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Review article

Overview of recent progress towards in-situ biogas upgradation techniques

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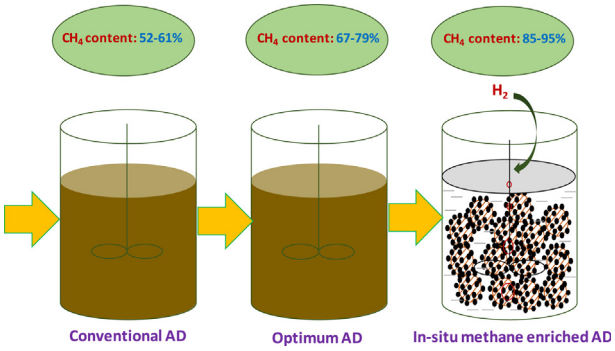
GRAPHICAL ABSTRACT



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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 with the *ex-situ* method, *in-situ* techniques, such as CO_2 desorption, pressurized reactor, H_2 addition (deployed to anaerobic digesters directly) and electromethanogenesis has also been gained significant attention recently. Comparative studies between *in-situ* and *ex-situ* method suggest 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 CO_2 to CH_4 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.

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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

1. 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]. 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 (when compared to thermochemical and thermal conversion techniques) is highly 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 have 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 is 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 the 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 CO_2, NH_3, H_2S 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 CO_2 in raw biogas, the cost of gas purification only becomes economically and energetically feasible if plant operational capacity exceeds 100 m^3 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 CO_2 and CH_4 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 H_2S from the off-gas (which is technically as expensive as removing CO_2 from biogas) [26]. Furthermore, in a novel electro-methanogenesis concept, several groups of bacteria can efficiently exchange electrons, directly producing biogas with 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 some 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 various methodologies with emphasis on emerging processes, which are envisaged to play a significant role in the future context of bioenergy.

2. Biomethane enrichment

Raw biogas produced by the anaerobic digestion generally consists of the gas species CH_4, CO_2, H_2S, NH_3 and H_2O, 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 CO_2 with 25–55% [12]. Besides anaerobic digestion, biogas can also be collected from landfills with a typical gas composition of 50–55% CH_4, 37–45% CO_2 and < 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 CO_2 and other contaminants. Moreover, the lower heating value of biogas for example is roughly 21.5 MJ/Nm^3, while it is around 35.8 MJ/Nm^3 for natural gas [33].

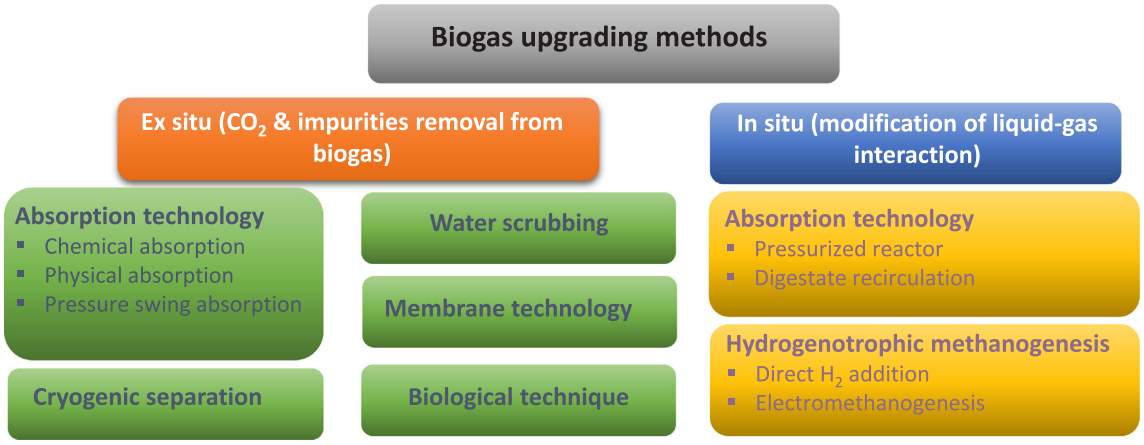

Fig. 1. Different modes of biogas upgrading techniques.

To enhance energy content, therefore, biogas needs to be upgraded [12]. Upgraded biogas can have reduced CO_2 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 regarding the levels of contaminants [19]. For instance, high levels of CO_2 within biogas is not desirable in internal combustion engines. A high CO_2 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, H_2S, NH_3, 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 H_2S 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 CH_4 concentrations of 80–96%, CO_2 of 2–3%, O_2 of 0.2–0.5%, H_2S of 5 mg/m^3, NH_3 of 3–20 mg/m^3, and siloxanes of 5–10 mg/m^3 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] (Fig. 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 Fig. 2. Table 1 shows currently available lab and commercial scale *in-situ* biogas upgrading technologies.

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 CO_2 and H_2S from the biogas, and also for growing microalgae for bioethanol production [41]. As much as 40% of the CO_2 and 100% of the H_2S was reportedly removed, with a higher amount of CO_2 removal reported by Kampanatsanyakorn et al. [42]. Despite this, *ex-situ* technique is outside the

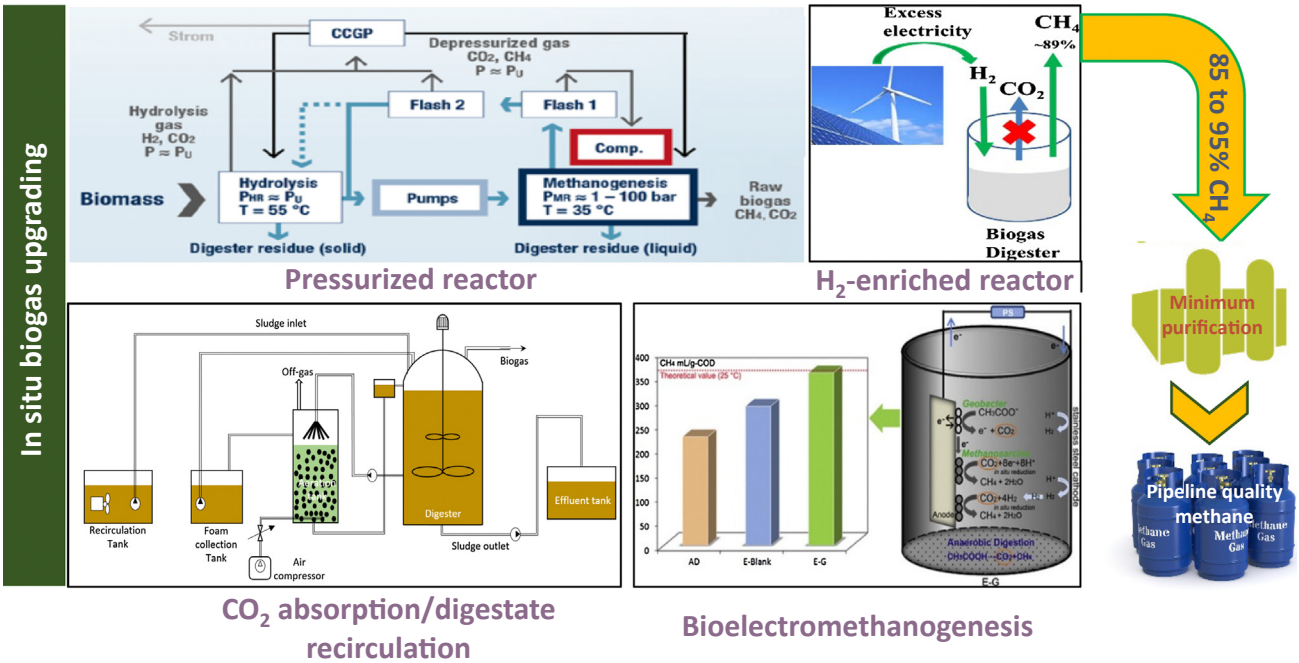

Fig. 2. Biogas upgrading using *in-situ* techniques.

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

Upgrading technology	Application properties	Enriched biogas properties				Other parameter	Gas leakage	Limitation/recommendation	Reference
		CH_4 (%)	CO_2 (%)	H_2S (%)	N_2 (%)				
Pressurized reactor									
Autogenerative high pressure digestion (AHPD)	**Range**: Lab scale, **Substrate**: Sodium acetate trihydrate, **Reactors**: (3 units) 0.6 L, 1.7 L & 13.5 L, **Final pressure**: 7.5 to 90.0 bar, **Operation time**: 40 to 160 h	91 to 96 (no trend)	1 to 6 (no trend)	N/D	1 to 8	N/D	Occurred at 13.5 bar pressure	Less CH_4 yield than expected from stoichiometry	[24]
Integration of a water scrubbing technique and two-stage pressurized anaerobic digestion in one process	**Range**: Medium scale, **Substrate**: Grass and maize silage hydrolystate, **Reactors**: 6 acidification reactors (50 L), 1 UASB reactor for pressurized methanogenesis (30 L), one 5 L flash tank, **Operating temperature**: 37 °C, **Pressure**: 1 & 9 bar, **OLR**: 13.1 to 25.2 kgCOD/m^3, **pH**: 6.5 to 6.7	32 to 87 (increase with pressure)	13 to 68 (decrease with pressure)	N/D	N/D	N/D	N/D	Methane losses due to the circulation of depressurized liquid from the methane reactor	[38]
Two-phase pressurized anaerobic digestion system	**Range**: Medium scale, **Substrate**: Maize silage, **Reactors**: 3 hydrolysis-acidification reactors (50 L) and 1 UASB reactor for methanogenesis (20 L), **Operating temperature**: 37 °C, **Pressure**: 1,3,6 & 9 bar, pH: 7.2 to 6.4 (decreased with pressure), Costs: 20% less than the conventional upgrading technique	66 to 76 (increase with pressure)	35 to 25 (decrease with pressure)	N/D	N/D	Ammonium nitrogen in the effluent increases with pressure	N/D	Decreased pH effecting CO_2 solubility and weakening methane enrichment	[45]
Aerated methanation reactor									
Sludge anaerobic digester connected with a bubbling desorption column	**Range**: Pilot scale, **Substrate**: municipal sewage sludge, **Reactor:** 30 m^3, the desorption column working volume: 90 dm^3 (first experiment, batch), 140 dm^3 (second experiment, continuous), **Stripping media**: Air, **Operating temperature**: 37 °C, **Air/sludge flow ratio (m^3/m^3)**: 0.75 to 16.0, **Digester pH**: 7.28 to 7.86	70 to 87% (increase with digester pH)	11 to 30% (decrease with pH)	N/D	0 to 11% (no trend)	N/D	8% in the biogas	Methane loss, high biogas N_2 and calcium carbonate deposition	[26]
Sludge anaerobic digester connected with a desorption column	**Range**: Full scale, **Substrate**: sewage sludge, **Reactor**: 1500 m^3 & a bubble column, ~420 L, **Stripping media**: Air, **Operating temperature**: mesophilic (37 to 41 °C), **pH**: 7.2 to 7.7	90 to 100%	**CO_2 desorption**: 0.07 to 0.23 m^3/m^3 sludge	**H_2S concentration:** decrease from 50 to 100 ppm in the desorption column	N/D	–	0.01 to 0.17 m^3 CH_4/m^3 CO_2 (in the desorption column); loss is lower than 2% at L/G < 0.5	Reduction in methane enrichment might have occurred due to the O_2 introduction via aeration	[29]
Semicontinuously mixed and fed reactor coupled with a CO_2 stripper using compressed nitrogen	**Range**: Bench scale, **Substrate**: Sorghum, **Reactor**: 12 L & stripper 2 L, **Stripping media**: Humidified sweep gas (compressed nitrogen) as a stripper, **Operating temperature**: 35 °C, **Leachate recylcle**: 0.5 to 3.5 L/kg/d, **pH**: 6.7 to 8.4, **Recycle ratio**: 0.65 to 12 L/LCO_2	71 to 98 (increase with pH)	**CO_2 production**: 0.25 to 0.95 L/kg/d	N/D	N/D	–	N/D	The digester configuration only suits to low solid system, plugging in the recycle line and unsteady physical condition	[47]
Solids concentrating digester with a buffled air stripper (methane enrichment process)	**Range**: Pilot scale, **Substrate**: organic fraction of MSW and primary sewage sludge, **Reactor:** 4500 L & a baffled stripper 1000 L, **Stripping media:** Air, **Operating temperature**: 35 °C, OLR: 3.2 kgVS/m^3/d, **Recycling:** 46 L-air/L-effluent	> 90%	N/D	N/D	N/D	–	N/D	Inhibition of anaerobic microbial population in the effluent exiting from the baffled stripper	[52]

(*continued on next page*)

Table 1 (*continued*)

Upgrading technology	Application properties	Enriched biogas properties				Other parameter	Gas leakage	Limitation/recommendation	Reference
		CH_4 (%)	CO_2 (%)	H_2S (%)	N_2 (%)				
Channel digester with gas stripping column	**Range**: Laboratory scale, **Substrate**: chicken manure, **Reactor**: 1000 L & a plastic packed air stripper column, 110 L, **Stripping media: Air**, OLR: 2.5 kgCOD/L, **Recycling ratio (L/G)**: 0.31 to 2.0 L/LCO_2, **Recirculation flow** (% digester volume): 200 to 400%, **pH**: 7.5 to 8.3	50 to 80% (increase with recirculation ratio)	26 to 38% (decrease with recirculation ratio)	**H_2S concentration**: 1.2 to 3.0 g/L (decrease with recirculation ratio)	N/D	–	0.3 to 0.8% in the effluent and 3.7 to 10.3% in the biogas (increase with recirculation flow)	Low rate of methane enrichment	[54]
Digester enriched with H_2									
Mesophilic and thermophilic digester with external H_2 addition	**Range**: Lab scale, **Substrate**: Cattle manure, **Reactor:** 2 CSTR of 1.5 (R1) and 2 L (R2) working volume, **Operating temperature**: 35 ± 1 °C (R1) and 55 ± 1 °C (R1) **HRT**: 25 days (R1) & 20 days (R2), **H_2 added (by a diffuser)**: 192 (R1) & 510 mL/L.day (R2), **OLR:** 0.6 & 1 gVS/L-d (R1 & R2), **Digester pH after H_2 adding**: ~7.78 (R1) & ~7.95 (R2)	~85% (thermo) & ~89% (meso)	~9% (thermo) and ~7% (meso)	N/D	N/D	**tVFA**: ~0.38 g/L (thermo) and ~0.16 g/L (meso)	N/D	Incomplete mass transfer from gaseous to liquid leading 92% H_2 utilization in therophilic reactor compared to 99% in the mesophilic one	[27]
Exogenous H_2 addition to batch reactors	**Range**: Lab scale, **Substrate**: U-^{13}C labelled maize leaf (Zea mays, > 97 atom % ^{13}C & unlabelled maize leaf (1.33 g feed), **Reactor:** batch bottle reactor, 120 mL, **Operating temperature**: 52 °C, **Experimental period:** 24 days, **H_2 added (by a gas tight syringe)**: at pressure 56 to 138 kPa and at volume 40 to 100 mL (between 0 & 15 days), **Digester pH after H_2 adding**: 7 to 8 (adjusted with HCl)	~88 to 89% (higher at unlabelled maize reactor)	~10 to 12% (lower at unlabelled maize reactor)	N/D	N/D	**Cumulative methane yield**: 296 mL (labelled maize), 282 mL (unlabelled maize); **Methane production rate:** 272 mL/L.d (labelled), 267 mL/L/d (unlabelled)	N/D	Excess H_2 addition leads to VFA accumulation	[39]
CSTR with co-digested substrates and exogenous H_2 addition	**Range**: Lab scale, **Substrate**: Cattle manure and whey, **Reactor:** 2 CSTR of 600 mL working volume, **Operating temperature**: 55 °C (R1) **HRT**: 15 days, **H_2 added (by a diffuser)**: 1.5 (0–20 days) & 1.7 L/L.day (20 days+), **Digester pH after H_2 adding**: ~7.7 to 7.9	53 to 75% (increase with H_2 addition rate)	6.6 to 13% (decrease with H_2 addition rate)	N/D	N/D	**Acetate**: 2 to 2.5 mM (increase with H_2 added) and **Proprionate**: 0.5 to 0.8 mM (decrease with H_2 added), Dissolved H_2: 330 to 380 Pa	N/D	Low upgraded methane and hence progress to full scale plant may require additional safety measure.	[59]
H_2 addition to a CSTR and batch reactors	**Range**: Lab scale, **Substrate**: Cattle manure, **Reactor:** 2 CSTR of 3.5 L working volume, **Operating temperature**: 55 °C (R1) **HRT**: 14 days, **H_2 added (by a pressure regulated valve)**: 28.6 mL/L/h at pressure of 0.25, 0.5 and 1 atm, **TS added**: 3%, **Digester pH after H_2 adding**: ca 8.3	65% (3% increase, in CSTR)	15% (23% decrease, in CSTR)	N/D	N/D	**Hydrogen consumption rate**: 16.2 to 270 mL/L/h (increase with mixing RPM); **Methane consumption rate:** 3.7 to 67.8 mL/L/h (increase with mixing RPM)	N/D	Low H_2 utilization efficiency. For improvement low pH level between 7 and 8 is proposed	[60]

(*continued on next page*)

Table 1 (*continued*)

Upgrading technology	Application properties	Enriched biogas properties				Other parameter	Gas leakage	Limitation/recommendation	Reference
		CH_4 (%)	CO_2 (%)	H_2S (%)	N_2 (%)				
Digester coupled with bioelectrochemical system									
AD and microbial electrolysis cell (MEC) connected system	**Range**: Lab scale, **Reactor:** 3 Stainless steel reactors (250 mL) - AD, AD-G, AD-MEC-G, **Substrate**: Sodium acaetate (10 g/L), **Operating temperature**: 25 ± 2 °C, **Experimental period:** 72 h, **Inoculum & bacteria**: Waste activated sludge inoculum (2 mL), Geobacter inoculum (2 mL) and methanosarcina sp. culture (2 mL), **Initial pH**: 6.8	**CH_4 yield, AD-G-MEC**: 642.9 mL (increase of 59.7% and 32.4% compared to AD & AD-G respectively)	N/D	N/D	N/D	**COD removal rate**: 216.8 mg COD/L.h (1.3 times increase compared to without Geobacter; **Current density**: 304.3 A/m^3 (1.8 times increase compared to without Geobacter)	N/D	Process understanding requires further development, especially, in regard to verify the suitability of electron donor	[76]
Bioelectrochemical system with mixed culture biocathode for biomethane enrichment	**Range**: Lab scale, **Reactor:** two-chambered (anode 414 mL, cathode 450 mL) with inoculum recirculation for 6 days (150 L/d), **Substrate**: Synthetic water medium (553 ± 16 mL), **Inoculum:** Diluted effluent from anaerobic digester (100 mL), **Operating temperature**: 34.7 ± 1.1° C, **Experimental period:** 420 days, **Power source**: -0.6 V (cathode potential until day 74), -0.8 V (cathode potential > 74 days), +0.6 V (anode potential), **Electrodes**: three units graphite rods (potentiostat, biocathode/working electrode & anode), **Digester pH**: 6.1 to 7.1 (batch), 7.1 ± 0.2 (continuous)	65 to 85% in the off-gas of biocathode reactor	**Microbial analysis:** Hydrogeno.methano. Methanobacterium sp. was found abundant in biocathode reactor	N/D	N/D	**Coulombic efficieny**: 75.3 ± 5.2% (batch), 68.9 ± 0.8% (continuous), Max. **CH4 production rate**: 5.2 mmol/m2/d (batch), 15 mmol/m2/d (continuous)	N/D	Cross-over reactions, such as oxygen and sulphate reduction, and methane oxidation were found to decrease Coulombic efficiency of the process	[78]
Integrated AD and MEC with catalyst	**Range**: Lab scale batch reactor, **Reactor:** Membrane free bottle (600 mL), **Substrate**: Sythesized medium, (C/N = 20, 23.3 g), **Inoculum**: Biogas plant effluent (376.7 mL), **Operating temperature**: 38 °C, **Experimental period:** 50 days, **Power source**: DC (0–120 V, an external resistor: 1000 Ω), **Electrodes** (deposited with catalyst Co-P): Anode (carbon cloth), cathode (mesh 316 L SS)	95% (in the experimental reactor)	N/D	N/D	N/D	**COD removal rate**: 6% increase than the control; **CH_4 yield**: 48% higher than control; **CH_4 production rate**: 1.65 times higher than control	N/D	For better process understanding further studies on different substrates was suggested	[81]
Integrated AD and MEC for WAS tretament	**Range**: Lab scale (polycarbonate MEC reactor), **Reactor:** 8 units (130 mL), **Substrate**: Acetate (1.5 g/L), **Inoculum:** WWTP aeration tank effluent, **Operating temperature**: 20 to 25 °C, **Experimental period:** 45 days, **Power source**: DC (0.8 V, an external resistor: 10 Ω), **Electrodes**: Anode (graphite brush) & covered with Pt catalyst layer, cathode (carbon cloth)	**CH_4 production rate**: 3 times higher than control (from 30.6 to 91.8 gCH_4/m^3)	N/D	N/D	N/D	**VSS removal rate**: 38 to 48% increase than the control. Carbon degradation of VFAs, polysaccharides and proteins was accelerated by 22%, 43% and 48% res.	N/D	More detailed exploration in microbial community dynamics due to electron transfer mechanism is necessary	[85]

(*continued on next page*)

Table 1 (*continued*)

Upgrading technology	Application properties	Enriched biogas properties				Other parameter	Gas leakage	Limitation/recommendation	Reference
		CH_4 (%)	CO_2 (%)	H_2S (%)	N_2 (%)				
Integrated AD and MEC with membrane (cathodic AD)	**Range:** Lab scale (polymethylmethacrylate), **Reactor:** 1.2 L (inner cylinder 700 mL, outer cylinder 500 mL), **Substrate:** Acetate (1.5 g/L, anode chamber) and glucose (2.5 g/L, cathode chamber), **Inoculum:** Sludge fermentation liquid, **Operating temperature:** 25 °C, **Experimental period:** 30 days, **Power source:** DC (0.8 V), **Electrodes:** Anode (carbon brush), cathode (stainless steel mesh)	**CH_4 production rate:** avg. 2.59 times higher (in cathodic AD), 51.53% higher in cathodic AD for sludge fermen. liquid)	N/D	N/D	N/D	**COD removal rate:** 15% increase than the control. Energy recovery efficiency reached to 100%	N/D	[a,c]Needs further investigation towards higher scale of operation and other substrates	[87]7

N/D: Not defined, [a,c]: Authors' comment

scope of this review, but a recent review by Singhal et al. [19] describes these techniques in more detail.

2.1. In-situ upgradation

2.1.1. 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% CH_4 and ~40% CO_2, in the pressurized digester due to the influence of high pressure, dissolved CO_2 in the liquid phase enhances. When the part of this dissolved CO_2 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 H_2, CH_4, CO_2, H_2S and NH_3 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 CO_2 is ~20 times, H_2S is ~72 times and NH_3 is ~39000 times more soluble than CH_4 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 (CO_2, H_2S and NH_3) to be reduced and released, reducing the requirement of compression for natural gas grid injection.

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 m^3/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 CO_2 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 CO_2 partial pressure

from 0.3 to 2.2 bar and a shift in the carbonic acid equilibrium towards gas phase CO_2, resulting in a reduction of biomethane upgradation. To prevent the carbonic acid equilibrium shift (see Section 2.1.3) towards gas phase CO_2 production and hence to achieve higher methane upgradation, a buffering capacity maybe required.

2.1.2. Recirculation of digestate via aerated methanation reactor

Likewise pressurized reactor technique, exploitation of the ADs inherent properties, (i.e, CO_2 and CH_4 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 CH_4 and CO_2, 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 CO_2, for example, at a pH of 7 and a temperature of 35 °C, CO_2 is 40 times more soluble than methane. Depending on the aqueous CO_2 concentration, the carbonate equilibrium can be shifted, either towards bicarbonate direction or carbonate ions concentration, following the reaction pattern as shown below [48] (Eq. (1)):

$$CO_3^{2-} + H^+ \leftrightarrow HCO_3^- + H^+ \leftrightarrow H_2CO_3 \rightarrow CO_2(aq.) + H_2O \quad (1)$$

When the aqueous CO_2 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 bicarbonate dominated carbonate systems, methane concentration has been observed to increase from 50% to 80% [49]. Hence, a liquid stream drawn from a digester, if stripped of CO_2, becomes unsaturated with dissolved CO_2. This can potentially absorb a significant portion of gaseous CO_2, but a very small fraction of insoluble CH_4, resulting in partial separation of CO_2 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 a higher concentration of CO_2 is formed) of the anaerobic digester is recirculated through a reactor column, stripping CO_2 using an external gas flow, and pumped back to the reactor. This allows for dissolving more CO_2 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 CO_2 stripping chamber operated with sweep gas (compressed nitrogen) as a stripping media. Using this configuration, high-quality biogas with a methane content of 95% was possible, but this resulted in a 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 types of digesters such as packed bed reactors 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 CO_2 stripping performance was shown to be dependent on the liquid and gas flow ratios (L/G ratio: liquid recycled/CO_2 produced) with optimum being 0.83, as this gives the lowest dissolved CH_4 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 to reduce N_2 concentration in the biogas (influenced by the aeration), the sludge recirculation rate adjustment is necessary. 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 H_2S removal technique [26]. However, the rate of CO_2 desorption, fluctuating pH, varying solid content, effluent inhibition, methane losses and carbonate deposition, remain the major technical barriers to be overcome.

2.1.3. Hydrogenotrophic methanogenesis via exogenous H_2 input

Besides the two major paths of methanogeneis (the acetoclastic (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 mol of CO_2 as a carbon source and 4 mol of H_2 as the electron donor to produce 1 mol of CH_4 via hydrogenotrophic methanogenesis (see Eq. (3)) [55].

$$\textit{Acetoclastic methanogensis}: \quad CH_3COOH = CH_4 + CO_2;\ \Delta G^0 = -36\ \text{kJ/mol} \quad (2)$$

$$\textit{Hydrogenotrophic methanogenesis}: \quad 4H_2 + CO_2 = CH_4 + 2H_2O;\ \Delta G^0 = -130.7\ \text{kJ/mol} \quad (3)$$

Typically, conventional anaerobic digestion produces around 30% of the methane component of biogas via hydrogenotrophic methanogenesis [27]. However, it has been hypothesized [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 CO_2 into methane with a reported CH_4 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 H_2 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 H_2 maybe introduced periodically in pulses [63]. Hydrogen enriched gases (i.e, coke oven gas: 92% H_2 & 8% CO) can also be a good alternative to pure H_2, 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 H_2 addition and the current natural gas infrastructure for transport of the upgraded biomethane, therefore

Table 2
Possible product and reactant pathways in anaerobic digestion and AD-MEC.

Mechanism	Reaction equation	Potential (V vs. SHE[1])	Minimum electrical energy input[2] (kWh/m^3CH_4)
Bioelectrochemical reactions in cathode			
Direct interspecies electron transfer (DIET)	$HCO_3^- + 9H^+ + [8e]^- \rightarrow CH_4 + [3H]_2O$	−0.24	2.1
Intermediate hydrogen production	$H^+ + [2e]^- \rightarrow H_2$	−0.41	3.6
Intermediate acetate production	$[2HCO]_3^- + [9H]^+ + [8e]^- \rightarrow [CH]_3COO^- + [4H]_2O$	−0.28	2.4
Intermediate formate	$[HCO]_3^- + 2H^+ + 2e^- \rightarrow HC[OO]^- + H_2O$	−0.41	3.5
Biochemical reactions in cathode			
Homoacetogenesis (intermediate hydrogen)	$2HCO_3^- + [4H]_2 + H^+ \rightarrow CH_3COO^- + [4H]_2O$	N.F.	N.F.
Homomethanogenesis (intermediate hydrogen)	$HCO_3^- + [4H]_2 + H^+ \rightarrow CH_4 + [3H]_2O$	N.F.	N.F.
Syntrophic acetate oxidation (intermediate acetate)	$CH_3COO^- + [4H]_2O \rightarrow 2HCO_3^- + [4H]_2 + H^+$	N.F.	N.F.
Acetoclastic methanogenesis (intermediate acetate)	$CH_3COO^- + H_2O \rightarrow HCO_3^- + [CH]_4 + H^+$	N.F.	N.F.
Intermediate formate to methane	$HCOO^- + [3H]_2 + H^+ \rightarrow [CH]_4 + 2H_2O$	N.F.	N.F.
Oxidation reaction anode			
Water splitting	$4H_2O \rightarrow 2O_2 + 8H^+ + [8e]^-$	−1.05	8.9

[1]Standard hydrogen electrode, [2]Energy input requirement for half reaction. A reduction half reaction couples with an oxidation half reaction to complete the whole reaction process, N.F.: not found.

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 CH_4 production rates [65], and the technical challenges associated with the optimization of the process [39]. For example, an H_2 injection exceeding 4:1 stoichiometric ratio between H_2 and CO_2 tends to deplete CO_2 resulting in a rise of the pH [59] and consequently the inhibition of autotrophic hydrogenotrophic methanogenesis (due to the lack of CO_2 availability) [63]. The pH increase due to the H_2 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].

H_2 dissolves very poorly in aqueous phase [66] and with the extent hydrogenotrophic methanogens can convert H_2 into CH_4 strongly depends on the efficiency that gaseous hydrogen can transform into liquids that can be utilized by the microorganisms. The H_2 liquid mass-transfer rate is typically expressed as [36] (Eq. (4)):

$$r_t = 22.4 k_L a (H_{2gTh} - H_{2l}) \quad (4)$$

where,

r_t: H_2 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)
k_La: gas transfer co-efficient (per day)
H_{2gTh}: H_2 concentration in the gas phase (mol/L)
H_{2l}: H_2 dissolved in the liquid phase (mol/L)

As Eq. (4) suggests, r_t can be enhanced by increasing k_La. To improve k_La 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].

H_2 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 H_2 by the syntrophic bacteria is utilized by the methanogens. Theoretically, the syntrophic acetate oxidation (see Table 3) is only thermodynamically favorable when H_2 is produced at low concentration (partial pressure, pp) [37], with the partial pressure ranging between 2.6 and 74 Pa [70]. However, direct H_2 injection to the anaerobic reactor for methane upgradation may increase H_2 partial pressure above these concentrations, resulting in the inhibition of syntrophic bacteria, and in the worst case process failure [39]. The H_2 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 H_2 partial pressure might also lead to propionate and butyrate accumulation, as these VFAs do not oxidize at a high H_2 partial pressure, while a low H_2 partial pressure enhances the CO_2 and CH_4 yield [27].

H_2 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 CH_4, CO_2 and acetate in the AD with ^{13}C labelled

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

	Reaction	$\Delta G^{\circ\prime}$ (kJ/mol)	$\Delta G'_{55}$ (kJ/mol)
Homoacetogenesis	$2HCO_3^- + [4H]_2 + H^+ \rightarrow CH_3COO^- + [4H]_2O$	−55	N.F.
Homomethanogenesis	$HCO_3^- + [4H]_2 + H^+ \rightarrow CH_4 + [3H]_2O$	−135.6	−122.5
Syntrophic acetate oxidation	$CH_3COO^- + [4H]_2O \rightarrow 2HCO_3^- + [4H]_2 + H^+$	+104.1	N.F.
Acetoclastic methanogenesis	$CH_3COO^- + H_2O \rightarrow HCO_3^- + [CH]_4 + H^+$	−31.0	−34.7

N.F.: not found.

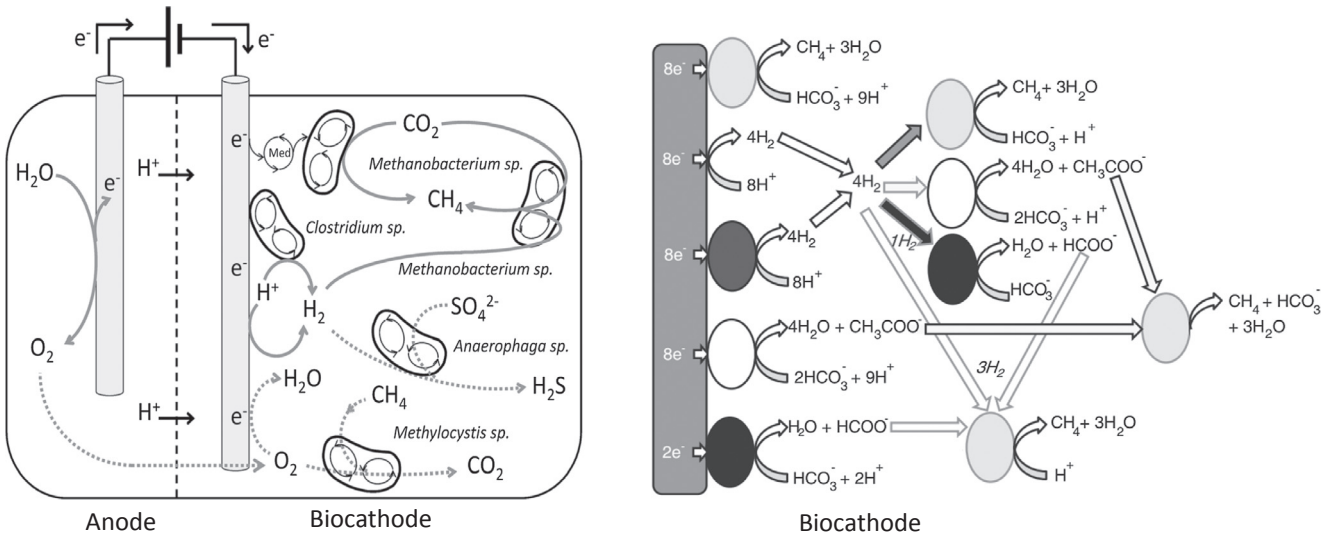

Fig. 3. Interactions of some methane producing microorganisms and possible mechanisms to produce bioelectrochemical methane (). adapted from [74,78]

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 a large-scale, continuous reactors is still unknown.

In parallel to the direct H_2 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 H_2S removal was observed. As H_2 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.

2.1.4. Electro-methanogenesis: A novel concept

The conversion of CO_2 to CH_4 through the technique called bioelectrochemical system (BES) or electro-methanogenesis is a promising novel technique [31]. The concept relies on the fact that by 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 CO_2 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 CO_2 into methane. Also, there can be as many as ten different electron donation mechanisms [74] (see Fig. 3 & Table 2) 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 the H_2 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].

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 H_2, 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 H_2. However, membrane- free designs are found to be a cost-effective solution, giving high H_2 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 was investigated and a range of potentials corresponding to particular routes of production were identified (a selection of these are shown in Table 2 [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 H_2 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 H_2 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.

3. 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, CO_2 desorption, H_2 addition and electromethanogenesis) 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 (e.g., digestate recirculation rate, H_2 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.

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