbon capture in the Olla Field (Olla, LO, USA), indicating that microbial methanogenesis converted about 13–19% of CO₂ initially injected. The review performed by Strobel et al. [177] summarizes the potential of underground methanation, giving information regarding two main projects: the project “Underground Sun Conversion” by the company RAG Austria AG was started in 2017 and explored an innovative approach for storing energy from intermittent renewable generation. The storage is performed underground in gaseous form at depths of over 1000 m. The aim is the use of RAG Austria AG’s patented technology called “Underground Sun Conversion” (USC), which consists of CO₂ and green hydrogen conversion into methane with field tests planned at RAG’s research facility in Pilsbach [178]. The other project is the Hychico-BRGM pilot project by the Argentinean company Hychico S.A. The company participated in the European Union program HyUnder. The pilot project intends the production of methane through controlled underground methanogenesis, also using hydrogen and CO₂ mixtures. The tasks of the project include the biological characterization of the site and the identification and optimization of operational parameters, such as injection flow rates, H₂:CO₂ ratio, and residence times, among others. The characteristics of the reservoir (temperature, physical–chemical properties) will also be studied [179].

Underground hydrogen storage can be seen as a large-scale bioreactor for which conditions can be set to transform CO₂ into methane using naturally occurring reactions [180]. However, there are several risks in this strategy that need to be investigated, such as the effect of pore-clogging [181], bacterial corrosion, gas–water–rock undesirable interactions, caprock sealing failure, and mechanisms that can compromise well integrity, such as rock cracking, embrittlement, cement degradation, along with the risk associated with handling this gas during transport to the site, injection, and posterior withdrawal [182–184], but undoubtedly this strategy can serve as a mean of large reservoirs for energy derived from intermittent generating sources or can be adapted by using smaller high-pressure bioreactors to enhance methanation rates. In fact, the study performed by Simon et al. [185], based on the analysis of several literature data, reported the high correlation observed between

volumetric gas injection (measured as the volume of gas injected per volume of reactor and minute, vvm) and process pressure when selecting *Methanothermobacter marburgensis* as microorganisms for study.

Solutions capable of being implemented in the near future are needed if an effective response is to be given to the challenge of decarbonizing the economy and increasing its circularity. Large-scale projects should be the focus of financial aid instead of increasing economic resources for small-scale experimental work, which cannot be easily extrapolated to the industrial sector. Scientific literature already counts with extensive information regarding small laboratory systems. This information should be used as a starting point for increasing the size of prototypes and providing technical solutions to commercial companies, which are the ones capable of transforming sustainability desires into reality.

5. Conclusions

Anaerobic digestion is a powerful ally for attaining the transition into a new economic model where the circularity of flows is essential for reducing the demand for raw materials and energy flows. Renewable energies can aid in reducing the dependence on fossil fuels, but the mismatch between generation and demand needs practical solutions and applying efficient strategies. Energy storage is fundamental to avoid an excessive over-dimensioning of installed power. The conversion of hydrogen into biogas by biological means benefits from the existence of large-scale reaction systems and experienced technical personnel. Excess electricity stored in the form of methane can be used directly to produce electricity back when needed in CHP engines of high efficiency or transported into the natural gas network as a substitute for this gas.

There are different ways of transforming hydrogen into methane. However, there are still research gaps that need to be addressed to improve existing processes. The gradual implementation of biogas as a substitute for natural gas and its distribution through current networks would reduce the pressure for new explorations to identify oil fields and their derivatives while reducing greenhouse gas emissions. Anaerobic digestion allows valorizing by-products and wastes of different origins and can aid in the transition to reach a hydrogen economy characterized by a high level of circularity.

Research is needed to evaluate conversion rates at large-scale and establish productivity when the process is integrated into existing digestion units. Ex situ methanation performed at high pressure and underground reactors will probably be a new exciting line of research where reactor configuration in the first case and structural constraints in the second will be essential aspects to focus on for attaining the implementation of this technology at an industrial scale.

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Abbreviations

ARES	Advanced Rail Energy Storage
CHP	Combined heat and power
CSTR	Continuously stirred tank reactor
Li-ion	Lithium-ion
LHV	Lower heating value
LNG	Liquefied natural gas
LOHCs	Liquid organic hydrogen carriers
MCH	Methylcyclohexane
MOFs	Metal–organic frameworks
MPR	Methane production rate
PAC	Pyrolysis aqueous condensate
PtG	Power-to-Gas
PtM	Power-to-Methane
PUF	Polyurethane foam
STP	Standard temperature and pressure conditions
USC	Underground Sun Conversion
VFA	Volatile fatty acids
VSS	Volatiles suspended solids
vvm	Volume of gas injected per volume of reactor and minute
WWTP	Wastewater treatment plant

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