Short review:

**Overview of recent progress towards in-situ biogas upgradation techniques**

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**Abstract**

Biogas, as derived from the anaerobic digestion process, offers a versatile possibility of renewable and sustainable energy usage. When enriched, upgraded biogas can yield high levels of biomethane, allowing its use as an alternative to natural gas via existing natural gas grids or being directly consumed by transport vehicles as fuel. Currently, biogas upgrading is experiencing a golden period of rapid development where many enrichment techniques are being revisited, modified or strengthened, and contemporary novel technologies are being proposed. Mainly, two broad categories of upgrading techniques are present in which conventional method primarily focuses on *ex-situ* approaches, treating produced biogas to methane by employing catalytic conversion (biological and chemical), membrane gas-permeation, desulphurization, physical and chemical scrubbing, absorption and adsorption. Over the years, a considerable effort has been made to improve efficiency and to enhance the economic viability of the above techniques and many commercial plants worldwide use *ex-situ* approaches as options to enrich biogas as biofuel for direct utilization to vehicles. Coupled to the *ex-situ* method, *in-situ* techniques, such as CO2 desorption, pressurized reactor, H2 addition (deployed to anaerobic digesters directly) and electromethanogenesis has also been gained huge attention recently. Comparative studies between *in-situ* and *ex-situ* method suggests that the former provides an increased economic performance for small to medium and small-scale facilities, allowing the upgrading of biogas above 85% v/v of methane. Additionally, innovations in bacterial species that are capable of direct exchange of electrons, escalating the biological conversion of CO2 to CH4 has also been demonstrated. This paper enlightens some of these aspects and reviews the state-of-the art of biogas enriching techniques emphasizing *in-situ* approaches.



**Figure for graphical abstract**

**Keywords:** Biogas, Upgrading, Biomethane, *In-situ*, Review

**Nomenclature**

AD Anaerobic digestion

AHPD Autogenerative high pressure digestion

BES Bioelectrochemical system

CHP Combined heat and power

DIET Direct interspecies electron transfer

FA Free ammonia

GHG Greenhouse gas

GW Giga watt

HRT Hydraulic retention time

L/G Liquid-to-gas

MEC Microbial electrolysis cells

MFC Microbial fuel cells

OLR Organic loading rate

SHE Standard hydrogen electrode

UASB Upflow anaerobic sludge blanket

VFA Volatile fatty acids

# Introduction

As the availability of fossil fuels is constantly decreasing, there is an increasing concern towards reducing energy usage and production derived carbon dioxide emissions [1]. As a consequence, the demand for accelerating the growth of alternative energy sources has gained more public attention than ever before [2]. Wind, solar and biomass are the three main sources of renewable energy expected to cover the bulk of the future energy supply worldwide, replacing fossil fuels [3]. Many energy policies already reflect this shift and target a substantial volume of alternative energy in their future energy mix based on available resources and complying with the Kyoto protocol [4]. Unlike wind and solar energy technologies (which are termed as intermittent renewable energy technologies), biomass is abundant, versatile, and has a continuous power generation capability (once reliable logistics are guaranteed) [5], and currently accounts for 10% of primary energy supply worldwide [6].

There can be different routes of biomass conversion technologies [7], among which, biochemical conversion that produces biogas using a variety of wastes and organic sources in a controlled anaerobic digestion process is suitable to fulfill part of the future sustainable energy production objective, as this method compared to thermochemical and thermal conversion technique is more economical and efficient [8]. Wastes like animal manure, sewage sludge, municipal solids and agricultural residues are specifically important in the context of biogas because they do not compete with agricultural food crops [9]. On a global scale, the amount of anaerobically digested substrate increases remarkably with an annual growth rate of ~25% [10]. Biogas production, therefore, has potential to generate a large amount of energy. The elevation of anaerobic digestion capacity to allow increased waste treatment and biogas production has been emphasized a great deal in previous studies [11-14]. Currently, the installed electricity production capacity of anaerobic digestion plants within the European Union has reached close to 7.9 GW which in addition to heat production may rise close to 29.5 GW by 2022 [15].

Nevertheless, biogas is not readily suited to all energy applications, primarily because of its low level of heating value (calorific value) and impurities. Currently, the majority of the commercial biogas plants are operated as combined heat and power (CHP) where biogas fueled engines produce the required heat and electricity to meet the energy demands on site and to the external consumers [16]. However, since the electrical efficiency of commercial gas engines are low (between 30 and 40%), electricity produced from biogas based CHP is not competitive in the free electricity market without substantial government subsidies. An alternative route, as developed over the last few decades, is the upgrading of biogas to a higher level of methane quantity. This can be used either as compressed biomethane locally or as renewable fuel directly injected into natural gas grid. The positive economic and energetic effect for substitution of fossil fuels with enriched biomethane from biogas instead of electricity derived directly from CHP has already been demonstrated [15] with the commercial interest growing continually.

In order to increase the methane content in biogas, especially for use as a transport fuel, a large number of innovative technologies have been developed [17, 18] and recently reviewed [19-22]. The technological focus has generally been towards extensive cleaning and downstream processing of biogas by deploying techniques such as drying, and the removal of CO2 , NH3, H2S and other trace impurities to achieve a methane content of 95-99% in biogas. However, impurity removal can be of cost and energy intensive including technical barriers associated with low sorbent efficiency (sorbents or chemicals: i.e.; alkaline amine, zeolites and metal-organic frameworks) [15] and plasticizing of membranes [23]. Past studies [24, 25] have suggested that due the large fraction of CO2 in raw biogas, the cost of gas purification only becomes economically and energetically feasible if plant operational capacity exceeds 100 m3 biogas/h. A large number of real applications, however, operate below this range and thereby the development of *ex-situ* technique up until now is underemphasized. Today, only a very few commercial plants upgrade biogas to a high fuel standard using *ex-situ* cleaning of the biogas globally [26].

Through the *in-situ* technique, when applied to the anaerobic process directly operating with the concept of CO2 and CH4 differential solubility and electro-methanogenesis, a cost-effective way of upgrading methane over a broad range of applications may become established. To date, a number of methods regarding *in-situ* methane enrichment have been proposed and interesting results were demonstrated [26-31]. Besides being cost-effective, *in-situ* upgrading is deemed to offer enhanced degradation of organic matter [30] with simultaneous removal of H2S from the off-gas (which is technically as expensive as removing CO2 from biogas) [26]. Furthermore, in a novel electro-methanogenesis concept, several groups of bacteria can efficiently exchange electrons, directly producing biogas with a high methane. Despite this, the research and development towards upscaling of various *in-situ* techniques are still ongoing.

Biogas upgrading using combined *ex-situ* and *in-situ* techniques have been reviewed by a number of published documents previously [12, 15]. However, literature review reporting *in-situ* biogas upgrading only is scarce, if not none. The aim of this review, therefore, is to define the state-of-the-art *in-situ* biogas upgrading techniques and to shed light on innovations that could be employed for future advancement in biogas production technologies. In particular, the work explores a various methodologies with emphasis on emerging processes, which are envisaged to play a significant role in future context of bioenergy.

# Biomethane enrichment

Raw biogas produced by the anaerobic digestion generally consists of the gas species CH4, CO2, H2S, NH3 and H2O, along with the trace amount of other organic and inorganic components. Methane has a large share within the biogas composition with 40 - 75%, followed by CO2 with 25 - 55% [12]. Besides anaerobic digestion, biogas can also be collected from landfills with a typical gas composition of 50-55% CH4, 37-45% CO2 and less than 1% non-methane organic and inorganic compounds [12, 32]. Regardless of the production routes, compared to its closest counterpart natural gas (fossil fuel), biogas is energetically inferior due to the high amount of CO2 and other contaminants. Moreover, the lower heating value of biogas for example is roughly 21.5 MJ/Nm3, while it is around 35.8 MJ/Nm3 for natural gas [33].

To enhance energy content, therefore, biogas needs to be upgraded [12]. Upgraded biogas can have a reduced CO2 emissions of 75 to 200%, when compared to that of fossil fuels [34]. Significant reductions in GHG emissions can also be achieved using liquid biofuels derived from upgraded biogas. However, depending on the applications, upgraded biogas needs to meet the requirements of downstream specifications in terms of the levels of contaminants [19]. For instance, high levels of CO2 within biogas is not desirable in internal combustion engines. A high CO2 content significantly reduces the energy content of the biogas, therefore, escalating the requirement of gas flow to the combustion engine. Furthermore, the presence of water, H2S, NH3, siloxanes and halocarbons with the levels above 1000 ppm tend to cause incomplete combustion and poisonous emissions, making the removal of these components also desirable. Other uses of biogas, such as turbines and micro-turbines for CHP generation require a very low content of water and siloxane contents (0.03–0.1 ppmv) with a tolerable H2S and halocarbon (Cl-/F-) level of 10,000 –70,000 ppmv and 200–1500 ppmv respectively [35].

The prescribed quality of biomethane for natural gas grid injection requires CH4 concentrations of 80–96 %, CO2 of 2–3 %, O2 of 0.2–0.5 %, H2S of 5 mg/m3, NH3 of 3–20 mg/m3, and siloxanes of 5–10 mg/m3 respectively [35]. For biogas to reach this quality, various approaches have been used, broadly classified as *in-situ* and *ex-situ* upgradation techniques [36, 37] (Figure 1). *In-situ* biogas upgrading involves liquid-gas phase interaction within the anaerobic reactor moderated in a way that leads to increases in the level of methane within the resulting biogas. By adding certain chemicals (i.e.; salts, carbon sources) or gases, or by adjusting some of the process parameters (i.e.; pressure and digestate flow), *in-situ* upgrading can be achieved [25, 38, 39]. Different methods of *in-situ* biogas upgrading techniques are briefly discussed in section 2.1 below and shown in Figure 2. Table 1 shows currently available lab and commercial scale *in-situ* biogas upgrading technologies.

**Figure 1: Different modes of biogas upgrading techniques**

**Figure 2: Biogas upgrading using in-situ techniques**

**Table 1: Existing in-situ biogas upgrading technologies with various scales of application**

*Ex-situ* upgrading enriches the biomethane content of the biogas that has already been extracted from the anaerobic digester. Since raw biogas is converted, *ex-situ* upgrading requires a downstream biogas processing making use of the techniques such as catalytic conversion, absorption, membrane separation, among others [40]. One novel *ex-situ* technique uses algae ponds for the removal of both CO2 and H2S from the biogas, and also for growing microalgae for bioethanol production [41]. As much as 40% of the CO2, and 100% of the H2S was reportedly removed, with a higher amount of CO2 removal reported by Kampanatsanyakorn et al. [42]. Despite this, *ex-situ* technique is outside the scope of this review, but a recent review by Singhal et al. [19] describes these techniques in more detail.

## In-situ upgradation

### Pressurized reactor

Biogas produced from anaerobic digestion (AD) can be upgraded to high methane content (above 85%) biogas by producing a high pressure within the reactor. Depending on the type of microorganisms used, the pressure in an anaerobic reactor potentially can reach close to1000 bar [43, 44], although existing technologies have so far only successfully operated within the pressure range of 1 - 90 bar [24]. Compared to the conventional two-stage atmospheric pressure AD system with a normal biogas composition of ~60% CH4 and ~40% CO2, in the pressurized digester due to the influence of high pressure, dissolved CO2 in the liquid phase enhances. When the part of this dissolved CO2 directly exits as effluent, the gas-phase biogas becomes rich in methane content with corresponding composition equaling to ~95% or higher [24]. The gas solubility in liquid phase is correlated to Henry’s gas constant [25], which for H2, CH4, CO2, H2S and NH3 is 0.00078, 0.0016, 0.0318, 0.115, and 62 mol/L/bar, respectively (at standard temperature and pressure – 0 °C & 1 atm) [24]. With a higher Henry’s constant, more gas can be dissolved into the liquid phase. This means that CO2 is ~20 times, H2S is ~72 times and NH3 is ~39000 times more soluble than CH4 at standard temperature and pressure. Because of the effect of solubility within the liquid phase, high pressure reactors allow undesired gas components’ presence in biogas (CO2, H2S and NH3) to be reduced and released, reducing the requirement of compression for natural gas grid injection.

Generally, the biogas emanating from the anaerobic digester is upgraded by external techniques such as, water scrubbing, pressure swing adsorption, cryogenic separation, catalytic conversion and membrane separation before being compressed for biomethane injection into the natural gas grid [40]. However, the external techniques are highly energetically and chemically intensive and, therefore, may not be suitable in terms of plant economic and environmental sustainability. A recent study suggested that external gas upgrading of biogas can only become economically viable when biogas production capacity exceeds 100 m3/h [24]. Many existing plants, however, are operated with significantly lower capacities, where the option of increasing in production volume to suitable levels is almost unrealistic unless substantial increases in the resource availability or infrastructure modifications, both that require substantial capital investment, are made. The *in-situ* biomethane upgradation by reactor pressurization can be adapted to many biogas production plants, requiring minimum modifications. In addition, pressurized upgradation can offer substantial financial savings of up to 20% in the long term [28] when compared to the conventional plant utilizing external upgrading plus biomethane injection to the natural gas grid. Implementation of the pressurized reactor technique for biomethane upgrading could therefore become a future option for biogas production.

The effect of pressure on the microbial ability for biogas production has been investigated previously [45], and it was found that the level of methane production remained almost unaffected regardless of the digester’s pressures at 1, 50 and 100 bar. According to the study by Bartlett et al. [43], microorganisms of various species have tremendous potential to survive over a broad range of pressures. Furthermore, bacteria that are found in sewage slurry or waste treatment sludge are piezosensitive or piezotolerant [44] and a study by Abe et al. [10] has also suggested that methanogens can tolerate an external pressure of up to 100 bar. As a consequence, the development of pressurized reactors in AD plants is slowly becoming an interesting field of research. Despite this, a study [46] exploring reactor pressure increases from 1 to 9 bar demonstrated that the CO2 dissolved in the liquid-phase was converted into bicarbonate and consequently decreased the measured pH level to 6.5. This was also associated with the increase in CO2 partial pressure from 0.3 to 2.2 bar and a shift in the carbonic acid equilibrium towards gas phase CO2, resulting in a reduction of biomethane upgradation. To prevent the carbonic acid equilibrium shift (see section 2.1.3) towards gas phase CO2 production and hence to achieve higher methane upgradation, a buffering capacity maybe required.

### Recirculation of digestate via aerated methanation reactor

Likewise pressurized reactor technique, exploitation of the ADs inherent properties, (i.e.; CO2 and CH4 differential solubility), an aerated methanation reactor (also known as a stripping column, or desorption column, or bubble column) can be designed and used for enhancing the methane content in biogas. According to Hayes et al. [25], the methane to carbon dioxide ratio in biogas produced via the aerated methanation technique is substantially higher than the ratios predicted from the stoichiometry of conversion. This is mainly due to the difference in solubilities of CH4 and CO2, which is a function of the pH, temperature and pressure [47]. Changes in pH and temperature can result in dramatic changes to the solubility of CO2 , for example, at a pH of 7 and a temperature of 35 °C, CO2 is 40 times more soluble than methane. Depending on the aqueous CO2 concentration, the carbonate equilibrium can be shifted, either towards bicarbonate direction or towards carbonate ions concentration, following the reaction pattern shown below [48] (eq.1):

$CO\_{3}^{2-}+ H^{+}\leftrightarrow HCO\_{3}^{-}+H^{+}\leftrightarrow H\_{2}CO\_{3}\rightarrow CO\_{2}\left(aq.\right)+H\_{2}O$ (1)

When the aqueous CO2 concentration is decreased, the carbonate balance shifts towards bicarbonate, which has a direct influence on the pH and, therefore, the concentration of methane in the biogas. Generally, with a pH rise of ca 0.3 to 0.4 units, in a bicarbonate dominated carbonate system, methane concentration has been observed to increase from 50% to 80% [49]. Hence, a liquid stream drawn from a digester, if stripped of CO2, becomes unsaturated with dissolved CO2, which then can potentially absorb a significant portion of gaseous CO2, but a very small fraction of insoluble CH4, resulting in partial separation of CO2 from gas stream and rise in pH with concomitant increase of methane content in the product gas [25]. This concept, first developed by Hayes and Isaacson [50], is currently utilized in aerated reactor systems. A certain portion of digestate from the bottom (where the solution of higher concentration of CO2 is formed) of the anaerobic digester is recirculated through a reactor column, stripping CO2 using an external gas flow, and pumped back to the reactor. This allows for dissolving more CO2 into the digestate until the desired quality of methane in the biogas is achieved.

Various types of aerated reactors using various stripping media (air or compressed nitrogen) have been developed, and implemented in different scales of operation. An aerated reactor, consisting of baffled column through which air is passed through, was first developed by Chen et al. [51] and later implemented by O’Keefe [52] for a pilot-scale study treating municipal solid waste. The results of this work [52] suggested that the average methane content in biogas can be increased to 90% with little or no washout of the anaerobic microorganisms from the digester. However, the inhibition of anaerobic populations of microorganisms in the effluent leaving the stripping tank was observed. To further investigate this, a specific methanogenic activity (SMA) test was proposed.

*In-situ* methane upgrading was also applied [47] to a semi-continuously fed reactor (using sorghum as feedstock), which was externally connected to a CO2 stripping chamber operated with sweep gas (compressed nitrogen) as a stripping media. Using this configuration, a high quality biogas with methane content of 95% was possible, but this resulted in rise of pH between 7.8 and 8.1 at which free ammonia (FA) inhibition is susceptible [53]. Additionally, the semi-continuous feeding of an anaerobic digester for constant gas production was found to be associated with the plugging of recycling line, a low-solid digestate requirement, and an unsteady physical condition. To improve these shortfalls, other type of digesters such as packed bed reactor were suggested.

A study by Boontawee et al. [54] on a laboratory scale digester equipped with a plastic packed stripping column using chicken manure as feedstock showed a methane enrichment within the range of 10-23%. Furthermore, the CO2 stripping performance was shown to be dependent on the liquid and gas flow ratios (L/G ratio: liquid recycled/CO2 produced) with optimum being 0.83, as this gives the lowest dissolved CH4 in the effluent. Additionally, a higher recirculation flow (% of digester volume) resulted in an increased methane fraction in the biogas, but a methane loss up to 10% from the aerated column was evidenced when the flow was maximized to 400%.

To investigate the methane loss as a result of the aeration in the desorption column, a pilot-scale anaerobic digestion of sewage sludge was monitored [26]. It was concluded that when the bubble column is operated in a homogeneous flow regime, where the superficial liquid flow remains below 0.4 cm/s and the superficial gas velocity above 0.8 cm/s (L/G ratio < 0.5), the methane loss is minimized to below 2%. A similar conclusion was made by the same research group in the subsequent article [29], which also suggested that in order to reduce N2 concentration in the biogas (influenced by the aeration), the sludge recirculation rate adjustment is necessary. A methane content of 87% in biogas was observed, but this also resulted in the deposition of calcium carbonate in the desorption column.

Recirculating digestate through an aerated methanation reactor is promising and cost-effective methane upgradation and H2S removal technique [26]. However, the rate of CO2 desorption, fluctuating pH, varying solid content, effluent inhibition, methane losses and carbonate deposition, remain the major technical barriers to be overcome.

### Hydrogenotrophic methanogenesis via exogenous H2 input

Besides the two major paths of methanogeneis (the acaetoclastic (eq. 2) and hydrogenotrophic (eq. 3) paths), the hydrogenotrophic route is thermodynamically more favorable and stable [55]. By utilizing hydrogenotrophic bacteria like *methanobacteriales*, *methanococcales*, *methanomicrobials* and *methanosarcenaceae* [56, 57], *in-situ* biological conversion of methane can be accomplished. The hydrogenotrophic methanogens, which generally can be found in anaerobic sludges [58], use 1 mole of CO2 as a carbon source and 4 moles of H2 as the electron donor to produce 1 mole of CH4 via hydrogenotrophic methanogenesis (see equation 3) [55].

$Acetoclastic methanogensis: $ $CH\_{3}COOH= CH\_{4}+CO\_{2}; ∆G^{0}=-31 kJ/mol (2)$

$Hydrogenotrophic methanogenesis: 4H\_{2}+ CO\_{2}= CH\_{4}+2H\_{2}O; ∆G^{0}=-130.7 kJ/mol$ (3)

Typically, conventional anaerobic digestion produces around 30% of the methane component of biogas via hydrogenotrophic methanogenesis [27]. However, it has been hypothesiszed [27] that adding hydrogen directly to anaerobic digester may change the microbial community composition promoting hydrogenotrophic methanogenesis pathways. This can also enhance the biological conversion of CO2 into methane with a reported CH4 yield increase of ca 20 - 40% [59, 60], and a possibility of up to 90% [27, 61, 62], when combined with *ex-situ* upgrading techniques. The H2 required for injection may be obtained from electrolysis utilizing surplus electricity from wind and solar [37], but since these sources of electricity are not available continuously, such additions of H2 maybe introduced periodically in pulses [63]. Hydrogen enriched gases (i.e.; coke oven gas: 92% H2 & 8% CO) can also be a good alternative to pure H2, where a methane purity of up to 99% has been observed [64].

The major advantage of the *in-situ* technique is that it allows existing biogas plants to be utilized for H2 addition and the current natural gas infrastructure for transport of the upgraded biomethane, therefore eliminating the need for hydrogen storage (which can be of safety concern) [55]. Nevertheless, the application of this technology thus far is limited to the lab scale studies [59, 60]. This is because of its low volumetric CH4 production rates [65], and the technical challenges associated with the optimization of process [39]. For example, an H2 injection exceeding 4:1 stoichiometric ratio between H2 and CO2 tends to deplete CO2 resulting in rise of pH [59] and consequently the inhibition of autotrophic hydrogenotrophic methanogenesis (due to the lack of CO2 availability) [63]. The pH increase due to the H2 addition was already evidenced and for a remedy co-digestion with acidic substrates was suggested [55]. Alternatively, hydrogen addition to a separate reactor enriched with hydrogenotrophic methanogens was also proposed [55].

H2 dissolves very poorly in aqueous phase [66] and with the extent hydrogenotrophic methanogens can convert H2 into CH4 strongly depends on the efficiency that gaseous hydrogen can transform into liquids that can be utilized by the microorganisms. The H2 liquid mass-transfer rate is typically expressed as [36] (equation 4):

$r\_{t}=22.4k\_{L}a (H\_{2gTh}-H\_{2l})$ (4)

where,

rt : H2 liquid mass transfer rate (L/(L.d))

22.4: gas volume to mole ratio (1 mol gas corresponds to 22.4 L gas at STP)

kLa: gas transfer co-efficient (per day)

H2gTh: H2 concentration in the gas phase (mol/L)

H2l: H2 dissolved in the liquid phase (mol/L)

As eq. 4 suggests, rt can be enhanced by increasing kLa. To improve kLa several attempts have been made. For example, the modulation of the mixing speeds [55, 67], gas recirculation [68], changing the diffusion device [59, 69], adding packing materials as a means to minimize gas bubble size (increasing gas-liquid mass transfer) [36], and modified reactor design using a trickle bed [37] and an upflow anaerobic sludge blanket (UASB) reactor [36]. The results obtained from these techniques were promising with the produced biomethane in the majority of these cases meeting the specified quality standard set by the users [37].

H2 also has a direct influence on the products and reactants of the different anaerobic digestion stages. In an efficient anaerobic digestion system, there is a balance between the syntrophic and methanogenesis activities, where the production of H2 by the syntrophic bacteria is utilized by the methanogens. Theoretically, the syntrophic acetate oxidation (see table 3) is only thermodynamically favorable when H2 is produced at low concentration (partial pressure, pp) [37], with the partial pressure ranging between 2.6 and 74 Pa [70]. However, direct H2 injection to the anaerobic reactor for methane upgradation may increase H2 partial pressure above these concentrations, resulting in the inhibition of syntrophic bacteria, and in the worst case process failure [39]. H2 injection may also stimulate the production of acetate through the homoacetogenesis route (see table 3) which if not converted to methane via acetoclastic methanogenesis (see table 3), the process inhibition might occur [39]. Previous findings stated that high H2 partial pressure may also lead to propionate and butyrate accumulation, as these VFAs do not oxidize at a high H2 partial pressure, while a low H2 partial pressure enhances the CO2 and CH4 yield [27].

Table 2: Possible product and reactant pathways in AD and AD-MEC

Table 3: Several pathways of products and reactants in anaerobic digestion

H2 addition to an anaerobic digester is a promising approach to the enrichment of methane in biogas. However, the extent of its impact on the interaction of the bio-chemical processing steps (eg. methanogenesis, homoacetogenesis and syntrophic acetate oxidation), is not sufficiently understood, and research undertaken in this area is still limited. Recently, a study by Mulat et al. [39] used carbon isotope composition determination of CH4, CO2 and acetate in AD with 13C labeled substrates. They found to yield interesting results in terms of understanding the process as well as characterizing the methanogens. However, their experiments were carried out on lab-scale batch digesters, therefore, the effect it has on large scale, continuous reactors is still unknown.

In parallel to the direct H2 addition for upgrading biogas, the introduction of other chemicals such as biochar from corn [71] or wall nut shell [72] to anaerobic digesters has been investigated and methane quality improvements, lowered costs, and improved H2S removal was observed. As H2 is not a readily available fuel and has a high production cost, adding other chemicals coupled with other approaches to produce endogenous hydrogen (such as microbial fuel cells (MFC)), are emerging, which, as of relevance, is partly covered in the sub-section below.

### Electro-methanogenesis: a novel concept

The conversion of CO2 to CH4 through the technique called bioelectrochemical system (BES) or electro-methanogenesis is a promising novel technique [31]. The concept relies on the fact that applying a current between two electrodes (an anode and a cathode) of an electrical circuit in the anaerobic digestion liquid (typically an microbial electrolysis cell, MEC), the organic matter is decomposed at the anode where electrons are transferred to the methanogens (methanosaeta and methanosarcina) by several exoelectrogenic microbial species (primarily *Shewanella*, *Geobacter* and *Pseudomonas*) leading to the conversion of biological CO2 into methane (eq. 3) [73] at the cathode. In this process, there are mainly two different steps where donated electrons are first converted into hydrogen which is afterwards used by the hydrogenotrophic methanogens to reduce CO2 into methane. In addition, there can be as many as ten different electron donation mechanisms [74] (see fig. 3 & table 3) contributing to the formation of methane via a number of other intermediates (such as acetate and formate). Furthermore, electrons can be donated directly to methanogens without an intermediate (direct interspecies electron transfer, DIET), where the process is considered to be more efficient due to the fact that energy is conserved as the production of intermediates is avoided [75]. When co-cultivating the microorganisms geobacter and methanosarcina, the DIET effect on an AD-MEC system was evidenced, from which improved methane yield (~32% increase) compared to that of H2 intermediate route was reported [76]. A combination of other pure and mixed cultures demonstrating DIET and increased methane yields have also been reported previously [31, 77].

**Figure 3: Interactions of some methane producing microorganisms and possible mechanisms to produce bioelectrochemical methane (adapted from [74, 78])**

In a typical bioelectrochemical reactor configuration enabling hydrogenotrophic methanogenesis, the anode and cathode chambers are usually separated by a membrane (proton exchange, anion-exchange, bipolar, or charge mosaic), allowing only protons (H+) (for proton exchange membrane) from the anode to pass to the cathode, allowing the production of H2, and subsequently methane [79]. Generally, the membrane prevents the crossover of fuels and microorganisms from the anode to the cathode chamber and maintains the purity of H2. However, membrane- free designs are found to be a cost-effective solution, giving high H2 production rates [80]. In a recent investigation using membrane-free AD-MEC with a synthetic medium, a methane enrichment exceeding 95% was observed [81].

The energy provided to an electrochemical cell (enabling the transfer of electron throughout the system), is provided using cathodic potential and commonly expressed by the term: ‘–V vs. standard hydrogen electrode (SHE)’. By regulating the cathodic potentials, different modes of reactions that lead to various intermediate products or direct electron transfer to methane conversion were investigated and a range of potentials corresponding to particular routes of production were identified (a selection of these are shown in Table 3 [74]. With the cathode potential of - 0.7 V vs. SHE or above, methane production via DIET in a past study was observed [82]. The other intermediate routes of methane production, particularly via acetate and formate as a result of the cathodic potential ranging from -0.4 to -0.8 V vs. SHE was also evidenced [83, 84]. Maintaining a constant cathodic potential of -0.8 V, Liu et al. [85] identified several intermediate routes of methane enrichment with a 3-fold increase in production via *Geobacter* through the H2 mediated pathway. A constant potential of -0.9 V vs. SHE also resulted in up to a 6-fold increase in methane production from a low temperature (10° C) bioelectrochemically-assisted AD, with H2 as a product in between [86]. In addition to adjusting the cathode potential, optimizing the performance of BES applying various approaches was investigated. Employing biocompatible cobalt-phosphate catalyst deposited on a carbon cloth cathode showed an improved methane production rate compared to that without the deposition [81]. Modifying the position of the electrodes in the cell was also reported to achieve a higher methane production rate [87]. More research towards the development of reactor design and identifying a suitable combination of microbial strains is ongoing.

Nevertheless, almost all the studies undertaken so far are limited to lab-scale and, therefore, the methane enrichment effect on full scale application has no solid proof as yet which clearly calls for further research in this field.

# Conclusions

The technology used for biogas production from anaerobic digestion is widespread. Modern biogas plants often incorporate advanced optimization techniques including state-of-the-art controlling systems to improve methane yields in the biogas. However, commercial utilization of biogas is still limited as the biogas needs to be cleaned, and cleaning can be energy and cost intensive given the gas quality mandated by end-users or national directives.

The analysis by this review reveals that by employing the *in-situ* method (pressurized reactor, CO2 desorption, H2 addition and electro-methanogenesis) the cost of biogas cleaning and upgrading can be substantially reduced while biomethane quality can be improved close to the level of natural gas, allowing biogas to be readily injected into the existing natural gas grid. Nevertheless, the *in-situ* technique, is still underdeveloped, and the majority of the results obtained so far are based on lab or small scale experiments, where the identified potential challenges are working parameters properties (for example: digestate recirculation rate, H2 concentration, reactor pressure and microbiological activity), and lack of process understanding. More efforts towards projecting the present knowledge to large-scale operations with an improved understanding of the process mechanisms, and overcoming several technological challenges, are thus required.

# Acknowledgement

The authors wish to thank Norwegian University of Science and Technology (NTNU) for providing funding of this study under partly the framework of ‘Hydrogen in Biogas (HyBiG)’ within the strategic research ‘ENERSENSE (Energy, sensor and storage)’.

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