https://doi.org/10.3311/PPch.19537

Periodica Polytechnica Chemical Engineering, 66(3), pp. 465–481, 2022

Current Status of Biological Biogas Upgrading Technologies

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Received: 15 November 2021, Accepted: 04 March 2022, Published online: 31 March 2022

Abstract

To limit global warming, ratio of renewable sources in the energy mix has to be considerably raised in the following years. While application of e.g. wind and solar power usually generates fluctuations in the electric grid, biogas produced in anaerobic processes is an easy-to-store renewable energy source. Raw biogas contains generally ~55–70% methane and ~30–45% carbon-dioxide. Although raw biogas can be utilized directly for combustion or combined heat and power generation (CHP), its methane content can be raised to >95% by upgrading technologies, thus it can be valorized. By upgrading and cleaning, the quality of the upgraded biogas may reach the quality of the natural gas and it may be injected to the gas grid or used as fuel for devices optimized for natural gas. Several physico-chemical upgrading methods are available on the market (e.g. high pressure water scrubbing, pressure swing adsorption, membrane technology, etc.) to remove the carbon-dioxide content of the biogas. Opposite to the physico-chemical methods, where basically the CO_2 removal is the main goal, in biological biogas upgrading technologies microorganisms are applied to convert the carbon-dioxide content of the biogas to methane (chemoautotrophic upgrading), or algal biomass (photoautotrophic upgrading). The expectations are high towards biological biogas upgrading technologies in the field of energy storage linked with carbon-dioxide capture. In this paper, latest research results concerning biological biogas upgrading are summarized, viability and competitiveness of this technology is discussed together with the most important future development directions.

Keywords

biogas upgrading, anaerobic digestion, biomethanation, power-to-gas, algal biotechnology

1 Introduction

In the frames of United Nations Framework Convention of Climate Change Conference (2015, Paris) the countries agreed on a long-term goal to limit the increase of the global temperature to well below 2 °C above pre-industrial levels. The agreement applies legally binding climate deal and a global action plan to limit the increase to 1.5 °C to mitigate the impact and the risks of the climate change [1]. The European Union is highly determined in climate politics, thus the current medium-term goal for 2030 described by the EU Climate and Energy Framework is to decrease greenhouse gas emission (GHG) by at least 40% compared to the 1990 base year level, reach at least 32% part of renewable energy in the energy portfolio, and improve energy efficiency by at least 32.5% [2]. As a long-term strategy, EU aims to reach climate-neutral society by 2050, which requires 80–95% GHG emission reduction and to reach the renewable energy fraction between 55 and 75% in the gross final energy consumption [3].

Biogas is an important energy source and a valuable energy carrier, produced by the anaerobic biodegradation of organic matter. As feedstocks of anaerobic digestion are most commonly waste materials (e.g. excess sludge of wastewater treatment, municipal solid waste, agricultural and industrial waste, etc.), biogas is considered to be one of the most useful renewable energy source. In accordance with the EU Climate and Energy Framework, the European Union is leader in production of biogas, and the amount of biogas produced is significantly growing. In 2015, total biogas production of the EU reached 654 PJ in energy equivalent, which equals to 18 billion m^3 of natural gas. This is more than sevenfold increase compared to the 92 PJ value of the year 2000 [1]. To reach the long-term goal of climate neutrality in 2050 further efforts are required in biogas production and utilization: it is estimated that the current total biogas production of ~17 Mtoe (million tons of oil equivalent) which equals to ~710 PJ has

Cite this article as: Lóránt, B., Tardy, G. M. "Current Status of Biological Biogas Upgrading Technologies", Periodica Polytechnica Chemical Engineering, 66(3), pp. 465–481, 2022. https://doi.org/10.3311/PPch.19537

to be increased up to ~72 Mtoe (3010 PJ) [4]. To facilitate this, research and development of biogas production, upgrading and utilization technologies are necessary.

The production of biogas by the anaerobic biodegradation of organic matter is a complex biochemical process catalyzed by a heterogenous microflora, involving several different bacterial and archaeal genera. It consists of four basic stages:

1. hydrolysis: degradation of complex organic matter to soluble organics (fatty acids, amino acids, sugars);
2. acidogenesis: production of volatile fatty acids;
3. acetogenesis: production of acetic acid, hydrogen and carbon dioxide;
4. methanogenesis: formation of methane mainly by specific archaeal genera [5].

These processes can be conducted both in thermophilic (~55 °C) and mesophilic (~35 °C) conditions, in anaerobic digesters, composters, landfills, depending on the feedstock type. Wide variety of biodegradable organic substrates (including agricultural waste, sewage- and waste activated sludge, municipal solid waste, industrial waste – see in Fig. 1) can be applied as feedstock for biogas production.

Biogas is the direct product of anaerobic biodegradation. Via anaerobic digestion, the predominant part of the carbon content of biodegradable organic substrates are converted eventually to CO_2 and CH_4, resulting in typically 55–70% methane and 30–45% carbon-dioxide in the produced biogas, providing 15–30 MJ Nm^{-3} higher heating value [6]. Besides CO_2 and CH_4, other contaminants and byproducts of anaerobic digestion are generally present in the biogas in smaller fractions: oxygen (0–3%), nitrogen (0–15%), water (1–5%), hydrogen-sulfide (0–10 000 ppm), ammonia (0–100 ppm).

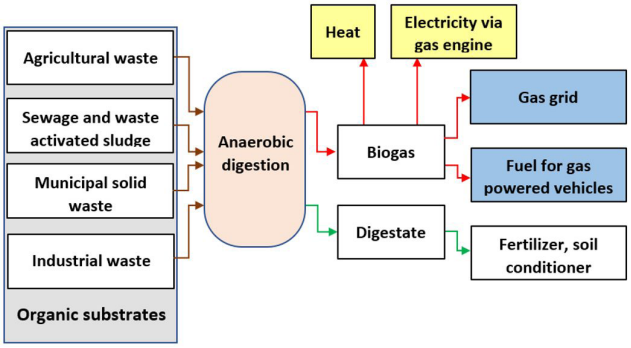

Fig. 1 General pathways of anaerobic digestion, biogas production and utilization (yellow – without considerable upgrading; blue – requires upgrading)

The methane content as well as the presence and the concentration of the other constituents highly determine the biogas quality and the way of biogas utilization. In certain technologies the biogas can be utilized without considerable pre-treatment, however, in most of the cases, the removal of some constituents and the increase of methane content is necessary. Generally, two steps of biogas treatment is distinguished:

1. biogas cleaning: the removal of toxic, corrosive and harmful compounds (e.g. hydrogen sulfide, ammonia etc.);
2. biogas upgrading: the significant increase of methane content via the removal of carbon-dioxide, or by converting the CO_2 content to CH_4.

By upgrading, biogas is valorized, the quality and the heating value is highly raised. The highest quality product of biogas upgrading is the so-called biomethane, which generally has characteristics (CH_4 content and purity) similar to natural gas and can be injected to gas grids. In case the Wobbe-index (indicator of the interchangeability of fuel gases, calculated from the heating value and the specific gravity) of the upgraded biogas is lower than the requirement for gas grid injection, mixing higher hydrocarbons (e.g. propane) into the gas is possible, as implemented for example in Germany [7].

The basic scheme of the material flows of biogas production by anaerobic digestion is summarized in Fig. 1. Biogas can be utilized directly by combustion for heat generation. This method may be applied without any biogas pre-treatment, thus it is a relatively low-cost and low-maintenance technology commonly applied on-site of the biogas production [8]. To generate electricity or for combined heat and power generation processes (CHP) the applied technology (gas engine or turbines) determines the required quality. Generally, e.g. hydrogen-sulfide removal is required and beneficial for the technology, but specific gas engines are available to operate with the original ~55–70% methane content of the biogas [9], thus biogas upgrading is not necessarily required in this case.

As natural gas has considerably higher (85–92%) methane content than biogas, for the injection of biogas to the gas grid or for the application as fuel for vehicles with CNG (compressed natural gas) engines, biogas upgrading is necessary [10]. Although biogas upgrading is demanding in terms of investment and operational costs, upgraded biogas is a higher value renewable energy source, and it can be perfectly stored. As a result, the application of

upgraded biogas is more flexible than the heat and electricity produced from original biogas. Consequently, biogas upgrading technologies and the produced high methane content upgraded gas are of great importance in balancing fluctuations of energy production caused by the application of other renewable (e.g. solar, wind, etc.) sources [11, 12]. Besides the more conventional physico-chemical gas upgrading technologies, the application and R&D of biotechnology-based gas upgrading methods gain more and more importance. Here, the latest scientific and technological results concerning these biotechnologies are summarized and compared with the conventional physico-chemical methods.

2 Biogas composition and conventional physico-chemical upgrading technologies

Typical biogas composition from anaerobic digestion and landfills are summarized, together with the typical natural gas composition and gas grid injection requirements of some countries in Table 1 [6, 10, 13, 14]. Except for methane, all the other components are undesirable: they decrease the heating value of the biogas and their presence may cause harmful effects in biogas utilization technologies.

Carbon dioxide is the second largest constituent of biogas after methane. Caused by the presence of 15–40% CO_2, both the heating value and the Wobbe-index of the biogas is considerably lower compared to natural gas, and the requirement of gas-grid injection, besides, it may cause corrosion in the utilization technology [6]. Hydrogen-sulfide is toxic, harmful to the environment, and by chemical and/or biological oxidation it can form highly corrosive sulfuric and sulfurous acid. H_2O and NH_3 impurities may also generate corrosive chemical reactions [6].

To reach the standard quality for gas injection or used in transportation as fuel, the application of efficient biogas upgrading and cleaning technologies are required [10]. Currently, most of the widely used biogas upgrading methods are based on physico-chemical (mainly sorption and separation) principles. The most important features, advantages and disadvantages of these methods are summarized in Table 2 [6, 15–17]. Main goal of these processes is to remove the CO_2 content, and by this, to reach the highest possible CH_4 concentration and consequently the highest possible heating value in the produced upgraded biogas.

High pressure water scrubbing (HPWS) and organic physical scrubbing (OPS) are based on the physical absorption of CO_2 in water (HPWS) or in organic solvent (OPS, e.g. methanol, N-methyl pyrrolidone), while chemical scrubbing process (CSP) exploits the reversible reaction of solvent (e.g. mono- and diethanolamine) and the absorbed substances [15, 18]. By HPWS and OPS, efficient H_2S removal can also be managed. In case of CSP, because of the higher temperature requirement for the desorption of H_2S from the solvent, a preceding H_2S removal step is recommended.

In pressure swing adsorption (PSA), CO_2 is adsorbed on the surface of the adsorbent (e.g. zeolites, activated carbon) under high pressure, and it is desorbed in low pressure conditions, regenerating the adsorbent [19]. Prior H_2S removal is required for PSA as it may irreversibly adsorbed. Temperature can also be the driving force for adsorption and desorption in a similar technology: temperature swing adsorption (TSA) [20].

Membrane technology is based on that specific compounds may pass through the semipermeable membrane, while other compounds remain in the retentate. The most abundantly applied membranes for biogas upgrading are organic materials like polysulfone, polyimide, polyetherimide and cellulose acetate [21]. In biogas upgrading, generally CO_2 passes through the membrane and CH_4 remains in the retentate. In specific cases, H_2S has to be removed prior membrane treatment as its presence may decrease the

Table 1 Typical biogas composition, lower (*L*) heating value, higher (*H*) Wobbe-index compared to the composition of natural gas and some standard requirements of grid injection and vehicle fuel in three EU member countries [6, 10, 13, 14]

Parameter	Unit	Biogas		Natural gas	Grid injection requirements		
		anaerobic digestion	landfill		Germany	France	Spain
Heating value (*L*)	MJ Nm^{-3}	23	16	30–40	–	–	–
Wobbe-index (*H*)	MJ Nm^{-3}	27	18	45–55	46.1–56.5	48.2–56.5	48.3–57.8
CH_4	Vol%	60–70	35–65	85–92	–	≥86	≥95
CO_2	Vol%	30–40	15–40	0–2	≤6 (dry)	<2.5 (dry)	2
H_2O	Vol%	1–5	1–5	–	–	–	–
N_2	Vol%	0–0.5	0–15	0–1	–	–	–
H_2S	ppm	0–10000	0–100	1–6	<5	<5	<15
NH_3	ppm	50–100	20–200	–	≤20	≤3	≤3

Table 2 General properties, advantages and disadvantages of the most important physico-chemical biogas upgrading technologies [6, 15–17]

Technology (working principle)	Typical final CH_4 conc. (Vol%) Specific energy requirement (kWh/m³ upgraded biogas)	Advantages	Disadvantages
High pressure water scrubbing (HPWS) (absorption)	>97% 0.2–0.43 kWh/m³	Combined CO_2 and H_2S removal Low methane loss (<2%) Used water can be regenerated Tolerant to impurities	High investment and operational costs Slow process Possible clogging and foaming caused by biomass growth Possible corrosion caused by H_2S High amount of water required even with regeneration
Organic physical scrubbing (OPS) (absorption)	>97% 0.4–0.51 kWh/m³	Combined removal of CO_2, H_2S, HCN, H_2O Low CH_4 loss More energy efficient than HPSW	Expensive, for small scale applications High energy requirement of solvent regeneration Solvent is expensive and requires special handling Generally high investment and operational costs Dilution of solvent with water reduces efficiency
Chemical scrubbing process (CSP) (absorption)	>99% 0.12–0.65 kWh/m³	High CO_4 concentration with low operational costs All the H_2S may be removed at low pressure Very low CH_4 loss (<0.1%) Faster than HPWS and solvent is easy to regenerate	High investment costs Heat required for solvent regeneration Solvent is expensive and difficult to handle Corrosion, decomposition of solvent, foaming, precipitation of salts
Pressure swing adsorption (PSA) (adsorption)	>95–98% 0.24–0.6 kWh/m³	Combined CO_2, N_2 and O_2 removal Compact technology available for small scale Fast installation and start-up Tolerant to impurities Low energy requirement	High investments and operational costs Previous H_2S and H_2O removal is required Off gas treatment is required Impurities may cause fouling and operating nuisances Valve malfunction may cause severe CH_4 losses
Membrane technology (separation)	>92–98% 0.27–0.38 kWh/m³	Combined removal of CO_2, H_2S, H_2O Relatively low operational and investment costs Small-scale units are also economically feasible High (>99%) methane purity can be achieved with membrane units operated in series No hazardous chemical requirement Easy and low-cost maintenance	Low CH_4 yield in single step membrane process Multiple steps of membrane processes is required for high-purity gas product Low membrane selectivity Methane losses are possible (<10%)
Cryogenic separation (separation)	>90–98% 0.4–0.44 kWh/m³	High purity CO_2 can be produced for further use Low additional energy costs to produce liquid biomethane (LBM) Environmentally friendly, no additional chemicals	High investment, operational and maintenance costs High energy requirement for cooling CO_2 residues may remain in CH_4

membrane performance. Generally multistage membrane technologies are favored against single-stage units, as both investment and operation cost may be lower and CH_4 purity is higher in multi-step membrane processes [22].

Cryogenic separation operates at high pressure (40–200 bar) and low temperature (generally below −70 °C) [23, 24]. In these conditions CO_2 and H_2S liquifies, while CH_4 remains in gas phase. By the process, liquid biomethane (LBM) can be produced which has the quality of liquid natural gas (LNG), but the energy consumption of this method is considerable (5–10% of the energy of the produced upgraded gas) [6, 13].

Although these CO_2 separation methods can provide grid-scale "natural gas", one should keep in mind that due to the removal of CO_2, the quantity of the upgraded gas will be significantly lower compared to the original biogas.

3 Biological biogas upgrading technologies

Relatively new approach in biogas valorization is the bio-technology-based upgrading. Opposite to the aforementioned physico-chemical methods, where basically the CO_2 removal is the main goal, in biological biogas upgrading technologies microorganisms are applied to convert the carbon-dioxide content of the biogas to methane (chemoautotrophic upgrading), or algal biomass (photoautotrophic upgrading). In this respect, biological upgrading is more progressive than conventional methods, as the total energy content of the products are considerably higher

than the energy content of the feed gas. During the chemoautotrophic process, the amount of methane (and thus, the energy content of the upgraded gas) is considerably increased, while it remains constant or (due to methane losses) even decreases in case of physico-chemical methods. At the same time, biotechnological upgrading methods may provide lower operational cost and decreased energy consumption compared to physico-chemical ugrading technologies, besides, they do not require expensive chemicals in general [25]. In addition, unlike in case of conventional physico-chemical CO_2 removal methods, the volume flow of the gas will not be affected by the biological upgrading, i.e. the volume of the incoming biogas and the outgoing grid-scale gas will be almost the same.

As a result, diverse novel biotechnological methods were developed to meet the carbon dioxide contamination limit of various applications. Based on the main metabolic type of the biomass applied, biotechnological biogas upgrading technologies are classified as chemoautotrophic and photoautotrophic approaches. Main advantages and disadvantages of the below detailed most important biological biogas upgrading methods are summarized in Table 3 [17, 26, 27].

3.1 Chemoautotrophic biogas upgrading

In chemoautotrophic biogas upgrading, by the help of hydrogenotrophic methanogenic bacteria, the carbon dioxide content of raw biogas is converted to methane according to Eq. (1) either directly inside the anaerobic digester (in-situ) or in a separate bioreactor (ex-situ). Typical methanogens from the Archaea phylum capable of this conversion are *Methanobacterium* sp., *Methanobrevibacter* sp., *Methanoculleus* sp., *Methanothermobacter* sp., *Methanococcus* sp., *Methanosarcina* sp., *Methanospirillum* sp., *Methanogenium* sp., *Methanomicrobium* sp. and *Methanospirilum* sp. [28, 29].

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \ \left(\Delta G = -131 \text{ kJ}\right) \quad (1)$$

The hydrogen required for the methanation process is generally produced by electrochemical water splitting. The energy requirement of this process is covered preferably by renewable sources to keep the process environmentally friendly (e.g. photovoltaic systems) [30].

Another possibility is to utilize excess electric energy from the grid for electrolysis and convert it into chemically bond energy stored in a combustible gas. The technology is called Power-to-Gas (PtG), and its significance is expected to increase greatly in the upcoming years, as strong local positive and negative electric residual loads will occur in the grid, caused by the fluctuations of renewable energy sources with a growing proportion in the energy mix. The storage of hydrogen, however, is complicated, requires specific, expensive technologies [31]. Converting hydrogen to methane via biological biogas upgrading, (power-to-methane, PtM) does not only offer an opportunity to balance the loads in electricity networks and increase the flexibility of the system [32, 33], but PtM can serve as a compact seasonal or multi-seasonal energy storage solution with acceptable efficiency. Presently this method seems to be the best (acceptable storge efficiency with acceptable costs) high-capacity seasonal energy storage exceeding four months storage time [34]. The produced biomethane can be stored in the existing gas-storage infrastructure without considerable energy-loss or further investment compared to other energy storing methods (batteries, hydro-storage, compressed air) [35].

Table 3 General properties, advantages and disadvantages of the most important biological biogas upgrading technologies [17, 26, 27]

Technology (working principle)	Typical final CH_4 conc. (Vol%)	Advantages	Disadvantages
In-situ chemoautotrophic (methanogenesis)	70–90	Relatively low investment costs Integrated with anaerobic digestion process No additional bioreactor required CO_2 capture	Generally lower CH_4 content in the upgraded biogas than the requirement of gas grid injection High electric energy requirement for hydrogen generation pH increase, H_2 dissolution nuisances
Ex-situ chemoautotrophic (methanogenesis)	>90–95	High methane recovery Upgraded biogas CH_4 content is appropriate for grid injection or CNG fuel CO_2 capture Simple microbiological/biochemical process	High investment and operational costs Separate biomethanation reactor is required High electric energy requirement for hydrogen generation Requires separate H_2S removal pH increase, H_2 dissolution nuisances
Photoautotrophic (photosynthesis)	>90–97	High methane recovery CO_2 valorization in the form of algal biomass Simultaneous H_2S removal Simultaneous wastewater treatment possibility	High investment costs and energy demand High risk of biological contamination Low photosynthetic CO_2 uptake, high natural sources requirement

3.1.1 In-situ biological upgrading

Principles of the technology

During in-situ biological upgrading, hydrogen is directly injected to the anaerobic digester, where via the metabolism of hydrogenotrophic methanogens it reacts with the carbon-dioxide present inside the bioreactor, and produce methane (see Fig. 2). Under optimal temperature and pH conditions, theoretically more than 95% of the potential methane can be recovered. To approximate this theoretical efficiency, in the actual technologies, innovative hydrogen injection methods and efficient pH control has to be applied. At the same time, it has to be taken into consideration that the excess hydrogen injection may influence the complex microbial and biochemical processes in the anaerobic digester causing undesired negative effects.

Hydrogen injection and dissolution

When the generated hydrogen is injected directly into conventional anaerobic digesters, a major drawback usually occurs: biogas reactors are not designed to overcome gas-liquid mass transfer limitations. Henry's constant of hydrogen (7.8×10^{-3} mol L^{-1} MPa^{-1}) is remarkably lower than that of CO_2 (0.318 mol L^{-1} MPa^{-1}) at standard temperature and pressure. As a consequence, the gas-liquid mass transfer rate of the hydrogen is generally the limiting factor of the hydrogen consumption of methanogens, and consequently, the methanogenesis [36–38], therefore high efficiency hydrogen injection and dissolution methods have to be implemented to ensure the appropriate performance of in-situ technologies.

Although mixing can improve gas-liquid mass transfer and increase CH_4 content from 57% to 75% as it was found by Luo and Angelidaki [28], but vigorous stirring is energy intensive and capable of perturbing the proper functioning of the anaerobic consortia leading to a reduction in methane production [28, 39]. For this reason, several hydrogen dosing strategies and reactor designs were developed lately

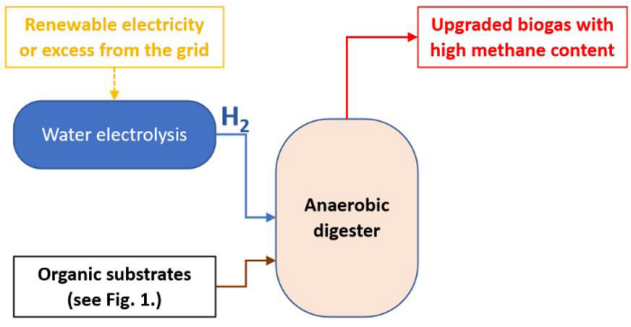

Fig. 2 Scheme of in-situ biological biogas upgrading

to mitigate mass transfer limitations. A Venturi-type system for H_2 injection was tested by Jensen et al. [40] that can be easily retrofitted to existing digesters, while H_2 conversion efficiency of 94% was achieved by using a submerged membrane module for biogas recirculation and H_2 sparging [41]. With the application of hollow fiber modules, hydrogen can penetrate liquid phase without bubble formation, thus ameliorating H_2 gas transfer coefficient from 30 to 430 h^{-1}, as it was demonstrated by Díaz et al. [42]. With this technology, hydrogen conversion efficiency can reach values as high as 98%, what further improves gas-to-liquid mass transfer rate [43]. Amongst several promising reactor designs, thermophilic upflow anaerobic sludge blanket (UASB) system is one in which effective in-situ biogas upgrading is possible reaching a methane content of 82% [44]. UASB reactors can be further improved by utilizing different solid carriers to immobilize key microorganisms and to enhance gas transfer to the biofilm. Better residence time of gas per reactor volume and increased mass transfer of hydrogen are some of the advantages owing to packing materials [45].

The pH balance

Carbon dioxide depletion due to the accelerated hydrogenotrophic methanogenesis caused by the excess hydrogen injection may lead to the increase of biogas slurry pH in in-situ upgrading technologies [46]. This alkalization generated by the reduction of bicarbonates acting as a critical natural buffer [30] can shift the pH to values higher than nine, where key microbial processes are blocked, as the optimum of methanogenic bacteria is around pH 7, while their activity is basically inhibited beyond pH 8 [47]. Even if complete inhibition can be avoided, the drift to alkalinity is still unfavorable because it decreases the methane yield, thus proper control of pH during anaerobic digestion process is of great importance [48].

Alkalization can be controlled by using acidic wastes in the anaerobic digesters such as food wastes that are prone to low pH due to high VFA levels [49]. For example, cheese whey wastewater can be a potential solution [50]. Simple [51] and complex, automated pH control systems were proposed recently as well [52], which could be integrated into in-situ hydrogen assisted biogas upgrading processes. Combining high-pressure anaerobic digestion (HPAD) with exogenous hydrogen injection is another possibility, since operational problems arising from both technologies may mitigate each other. On one hand, HPAD is susceptible to acidification due to the excessive

CO_2 dissolution at high pressure; on the other hand, H_2 injection is responsible for alkalization. With a careful process control, both drawbacks might be solved [53], while improved hydrogen availability in the biogas slurry is also achievable [54].

Effect of hydrogen injection on microbial community

Concerning the microbial community of the anaerobic digestion during in-situ upgrading, exogenous hydrogen influences microorganisms and their metabolic pathways by altering reaction conditions and equilibriums. Hydrogen producing aceto- and acidogenic bacteria, hydrogen consuming homoacetogenic and hydrogenotrophic methanogenic microorganisms are also affected. For instance, in conventional anaerobic digesters a relatively low H_2 level (partial pressure <10 Pa) is maintained by interspecies hydrogen transfer between acetogenic and hydrogenotrophic microorganisms. Even though hydrogen injection resulting in an elevated H_2 level favors methanogenic activity, it adversely affects and ultimately inhibits the breakdown of longer chained volatile fatty acids into acetate [55]. Besides, the surplus of hydrogen stimulates homoacetogenesis as well: up to 40% of H_2 can be consumed through the Wood-Ljungdahl pathway (also known as the reductive acetyl-coenzyme A pathway, that enables the use of hydrogen as an electron donor and carbon dioxide as an electron acceptor), contributing to acetate production and acetoclastic methanogenesis to a great extent, that is less favorable from the point of view of methane formation [56].

Feasibility and perspective

Despite all the aforementioned difficulties originated from exogenous hydrogen dosage, substantial efforts were made to overcome them since in-situ biogas upgrading is considered economically and energetically more feasible for smaller scale biogas plants (biogas production below 500 $m^3\ d^{-1}$) than conventional physico-chemical or ex-situ biological upgrading methods due to the considerably lower investment cost [38]. Thus, by employing in-situ technologies, the cost of biogas upgrading can be reduced considerably while biomethane quality may be improved close to the level of natural gas [57].

Even though significant progress has been achieved in the field of in-situ biological biogas upgrading, most technologies (apart from some rare exceptions) have only been tested at lab- and pilot-scale. Jensen et al. [40] tested a Venturi-type H_2 injector in a full-scale 1200 m^3 anaerobic digester, but hydrogen consumption efficiencies were modest (10–26%). Later on, the same research group modified their system based on previous results and demonstrated the potential of a Venturi-based mixing system for H_2 injection to facilitate gas-liquid mass transfer by achieving 49% maximum conversion efficiency and a maximum methane content of 65% in the upgraded biogas [58]. Additional examples of large-scale application is scarce in the literature, thus further work is needed to move closer to real-life applications and maturing the technology for commercialization [25, 59].

While in-situ biological biogas upgrading may considerably increase the methane content and the heating value of the biogas produced in the anaerobic digester, the quality of the produced upgraded biogas generally does not reach the requirement of gas-grid injection or the CNG vehicle fuel. As a result, in order to reach the requirements summarized in Table 1, considerable technological improvement or joint application of conventional physico-chemical upgrading methods may be required, as well as biogas cleaning for the removal of contaminants like H_2S, NH_3, H_2O, etc.

3.1.2 Ex-situ biological upgrading

Principles of the technology

During ex-situ biological upgrading, biogas from the AD and the exogenous hydrogen are fed into a separate bioreactor, where (pure or enriched) hydrogenotrophic archaea convert the CO_2 content of the biogas to CH_4 (see Fig. 3). Opposite to in-situ technologies, this type of biomethanation is independent of the anaerobic digestion process, so the drawbacks arising from exogenous H_2 dosing into the digester and a number of other biological and mechanical issues are evitable. Thus, application of an ex-situ biological upgrading method does not disturb the stability of the anaerobic digestion [60]. In addition, due to the simpler biochemical process, its stability is only dependent on the availability of carbon dioxide, hydrogen, essential nutrients and the physiological state of hydrogenotropes, so it

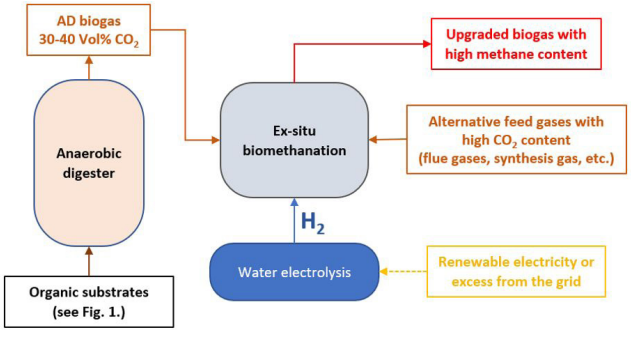

Fig. 3 Scheme of ex-situ biological biogas upgrading

is far more controllable than in-situ methods [30, 55]. As a result, ex-situ biogas upgrading is preferable in spite of the additional investment and operational costs needed for the separate bioreactor for biomethanation [61].

Similarly to in-situ technologies, the low solubility of hydrogen and the low gas-liquid mass transfer rate limits the bioavailability of hydrogen, hindering the upgrading process [62, 63] in ex-situ technologies. Therefore, considerable efforts have been devoted lately to mitigate these disadvantages by the improvement of H_2 conversion efficiency and the quality of effluent gas stream [64]. According to recent studies, molar ratio of H_2 and CO_2 [65]; operational conditions such as pressure [66] and temperature along with inoculum origin [67]; pH control [68]; mixing and gas recirculation rate [39]; gas loading rates [69] and reactor design are key factors for ex-situ biogas upgrading [62].

Alternative feed-gases

Another reason for the increasing interest towards ex-situ bioconversion is that not only raw biogas, but different industrial CO_2 sources can also be utilized as feed gas, such as flue gases [70, 71]. By implementing an industrial scale carbon capture, utilization and storage (CCUS) technology, carbon footprint reduction and greening of many, otherwise heavily polluting industries (e.g. steel and cement production) might be possible [72, 73]. Furthermore, the possibility of using various carbon dioxide sources gives more flexibility, while volumetric CH_4 production rates are usually higher for ex-situ biomethanation [74]. The use of synthesis gas (also know as syngas, a mixture mainly of CO, H_2 and CO_2 generated during thermal decomposition of carbonaceous material in absence of oxidizing agent) as substrate is also of great promise, as it has been reported on several occasions. With stoichiometric H_2 addition, methane contents as high as 95–98% were achieved [75, 76]. This thermo-biochemical route of biomass valorization and biomethane production is considered to be competitive and advantageous for small-scale installations compared to the physicochemical Sabatier process, which produces methane and water from a reaction of hydrogen with carbon-dioxide at high temperatures (300–400 °C) and pressures (3 MPa) in the presence of a nickel catalyst [77]. Another huge advantage of biological upgrading compared to the Sabatier-reaction is that it can tolerate contaminants such as hydrogen sulfide or siloxanes, and work with mixed CH_4/CO_2 feed gas. During high-temperature chemical methanization, contaminants (even methane) can lead to undesired chemical reactions, like methane reformation [78].

Bioreactor design and operation

An efficient way to overcome hydrogen mass transfer limitation is the appropriate bioreactor design. Kougias et al. [62] compared the conversion efficiency and the effluent quality of a serial upflow, a continuously stirred tank and a bubble column type reactor. Furthermore, the effect of gas recirculation at two rates was investigated. Methane contents higher than 98% in the output gas were achieved with the serial upflow and the bubble column reactor, while the increased gas recirculation rate enhanced the biogas upgrading efficiency by improving the gas-liquid mass transfer rate of H_2 [62].

Also, anaerobic trickle-bed reactors (TBR) have drawn considerable attention in recent days, as it may overcome process scale-up constraints [60]. The bed space is not submerged, but a recirculated fluid stream containing essential nutrients tricks the surface of the carrier covered with immobilized microorganisms, thus creating a three-phase gas-liquid-biofilm system [79]. This configuration provides large contact area, a higher concentration gradient as the driving force for mass transfer and a shorter diffusion path between methanogenic archaea and gas phase [70]. In addition, the mass transfer barrier in the gas phase can be more or less neglected, as diffusion coefficients can be about four orders of magnitude higher in gas compared to aqueous medium [80], so the transfer of gases to biofilm is much better compared to traditional fixed-bed reactors [79]. Accordingly, several studies reported nearly full (~99%) or slightly lower H_2 conversion efficiencies in TBR along with methane contents higher than 95% [81], in spite of rapid H_2 load changes due to fluctuating availability of excess renewable energy [82]. However, the selected carrier material is of significant importance, while the adequate supply of micronutrients through carrier irrigation was identified as imperative for stable and long-term operation [83, 84]. So far, there is only one study investigating the long-term ex-situ biomethanation of biogas using a mesophilic TBR, in which biogas from a pilot-scale anaerobic digester was converted to a gas containing 97% CH_4 [65].

Another solution for the mass transfer limitation is the countercurrent recirculation of the liquid-phase to enhance surface contact and time with the injected gas in the reactor. Accordingly, 80–89% methane contents along with H_2

conversion efficiencies >93% were reported in a laboratory-scale immobilized biomethanation bioreactor (IBBR). In this technology, higher recirculation ratios (hydraulic retention times were lower than 30 min) were applied enabled by the immobilization of microorganisms within a polymeric-based matrix that prevented washout and the structural and functional damage of the biomass [85].

Also, fed-batch reactor configuration proved to be a promising alternative to the conventionally used flow-through systems, as high H_2 loading rate, complete conversion of H_2/CO_2 to CH_4 and low operation cost were reported in a recent study. Since flow-through reactors are optimized to maximum H_2 conversion efficiency, generally low hydrogen injection rates are applied that limit methane production rates. In spite of the intermittent operation of the fed-batch reactor, a remarkable 1000 mL L^{-1} d^{-1} H_2 consumption rate was attained, while methane was enriched up to 95% [86].

Gas injection and dissolution

Different mixing techniques (gas recycle vs. mechanical) and operating temperatures were investigated by Yun et al. [87]. Combination of thermophilic conditions and gas recycle was the most effective. An almost complete conversion of H_2 and high calorific biomethane (96% CH_4) was achieved during long term operation of the 6.3 L reactor by applying intensive gas recycling (200 L L^{-1} d^{-1}) through a glass fiber disc (pore size of 20 μm) [87].

The effect of gas diffusers with different pore sizes was examined as well in up-flow reactors (1 L) at thermophilic conditions. Continuous gas recirculation was applied as means of mixing. By achieving a more efficient dispersion of CO_2 and H_2 in the liquid phase with silicon carbide diffuser (d_{pores} = 7 μm) and low input gas flow rate (gas retention time of 10 h), CH_4 concentration of 99 ± 0.1% in output gas was obtained. Although higher input gas flow rate led to higher methane production rate, but output CH_4 content decreased because of insufficient H_2 solubilization and lower H_2 utilization efficiency [88].

The pH balance

Similarly to in-situ biomethanation, H_2 addition can cause alkalization due to the disruption of the bicarbonate buffer system, negatively influencing the process stability [62, 74]. Bassani et al. [89] investigated the effect of pH from 6.0 to 10.0 on enriched hydrogenotrophic culture of an ex-situ system, and reported that methane production decreased significantly when pH was increased from 8.0 to 8.5 and completely stalled at pH 10. Results indicate that despite the deterioration in CH_4 yields, hydrogenotropes are tolerant up to a pH of 8.5 [89].

Apart from the depletion of bicarbonates, ammonia accumulation as a result of protein degradation and the buildup of volatile fatty acids can also alter the pH of an anaerobic digester during in-situ biogas upgrading. In case of ex-situ methanogenesis, the risk of pH increase due to ammonia accumulation is nonexistent. On the other hand, acetate accumulation linked to the increased activity of homoacetogenic bacteria can decrease the pH, if syntrophic acetate oxidizing bacteria and acetoclastic methanogens cannot keep the acetate levels low [68, 90]. Adjustment of CO_2 partial pressure by CO_2/H_2 feed ratio was proved to be an effective method for pH control [91], but the use of buffer media also has some potential as a short-term solution [68].

Feasibility and perspective

Bio-methanation reactors can be operated as standalone biogas-upgrading technologies, in this case biogas from e.g. anaerobic digestion can be directly used as feed gas. Combining physico-chemical upgrading technologies with ex-situ bio-methanation, the high CO_2 content downstream gas of the physico-chemical technology can be utilized as the feed-gas of ex-situ bio-methanation [92]. Techno-economic analysis and comparison of three scenarios (1 - amine scrubbing; 2 - standalone ex-situ bio-methanation; 3 - combined amine scrubbing and ex-situ bio-methanation) showed that if the main goal is the storage of surplus renewable electricity as methane, the direct methanation of biogas is more economically advantageous than capturing the CO_2 from amine scrubbing and subsequently converting CO_2 to CH_4 via bio-methanation [93].

The investment and operational costs of ex-situ biogas upgrading are considerably higher than in-situ upgrading. At the same time, by the application of ex-situ biogas upgrading, gas-grid injection requirement of methane content can be reached in the produced upgraded biogas, thus this technology can be considered as a potential competitor of the physico-chemical upgrading methods detailed in Table 2. As water electrolysis requires electricity, the competitiveness of the power-to-gas technologies, and thus, ex-situ biomethanation is highly dependent on the electricity prize: the lower is the electricity prize, the higher is the competitiveness of these technologies

against physico-chemical methods (e.g. amine-scrubbing, membrane separation) in terms of methane production costs [94]. A case study showed that if excess electricity purchased for 50% of the regular electricity prize for hydrogen production, ex-situ biological upgrading may have better economic performance than water scrubbing, however, if regular electricity is purchased water scrubbing outperforms biomethanation [35].

Currently, similarly to the in-situ technologies, full-scale applications of ex-situ biological upgrading are rather scarce, these technologies are relatively new and requires maturation to allow reduction in investment and operational costs to reach economic feasibility [93].

3.2 Photoautotrophic biogas upgrading

3.2.1 Principles of the technology

Microalgae are autotrophic microorganisms, and as such, able to produce biomass by converting light energy into chemical energy and fixing CO_2. Algal biomass can be utilized as feedstock for anaerobic digestion [95], as food and several valuable algal components (e.g. the oil or the carbohydrate content) are attracting special attention nowadays [96–98].

During direct photoautotrophic biogas upgrading, raw biogas is injected into either an open or a closed photobioreactor, where microalgae are fixing the CO_2 content while producing valuable new biomass (see Fig. 4). The produced algal biomass can be applied as a feedstock for the anaerobic digestion enhancing the biogas production or further utilized in separate technologies.

A significant advantage of the process is that simultaneous CO_2 and H_2S removal is possible [99]. Removal of nutrients (different forms of nitrogen and phosphorus) and various contaminants from wastewater or anaerobic digestion effluent used as culture medium in the reactor is also achievable by the algal cultivation [100–102]. Thus, photoautotrophic biogas upgrading may have multi-fold benefits.

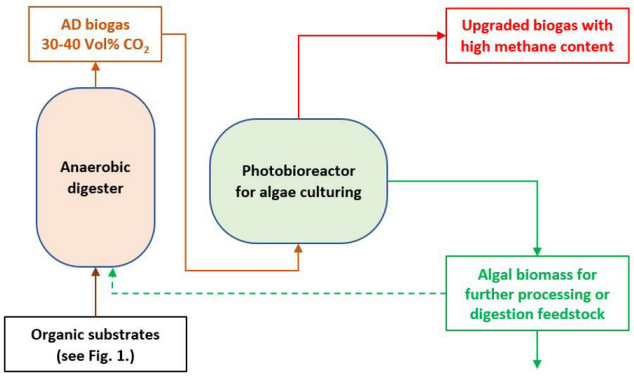

Fig. 4 Scheme of photoautotrophic biogas upgrading

3.2.2 Technological challenges

Main challenges of the technology are the low solubility of CO_2 and its mass transfer, limiting cell growth of microalgae and its carbon dioxide removal [103]. For the very same reason, up to 90% of the input CO_2 may leave the bioreactor unutilized [104]. Despite of the low solubility of CO_2, its increasing concentration may lead to the acidification of culture medium, which is adverse to microalgal growth [105]. Geographical and seasonal availability of sunlight have to be taken into account as well, since microalgae biomass production is often limited by the light energy. Therefore, artificial lighting systems with durable, reliable, and efficient light source would be preferred, but installing and operating these systems are often costly [106]. CH_4 is also dissoluble in the medium, resulting in a significant methane loss in photobioreactors with larger volumes. Moreover, in case of direct upgrading (detailed below), harvesting of the upgraded biogas requires a closed system. This requirement can limit the design of bioreactors and microalgal growth. Last but not least, O_2 contamination in the final biogas as a result of microalgal photosynthesis pose further challenges [107].

3.2.3 Developed/developing technological solutions

To mitigate the above-mentioned limitations, several technological solutions and innovative bioreactor systems have been proposed.

By using a microalgae bag photobioreactor with optimized lighting control and light wavelength, average CO_2 removal efficiency of ~85% and final CH_4 contents higher than 90% were achieved, while simultaneous biogas slurry decontamination was successfully accomplished: 85.5% of COD, 92.4% of total phosphorus and 87.1% of total nitrogen was removed in average [108].

Marine microalgae *Tetraselmis suecica* was cultured using biogas as carbon source and anaerobic digested piggery effluent as nutrient source. Average CO_2 uptake of 94% was recorded at 7.5 pH that also supported high biomass productivities with increased lipid and carbohydrate yield. Total nitrogen and phosphorus removal efficiencies reached 96% and 72%, respectively, and theoretical methane concentrations calculated from CO_2 uptake were in the range of 96% [109].

Indirect photoautotrophic biogas upgrading is another approach to overcome the limitations of direct photoautotrophic upgrading. In this approach, CO_2 is captured from the biogas efficiently by carbonate solution at alkaline condition in an absorption column, forming bicarbonates. Then, bicarbonate serves as the carbon source

in the photobioreactor. During carbon dioxide biofixation by microalgae, carbonate is regenerated from the bicarbonates and can be recycled for the next biogas upgrading cycle. Although this technology requires halophilic and alkaliphilic strains, it has several advantages: energy intensive gas sparging is unnecessary, carbon dioxide can be temporarily stored in the form of bicarbonate and the high ion concentration along with alkaline conditions can prevent microbial contamination of the bioreactor [110].

Marín et al. [111] tested three operational strategies of an outdoors pilot scale photobioreactor connected with an external absorption unit. When a greenhouse was applied during winter conditions, microalgae productivities typical for continental weather conditions were successfully maintained while CH_4 concentrations in the biomethane ranged from 89.5% to 98.2%. By introducing direct air stripping of CO_2 in the photobioreactor that provided an effective CO_2 and H_2S removal, methane concentrations increased to 93.0%–98.2% in the outlet gas of the absorption unit. Finally, methane concentrations in the upgraded biogas during summer conditions were between 96.3%–97.9% when digestate was used as make-up water. Moreover, complete H_2S removal was achieved under all strategies tested [111].

3.2.4 Feasibility and perspective

Microalgae cultivation based photoautotrophic biogas upgrading technology is still under development facing several challenges, yet it is a promising future solution for biological CO_2 and H_2S removal from raw biogas. Several different photosynthetic systems with various microalgae strains have been tested to this day to enhance CO_2 fixation. The cost of photoautotrophic biomethanation is principally dependent on the configuration. Generally, indirect upgrading systems using open ponds are cheaper and exhibits better performance than indirect systems with photobioreactors, but due to the problems arising from. land-limitation, the latter version is preferred [112]. Since operational modes and conditions (such as temperature, pH, lighting intensity and wavelength spectrum, etc.) can affect process efficiency, optimized parameters were proposed as well, but often without cost-benefit analysis.

Choosing the most suitable microalgal strain for culturing is of utter importance as well. Preferably it has high carbonic anhydrase activity, can tolerate alkaline conditions and high CO_2 concentrations, capable of mixotrophic growth and easy to harvest [113]. Harvesting microalgae can be technically challenging because of small cell size (<30 μm), growth in dilute suspension (0.02–0.05% dry solids), negligible density difference of cells to their culture medium, negatively charged surface (zeta potential), and their high growth rates which needs frequent harvesting compared to land crops [114]. As most harvesting technology capable of separating unicellular microalgae efficiently is considerably energy intensive (e.g. centrifugation) [115], the cultivation of filamentous species (filament length between 50 and 500 μm) is advantageous since their separation is significantly easier [113]. Co-cultivation of microalgae and fungi is also promising due to the higher economic and energy efficiency: energy consumption for CO_2 removal were 19.9–23.3% USD^{-1}, compared to the 3.78–22.34% USD^{-1} value of traditional monocultures [116].

In summary, to achieve an energetically balanced and economically feasible photoautotrophic biogas upgrading technology, system configuration, operational conditions and microalgae strain have to be selected carefully. Despite of the high capital costs, environmental benefits of the microalgae-based CO_2 removal may counteract those high expenses to some extent, but economic feasibility would be determined mainly by the value of algal biomass, or by the use of algal reactors for other purposes, such as wastewater treatment [112, 117].

4 Conclusions, outlook

Anaerobic processes are currently widely applied to produce biogas, which is generally considered to be a important renewable energy source. Produced biogas is much easier to store, without considerable loss compared to other renewables (e.g. electricity from solar or wind). The quality and the heating value of the raw biogas, however, is considerably lower than that of the natural gas and the quality requirements of gas-grid injection, primarily because of its 15–40% carbon-dioxide content. To valorize the biogas and raise its methane content, gas upgrading technologies are applied. Besides the more conventional physico-chemical biogas upgrading methods (HPWS, PSA, membrane separation, etc.), biological biogas upgrading gained more and more interest, as by these biotechnologies, the carbon-dioxide content of the biogas is directly transformed to methane (chemoautotrophic approach) or valuable algal biomass (photoautotrophic approach), considerably raising the total heating value of the end-products.

The expectations are high towards the biological biogas upgrading technologies in the field of energy storage linked with carbon-dioxide capture. To this day, predominantly lab- and pilot-scale researches are available in the literature,

but full-scale applications are rather scarce. As chemoautotrophic upgrading requires external hydrogen supply produced mainly by electrolysis, the economic feasibility of this approach highly depends on the energy efficiency and the prize of the electric energy applied. Current research and development efforts aim mainly to raise the hydrogen injection and conversion efficiency. In photoautotrophic approach, the CO_2 injection and conversion efficiency are aimed to be raised in most of the current development, while the payback by further utilization of the algal bioreactors for nutrients removal and valorization of algal biomass are key factors of economical feasibility.

Besides technological improvements, governmental regulations may also highly influence the viability of these biotechnologies. Along with the aims of EU Climate and Energy Framework, with appropriate governmental subsidies for biomethane, the competitiveness and economic feasibility of these technologies can be highly increased.

Acknowledgements

This work was performed in the frame of the 2020-3.1.1-ZFR-KVG-2020-00006 project, implemented with the support provided from the National Research, Development and Innovation Fund of Hungary, financed under the 2020-3.1.2-ZFR-KVG funding scheme.

The research reported in this paper is part of project no. TKP2021-EGA-02, implemented with the support provided by the Ministry for Innovation and Technology of Hungary from the National Research, Development and Innovation Fund, financed under the TKP2021 funding scheme.

References

[1] Scarlat, N., Dallemand, J.-F., Fahl, F. "Biogas: Developments and perspectives in Europe", Renewable Energy, 129(A), pp. 457–472, 2018. https://doi.org/10.1016/j.renene.2018.03.006

[2] European Comission "2030 climate & energy framework", [online] Available at: https://ec.europa.eu/clima/eu-action/climate-strategies-targets/2030-climate-energy-framework_en [Accessed: 07 October 2021]

[3] Scarlat, N., Dallemand, J.-F., Monforti-Ferrario, F., Banja, M., Motola, V. "Renewable energy policy framework and bioenergy contribution in the European Union - An overview from National Renewable Energy Action Plans and Progress Reports", Renewable and Sustainable Energy Reviews, 51, pp. 969–985, 2015. https://doi.org/10.1016/j.rser.2015.06.062

[4] Hughes, J. "EU's methane strategy hinged on massive deployment of on-farm biogas", Industry news, World Biogas Association, [online] 27 October 2020, Available at: https://www.worldbiogasassociation.org/eus-methane-strategy-hinged-on-massive-deployment-of-on-farm-biogas/ [Accessed: 08 October 2021]

[5] Adekunle, K. F., Okolie, J. A. "A Review of Biochemical Process of Anaerobic Digestion", Advances in Bioscience and Biotechnology, 6(3), pp. 205–212, 2015. https://doi.org/10.4236/abb.2015.63020

[6] Awe, O. W., Zhao, Y., Nzihou, A., Minh, D. P., Lyczko, N. "A Review of Biogas Utilisation, Purification and Upgrading Technologies", Waste and Biomass Valorization, 8(2), pp. 267–283, 2017. https://doi.org/10.1007/s12649-016-9826-4

[7] Aryal, N., Kvist, T. "Alternative of Biogas Injection into the Danish Gas Grid System—A Study from Demand Perspective", ChemEngineering, 2(3), Article number: 43, 2018. https://doi.org/10.3390/CHEMENGINEERING2030043

[8] Kapoor, R., Ghosh, P., Tyagi, B., Vijay, V. K., Vijay, V., Thakur, I. S., Kamyab, H., Nguyen, D. D., Kumar A. "Advances in biogas valorization and utilization systems: A comprehensive review", Journal of Cleaner Production, 273, Article number: 123052, 2020. https://doi.org/10.1016/j.jclepro.2020.123052

[9] Kurtgoz, Y., Karagoz, M:, Deniz, E. "Biogas engine performance estimation using ANN", Engineering Science and Technology, an International Journal, 20(6), pp. 1563–1570, 2017. https://doi.org/10.1016/j.jestch.2017.12.010

[10] Muñoz, R., Meier, L., Diaz, I., Jeison, D. "A review on the state-of-the-art of physical/chemical and biological technologies for biogas upgrading", Reviews in Environmental Science and Biotechnology, 14(4), pp. 727–759, 2015. https://doi.org/10.1007/s11157-015-9379-1

[11] Østergaard, P. A. "Comparing electricity, heat and biogas storages' impacts on renewable energy integration", Energy, 37(1), pp. 255–262, 2012. https://doi.org/10.1016/j.energy.2011.11.039

[12] Hahn, H., Krautkremer, B., Hartmann, K., Wachendorf, M. "Review of concepts for a demand-driven biogas supply for flexible power generation", Renewable and Sustainable Energy Reviews, 29, pp. 383–393, 2014. https://doi.org/10.1016/j.rser.2013.08.085

[13] Sun, Q., Li, H., Yan, J., Liu, L., Yu, Z., Yu, X. "Selection of appropriate biogas upgrading technology-a review of biogas cleaning, upgrading and utilisation", Renewable and Sustainable Energy Reviews, 51, pp. 521–532, 2015. https://doi.org/10.1016/j.rser.2015.06.029

[14] Porowska, D. "Review of Research Methods for Assessing the Activity of a Municipal Landfill Based on the Landfill Gas Analysis", Periodica Polytechnica Chemical Engineering, 65(2), pp. 167–176, 2021. https://doi.org/10.3311/PPCH.16476

[15] Ullah Khan, I., Hafiz Dzarfan Othman, M., Hashim, H., Matsuura, T., Ismail, A. F., Rezaei-DashtArzhandi, M., Wan Azelee, I. "Biogas as a renewable energy fuel – A review of biogas upgrading, utilisation and storage", Energy Conversion and Management, 150, pp. 277–294, 2017. https://doi.org/10.1016/j.enconman.2017.08.035

[16] Adnan, A. I., Ong, M. Y., Nomanbhay, S., Chew, K. W., Show, P. L. "Technologies for Biogas Upgrading to Biomethane: A Review", Bioengineering, 6(4), Article number: 92, 2019. https://doi.org/10.3390/bioengineering6040092

[17] Khan, M. U., Lee, J. T. E., Bashir, M. A., Dissanayake, P. D., Ok, Y. S., Tong, Y. W., Shariati, M. A., Wu, S., Ahring, B. K. "Current status of biogas upgrading for direct biomethane use: A review", Renewable and Sustainable Energy Reviews,149, Article number: 111343, 2021. https://doi.org/10.1016/j.rser.2021.111343

[18] Carranza-Abaid, A., Wanderley, R. R., Knuutila, H. K., Jakobsen, J. P. "Analysis and selection of optimal solvent-based technologies for biogas upgrading", Fuel, 303, Article number: 121327, 2021. https://doi.org/10.1016/j.fuel.2021.121327

[19] Riboldi, L., Bolland, O. "Overview on Pressure Swing Adsorption (PSA) as CO_2 Capture Technology: State-of-the-Art, Limits and Potentials", Energy Procedia, 114, pp. 2390–2400, 2017. https://doi.org/10.1016/j.egypro.2017.03.1385

[20] Vogtenhuber, H., Hofmann, R., Helminger, F., Schöny, G. "Process simulation of an efficient temperature swing adsorption concept for biogas upgrading", Energy, 162, pp. 200–209, 2018. https://doi.org/10.1016/j.energy.2018.07.193

[21] Baena-Moreno, F. M., le Saché, E., Pastor-Pérez, L., Reina, T. R. "Membrane-based technologies for biogas upgrading: a review", Environmental Chemistry Letters, 18(5), pp. 1649–1658, 2020. https://doi.org/10.1007/s10311-020-01036-3

[22] Scholz, M., Melin, T., Wessling, M. "Transforming biogas into biomethane using membrane technology", Renewable and Sustainable Energy Reviews, 17, pp. 199–212, 2013. https://doi.org/10.1016/j.rser.2012.08.009

[23] Yousef, A. M., El-Maghlany, W. M., Eldrainy, Y. A., Attia, A. "New approach for biogas purification using cryogenic separation and distillation process for CO_2 capture", Energy, 156, pp. 328–351, 2018. https://doi.org/10.1016/j.energy.2018.05.106

[24] Sahota, S., Shah, G., Ghosh, P., Kapoor, R., Sengupta, S., Singh, P., Vijay, V., Sahay, A., Vijay, V. K., Thakur, I. S. "Review of trends in biogas upgradation technologies and future perspectives", Bioresource Technology Reports, 1, pp. 79–88, 2018. https://doi.org/10.1016/j.biteb.2018.01.002

[25] Khan, M. U., Lee, J. T. E., Bashir, M. A., Dissanayake, P. D., Ok, Y. S., Tong, Y. W., Shariati, M. A., Wu, S., Ahring, B. K. "Current status of biogas upgrading for direct biomethane use: A review", Renewable and Sustainable Energy Reviews, 149, Article number: 111343, 2021. https://doi.org/10.1016/J.RSER.2021.111343

[26] Fu, S., Angelidaki, I., Zhang, Y. "*In situ* Biogas Upgrading by CO_2-to-CH_4 Bioconversion", Trends in Biotechnology, 39(4), pp. 336–347, 2021. https://doi.org/10.1016/j.tibtech.2020.08.006

[27] Mulat, D. G., Mosbæk, F., Ward, A. J., Polag, D., Greule, M., Keppler, F., Nielsen, J. L., Feilberg, A. "Exogenous addition of H_2 for an *in situ* biogas upgrading through biological reduction of carbon dioxide into methane", Waste Management, 68, pp. 146–156, 2017. https://doi.org/10.1016/j.wasman.2017.05.054

[28] Luo, G., Angelidaki, I. "Co-digestion of manure and whey for in situ biogas upgrading by the addition of H_2: process performance and microbial insights", Applied Microbiology and Biotechnology, 97(3), pp. 1373–1381, 2012. https://doi.org/10.1007/S00253-012-4547-5

[29] Bajpai, P. "Basics of Anaerobic Digestion Process", In: Anaerobic Technology in Pulp and Paper Industry, Springer, Singapore, Singapore, 2017, pp. 7–12. https://doi.org/10.1007/978-981-10-4130-3_2

[30] Angelidaki, I., Treu, L.,Tsapekos, P., Luo, G., Campanaro, S., Wenzel, H., Kougias, P. G. "Biogas upgrading and utilization: Current status and perspectives", Biotechnology Advances, 36(2), pp. 452–466, 2018. https://doi.org/10.1016/J.BIOTECHADV.2018.01.011

[31] Tarhan, C., Çil, M. A. "A study on hydrogen, the clean energy of the future: Hydrogen storage methods", Journal of Energy Storage, 40, Article number: 102676, 2021. https://doi.org/10.1016/j.est.2021.102676

[32] Thema, M., Bauer, F., Sterner, M. "Power-to-Gas: Electrolysis and methanation status review", Renewable and Sustainable Energy Reviews, 112, pp. 775–787, 2019. https://doi.org/10.1016/J.RSER.2019.06.030

[33] Gorre, J., Ruoss, F., Karjunen, H., Schaffert, J., Tynjälä, T. "Cost benefits of optimizing hydrogen storage and methanation capacities for Power-to-Gas plants in dynamic operation", Applied Energy, 257, Article number: 113967, 2020. https://doi.org/10.1016/J.APENERGY.2019.113967

[34] Kummer, K., Imre, A. R. "Seasonal and Multi-Seasonal Energy Storage by Power-to-Methane Technology", Energies, 14(11), Article number: 3265, 2021. https://doi.org/10.3390/EN14113265

[35] Nashmin Elyasi, S., He, L., Tsapekos, P., Rafiee, S., Khoshnevisan, B., Carbajales-Dale, M., Mohtasebi, S. S., Liu, H., Angelidaki, I. "Could biological biogas upgrading be a sustainable substitution for water scrubbing technology? A case study in Denmark", Energy Conversion and Management, 245, Article number: 114550, 2021. https://doi.org/10.1016/j.enconman.2021.114550

[36] Maegaard, K., Garcia-Robledo, E., Kofoed, M. V. W., Agneessens, L. M., de Jonge, N., Nielsen, J. L., Ottosen, L. D. M., Nielsen, L. P., Revsbech, N. P. "Biogas upgrading with hydrogenotrophic methanogenic biofilms", Bioresource Technology, 287, Article number: 121422, 2019. https://doi.org/10.1016/J.BIORTECH.2019.121422

[37] Li, Y., Su, D., Luo, S., Jiang, H., Qian, M., Zhou, H., Street, J., Luo, Y., Xu, Q. "Pyrolysis gas as a carbon source for biogas production *via* anaerobic digestion", RSC Advances, 7(66), pp. 41889–41895, 2017. https://doi.org/10.1039/C7RA08559A

[38] Zhao, J., Li, Y., Dong, R. "Recent progress towards in-situ biogas upgrading technologies", Science of The Total Environment, 800, Article number: 149667, 2021. https://doi.org/10.1016/J.SCITOTENV.2021.149667

[39] Wahid, R., Horn, S. J. "The effect of mixing rate and gas recirculation on biological CO_2 methanation in two-stage CSTR systems", Biomass and Bioenergy, 144, Article number: 105918, 2021. https://doi.org/10.1016/J.BIOMBIOE.2020.105918

[40] Jensen, M. B., Kofoed, M. V. W., Fischer, K., Voigt, N. V., Agneessens, L. M., Batstone, D. J., Ottosen, L. D. M. "Venturi-type injection system as a potential H_2 mass transfer technology for full-scale *in situ* biomethanation", Applied Energy, 222, pp. 840–846, 2018. https://doi.org/10.1016/J.APENERGY.2018.04.034

[41] Alfaro, N., Fdz-Polanco, M., Fdz-Polanco, F., Díaz, I. "H_2 addition through a submerged membrane for in-situ biogas upgrading in the anaerobic digestion of sewage sludge", Bioresource Technology, 280, pp. 1–8, 2019. https://doi.org/10.1016/J.BIORTECH.2019.01.135

[42] Díaz, I., Pérez, C., Alfaro, N., Fdz-Polanco, F. "A feasibility study on the bioconversion of CO_2 and H_2 to biomethane by gas sparging through polymeric membranes", Bioresource Technology, 185, pp. 246–253, 2015. https://doi.org/10.1016/J.BIORTECH.2015.02.114

[43] Zhao, L., Wang, Z., Ren, H.-Y., Nan, J., Chen, C., Ren, N. Q. "Improving biogas upgrading and liquid chemicals production simultaneously by a membrane biofilm reactor", Bioresource Technology, 313, Article number: 123693, 2020. https://doi.org/10.1016/J.BIORTECH.2020.123693

[44] Bassani, I., Kougias, P. G., Angelidaki, I. "In-situ biogas upgrading in thermophilic granular UASB reactor: key factors affecting the hydrogen mass transfer rate", Bioresource Technology, 221, pp. 485–491, 2016. https://doi.org/10.1016/J.BIORTECH.2016.09.083

[45] Daglioglu, S. T., Ogut, T. C., Ozdemir, G., Azbar, N. "Comparative Evaluation of Two Packing Materials (Glass Pipe and Ceramic Ball) for Hydrogenothrophic Biomethanation (BHM) of CO_2", Waste and Biomass Valorization, 12(7), pp. 3717–3726, 2020. https://doi.org/10.1007/S12649-020-01242-8

[46] Garcia-Robledo, E., Ottosen, L. D. M., Voigt, N. V., Kofoed, M. W., Revsbech, N. P. "Micro-scale H_2–CO_2 Dynamics in a Hydrogenotrophic Methanogenic Membrane Reactor", Frontiers in Microbiology, 7, Article number: 1276, 2016. https://doi.org/10.3389/FMICB.2016.01276

[47] Choi, Y., Ryu, J., Lee, S. R. "Influence of carbon type and carbon to nitrogen ratio on the biochemical methane potential, pH, and ammonia nitrogen in anaerobic digestion", Journal of Animal Science and Technology, 62(1), pp. 74–83, 2020. https://doi.org/10.5187/JAST.2020.62.1.74

[48] Zhou, J., Zhang, R., Liu, F., Yong, X., Wu, X., Zheng, T., Jiang, M., Jia, H. "Biogas production and microbial community shift through neutral pH control during the anaerobic digestion of pig manure", Bioresource Technology, 217, pp. 44–49, 2016. https://doi.org/10.1016/J.BIORTECH.2016.02.077

[49] Okoro-Shekwaga, C. K., Ross, A. B., Camargo-Valero, M. A. "Improving the biomethane yield from food waste by boosting hydrogenotrophic methanogenesis", Applied Energy, 254, Article number: 113629, 2019. https://doi.org/10.1016/J.APENERGY.2019.113629

[50] Fontana, A., Kougias, P. G., Treu, L., Kovalovszki, A., Valle, G., Cappa, F., Morelli, L., Angelidaki, I., Campanaro, S. "Microbial activity response to hydrogen injection in thermophilic anaerobic digesters revealed by genome-centric metatranscriptomics", Microbiome, 6, Article number: 194, 2018. https://doi.org/10.1186/S40168-018-0583-4

[51] Wang, W., Xie, L., Luo, G., Zhou, Q., Angelidaki, I. "Performance and microbial community analysis of the anaerobic reactor with coke oven gas biomethanation and in situ biogas upgrading", Bioresource Technology, 146, pp. 234–239, 2013. https://doi.org/10.1016/J.BIORTECH.2013.07.049

[52] Ravi, P. P., Lindner, J., Oechsner, H., Lemmer, A. "Effects of target pH-value on organic acids and methane production in two-stage anaerobic digestion of vegetable waste", Bioresource Technology, 247, pp. 96–102, 2018. https://doi.org/10.1016/J.BIORTECH.2017.09.068

[53] Kim, S., Mostafa, A., Im, S., Lee, M.-K., Kang, S., Na, J.-G., Kim, D.-H. "Production of high-calorific biogas from food waste by integrating two approaches: Autogenerative high-pressure and hydrogen injection", Water Research, 194, Article number: 116920, 2021. https://doi.org/10.1016/J.WATRES.2021.116920

[54] Rusmanis, D., O'Shea, R., Wall, D. M., Murphy, J. D. "Biological hydrogen methanation systems – an overview of design and efficiency", 10(1), pp. 604–634, 2019. https://doi.org/10.1080/21655979.2019.1684607

[55] Voelklein, M. A., Rusmanis, D., Murphy, J. D. "Biological methanation: Strategies for in-situ and ex-situ upgrading in anaerobic digestion", Applied Energy, 235, pp. 1061–1071, 2019. https://doi.org/10.1016/J.APENERGY.2018.11.006

[56] Liu, R., Hao, X., Wei, J. "Function of homoacetogenesis on the heterotrophic methane production with exogenous H_2/CO_2 involved", Chemical Engineering Journal, 284, pp. 1196–1203, 2016. https://doi.org/10.1016/J.CEJ.2015.09.081

[57] Sarker, S., Lamb, J. J., Hjelme, D. R., Lien, K. M. "Overview of recent progress towards in-situ biogas upgradation techniques", Fuel, 226, pp. 686–697, 2018. https://doi.org/10.1016/J.FUEL.2018.04.021

[58] Jensen, M. B., Jensen, B., Ottosen, L. D: M., Kofoed, M. V. W. "Integrating H_2 injection and reactor mixing for low-cost H_2 gas-liquid mass transfer in full-scale *in situ* biomethanation", Biochemical Engineering Journal, 166, Article number: 107869, 2021. https://doi.org/10.1016/J.BEJ.2020.107869

[59] Fu, S., Angelidaki, I., Zhang, Y. "*In situ* Biogas Upgrading by CO_2-to-CH_4 Bioconversion", Trends in Biotechnology, 39(4), pp. 336–347, 2021. https://doi.org/10.1016/J.TIBTECH.2020.08.006

[60] Sposob, M., Wahid, R., Fischer, K. "*Ex-situ* biological CO_2 methanation using trickle bed reactor: review and recent advances", Reviews in Environmental Science and Bio/Technology, 20(4), pp. 1087–1102, 2021. https://doi.org/10.1007/S11157-021-09589-7

[61] Ahern, E. P., Deane, P., Persson, T., Gallachóir, B. Ó., Murphy, J. D. "A perspective on the potential role of renewable gas in a smart energy island system", Renewable Energy, 78, pp. 648–656, 2015. https://doi.org/10.1016/J.RENENE.2015.01.048

[62] Kougias, P. G., Treu, L., Benavente, D. P., Boe, K., Campanaro, S., Angelidaki, I. "*Ex-situ* biogas upgrading and enhancement in different reactor systems", Bioresource Technology, 225, pp. 429–437, 2017. https://doi.org/10.1016/J.BIORTECH.2016.11.124

[63] Kougias, P. G., Tsapekos, P., Treu, L., Kostoula, M., Campanaro, S., Lyberatos, G., Angelidaki, I. "Biological CO_2 fixation in up-flow reactors via exogenous H_2 addition", Journal of Biotechnology, 319, pp. 1–7, 2020. https://doi.org/10.1016/J.JBIOTEC.2020.05.012

[64] Jensen, M. B., Ottosen, L. D. M., Kofoed, M. V. W. "H_2 gas-liquid mass transfer: A key element in biological Power-to-Gas methanation", Renewable and Sustainable Energy Reviews, 147, Article number: 111209, 2021. https://doi.org/10.1016/J.RSER.2021.111209

[65] Rachbauer, L., Voitl, G., Bochmann, G., Fuchs, W. "Biological biogas upgrading capacity of a hydrogenotrophic community in a trickle-bed reactor", Applied Energy, 180, pp. 483–490, 2016. https://doi.org/10.1016/J.APENERGY.2016.07.109

[66] Ullrich, T., Lindner, J., Bär, K., Mörs, F., Graf, F., Lemmer, A. "Influence of operating pressure on the biological hydrogen methanation in trickle-bed reactors", Bioresource Technology, 247, pp. 7–13, 2018. https://doi.org/10.1016/J.BIORTECH.2017.09.069

[67] Figeac, N., Trably, E., Bernet, N., Delgenès, J.-P., Escudié, R. "Temperature and Inoculum Origin Influence the Performance of Ex-Situ Biological Hydrogen Methanation", Molecules, 25(23), Article number: 5665, 2020. https://doi.org/10.3390/MOLECULES25235665

[68] Ashraf, M. T., Sieborg, M. U., Yde, L., Rhee, C., Shin, S. G., Triolo, J. M. "Biomethanation in a thermophilic biotrickling filter — pH control and lessons from long-term operation", Bioresource Technology Reports, 11, Article number: 100525, 2020. https://doi.org/10.1016/J.BITEB.2020.100525

[69] Sposob, M., Wahid, R. "Comparison and Gas Loading Impact on Counter- and Concurrent Trickle-Bed Reactor Configurations for *Ex-Situ* Biomethanation", Research Square, [preprint] 25 October 2021. https://doi.org/10.21203/RS.3.RS-989066/V1

[70] Zabranska, J., Pokorna, D. "Bioconversion of carbon dioxide to methane using hydrogen and hydrogenotrophic methanogens", Biotechnology Advances, 36(3), pp. 707–720, 2018. https://doi.org/10.1016/J.BIOTECHADV.2017.12.003

[71] Seifert, A. H., Rittmann, S., Bernacchi, S., Herwig, C. "Method for assessing the impact of emission gasses on physiology and productivity in biological methanogenesis", Bioresource Technology, 136, pp. 747–751, 2013. https://doi.org/10.1016/J.BIORTECH.2013.03.119

[72] Sun, Y., Lin, Z., Peng, S. H., Sage, V., Sun, Z. "A Critical Perspective on CO_2 Conversions into Chemicals and Fuels", Journal of Nanoscience and Nanotechnology, 19(6), pp. 3097–3109, 2019. https://doi.org/10.1166/JNN.2019.16588

[73] Schiebahn, S., Grube, T., Robinius, M., Tietze, V., Kumar, B., Stolten, D. "Power to gas: Technological overview, systems analysis and economic assessment for a case study in German", International Journal of Hydrogen Energy, 40(12), pp. 4285–4294, 2015. https://doi.org/10.1016/J.IJHYDENE.2015.01.123

[74] Wahid, R., Mulat, D. G., Gaby, J. C., Horn, S. J. "Effects of H_2:CO_2 ratio and H_2 supply fluctuation on methane content and microbial community composition during in-situ biological biogas upgrading", Biotechnology for Biofuels, 12, Article number: 104, 2019. https://doi.org/10.1186/S13068-019-1443-6

[75] Li, C., Zhu, X., Angelidaki, I. "Carbon monoxide conversion and syngas biomethanation mediated by different microbial consortia", Bioresource Technology, 314, Article number: 123739, 2020. https://doi.org/10.1016/J.BIORTECH.2020.123739

[76] Li, C., Zhu, X., Angelidaki, I. "Syngas biomethanation: effect of biomass-gas ratio, syngas composition and pH buffer", Bioresource Technology, 342, Article number: 125997, 2021. https://doi.org/10.1016/J.BIORTECH.2021.125997

[77] Gavala, H. N., Grimalt-Alemany, A., Asimakopoulos, K., Skiadas, I. V. "Gas Biological Conversions: The Potential of Syngas and Carbon Dioxide as Production Platforms", Waste and Biomass Valorization, 12(10), pp. 5303–5328, 2021. https://doi.org/10.1007/S12649-020-01332-7

[78] Leonzio, G. "Process analysis of biological Sabatier reaction for bio-methane production", Chemical Engineering Journal, 290, pp. 490–498, 2016. https://doi.org/10.1016/J.CEJ.2016.01.068

[79] Burkhardt, M., Busch, G. "Methanation of hydrogen and carbon dioxide", Applied Energy, 111, pp. 74–79, 2013. https://doi.org/10.1016/J.APENERGY.2013.04.080

[80] Aryal, N., Kvist, T., Ammam, F., Pant, D., Ottosen, L. D. M. "An overview of microbial biogas enrichment", Bioresource Technology, 264, pp. 359–369, 2018. https://doi.org/10.1016/J.BIORTECH.2018.06.013

[81] Porté, H., Kougias, P. G., Alfaro, N., Treu, L., Campanaro, S., Angelidaki, I. "Process performance and microbial community structure in thermophilic trickling biofilter reactors for biogas upgrading", Science of The Total Environment, 655, pp. 529–538, 2019. https://doi.org/10.1016/J.SCITOTENV.2018.11.289

[82] Strübing, D., Moeller, A. B., Mößnang, B., Lebuhn, M., Drewes, J. E., Koch, K. "Load change capability of an anaerobic thermophilic trickle bed reactor for dynamic H_2/CO_2 biomethanation", Bioresource Technology, 289, Article number: 121735, 2019. https://doi.org/10.1016/J.BIORTECH.2019.121735

[83] Ashraf, M. T., Yde, L., Triolo, J. M., Wenzel, H. "Optimizing the dosing and trickling of nutrient media for thermophilic biomethanation in a biotrickling filter", Biochemical Engineering Journal, 176, Article number: 108220, 2021. https://doi.org/10.1016/j.bej.2021.108220

[84] Jensen, M. B., Poulsen, S., Jensen, B., Feilberg, A., Kofoed, M. V. W. "Selecting carrier material for efficient biomethanation of industrial biogas-CO_2 in a trickle-bed reactor", Journal of CO2 Utilization, 51, Article number: 101611, 2021. https://doi.org/10.1016/J.JCOU.2021.101611

[85] Baransi-Karkaby, K., Hassanin, M., Muhsein, S., Massalha, N., Sabbah, I. "Innovative *ex-situ* biological biogas upgrading using immobilized biomethanation bioreactor (IBBR)", Water Science & Technology, 81(6), pp. 1319–1328, 2020. https://doi.org/10.2166/WST.2020.234

[86] Szuhaj, M., Wirth, R., Bagi, Z., Maróti, G., Rákhely, G., Kovács, K. L. "Development of Stable Mixed Microbiota for High Yield Power to Methane Conversion", Energies, 14(21), Article number: 7336, 2021. https://doi.org/10.3390/EN14217336

[87] Yun, Y.-M., Sung, S., Kang, S., Kim, M.-S., Kim, D.-H. "Enrichment of hydrogenotrophic methanogens by means of gas recycle and its application in biogas upgrading", Energy, 135, pp. 294–302, 2017. https://doi.org/10.1016/J.ENERGY.2017.06.133

[88] Ghofrani-Isfahani, P., Tsapekos, P., Peprah, M., Kougias, P., Zhu, X., Kovalovszki, A., Zervas, A., Zha, X., Jacobsen, C. S., Angelidaki, I. "*Ex-situ* biogas upgrading in thermophilic up-flow reactors: The effect of different gas diffusers and gas retention times", Bioresource Technology, 340, Article number: 125694, 2021. https://doi.org/10.1016/J.BIORTECH.2021.125694

[89] Bassani, I., Kougias, P. G., Treu, L., Angelidaki, I. "Biogas Upgrading via Hydrogenotrophic Methanogenesis in Two-Stage Continuous Stirred Tank Reactors at Mesophilic and Thermophilic Conditions", Environmental Science & Technology, 49(20), pp. 12585–12593, 2015. https://doi.org/10.1021/acs.est.5b03451

[90] Hattori, S. "Syntrophic Acetate-Oxidizing Microbes in Methanogenic Environments", Microbes and Environments, 23(2), pp. 118–127, 2008. https://doi.org/10.1264/JSME2.23.118

[91] Savvas, S., Donnelly, J., Patterson, T. P., Dinsdale, R., Esteves, S. R. "Closed nutrient recycling via microbial catabolism in an eco-engineered self regenerating mixed anaerobic microbiome for hydrogenotrophic methanogenesis", Bioresource Technology, 227, pp. 93–101, 2017. https://doi.org/10.1016/J.BIORTECH.2016.12.052

[92] Vo, T. T. Q., Rajendran, K., Murphy, J. D. "Can power to methane systems be sustainable and can they improve the carbon intensity of renewable methane when used to upgrade biogas produced from grass and slurry?", Applied Energy, 228, pp. 1046–1056, 2018. https://doi.org/10.1016/j.apenergy.2018.06.139

[93] Vo, T. T. Q., Wall, D. M., Ring, D., Rajendran, K., Murphy, J. D. "Techno-economic analysis of biogas upgrading via amine scrubber, carbon capture and ex-situ methanation", Applied Energy, 212, pp. 1191–1202, 2018. https://doi.org/10.1016/j.apenergy.2017.12.099

[94] Collet, P., Flottes, E., Favre, A., Raynal, L., Pierre, H., Capela, S., Peregrina, C. "Techno-economic and Life Cycle Assessment of methane production via biogas upgrading and power to gas technology" Applied Energy, 192, pp. 282–295, 2017. https://doi.org/10.1016/j.apenergy.2016.08.181

[95] Feng, R., Li, Q., Zaidi, A. A., Peng, H., Shi, Y. "Effect of Autoclave Pretreatment on Biogas Production through Anaerobic Digestion of Green Algae", Periodica Polytechnica Chemical Engineering, 65(4), pp. 483–492, 2021. https://doi.org/10.3311/PPch.18064

[96] Vavitsas, K., Kugler, A., Satta, A., Hatzinikolaou, D. G., Lindblad, P., Fewer, D. P., Lindberg, P., Toivari, M., Stensjö, K. "Doing synthetic biology with photosynthetic microorganisms", Physiologia Plantarum, 173(2), pp. 624–638, 2021. https://doi.org/10.1111/PPL.13455

[97] Castiglia, D., Landi, S., Esposito, S. "Advanced Applications for Protein and Compounds from Microalgae", Plants, 10(8), Article number: 1686, 2021. https://doi.org/10.3390/PLANTS10081686

[98] Fabris, M., Abbriano, R. M., Pernice, M., Sutherland, D. L., Commault, A. S., Hall, C. C., Labeeuw, L., McCauley, J. I., Kuzhiuparambil, U., Ray, P., Kahlke, T., Ralph, P. J. "Emerging Technologies in Algal Biotechnology: Toward the Establishment of a Sustainable, Algae-Based Bioeconomy", Frontiers in Plant Science, 11, Article number: 279, 2020. https://doi.org/10.3389/FPLS.2020.00279

[99] Rodero, M. d. R., Lebrero, R., Serrano, E., Lara, E., Arbib, Z., García-Encina, P. A., Muñoz, R. "Technology validation of photosynthetic biogas upgrading in a semi-industrial scale algal-bacterial photobioreactor", Bioresource Technology, 279, pp. 43–49, 2019. https://doi.org/10.1016/J.BIORTECH.2019.01.110

[100] Nakai, S., Oktavitri, N. I., Itamura, N., Okuda, T., Nishijima, W., Matsumoto, M. "Use of Anaerobic Digestion Effluent and Secondary Treated Sewage Plant Discharge for Algal Cultivation and Prevention of Algal Pond Crash", Journal of Chemical Engineering of Japan, 53(4), pp. 177–182, 2020. https://doi.org/10.1252/JCEJ.19WE044

[101] Škufca, D., Kovačič, A., Prosenc, F., Griessler Bulc, T., Heath, D., Heath, E. "Phycoremediation of municipal wastewater: Removal of nutrients and contaminants of emerging concern", Science of The Total Environment, 782, Article number: 146949, 2021. https://doi.org/10.1016/J.SCITOTENV.2021.146949

[102] Sutherland, D. L., Park, J., Heubeck, S., Ralph, P. J., Craggs, R. J. "Size matters – Microalgae production and nutrient removal in wastewater treatment high rate algal ponds of three different sizes", Algal Research, 45, Article number: 101734, 2020. https://doi.org/10.1016/J.ALGAL.2019.101734

[103] Ibañez, M. V., Leonardi, R. J., Morelli, M. N., Irazoqui, H. A., Heinrich, J. M. "A colourimetric method for the measuring of the mass transfer kinetics of carbon dioxide in aqueous media", Algal Research, 45, Article number: 101717, 2020. https://doi.org/10.1016/J.ALGAL.2019.101717

[104] Kim, G.-Y., Heo, J., Kim, K., Chung, J., Han, J.-I. "Electrochemical pH control and carbon supply for microalgae cultivation", Chemical Engineering Journal, 426, Article number: 131796, 2021. https://doi.org/10.1016/J.CEJ.2021.131796

[105] Gao, K. "Approaches and involved principles to control pH/pCO_2 stability in algal cultures", Journal of Applied Phycology, 33(6), pp. 3497–3505, 2021. https://doi.org/10.1007/S10811-021-02585-Y

[106] Juškaitė, L., Zagorskis, A. "Microalgae Strains *Monoraphidium Griffithi and Chlorella sp.* for the Carbon Dioxide Capture from Biogas", In: 11th International Conference "Environmental Engineering", Vilnius, Lithuania, 2020, Article ID: enviro.2020.720. https://doi.org/10.3846/ENVIRO.2020.720

[107] Nguyen, L. N., Kumar, J., Vu, M. T., Mohammed, J. A. H., Pathak, N., Commault, A. S., Sutherland, D., Zdarta, J., Tyagi, V. K., Nghiem, L. D. "Biomethane production from anaerobic co-digestion at wastewater treatment plants: A critical review on development and innovations in biogas upgrading techniques", Science of The Total Environment, 765, Article number: 142753, 2021. https://doi.org/10.1016/J.SCITOTENV.2020.142753

[108] Yan, C., Zhu, L., Wang, Y. "Photosynthetic CO_2 uptake by microalgae for biogas upgrading and simultaneously biogas slurry decontamination by using of microalgae photobioreactor under various light wavelengths, light intensities, and photoperiods", Applied Energy, 178, pp. 9–18, 2016.
https://doi.org/10.1016/J.APENERGY.2016.06.012

[109] Herold, C., Ishika, T., Nwoba, E. G., Tait, S., Ward, A., Moheimani, N. R. "Biomass production of marine microalga *Tetraselmis suecica* using biogas and wastewater as nutrients", Biomass and Bioenergy, 145, Article number: 105945, 2021.
https://doi.org/10.1016/J.BIOMBIOE.2020.105945

[110] Xia, A., Herrmann, C., Murphy, J. D. "How do we optimize third-generation algal biofuels?", Biofuels, Bioproducts and Biorefining, 9(4), pp. 358–367, 2015.
https://doi.org/10.1002/BBB.1550

[111] Marín, D., Carmona-Martínez, A. A., Blanco, S., Lebrero, R., Muñoz, R. "Innovative operational strategies in photosynthetic biogas upgrading in an outdoors pilot scale algal-bacterial photobioreactor", Chemosphere, 264(1), Article number: 128470, 2021.
https://doi.org/10.1016/J.CHEMOSPHERE.2020.128470

[112] Wu, L., Wei, W., Song, L., Woźniak-Karczewska, M., Chrzanowski, Ł., Ni, B.-J. "Upgrading biogas produced in anaerobic digestion: Biological removal and bioconversion of CO_2 in biogas", Renewable and Sustainable Energy Reviews, 150, Article number: 111448, 2021.
https://doi.org/10.1016/J.RSER.2021.111448

[113] Bose, A., Lin, R., Rajendran, K., O'Shea, R., Xia, A., Murphy, J. D. "How to optimise photosynthetic biogas upgrading: a perspective on system design and microalgae selection", Biotechnology Advances, 37(8), Articel number: 107444, 2019.
https://doi.org/10.1016/J.BIOTECHADV.2019.107444

[114] Singh, G., Patidar, S. K. "Microalgae harvesting techniques: A review", Journal of Environmental Management, 217, pp. 499–508, 2018.
https://doi.org/10.1016/J.JENVMAN.2018.04.010

[115] Dassey A. J., Theegala, C. S. "Harvesting economics and strategies using centrifugation for cost effective separation of microalgae cells for biodiesel applications", Bioresource Technology, 128, pp. 241–245, 2013.
https://doi.org/10.1016/J.BIORTECH.2012.10.061

[116] Zhang, W., Zhao, C., Cao, W., Sun, S., Hu, C., Liu, J., Zhao, Y. "Removal of pollutants from biogas slurry and CO_2 capture in biogas by microalgae-based technology: a systematic review", Environmental Science and Pollution Research, 27(23), pp. 28749–28767, 2020.
https://doi.org/10.1007/s11356-020-09282-2

[117] Meier, L., Martínez, C., Vílchez, C., Bernard, O., Jeison, D. "Evaluation of the feasibility of photosynthetic biogas upgrading: Simulation of a large-scale system", Energy, 189, Article number: 116313, 2019.
https://doi.org/10.1016/J.ENERGY.2019.116313