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Recent progress towards in-situ biogas upgrading technologies

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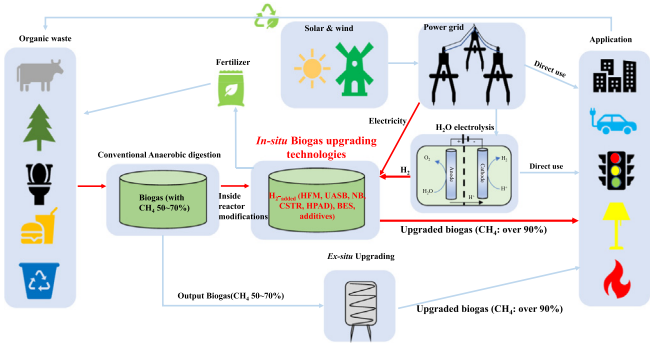
HIGHLIGHTS

- In-situ biogas upgrading technologies are reviewed.
- H_2-addition technology is the most prominent in-situ technology.
- Hydrogenotrophic methanogens are critical microorganisms in upgrading technologies.
- HFM reactor shows the highest average CH_4 content (92.5%).
- The combination between H_2-addition technology and HPAD/BES is promising.

GRAPHICAL ABSTRACT



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ABSTRACT

Biogas is mainly produced from the anaerobic fermentation of biomass, containing methane with an extensive range between about 50% and 70%. Higher methane content biogas has higher energy and heat value, which needs biogas upgrading. There are mainly two types of biogas upgrading technologies (ex-situ and in-situ). This manuscript presents a review of technologies on in-situ biogas upgrading. These technologies comprise H_2 addition technology (e.g., continuous stirring tank reactor (CSTR), hollow fiber membrane (HFM), nano-bubble (NB) technology, upflow anaerobic sludge blanket (UASB)), high-pressure anaerobic digestion (HPAD), bioelectrochemical system (BES), and additives (e.g., ash, biochar, and iron powder). The results confirm the excellence of H_2-addition technology, with the highest average CH_4 content obtained (HFM: 92.5%) and one of the few full-scale cases reported (Danish GasMix ejector system: 1110 m^3). Meanwhile, newly pop-up technology such as HPAD delivers appropriate CH_4 content (an average of 87%) and is close to the full-scale application (https://bareau.nl/en/for-professionals/). More importantly, the combo between HPAD and H_2-addition technology is prominent as the former improves the low gas-to-liquid obstacle confronted by the latter. Additionally, recently emerging BES can't stand out yet because of limited efficiency on CH_4 content or constraint full-scale application behaviors (disability to operate at high current density). However, its combination with H_2-

Abbreviations: AD, anaerobic digestion; AEM, anion exchange membrane; AM, acetoclastic methanogenesis; BES, bioelectrochemical system; CE, coulombic efficiency; CWSB, coarse walnut shell biochar; CEM, cation exchange membrane; COD, chemical oxygen demand; CSTR, continuous stirring tank reactor; DM, dry matter; DET, direct electron transfer; DIET, direct interspecies electron transfer; FWSB, fine walnut shell biochar; GHG, greenhouse gas; HPAD, high-pressure anaerobic digestion; HFM, hollow fiber membrane; HRT, hydraulic retention times; HM, hydrogenotrophic methanogenesis; IEA, international energy agency; IET, interspecies electron transfer; LNG, natural-gas liquefaction; MEC, microbial electrolysis cell; MBR, membrane bioreactor; NGG, natural gas grid; NB, nano-bubble; OLR, organic loading rate; PR, primary reactor; PB, photobioreactor; PtG, power to gas; PEM, proton exchange membrane; SR, secondary reactor; STP, standard temperature and pressure; SMY, specific methanogenic yield; SHE, standard hydrogen electrode; TS, total solids; UASB, upflow anaerobic sludge blanket; VFAs, volatile fatty acids; ZVI, zero-valent iron.

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addition technology to form the Power to Gas (PtG) concept is promising, and its commercial application is available (http://www.electrochaea.com/). Hydrogenotrophic methanogens are imperative players in all reviewed technologies for the generation of upgraded CH_4.

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1. Introduction

Fossil fuels dominate as the primary energy supply for industrial processes and daily livelihood (Adnan et al., 2019). However, the use of fossil fuels imposes a big threat to the environment, with the significant threat being greenhouse gas (GHG) emissions. Nowadays, many governments have released climate announcements aiming to reduce GHG emissions. In 2018, the total primary energy supply came globally from natural gas (23%), oil (31%), coal (27%), renewable energy (18%), with small shares from nuclear. While in China, renewable sources contributed to less than 15% of total energy consumption in 2019. The execution of the climate agreement signed in 2019 would result in at least 70% of electricity obtained from renewable sources by 2030 (IEA, 2020).

Biogas is a credible renewable energy source that is generally produced from anaerobic digestion (AD) of biomass. The potential to generate biogas from currently available substrates ranges between 10,100 and 14,000 TWh at the global scale. If fully exploited, the produced energy will contribute to 6-9% of the world's primary energy consumption and could be one of the proper substitutions of fossil fuels (energy from biogas will replace 23-32% of the world's coal consumption) (WBA, 2019). In general, raw biogas consists of 50-70% of CH_4 and 30-50% of CO_2 as well as some trace components such as H_2S, N_2, O_2, CO, and NH_3 (Adnan et al., 2019; Angelidaki et al., 2018; Appels et al., 2011).

Except for CH_4, other gasses in biogas are redundant, as they don't promote energy generation. It is believed that biogas with higher than 90% of CH_4 increases its heating value and enables its quality as natural gas (Table S1) (Bassani et al., 2016). Therefore, high concentrations of CO_2 and trace contaminants (H_2S, N_2, O_2, water, and NH_3) limit the application of biogas. Thus, during the practical upgrading process, the removal of CO_2 is the primary goal. Meanwhile, such a method is also accompanied by impurities removal (in most cases H_2S and NH_3) for qualified biomethane production.

To note, various upgrading treatments have been developed, which can be grouped into in-situ and ex-situ technologies. Ex-situ technologies include water scrubbing, pressure swing adsorption, physical scrubbing, chemical adsorption, cryogenic separation, membrane separation, and biological upgrading techniques (Angelidaki et al., 2018). The number of biogas upgrading plants delivers an increasing trend in the last two decades (Fig. 1). These ex-situ strategies are extensively implemented in large-scale biogas plants ($5000 > Q \geq 500$ m^3 biogas/day, NY/T 337-2011) (Adnan et al., 2019; Angelidaki et al., 2018; Papacz, 2011). However, ex-situ technologies need additional equipment and materials and periodic replacement of solution and membrane, which are costly and heavily dependent on the size of the AD plant (Papacz, 2011). According to previous reports, ex-situ technologies only become economically and energetically feasible when the operational capacity of the AD plant exceeds 2400 m^3 biogas/day (Adnan et al., 2019; Sarker et al., 2018). For medium ($500 > Q \geq 150$ m^3 biogas/day) and small-scale ($150 > Q \geq 5$ m^3 biogas/day, NY/T 337-2011) digesters, the upgrading equipment is neither available nor cost-effective (Li et al., 2017; Lindeboom et al., 2011; J. Zhao et al., 2020; L. Zhao et al., 2020). Currently, 110,448 biogas facilities are operating in China, with 6972 being large-scale, accounting for 6% of the total biogas installations (WBA, 2019). In this context, medium and small-scale biogas plants are the dominant ones (94%), motivating the establishment of compatible in-situ biogas upgrading facilities.

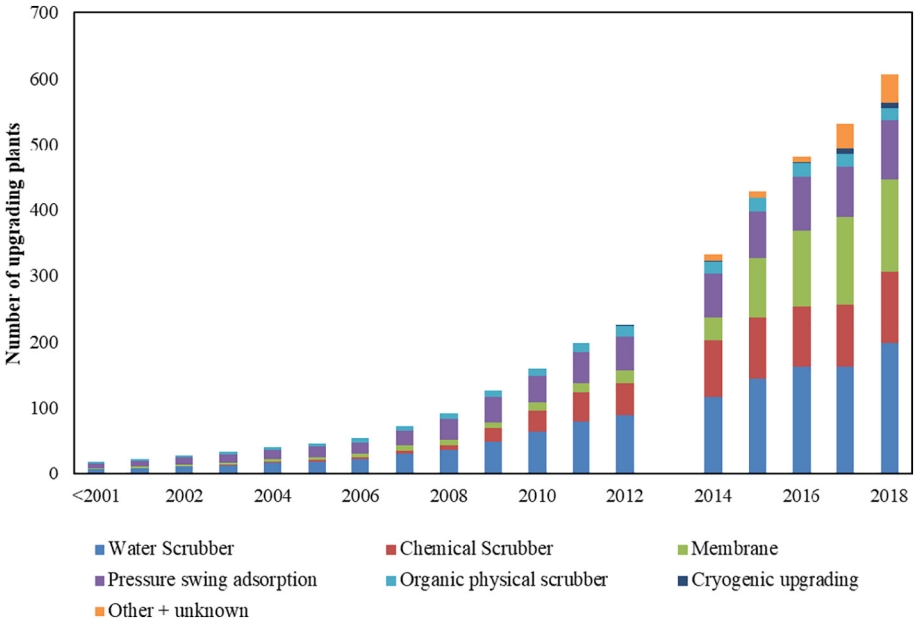

Fig. 1. Biogas upgrading plants in IEA bioenergy among 37 member countries.
(Data obtained from http://task37.ieabioenergy.com/plant-list.html, IEA Bioenergy 2019, data in 2013 is lacking)

In-situ technologies include H_2 addition (Bassani et al., 2016; Jensen et al., 2021), high-pressure anaerobic digestion (HPAD) (Lindeboom et al., 2011; J. Zhao et al., 2020; L. Zhao et al., 2020), bioelectrochemical system (BES) (Fu et al., 2020; Liu et al., 2017), and additives (e.g., ash, biochar, iron powder) (Feng et al., 2014; Linville et al., 2017; Yin et al., 2019) (Fig. 2). Henry's law plays a vital role in in-situ upgrading technologies, especially in HPAD and H_2 addition reactors. In the last decade, in-situ upgrading technologies have attracted broad attention. Presumably, it is ascribed to the exclusive advantages of much smaller carbon footprints since CO_2 is captured and converted to new products (Fu et al., 2021). But recent progress on in-situ technologies has been rarely gathered (Adnan et al., 2019; Angelidaki et al., 2018; Kadam and Panwar, 2017; Sun et al., 2015). Thus, in this review, in-situ biogas-upgrading technologies are presented regarding the principle, utilization, resultant CH_4 content, microbial community, and practical application potential. By gathering relevant information, the ideal biogas upgrading facilities are exhibited to satisfy the requirement of medium and small-scale AD plants.

2. Different technologies used for in-situ biogas upgrading

2.1. H_2 addition

H_2 addition is one of the most exploited techniques in the laboratory for biogas upgrading (Table 1), which relies on the hydrogenotrophic methanogenesis (HM) pathway to convert H_2 and CO_2 to CH_4. The origin of H_2 should be derived from a renewable source to make the entire process renewable. Thus, the exploitation of renewable electricity (windmills and photovoltaics) for water electrolysis (harvest H_2 as a result) is tempting (Angelidaki et al., 2018; Bassani et al., 2016). This method also stores the surplus renewable energy, known as the power to gas (PtG) technology. H_2 itself is already considered a valuable fuel for the future energy market.

Nevertheless, technology and infrastructure for large-scale H_2 storage and delivery are not mature. The low density of H_2 (0.09 kg/m^3) hampers its transportation as it requires larger pipes and more compression power compared to CH_4 (0.657 kg/m^3) at similar operational conditions (Wahid and Horn, 2021). Moreover, the capital cost of large-transmission grids of H_2 is nearly 1.5-1.8 times more than CH_4 (Wahid and Horn, 2021). Moreover, the volumetric energy density of H_2 (10.88 MJ/m^3) is inherently lower than that of CH_4 (36 MJ/m^3) (Angelidaki et al., 2018). Thus, it would be attractive to use H_2 to upgrade biogas rather than using it as a fuel itself. The upgrading process using H_2 could exploit the biogas plants' existing facilities and reduce the initial investment cost. Furthermore, the conversion of excess CO_2 to CH_4 enhances the CH_4 yield and the energy value of the output gas.

2.1.1. Mechanism, challenges, and opportunities

2.1.1.1. Mechanism. Regarding the two major pathways of methanogenesis (acetoclastic methanogenesis (AM, Eq. (1)) and HM Eq. (2)), HM is thermodynamically more favorable and stable than AM (Sarker et al., 2018). Several studies, including pilot-scale, have investigated hydrogenotrophic methanogens in bioreactors to upgrade biogas to biomethane (Dupnock and Deshusses, 2021). In principle, hydrogenotrophic methanogens use 4 mol of H_2 as the electron donor and 1 mol of CO_2 as the carbon source and electron acceptor to produce 1 mol of CH_4 through the so-called Wolfe cycle (Fig. S1) (Eq. (2)) (J. Zhang et al., 2020a). Or, CO_2 is converted into acetic acid, catalyzed by homoacetogenic bacteria via the Wood-Ljungdahl pathway (Eq. (3)), and then acetoclastic methanogens use acetic acid to generate CH_4 (Eq. (1)) (Fig. S1) (Fu et al., 2021). It is noteworthy that HM is widely distributed within the methanogenic community. Except for *Methanosaeta*, other prominent methanogens such as *Methanosarcina* (both AM and HM), *Methanobacterium*, *Methanculleus* all could use the HM pathway for CH_4 production.

Typically, conventional AD (without apparent inhibition) produces around 30% CH_4 via the HM pathway (Nzila, 2017). When the conditions are not optimal, acetoclastic methanogens are generally inhibited (these archaea are considered more sensitive to toxicants or changes in environmental conditions compared with hydrogenotrophic methanogens). This results in the dominance of the HM pathway, but it will lead to acetate accumulation, which ultimately will also inhibit the hydrogenotrophic methanogens. In some situations (for example, high ammonia, high temperature), syntrophic acetate oxidizers may become the dominant acetate-utilizers, oxidizing acetate to CO_2 and H_2, which is

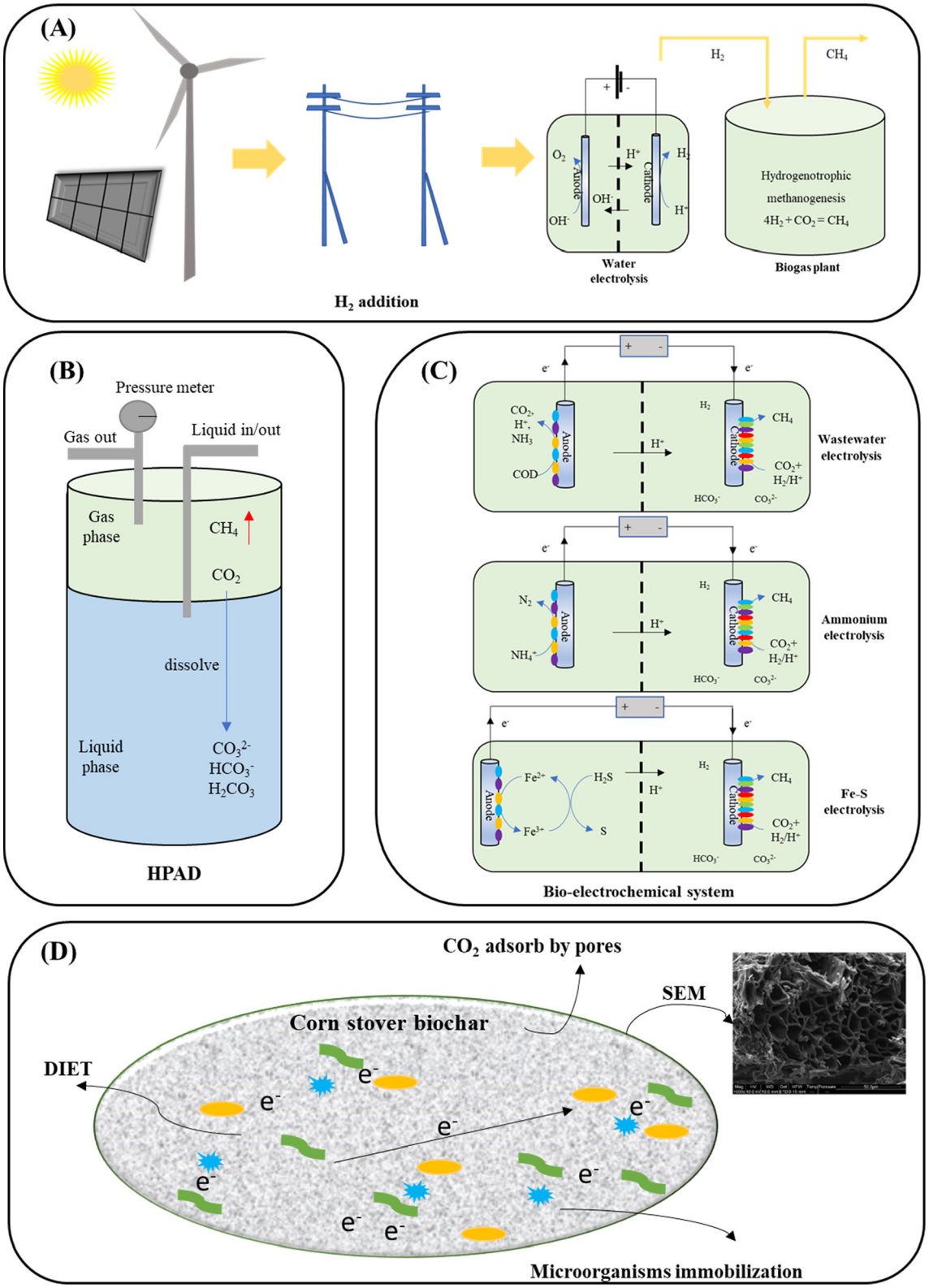

Fig. 2. Different technologies used for in-situ biogas upgrading (A) H_2 addition in an AD plant, (B) high-pressure anaerobic digestion (HPAD), (C) bio-electrochemical technologies, and (D) additives from corn stover biochar is shown as an example.
(SEM images from (Shen et al., 2017))

further consumed by HM (Duarte et al., 2021; Dyksma et al., 2020). Moreover, the addition of H_2 directly to AD also switches the methanogenic metabolic pathway towards the HM pathway (Table 1). In H_2-supplemented systems, *Methanoculleus*, *Methanobacterium*, and *Methanothermobacter* are dominant archaea (Table 1). The pure culture of these microorganisms could act as bioaugmentation culture to accelerate the HM process, promoting the conversion rate of H_2 and CO_2 to CH_4 (Dahl Jønson et al., 2020).

Table 1
Summary of H_2 addition for biogas upgrading.

Reactor type	Substrate	Operation condition	Conclusion	Microbes	H_2 utilization efficiency (%)	CH_4 production rate	CH_4 (%)	Reference
Two-stage CSTR	Cow manure food waste H_2:CO_2 (2:1, 4:1)	55 °C 10 L (6 L)[a] Primary + upgrading reactor	①CH_4 production rate was maximum at 140 rpm and 12.2 mL/min gas recirculation rate. ②H_2 gas-to-liquid transfer rate should be improved.	–	13%-39%	0.03-0.14 L/L/d	41% (26% for inlet)	(Wahid and Horn, 2021)
CSTR	H_2:CO_2 (2:1-10:1) Sludge and straw	38 °C 2 L HRT 20 days Pressure < 1.2 bar	①High H_2 content caused pH increase ②High H_2 content caused acetate accumulation, which was produced by the homoacetogens. ③Pulse H_2 injection enhanced H_2 uptake rates.	Methanobacterium	58%-99%	CH_4 production increased 136%-199%	77-100% (59% for control)	(Agneessens et al., 2017)
CSTR+HPAD	Food waste H_2	Pressure 3, 5, 7 bar 3.0 L(2.3 L) 37 °C	①The pH dropped when pressure increases. ②The addition of H_2 helped increases pH in the HPAD reactor. ③High amount of H_2 caused CH_4 yield drop and VFAs accumulation due to lack of CO_2 and high H_2 partial pressure	Methanobacterium Methanosarcina Methanosaeta	>96%	0.8-1.4 biogas L/L/d	92% (52.4% for control)	(Kim et al., 2021)
CSTR	Cattle manure, H_2 Propionate, butyrate	Batch, 118 mL Continuous, 4.5 L 55 °C	①The H_2 consumption rate was affected by P_{H2}, and mixing intensity. ②The addition of H_2 increased pH due to consumption of bicarbonate, which then inhibits methanogenesis. ③The propionate and butyrate level were not significantly affected by the H_2 addition.	–	>80%	3.7-67.8 mL/L/h 22% higher than control	65% (62% for control)	(Luo et al., 2012)
CSTR	H_2:CO_2:CH_4 = 60:15:25	37 °C, 55 °C 1 L (0.6 L)	①Thermophilic condition had a higher (60%) H_2 bioconversion rate than mesophilic condition. ②Gas-to-liquid mass transfer was the rate-limiting factor for efficient H_2 utilization.	Methanobacteriales	2.9-22.8 L/L/d	0.9-5.3 L/L/d	95%	(Luo and Angelidaki, 2012)
CSTR	Manure, acidic whey, H_2	1 L (0.6 L) Continuous 55 °C HRT 15 days	①The best stirring speed was 150 rpm, and using a ceramic diffuser was better than the column. ②The addition of H_2 had a positive effect on the methanogenesis but no obvious effect on the acetogenesis.	Methanothermobacter	1.2-1.5 L/L/d	0.76-0.89 L/L/d	75% (57% for control)	(Luo and Angelidaki, 2013a)
Batch	Glucose, H_2	37 °C 0.5 L Batch mode	①The best ratio of H_2:CO_2 was 4:1. ②pH increased above 8, which influenced the process stability. ③High H_2 content caused VFAs accumulation and reduced CH_4 yield.	Methanobacterium	2.32 mL/L/h 98%	0.59 mL/L/h	94% (67% for control)	(Wahid et al., 2019)
Batch	Maize leaf substrate, H_2	52 °C 120 mL Batch mode	①High H_2 addition could inhibit VFAs degradation. ②High H_2 addition stimulated homo-acetogens for production acetate from CO_2 and H_2.	Methanobacterium	>92.2% 471-510 mL/L/d	118-127 mL/L/d	89% (64% for control)	(Mulat et al., 2017)
CSTR	Grass silage	55 °C 9.5 L OLR: 3-8 g VS/L/d	Elevated H_2 concentration hampered the in-situ acetogenesis process	-	33-72%	0.33-2.52 L/L/d	60%	(Voelklein et al., 2019)
Batch	Cattle manure, H_2 NH_4Cl (1 and 7 g NH_4^+-N/L)	118 mL (40 mL) Batch mode 37 °C, 55 °C P_{H2}: 0, 0.25, 0.5, 1 atm	①High ammonia inhibited methane production in both mesophilic and thermophilic conditions. ②Ammonia level increase, the pathway change from AM to HM, and syntrophic bacteria increase. ③H_2 injection under high ammonia concentration could promote the growth of some hydrolytic and fermentative bacteria ④The ammonia toxicity was alleviated at thermophilic conditions.	*Methanothermobacter thermautotrophicus*	-	320 mL/(gVSS/h)	CH_4 yield was highest when the P_{H2} was 0.5 atm	(Wang et al., 2020, 2016)

(continued on next page)

Table 1 (*continued*)

Reactor type	Substrate	Operation condition	Conclusion	Microbes	H_2 utilization efficiency (%)	CH_4 production rate	CH_4 (%)	Reference
Batch	Glucose, H_2	37 °C, 55 °C, 150 rpm 540 mL (100 mL)	①Stop the methanogenesis step, using CO_2 to produce chemicals, such as VFAs. ②thermophilic inoculum had a higher ability to inhibit methanogenesis and produced higher acetate. ③Gas ratio H_2:CO_2 = 2:1 was the best ratio to get high CH_4 content and acetate yield.	Moorella sp.4	<90%	-	77%	(Omar et al., 2019)
CSTR	H_2 (3-30 mmol) Cattle manure	Fed-batch semi-continuous 6.6 L (5 L) 39 °C	①More acetic acid produced by the addition of H_2. ②Poor Gas-to-liquid transfer was a significant problem.	-	-	-	65-72%	(Sarker et al., 2020)
Batch	H_2:CO_2:CH_4 4 ratio	37 °C Batch mode 540 mL (100 mL)	①thermal treatment didn't suspend the methanogenic activity of the inoculum. ②chemical treatment enhanced biogas upgrading and acetate production. ③Gas ratio H_2:CO_2 = 2:1 wan best to gas high CH_4 content.	*Acetoanaerobium noterae* 10 (acetate produce)	>98%	-	96%	(Omar et al., 2018)
Batch	Food waste 5% H_2, 95% N_2	160 mL (75 mL) 37 °C Batch mode	①H_2 addition improved biomethane yield and biogas quality from food waste. ②High acidification potential of food waste helped to buffer excessive pH increase.	-	-	12.1% higher than the control	77.2% (65%)	(Okoro-Shekwaga et al., 2019)
CSTR	H_2:CO_2 = 4:1 Swine manure	37 °C, (11.6 L)	①CH_4 yield increased by 29.6% after H_2 addition. ②H_2 was mainly indirectly converted into CH_4 via homoacetogensis.	Methanosaeta (AM) Clostridium (homoacetogenic)	1.93 L/d	29.6% after H_2 addition	70% (62%)	(Zhu et al., 2020)
CSTR (simultaneous in-situ and ex-situ)	H_2	1 L (0.5 L), 200 rpm, 37 °C,HRT 15 days OLR 2, 3, 4, 5 g COD/L/d	CH_4 increase by more than 3-fold than the original. Need to add some buffer to prevent an inhibitory rise of pH.	Methanobacteriales Methanomicrobiales	-	2.76 L/L/d	95% (50% for initial)	(Tao et al., 2019)
CSTR	H_2:CO_2 = 0:1, 1:1, 4:1	35 °C 55 °C (11.2 L)	①Temperature was a crucial factor in impacting the succession of microbial community structure. ②Continuous stirring was harmful to the stabilization of the mesophilic system.	35 °C: Methanosaeta 55 °C: Methanosarcina, Methanoculleus	0.9-1.9 L/d (M) 1.9-6.4 L/d (T)	CH_4 yield was 13% higher than control.	62-70% (M) 66-78% (T)	(Zhu et al., 2019b)
CSTR	H_2:CO_2 = 4:1	60 °C, 700 rpm 101 kPa & 122 kPa	Pressure increased the H_2 mass transfer flux.	*Methanothermobacter thermautotrophicus*	<97%	21 L/L/d	62% (17%)	(Martin et al., 2013)
Single (R1) or two-stage CSTR (R2&R3)	H_2 Cheese whey permeate, cheese waste powder	3 L 150 rpm, 55 °C HRT 15 days	①H_2 addition helped single rector increased the CH_4 content by 7% (power-to-methane). ②In the two-stage CSTR, some short-chain fatty acids were produced, which could be used for power-to-chemical.	Single: *Methanothermobacter wolfeii* Two-stage: *Coprothermobacter proteolyticus* *Anaerobaculum hydrogeniformans*	303-648 mL/L/d	142-152 mL/gCOD	Single: 51.6% (44.6%) Two-stage: 39.7% (57.3%)	(Fontana et al., 2018)
CSTR	H_2:CO_2 = 1:1-4:1 Sodium formate	55 °C 11.2 L	①Continuous mixing was favorable for thermophilic in-situ biogas upgrading by H_2. ②After H_2 added, strict HM played a crucial role in the in-situ biogas upgrading system. ③Formate was more beneficial for acetogenesis of propionate degradation compared to H_2.	Methanoculleus Methanobrevibacter Methanobacterium	1.88-6.63 L/d	222.3-291.6 L/kg VS	80%	(Zhu et al., 2019a)
CSTR	H_2, CO2, CO = 4:1	330 mL (100 mL) 37 °C, 60 °C	①Thermophilic condition increased CH_4 production rate. ②At mesophilic condition, AM contributed to 65% of CH_4 production.	37 °C: Acetobacterium sp., Methanospirillum hungateii 60 °C: *Thermincola carboxydiphila*,	-	0.24 mol/mol H_2	81-92%	(Grimalt-Alemany et al., 2020)

$$AM: CH3COO^- + H2O \rightarrow CH4 + HCO3^-,\ \Delta G0' = -31\ kJ/reaction \quad (1)$$

$$HM: 4H2 + CO2 \rightarrow CH4 + 2H2O,\ \Delta G0' = -130.7 kJ/reaction \quad (2)$$

$$Homoacetogensis: 4H2 + 2CO2 \rightarrow CH3COOH + 2H2O,\ \Delta G0' = -104.5\ kJ/reaction \quad (3)$$

2.1.1.2. Challenges and opportunities. Although biological biogas upgrading offers technical advantages, H_2-added biogas upgrading is still challenging (Bassani et al., 2016). The primary constraints and corresponding solutions are demonstrated below:

2.1.1.2.1. Increased pH induced by CO_2 consumption. Together with the injection of H_2 into the digester, the depletion of CO_2 proceeds, leading to a rise of pH due to the removal of bicarbonate (a primary form of CO_2 in the liquid phase). Bicarbonate (HCO_3^-) acts as a critical buffer in AD. Hence, it also causes volatile fatty acids (VFAs) accumulation and inhibits the activity of hydrogenotrophic methanogens (Mulat et al., 2017; Wahid et al., 2019). Thus, it is one of the main drawbacks of in-situ H_2 addition configuration. To overcome this technical challenge, researchers adopted co-digestion with acidic waste to compensate for the increase of pH (pH > 8), such as food waste (Okoro-Shekwaga et al., 2019) and cheese whey wastewater (Fontana et al., 2018). In addition, the combination of H_2 injection and HPAD could be an excellent way to solve high pH in H_2-injected reactors. Since injected H_2 could use surplus CO_2 dissolved in the liquid phase of HPAD to mitigate the decreasing pH and further convert CO_2 into CH_4 internally. Kim et al. (Kim et al., 2021) claimed that after the addition of H_2 into the HPAD reactor, the CH_4 content increased up to 92.1% compared to 77.4% of the control, and pH increased from 6.7 to 8.7 at 5 bar when treating food waste. Thus, these two technologies could make up for each other's shortcomings.

2.1.1.2.2. Increased H_2 partial pressure causes inhibition. Another essential aspect that needs to be considered during the H_2 injection process is the concentration of H_2. The HM pathway is only thermodynamically feasible when H_2 concentration is deficient (10^{-4}-10^{-6} atm) (Zhao et al., 2018). High H_2 concentration inhibits methanogenesis and promotes the accumulation of electron sinks such as butyrate, propionate, lactate, and ethanol in the reactors (Angelidaki et al., 2018; Omar et al., 2019). Thus, H_2 concentration is a vital parameter in the H_2 addition reactors. The optimal H_2 to CO_2 ratio is still ambiguous at the moment. Some researchers demonstrated that the best ratio of H_2 to CO_2 was 2:1 when simultaneous biogas upgrading and biochemical production could be achieved (Omar et al., 2018; Omar et al., 2019). While other researchers found the best ratio was 4:1 for biogas upgrading or biomethane production (Rachbauer et al., 2016; Wahid et al., 2019). A systematic evaluation of varying H_2 to CO_2 ratios with different common substrates and different inoculum sources should be carried out to determine the optimal ratio.

2.1.1.2.3. Low gas-to-liquid transfer rate. The H_2 gas-to-liquid transfer ratio should be well studied in H_2 addition reactors for efficient uptake of H_2 (in the gas phase) by hydrogenotrophic methanogens (in the liquid phase) (Agneessens et al., 2017; Díaz et al., 2015; Luo and Angelidaki, 2012). In such a sense, Henry's constant is 7.8×10^{-3} mol/L/MPa for H_2, which is remarkably lower than that of CO_2 (0.318 mol/L/MPa) (standard temperature and pressure (STP), 0 °C and 1 atm). Therefore, the efficiency of the H_2 utilizing rate strongly depends on the H_2 gas-to-liquid transfer rate, as determined in (Eq. (4)) (Bassani et al., 2016):

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

where; r_t is the H_2 gas-to-liquid mass transfer rate, (L/(L.day)); 22.4 is gas volume to mole ratio (1 mol gas corresponds to 22.4 L gas at STP); k_La is gas transfer coefficient (per day); H_{2gTh} is H_2 concentration in the gas phase (mol/L); H_{2l} is H_2 dissolved in the liquid phase (mol/L).

As Eq. (4) implies, r_t can be promoted by k_La. The value of k_La is influenced by reactors' configuration and operating conditions (Rusmanis et al., 2019). Thus, k_La can be modified by changing the H_2 diffusion device (Luo and Angelidaki, 2013a; Yun et al., 2017), adjusting the mixing speed (Luo and Angelidaki, 2013a), and adopting gas recirculation (Guiot et al., 2011). Modified reactors design such as upflow anaerobic sludge blanket (UASB) reactor and nano-bubble diffuser can be potential options for diffusion devices. Furthermore, HPAD could be introduced to increase the gas-to-liquid transfer rate (based on Henry's constant) of CO_2/H_2 (the H_2 utilization rate reaches up to 99%) (Agneessens et al., 2017; Rusmanis et al., 2019). Additionally, the application of biogas recirculation through the membrane for gas sparging has increased H_2 and CO_2 conversion efficiency up to 95% in different trials (Alfaro et al., 2018; Alfaro et al., 2019; Díaz et al., 2015). All these intensifications are designed to intentionally enhance the contact (prolong the contact time) between hydrogenotrophic methanogens in the liquid phase and H_2 in the gas phase. The following section will thoroughly elaborate on the different reactor types, as well as varying modules (Section 2.1.2, Fig. S3).

2.1.2. Existing reactor set-ups for H_2-added biogas upgrading

2.1.2.1. Continuous stirring tank reactor (CSTR). CSTR is the most common type of reactor used in AD. A set of impellers controlled by a motor vigorously stirs the reactor. Gas retention and interface area are maximized through the reduction of bubble size via intensive mixing. High-speed mixing requires high energy input that could break biomass granules and the structure/cell of the microorganisms, which further causes acetic acid accumulation in the system (Rusmanis et al., 2019; Wahid and Horn, 2021). It has been suggested that the optimal speed used in the upgrading system is around 140-170 rpm, with the CH_4 production rate being 0.9-5.3 L/L/d (Luo and Angelidaki, 2013a; Wahid and Horn, 2021). Although an improved mixing speed could increase CH_4 content from 57% to 75% (Luo and Angelidaki, 2013a), it still does not meet the CH_4 quality for the natural gas grid (NGG). Therefore, gas recirculation and gas diffusion device are required to help further increase CH_4 content. In this regard, Wahid and Horn (Wahid and Horn, 2021) obtained the highest CH_4 production rate (0.13 L/L/d) when the gas was recirculated at 12.2 mL/min, and the CH_4 concentration increased from 77% to 80%.

2.1.2.2. Hollow fiber membrane (HFM) reactor. HFM reactor relies on hollow fibers to realize bubbleless gas transfer (Fig. S3) (Luo and Angelidaki, 2013b). The inner diameter (e.g., 200 μm) and outer diameter (e.g., 280 μm) of hollow fibers are tiny, enabling substantial fibers (e.g., 320 fibers). These characteristics allow hollow membrane high surface area (e.g., 844 cm^2) (J. Zhao et al., 2020; L. Zhao et al., 2020). When H_2 goes inside the fibers, the pressure in the thread could force the H_2 to penetrate the liquid phase from the tiny pores on the membrane without bubble formation. Thus, the HFM reactor could increase the H_2 conversion efficiency to around 98%, which improves the low H_2 gas-to-liquid transfer rate (J. Zhao et al., 2020; L. Zhao et al., 2020). The gas sparging through HFM results in k_{La} values of 430/h for H_2 (Díaz et al., 2015). Meanwhile, the microbes could attach to the outer membrane to form biofilm. Wang et al. (Wang et al., 2013) indicated that *Methanosaeta* and *Treponema* (homoacetogens-related genus) prevailed on the biofilm, while *Methanoculleus* was prevalent in the liquid. Such observation suggested that homoacetogenesis and AM were the main pathways on the biofilm, while HM was the main pathway in the liquid phase (Wang et al., 2013). The presence of acetic acid, *Methanosaeta*, and homoacetogens-related bacteria indicated that HM and AM pathways co-existed in H_2-added HFM reactors (Li et al., 2020; Wang et al., 2013). Nevertheless, Luo and Angelidaki (Luo and Angelidaki, 2013b) reported that the biofilm was harmful to the process because it blocked the diffusion of H_2 to the liquid to some extent. And the biofilm contributed merely 22-36% to the H_2 consumption in the CH_4 formation process. This result is conflicting with another study using HFM for H_2S removal, where only the biofilm promoted the oxidation of the gaseous substrate

Table 1 (*continued*)

Reactor type	Substrate	Operation condition	Conclusion	Microbes	H_2 utilization efficiency (%)	CH_4 production rate	CH_4 (%)	Reference
				Methanothermobacter sp.				
Batch	H_2:CO_2 = 4:1	24 °C, 35 °C, 55 °C, 65 °C 600 mL (200 mL) 210 rpm	①Main limitation was the low-gas-to-liquid transfer rate and solubility of H_2. ② High temperature enhanced CH_4 production rate, while it increased the instability of the system. ③The optimal temperature range 35 °C -55 °C.	Methanothermobacter	643-994 mL/L/d	112-309 mL/L/d	-	(Figeac et al., 2020)
Batch	H_2:CO_2 = 4:1	55 °C, 65 °C 1.14 L Batch mode	①The efficiency was better at 65 °C than 55 °C. ②Reseeding of the process was required as when inoculum ages, efficiencies decreased	Methanothermobacter	–	0.46 L/L/d	85%-92%	(Guneratnam et al., 2017)
CSTR	H_2, sludge	1.4 L (0.3 L) 38 °C HRT 20 days	①Acetate accumulation increased at increasing OLR. P②Homoacetogeneis consumed up to 60% of H_2 at a low CO_2 level and became less critical after repeated H_2 injections.	Methanomicrobiales	60-80%	8-18 mmol/L/d	71%-94% (50%)	(Agneessens et al., 2018)
Biofilms	H_2:CO_2 = 4:1	38 °C 1.2 L (0.3 L)	①H_2 addition resulted in CO_2 limitation and pH increase. ②HM was highly dependent on CO_2 concentration. ③A methanogenic biofilm was established on carrier materials.	Methanoculleus	<2 nmol/cm^3/s	8 L/L/d	95% (50% for control)	(Maegaard et al., 2019)
Two-stage CSTR	R1: Cattle manure R2: H_2 and biogas from R1	37 °C, 55 °C R1 (1.5 L) R2 (2 L)	①At thermophilic conditions, higher efficiency of CH_4 production and CO_2 conversion were recorded. ②The addition of H_2 favored the proliferation of potential homoacetogens	Methanoculleus Desulfovibrio	37 °C: 178 mL/L/d 55 °C: 470 mL/L/d	37 °C: 38 mL/L/d 55 °C: 92 mL/L/d	37 °C: 89% (69.7%) 55 °C: 85% (67.1%)	(Bassani et al., 2015; Treu et al., 2018a)
Two-stage CSTR	Cattle manure (PR) H_2 (SR)	55 °C PR: 1.5 L (biogas reactor), HRT 15 days SR: 2 L (upgrading reactor), HRT 20 days	①Acetate was produced by homoacetogens. ②The pH of SB was higher than that of PR.	Methanoculleus Methanothermobacter	ND	85-113 mL/L/d (from H_2)	99% for SR (67% for PR)	(Treu et al., 2018b)
UASB	Potato-starch wastewater, H_2	1.4 L 55 °C	①H_2 low gas-to-liquid mass transfer rate limited the availability of H_2 for methanogens ②H_2 distribution can be improved using porous insert devices, like a ceramic sponge. ③Gas recirculation and chamber configuration helped to maximize CO_2 conversion to CH_4.	-	<1.873 L/L/d 94%	1.188-1.528 L/L/d	82%	(Bassani et al., 2016)
UASB	H_2:CO_2 = 4:1 Packing materials (ceramic ball, glass pipe)	4.5 L 37 °C	①Packing material that provided efficient cell immobilization can increase biomethane efficiency. ②Glass pipe (85%) has higher H_2 utilization efficiency than ceramic ball (55%)	-	55% (ceramic) 85% (glass)	3.9 m^3/m^3/d (ceramic) 4.8 m^3/m^3/d (glass)	ceramic ball: 65% glass pipe: 78%	(Daglioglu et al., 2020)
UASB reactor + degassing unit membrane	Synthetic wastewater (15 g/L glucose)	UASB: 1 L Degassing unit: 0.4 L 37 °C	①pH increased. ②The COD removal efficiency and CH_4 yield were not affected by the gas desorption.	-	-	-	>90% (51.7% for control)	(Luo et al., 2014)
Two-stage UASB	Synthetic wastewater, glucose H_2/CO_2/CO/CH_4	35 °C OLR 1-5 gCOD/L/d 2.1 L (0.7 L) HRT 1 day	①Syntrophic bacteria and methanogens facilitated biogas upgrading with syngas ②CO in H_2-rich syngas didn't inhibit methanogenesis.	Methanoseata	<99%	-	>90%	(Xu et al., 2020)
Two-stage R1: CSTR R2: upflow reactor	R1:cattle manure, potato starch, H_2 R2:digestate from R1	53 °C PR1: in-situ, (3 L), HRT 15 days PR2: ex-situ, (850	①VFAs accumulation in the in-situ reactor. ②Hydrogenotrophic methanogens and homoacetogens were rich in reactors.	Methanothermobacter	-	R2: 355-427 mL/L/d	R1:87% R2:95%	(Corbellini et al., 2018)

		mL)					
UASB	H_2:CO_2 = 4:1	37 °C. 55 °C, (6.3 L)	①The highest performance achieved by applying gas recycle under thermophilic conditions.	*Methanoculleus chikugoensis* (37 °C) Methanothermococcus (55 °C)	<1.6 L/L/d	0.4-4.8 L/L/d	96%	(Yun et al., 2017)
Top-mounted agitator Venturi-based gas mix system	Manure, H_2	1200 L 52 °C, HRT 14 days	①H_2 conversion rate was controlled by H_2 gas-liquid mass transfer. ②venturi-based mixing system for H_2 injection to facilitate H_2 gas-liquid mass transfer in in-situ biomethanation. ③Headspace recirculation improved H_2 consumption	-	24% 70.3 L/m^3/h	-	63%	(Jensen et al., 2018; Jensen et al., 2021)
Biofilm plug-flow reactor	H_2:CO_2 = 4:1	0.75 L 37 °C	①High rate methanogenesis was observed without gas-liquid agitation. ②More active methanogens existed on biofilm.	Methanosaetaceae Methanobacteriales	-	<40 *v*/v/d	<90%	(Savvas et al., 2017)
Ceramic membrane	H_2:CO_2 = 4:1 loading rate 10-30 LH_2/m^3/d	Pilot-scale, 60 L 55 °C	①Ceramic MBR could efficiently transfer H_2 to CH_4, K_{La} was 268/h. ②CH_4 production rate was 0.18 L/m^3; H_2 transform rate was 95%.	*Methanothermobacter thermautotrophicus*	95%	0.22 m^3CH_4/m^3H_2	-	(Alfaro et al., 2018)
HFM	H_2:CO_2 = 4:1	40 L (31 L) 55 °C	①H_2 mass transfer to the liquid phase was identified as the limiting step for the conversion. ②Gas sparging through a membrane module can efficiently increase the gas-to-liquid transfer rate.	-	95%	0.22-0.23 m^3/m^3 H_2	95% (60% for control)	(Díaz et al., 2015)
HFM (CSTR)	H_2 Cattle manure and whey	1 L (0.6 L) 55 °C, 150 rpm HRT 15 days	①Increase H_2 flow rate could increase CH_4 content. ②pH increased to 8.3, which hampered the AD. ③Biofilm formed on the membrane will decrease H_2 diffusion to the liquid.	-	-	-	96.1% (53%)	(Luo and Angelidaki, 2013b)
HFM	H_2 Sewage sludge	35 °C, (20 L) HRT 20 days	①94% H_2 utilization efficiency. ②CH_4 production yield increased by 42%. ③Gas recirculation and H_2 supply through a submerged membrane for biogas upgrading.	Methanoculleus sp. Methanospirillum sp. Methanolinea sp. Methanobacterium sp.	100%	Biogas 30 mL/L/d (from H_2)	73% Had high CH_4 production rate.	(Alfaro et al., 2019)
HFM	H_2 and biogas (60% CH_4, 40% CO_2)	200 mL reactor tube 250 mL (150 mL) biogas reactor Bench-scale,30 °C, pH 7.0-7.5	①Acetate and ethanol generated by homoactogen during the upgrading process. ②Increase P_{H2} could help further increase CH_4 content.	Clostridium ragsdalei P11	95%	-	97.6% (60% at initial)	(J. Zhao et al., 2020; L. Zhao et al., 2020)
HFM	H_2:CH_4:CO_2 = 66:18:16 NH_4Cl (3.5-6.5 g/L)	7.85 L (7 L) 55 °C	The optimum ammonia nitrogen for biogas upgrading was 5.5 g/L	Methanobacterium Methanosaeta	91-99%	CH_4 yield increase 35.2-64%	94.1%	(Li et al., 2020)
HFM	Coke oven gas (92% H_2, 8% CO) Sewage sludge	3 L (2 L), CSTR 37 °C, 200 rpm HRT 10 days	①HM and AM existed in the reactor, HM existed in the liquid part, and AM lived on biofilm. ②pH increased after H_2 addition.	Methanoculleus Methanosaeta Treponema (homoacetogenetic)	96%	554-1305 mL/d	99%	(Wang et al., 2013)
NB	Waste activated sludge Air-NB, N_2-NB, CO_2-NB, H_2-NB	0.25 L batch study 36 °C	①NBs with the negative zeta potential could be stable in reactors for 2 weeks. ②The CH_4 production enhanced by 14-21%, H_2-NB had the best performance.	-	-	45 mL/g-VS/d	60% (55% for control)	(Wang et al., 2019)
NB	Swine manure Air-NB, CO_2-NB, H_2-NB	0.25 L, Batch mode 35 °C	①The cumulative CH_4 production from the NB added reactor was 19-39% higher than the control group. ②NB addition not only accelerated hydrolysis rates of proteins and carbohydrates but also enhanced the production of VFAs	-	-	192-225 mL/g-VS	60% (50% for control)	(Fan et al., 2020)

Note:
'-' not mentioned;
PR: primary reactor;
SR: secondary reactor;
MBR: membrane bioreactor;
OLR: organic loading rate.
[a] The volume in parenthesis is the working volume of the reactor.

(Sahinkaya et al., 2011; Zhao et al., 2011). Probably, such divergence comes from the different hydraulic retention times (HRT) adopted in those studies. When the HRT is short, few microorganisms exist in the system, and thereby the gases are consumed primarily by the microorganisms attached to the fibers. In contrast, the HRT in Luo's study is relatively long (HRT 15 days), which permits the submerse growth (Luo and Angelidaki, 2013b). Besides HRT, different mixing intensities also influence the structure of biofilm. A high speed could decrease the thickness of biofilm. However, an increase in mixing power is not practical for AD reactors due to the rise in operating costs. Moreover, this effort also leads to high gas permeation rate, which is not suitable for H_2 conversion (Celmer et al., 2008). Thus, in the HFM reactor, there is a 'trade-off' when setting parameters like HRT and stirring speed to maximize conversion efficiency.

2.1.2.3. Nano-bubble (NB) technology. NB technology has recently been recognized as a unique biogas upgrading technology. NBs are gaseous spherical bubbles with a diameter ranging from 50 to 200 nm (ISO 20480-1:2017). The generated NBs are characterized with excellent characteristics such as long residence time, improved gas solubility, low buoyancy, high negative zeta potential, and high surface charge (Lyu et al., 2019). Owing to these features, NBs are stable in solution from days to months. Another intriguing characteristic of NB comes from its capacity to enhance enzyme activity by promoting water mobility, such as hydride carrier Coenzyme F_{420} (hydrogenotrophic methanogenesis). Based on the mechanism of NB, the application of H_2-NB seems tempting. In this regard, biogas upgrading by H_2-NB has been evaluated in various studies (Bassani et al., 2015; Fan et al., 2020; Wang et al., 2019). Fan et al. (2020) reported that the CH_4 yield was increased by 39.3%, and CH_4 content was increased from 50% to 60% in the H_2-NB reactor. Wang et al. (Wang et al., 2019) found that the addition of NB water enhanced the CH_4 yield by 14%-21%, and CH_4 content was increased to 60% compared to 55% of the control reactor. Since NB technology is still in its infancy, future investigation on the effect of H_2-NB in hydrogenotrophic methanogenesis is appreciated.

2.1.2.4. Upflow anaerobic sludge blanket (UASB) reactor. The UASB reactor relies on the blanket formed by the granular sludge possessing highly active biomass (Mainardis et al., 2020). Wastewater (low suspended solids content) flows through the blanket from a bottom-up direction and is thoroughly contacted with the anaerobic microorganisms throughout the process (Fig. S3) (Bassani et al., 2016). Typically a UASB process could provide higher CH_4 content (91% after H_2 addition) in the biogas than a CSTR process does (86% after H_2 addition) because more contact time and area between microorganisms and H_2 is guaranteed in the UASB reactor (Corbellini et al., 2018; Nizami et al., 2012). The typical UASB configuration has been modified by introducing packing materials, contributing to immobilizing functional microbes (hydrogenotrophic methanogens) (Daglioglu et al., 2020). Meanwhile, the packing materials used in the UASB reactor could further affect the CH_4 content (78% vs. 65%) and H_2 utilization efficiency (85% vs. 55%) for glass pipe and ceramic balls, respectively (Daglioglu et al., 2020). A longer gas retention time was monitored in the glass pipe bioreactors (2.58 h compared to 2.08 h for ceramic balls), prolonging the contact time between gas and microorganisms. Like the HFM reactor, the UASB reactor can be tall, increasing the contact time and promoting the H_2 conversion efficiency. Meanwhile, the optimal upflow velocity is essential in the UASB system, which helps provide adequate mixing of the gas and biomass (Daud et al., 2018). However, the higher upflow velocity reduces the contact time between sludge and wastewater and smashes the sludge granules (Daud et al., 2018). Therefore, upflow velocity significantly impacts both biological performance and physicochemical effluent characteristics (Ozgun et al., 2013). Thus, the optimal upflow velocity should be carefully determined in the UASB system. Additionally, the gas collected from the top part could be recycled into the UASB reactor until the CH_4 content meets the requirements. By doing so, the CH_4 content enjoys a substantial increment (from 58% to 82%) (Bassani et al., 2016).

2.2. High-pressure anaerobic digestion (HPAD)

Compared to the regular pressure counterpart, high-pressure anaerobic digestion (HPAD) reactor can ultimately produce qualified biogas (CH_4 content >88%). This strategy integrates biogas generation, upgrading, and pressurization in a single step (Lindeboom et al., 2011; J. Zhao et al., 2020; L. Zhao et al., 2020) or two-stage (Chen et al., 2014b; Merkle et al., 2017b) (Table 2).

2.2.1. Mechanism

The main principle of the HPAD technology is Henry's law, where CO_2 dissolves better than CH_4 in the liquid phase when the pressure increases. Henry's constant for CH_4, CO_2, H_2S, and NH_3 is 0.016, 0.318, 1.15, and 620 mol/L/MPa (STP, 0 °C and 1 atm), respectively (J. Zhao et al., 2020; L. Zhao et al., 2020). Moreover, the improved contact between CO_2 and methanogens could also enhance CO_2 uptake by methanogens. As a result, the CH_4 content in the outlet gas increases under pressure. Together with CO_2, other pollutant gas (H_2S and NH_3) also dissolves quickly into the liquid phase under pressure.

2.2.2. HPAD applications, challenges, and opportunities

When the substrate is fixed, the CH_4 content in the headspace biogas responds linearly to the pressure within a range from 1 bar to 10 bar. When the pressure is increased higher than 10 bars, other factors, such as pH and saturability, will take over the function of pressure to determine the CH_4 content. Moreover, some researchers indicated that when the pressure was increased to 31.5 bar, the specific methanogenic yield (SMY) decreased by 30% compared to digestion at ambient pressure (Lindeboom et al., 2011). In fact, 10 bar (around 90% CH_4) already meets the pressure requirement for NGG and natural-gas liquefaction (LNG) (J. Zhang et al., 2020a, 2020b; L. Zhang et al., 2020a, 2020b; Y. Zhang et al., 2020). Further increase of pressure would only increase the cost of this technology. Hence, in most cases (Table 2), the optimal operating pressure is set around 10-20 bar.

$$H2O + CO2 \leftrightarrow H2CO3 \leftrightarrow HCO3- + H+ \leftrightarrow CO32- + 2H+ \quad (5)$$

Although HPAD technology can upgrade biogas, it relies mainly on physical principles to dissolve the CO_2 in the reactor's liquid phase. Thus the upgrading ability is determined by the volume of the liquid phase. If the liquid is not changed frequently, its buffer capacity will reach saturation. When the buffer capacity is saturated, pH will drop below 6 in a single-stage system because of the formation of H_2CO_3 (Eq. (5)). Low pH hurts CH_4 content (Lindeboom et al., 2012). Lemmer et al. (2015b) implemented a water scrubbing technique to increase pH in the HPAD reactor. After decompression, CO_2 is released from the liquid phase, and the liquid phase can be reused (Lemmer et al., 2015b; Merkle et al., 2017b). Water scrubbing increased pH from 6.5 to 6.7, and consequently, the CH_4 content increased from 75% to 87% (Lemmer et al., 2015b). However, water scrubbing requires an additional recirculating system, which increases the overall investment. Lindeboom et al. (Lindeboom et al., 2013b) applied silicate minerals (e.g., wollastonite, olivine, and anorthosite) for CO_2 scavenging. They demonstrated that pH increased from 6.0 to 7.5, and CH_4 content increased to around 87% at 3-9 bar. However, this method required substantial chemicals, and the produced precipitate might block the outlet pipe. Alternatively, to avoid problems with pH, wastewater with high alkalinity content can be an option. J. Zhao et al. (2020) and L. Zhao et al. (2020b) stated that HPAD could be applied to treat highly alkaline (14.4 g/L $CaCO_3$) wastewater without pH modification. Hence, HPAD technology for biogas upgrading can be applied with close pH monitoring or for the treatment of high-alkalinity waste streams. Or, HPAD can be coupled with external voltage to form bioelectrochemical

Table 2
Summary of high-pressure technology used for biogas upgrading.

Reactor type	Substrate	Operation condition	Conclusion	Microbes	CH_4 (%)	Reference
H_2 addition (single-stage)	Sewage sludge H_2 injection	1.5-3 bar, 35 °C HRT 20 days 35 L, 300 kPa	①Pressure could increase the gas-to-liquid transfer rate, H_2 conversion reached 99%. ②Exogenous H_2 could help upgrade biogas.	-	95.2%	(Díaz et al., 2020)
H_2 addition	Food waste, H_2	3, 5, 7 bar, 37 °C 3.0 L (2.3 L)	①pH decreased caused by high pressure ②Addition of H_2 could increase pH	Methanobacterium Methanosarcina Methanosaeta	92%(52.4% for control)	(Kim et al., 2021)
Single-stage, CSTR	synthetic wastewater (glucose, acetic acid)	37 °C 11 bar, 2 L	①CO_2 dissolved in the liquid phase under the pressure ②HPAD reactor could deal with high alkalinity content wastewater	*Methanosaeta concilii* Methanobrevibacter	88% (64% for control)	(J. Zhao et al., 2020; L. Zhao et al., 2020)
Single-stage	Propionic and butyrate	0.2 L, 35 °C 0.3-8 bar	Increasing P_{CO2} decreased the syntrophic propionic and butyrate oxidation	-	-	(Ceron-Chafla et al., 2020)
Single-stage, batch	$NaCH_3COO{\cdot}3H_2O$	30 °C, 3-90 bar	The SMY decreased by 30% compared to atmospheric conditions.	-	90-95%	(Lindeboom et al., 2011)
Single-stage, batch	VFAs	30 °C, 1-20 bar	Substrate and cation inhibition reduced conversion rates	-	>94%	(Lindeboom et al., 2013a)
single-stage, batch	Sodium acetate	30 °C, 1-20 bar	P_{CO2} was below ideal theoretical equilibrium. pH was lower than 6.	-	CH_4 > 95% (pH 7); CH_4 > 80% (pH 5-6)	(Lindeboom et al., 2012)
Batch	Glucose	30 °C, 1-10 bar	The addition of silicate can buffer glucose acidification and sequestrate CO_2.	-	75-88%	(Lindeboom et al., 2013b)
Batch	Sodium acetate, Glucose, Propionate	30 °C, 1-20 bar	P_{CO2} could inhibit propionate degradation (5 bar).	*Methanosaeta concilii*; *Methanobacterium formicicum*	-	(Lindeboom et al., 2016)
CSTR	Activated sludge	37 °C,1-6 bar	Phosphate solubility increased, COD removal decreased.	Methanocellaceae	85%	(Latif et al., 2018)
Two-stage, batch Methane filter	A mixture of grass and maize silage hydrolysate	37 °C, 10, 20, 30 bar, and 1, 50, 100 bar	The initial pressures didn't significantly influence pressure increase, degradation of organics, and SMY.	-	-	(Lemmer et al., 2017; Merkle et al., 2017a)
Two-stage, Methane filter	Maize silage	37 °C, continuous 9-50 bar flow rate: 0, 20, 40 L/day	Water scrubbing can help increase pH from 6.5 to 6.7.	-	75-87%	(Lemmer et al., 2015b; Merkle et al., 2017b)
Two-stage, Methane filter	Leachate from maize silage/grass and maize silage	37 °C 1, 3, 6, 9 bar	The SMY dropped. Higher NH_4 lead to higher pH and CH_4 content but lower SMY.	-	pH from 7.2 to 6.5, CH_4 from 66 to 75%	(Chen et al., 2014a; Lemmer et al., 2015a)
Two-stage (Hydrolysis reactor, HR; Methanogenesis reactor, MR)	HR: maize and grass silage MR(fixed-bed reactor): effluent percolate from HR	HR: 55 °C MR: 37 °C, 21 L <100 bar	①HPAD cost savings of 20%. ②Combine microfiltration and HPAD could further increase CH_4 content. ③Microfiltration unit reduced the HRT in the HPAD process to 1.5 days.	-	75%-94%	(Bär et al., 2018)
Two-stage, Methane filter reactor	leachate from maize silage	37 °C 1.5, 9 bar	①Best performance was 9 bar and 12.5 kg m^3d^{-1}. ②Higher OLR became unstable.	-	74.5%	(Chen et al., 2014b)
Two-stage, Biofilm reactor	Food waste	37 °C, continuous 3-17 bar	pH decreased from 7.22 to 6.98, and COD removal decreased 93 to 80%, the SMY decreased.	Methanosaeta, Methanospirillum	91%	(Li et al., 2017)
electromethanogenic reactor (Stainless-steel single-chamber reactors)	Sodium acetate	55 °C, 50 bar Fed-batch 700 mV	The methane-production rate of the reactors showed an applied-voltage dependence.	Methanothermobacter Thermincola	-	(Kobayashi et al., 2017)

Note: '-' not mentioned.

Table 3
Bio-electrochemical technology used for biogas upgrading.

Reactor type	CO_2 removal efficiencies/CE	Anode	Cathode	Operation condition	Conclusion	Microbes	CH_4 (%)	Reference
Two-chamber + PEM	98% (enrich inoculum) 62% (control)	Solium acetate, Porous carbon felt, anolyte	CO_2, Porous carbon felt, Catholyte, -0.8 V, 1.65 atm CH_4 produce	300 mL (250 mL), 22 °C HRT 7 days	①Pre-enriched inoculum enhanced biocathode CH_4 production. ②The archaeal communities were similar, while the bacterial communities were different.	Methanobrevibacter arboriphilus	0.586 mmol CH_4/d for enriched (0.153 for control)	(Dykstra and Pavlostathis, 2017b)
Two-chamber + PEM	89%-135% (CE)	Graphite felt O_2 produce	Graphite felt Substrate: CO_2 CH_4 produce -0.85, -0.90, -0.95 V	1.4 L (0.7 L)[b]	①CH_4 production was enhanced at lower pH (pH 6.5). ②CH_4 production rate was higher than this pure strain.	Methanothermobacter sp. THM-2 (pure)	CH_4 production rate is 6.36 L/m^2/d[a]	(Lee et al., 2020)
Two-chamber + AEM	88% (20A m^{-2}) 99% (40A m^{-2})	Na_2SO_4 solution (anolyte), Iridium mixed metal oxide coated titanium-electrode mesh O_2 produce	HEPES buffer (catholyte) Biogas from R1, Stainless-steel wire mesh H_2& CH_4	0.2 L, 20 °C	①Upgraded cathode off-gas (CH_4, H_2) generated more microbial protein than raw biogas. ②CO_2 and CH_4 were separated by electrochemical. ③H_2 content increased, and CH_4 decreased when current increase.	-	45%	(Acosta et al., 2020)
Two-chamber + CEM	80-88% (CE)	N_2:CO_2 = 4:1 Graphite electrodes	Glucose -700 mV Graphite electrodes	Batch and continuous 37 °C, 1 L (0.8 L)	Hydrogenotrophic methanogenesis and alkali production followed by CO_2 absorption were likely to be major contributors to biogas upgrading in these systems	*Methanobacterium Petrolearium*	>70%	(Xu et al., 2014)
Single-chamber	–	Cow manure Stainless steel electrode		35 °C Batch mode 100-2500 mV	①Electrode promoted lignocellulose degradation ②Electric polarity was: cathode > anode > blank ③Cathodic micro-voltage was: 250 mV > 500 mV > 100 mV	-	84% (77% control)	(Qu et al., 2014)
Two-chamber + CEM	11-75% (CE)	410 mL H_2O as electron donor O_2 produce	420 mL; -600, -800 mV Synthetic gas (55% CH_4, 45% CO_2)	35 °C Batch mode	O_2 diffusion from the anode compartment, which decreased the reactor efficiency.	Methanobacterium sp.	65-85%	(Batlle-Vilanova et al., 2015)
Single-chamber & Two-chamber + CEM	60.2-80.9% (electron balance)	Glucose Carbon felt 0 to -1.2 V		Single-chamber 55 °C, 400 mL (350 mL) Two-chamber 55 °C, 500 mL (350 mL)	①Single chamber had higher VFAs concentration, especially for propionate. ②Two-chamber reactor had higher CH_4 content and more stable.	-	98% (two-chamber)	(Liu et al., 2017)
Two-chamber + CEM	25-33% (CE)	Stainless steel mesh Sodium acetate	Stainless steel mesh $NaHCO_3$ -800 mV	0.5 L for each; Continuous; HRT 6.8 h; 23 °C	①No significant differences between different inocula for CH_4 production and CH_4 recovery efficiency. ②Hydrogenotrophic methanogens were dominated in the biocathode.	Methanobrevibacter	83% CH_4 production rate 0.23 L/m^3/d	(Cerrillo et al., 2017)
Single-chamber	–	Stainless steel mesh, Carbon cloth Glucose, xylose, cellulose		38 °C, 600 mL (400 mL)	The CH_4 yield was enhanced by 48%. The CH_4 production rate increased 1.65 times.	-	88%	(Hagos et al., 2018)

Single-chamber	66.7% (Energy efficiency)	Acetate (10 g/L) Stainless steel 0.4, 1.0 V		180 mL Batch mode	①CH_4 yield increased 2.3 times, COD removal rate was tripled, and carbon recovery was increased by 56.2%. ②The overall energy efficiency was 66.7%.	Methanospirillum	98%	(Bo et al., 2014)
BES + H_2 injection AD1-MEC-AD2	–	Carbon cloth	Carbon cloth biogas and H_2: CO_2 = 4:1	AD1, 2.3 L MEC: 2.1 L (0.5-1.5 V) AD2, 0.8 L, 37 °C	①Combination of MEC with AD improved AD performance. ②H_2 circulation contributed to the high quality and yield of CH_4.	Methanobacteriales Methanomicrobiales Methanosarcinales	CH_4 yield 500 mL/g COD	(Yanuka-Golub et al., 2019)
BES	6.7-25.4% (CE)	Graphite fabric sheet with multiwall carbon nanotube and Ni sludge		0.5 V, 1.0 L 35 °C	①CH_4 production strongly depended on electroactive microorganisms' concentration in bulk solution. ②IET was the main pathway that existed in the system.	*Methanocorpusculum bavaricum* *Clostridium quinii*	62.3-207 mL/d	(Feng et al., 2018)
High-pressure + single-chamber BES	70% (current-capture efficiency)	sodium acetate stainless-steel		55 °C, 50 bar Fed-batch 700 mV	The methane-production rate of the reactors showed an applied-voltage dependence.	Methanothermobacter Thermincola	CH_4 production rate 168 mmol/m^2/d	(Kobayashi et al., 2017)
Two-chamber + PEM	85.2% (CE)	Carbon paper $FeSO_4 \cdot 7H_2O$	Carbon paper CO_2	0.15 L for each, Batch & Continuous, 37 °C	①This system combined biogas purification, H_2S removal, and sulfur recovery. ②Fe^{2+} could simulate sulfide removal and CH_4 formation	*Methanococcus maripaludis* S2	98.3% CH_4 production rate 20.6 μmol·h^{-1}	(Fu et al., 2020)
BES	–	Carbon cloth stainless Dairy manure 1, 2, 3 V		Bench-scale 25 °C, 35 °C 160 mL (100 mL)	①Remove H_2S and increase CH_4 content. ②3 V was better for H_2S removal. ③Stainless steel electrodes removed most sulfide without interfering with CH_4 production.	-	87%	(Lin et al., 2016)
Two-chamber + AEM	100%	Iridium mixed metal oxide coated titanium-electrode mesh	Stainless steel wire mesh CH_4:CO_2(H_2S) = 60:40	0.5 L (0.2 L) for each	①Membrane electrolysis allowed to simultaneously remove CO_2 and add H_2 to the biogas. ②H_2S absorption in the alkaline catholyte removed up to 98% of the incoming H_2S.	-	>98%	(Verbeeck et al., 2019)
Two-chamber + CEM	1.5-3.5% (CE)	Carbon felt Digested pig slurry N_2 produce	Granular graphite biogas	55 °C, 500 mL (265 mL)	①Ammonium removal in the MEC anode compartment achieved 14.46 g N-NH^{4+} m^{-2} d^{-1}, removal efficiency 18-30%.	Methanomassiliicoccus	CH_4 production rate 79 L/m^3/d	(Cerrillo et al., 2018)
H-cell reactor	10% (Nitrogen removal efficiency)	titanium mesh drums Wastewater	Steel brushes	<550 mV No membrane Batch mode	①N_2 will replace with O_2 produce at the anode. ②The drums were better in removing COD, while steel brushes produced CH_4 faster.	-	(56% COD removal rate)	(Siegert and Tan, 2019)
Two-chamber + AEM	105 mmol/d 85 (CE) 62 mmol/d 53% (CE)	Anolyte Acetate	800 g graphite granules Catholyte CO_2 N_2 = 3:7	0.86 L 0.2, -0.1 V	①CO_2 adsorption in BES cathode was driven by net alkalinity generation. ②Alkalinity generation was due to selective ion transport across separation membranes. ③AEM allowed a higher CO_2 removal due to HCO_3^- transport from cathode to anode.	-	34 meq/Ld 47% 83 meq/Ld 81%	(Zeppilli et al., 2016)
Two-chamber + PEM + zero-valent Iron (ZVI)	11-19% (CE) 62-97%(cathode capture efficiency) 80-99% acetate removal rate	Carbon felt anolyte	Carbon felt -0.65 to -0.80 V Sodium acetate CO_2, 1.65 atm Catholyte ZVI:1, 2 g/L	Batch, 22 °C 300 mL (250 mL)	①The CH_4 yield was 2.9-fold higher. ②ZVI assisted in the start-up of an elctromethanogenic biocathode and maintained microbial activity during voltage interruptions.	Methanobrevibacter arboriphilus Proteobacteria	0.60-2.73 mmol CH_4	(Dykstra and Pavlostathis, 2017a)

Note: '-' not mentioned; CE: coulombic efficiency; MEC: Microbial electrolysis cell.

[a] The CH_4 production per unit cathode surface area.

[b] The volume in parenthesis is the working volume of the reactor.

HPAD to convert the surplus dissolved CO_2 into CH_4 (Kobayashi et al., 2017). Another option is the combination of HPAD and H_2 addition, as underlined above (Section 2.1.1.2).

The methanogenic community in HPAD might be affected by various internal conditions such as pressure, pH, and temperature. Lindeboom et al. (2011) claimed that methanogens are resistant to pressure and could tolerate an external pressure of up to 100 bar. But the relevant knowledge of the methanogenic community at elevated pressures is rare. Whereas the change of pH induced by the dissolution of CO_2 under high pressure could strongly affect the activity (SMY decreased by 30%) and composition of the methanogenic community (50% *Metahanosaeta* at 11 bar) in the HPAD system (Li et al., 2017; Lindeboom et al., 2011, 2016; J. Zhao et al., 2020; L. Zhao et al., 2020). As for temperature, *Methanosaeta*, *Methanospirillum*, *Methanobrevibacter* are abundant at mesophilic conditions, while *Methanothermobacter* is rich at thermophilic conditions (Kobayashi et al., 2017; Li et al., 2017; Lindeboom et al., 2016; J. Zhao et al., 2020; L. Zhao et al., 2020).

Collectively, the development of HPAD reactors offers some clear advantages for biogas upgrading. However, low pH caused by the dissolved CO_2 is still a significant bottleneck for the wide distribution of this technique. Conversion of the dissolved CO_2 into CH_4 could be ideal for solving this problem and decreasing CO_2 emissions. Reduction of dissolved CO_2 could be achieved through the direct addition of H_2 or bioelectrochemical technology implementation. Despite current constraints confronted by HPAD, continuous operation of the HPAD reactor would considerably reduce capital expenditure (around 20%) compared to a conventional AD, including ex-situ upgrading and biomethane injection into the NGG (Budzianowski and Postawa, 2017; Sarker et al., 2018).

2.3. Bioelectrochemical system (BES)

BES for biogas upgrading has several advantages. The process can be performed at low temperatures; the process produces less sludge and requires no aeration cost, making the process eco-friendly (Kumar et al., 2017).

2.3.1. Mechanism

BES harbors the oxidation reaction at the bioanode (take wastewater chemical oxygen demand (COD) as an example: $C_xH_yO_zN + (2x\text{-}z)\ H_2O \rightarrow xCO_2 + [y + (2x\text{-}z)]\ [e^- + H^+] + NH_3$ (Eq. (6)), while the reduction of CO_2 to CH_4 at the biocathode is also known as electromethanogenesis. Electromethanogenesis can proceed via several known mechanisms (Fig. S2) (Fu et al., 2021): 1) Interspecies electron transfer (IET): H_2 produced at the cathode at the expense of H^+ reduction, which is catalyzed by extracellular enzymes: $2H^+ + 2e^- \leftrightharpoons H_2$ (Eq. (7)), H_2 can then be captured by hydrogenotrophic methanogens for CO_2 reduction: $CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$ (Eq. (2)) (Fig. S2C). When the applied voltage is sufficient to overcome thermodynamic limitations and losses, H_2 can also be produced abiotically at the cathode. 2) Direct electron transfer (DET): Cheng et al. (2009) proved the existence of DET, where methanogens can use electrons directly to reduce CO_2 into CH_4 by physical contact on cathode without the intermediate production of H_2. $CO_2 + 8H^+ + 8e^- \leftrightharpoons CH_4 + 2H_2O$ (Eq. (8)) (Cheng et al., 2009; Hagos et al., 2018) (Fig. S2D). 3) Homoacetogenesis plus AM: H_2 and CO_2 are first converted into acetate by homoacetogenic bacteria, and then the formed acetate is degraded by AM to generate CH_4 (Fig. S2E). At relatively low external potential, DET dominates in electromethanogenesis. In this context, it enables BES to get rid of the common gas-to-liquid transfer rate problem in exogenous H_2 injection technologies to a certain extent. In the subsections, factors influencing the efficiency of the conversion of CO_2 into CH_4 (biogas upgrading efficiency) are discussed (Table 3).

2.3.2. BES applications

2.3.2.1. Single-chamber or two-chamber BES?. According to the reactor configurations, two types of BES reactors, namely single-chamber BES and two-chamber BES, are available. Single-chamber BES is featured by membrane-free characteristics (without anion exchange membrane (AEM) and cation exchange membrane (CEM)). In this context, Qu et al. (2014) investigated the effect of the individual electrode (anode or cathode) at different micro-voltages (100, 250, 500, 2500 mV) on the AD of cow manure in single electrode-assisted fermenters (Li et al., 2021; Qu et al., 2014). They affirmed the enhancement of the average CH_4 content (77.9%) in the voltage-added (2500 mV) cathode-assisted reactors than that of the control (67.4%). In another study, Bo et al. (2014) argued that the CH_4 content could excess 98%, and CH_4 yield was increased 2.3 times through the addition of only a small voltage (1.0 V) in a barrel-shaped single chamber BES. The merit of single-chamber BES comes from its simple set-up, no additional membrane unit, and low voltage input (due to its low internal ohmic resistance). However, the concern arises considering the production of O_2 at the anode if the applied voltage exceeds the principle voltage required for water split (1.23 V at the standard condition), which is harmful to the oxygen-sensitive methanogens. One solution could be the supplementation of electron donors (COD, H_2S, NH_4^+) other than water since these compounds can be oxidized to provide electrons at a potential much lower than that of water. For instance, the applied voltage to oxidize NH_4^+ (136 mV) can be much lower than for the water splitting (1.23 V) with appropriate catalysts in place (Table S2) (Siegert and Tan, 2019). The AD process and BES integration have been tested using real effluents as anodic substrates (Zeppilli et al., 2017), allowing simultaneous N_2 production at the bioanode and CO_2 removal at the biocathode. In another study, Fu et al. (2020) used a single BES reactor to treat synthetic wastewater for simultaneously CO_2 reduction and sulfur recovery. This system comprises a ferrous ion (Fe^{2+}) mediated abiotic anode for H_2S oxidation and a methanogen-inoculated biocathode for CO_2 removal. In the anodic chamber, H_2S was removed and selectively converted into elemental sulfur particles. The CH_4 production rate of 20.6 μmol/h and high upgrading level (98.3% CH_4) was achieved in the cathode chamber. This system holds great potential for practical application as concurrent biogas upgrading and sulfur recovery can be achieved.

Alternatively, the dual-chamber BES can be adopted for biogas upgrading regardless of the potential to maximize the upgrading rate and efficiency. In this context, Liu et al. (2017) evaluated the biogas upgrading efficiency of single-chamber and two-chamber reactors. Compared with single-chamber BES, two-chamber BES was more stable, with lower VFAs concentration (420 vs. 775 mmol/e), higher CH_4 yield (CH_4 yield was enhanced by 40% vs. 10% compared to control), and significantly higher CH_4 content (98% vs. 60%). Thus, they concluded that two-chamber BES reactors are more suitable for continuous biogas upgrading in future research and application (Liu et al., 2017). Besides applied voltage, different membrane types could also influence the reactor's behaviour. Zeppilli et al. (2016) stated that in AEM-BES, 5.4 g/L·d of CO_2 was removed through the membrane due to molecular diffusion and ionic transport. In contrast, in the proton exchange membrane (PEM)-BES, only 3.2 g/L·d of CO_2 was removed by the osmotic overflow.

2.3.2.2. Biocathode materials. Currently, biocathode materials mainly include carbonaceous fabric materials, metal-based materials, and a combination of them. In a recent study, Zhen et al. (2018) compared five different carbon-based cathode materials (carbon stick, carbon twined with Ti wire or covered with carbon fiber, graphite felt, and carbon cloth) regarding their long-term performance in CO_2 electromethanogenesis. Results indicated that carbon stick covered with graphite felt enjoyed the most pronounced CO_2 reduction rate (90%), significantly higher than that of carbon stick (40%). Such phenomenon was owing to the proliferation of the robust electromethanogenic cathodic biofilm brought by the composite electrode, enabling more effective CO_2 utilization and electron uptake. Likewise, Kim et al. (2017) reported an improved CH_4 content (83%) obtained in a Ni-doped granular activated carbon biocathode than that of the control (73%).

2.3.2.3. Mineral addition for CO_2 sequestration. Besides reactor configurations and cathodic materials, which can promote the conversion rate of CO_2 into CH_4, the implementation of cheap chemicals coupled with BES can be an alternative for further CO_2 reduction and acceptable CH_4 content. In this context, J. Zhang et al. (2020a, 2020b), L. Zhang et al. (2020a, 2020b) and Y. Zhang et al. (2020) adopted wollastonite to achieve in-site CO_2 sequestration by forming calcite precipitates. As a result, they attained the ultimate CH_4 content of 95.9% (control without wollastonite: 90%), followed by an enhancement of CH_4 yield (16.9%) (J. Zhang et al., 2020a, 2020b; L. Zhang et al., 2020a, 2020b; Y. Zhang et al., 2020). Moreover, the generated precipitates barely aggregated on biocathode and did not significantly affect the morphology of cathode biofilm.

Collectively, BES can be introduced for biogas upgrading, especially when the electricity is coming from renewable sources (windmill, photovoltaic, etc.). However, most BES is temporarily limited to lab-scale, indicating the requirement of an improved upgrading efficiency (operation under high current density) before its full-scale application (Rousseau et al., 2020).

2.4. Additives

2.4.1. Ash

Sludge ash, a substance originating from municipal solid waste incineration, has been reported as an AD booster for improved biogas production (Montalvo et al., 2017; Yin et al., 2018). This is because it contains many trace metal elements (Zn, Ni, Fe, etc.) (Yin et al., 2019). Trace elements from ash are essential components of enzymes and cofactors in CH_4 production. Moreover, the high concentration of alkali oxide metals (CaO, MgO, etc.) enables the high buffer capacity of ash, which can efficiently prevent VFAs accumulation and provide a suitable environment for the growth of methanogens. Nevertheless, a high dosage of sludge ash into the system should be avoided, as it suppresses the activity of methanogens.

In comparison, stepwise addition of sludge ash is recommended. A study conducted by Yin et al. (2019) indicated a linear correlation between ash dosages and CO_2 sequestration. The gradual addition of ash may not stimulate the hydrolytic and acidifying enzyme activities immediately but favors the action of coenzyme F_{420}, compared to the instantaneous addition group. As a result, the stepwise addition of ash enriched the proportion of *Methanomassiliicoccus* (34.48%) and promoted amounts of CO_2 captured (Yin et al., 2019). After adding the sludge ash to the AD system, the CH_4 yield was improved by up to 26.6%, and the CH_4 content was boosted from 76.1% to 86.6% at thermophilic conditions (Yin et al., 2018). At mesophilic conditions, the CH_4 yield was strengthened by 39.2%, and the CH_4 content was enhanced from 69.1% to 79.4% by stepwise adding the ash (Yin et al., 2019).

2.4.2. Biochar

Biochar possesses a high surface area (105 m^2/g), a high ash content (45.2% dry weight), and high concentrations of oxide metals (14.2% K_2O, 3.9% CaO, and 4.2% MgO of the ash content, respectively) (Shen et al., 2015). The trace element (Fe, Co, Ni, Mn) in biochar could act as a cofactor to enhance the biogas upgrading process (Romero-Güiza et al., 2016; Wambugu et al., 2019). Moreover, the pores in biochar could adsorb CO_2 (Shen et al., 2015). Additionally, the microorganisms could attach to the surface of biochar to avoid being washed out. Owing to these advantages, biochar improves CH_4 concentration and production rate (Table 4) (Masebinu et al., 2019). The sludge-based biochar and ash share an identical element composition. However, the mechanisms for the enhancement are different. Notably, the introduction of biochar promotes the direct interspecies electron transfer (DIET) pathway (Fig. 2D and Fig. S2), which seldomly happens in ash-addition reactors (Yin et al., 2019). Moreover, the alkaline metals of biochar lead to a slight increase of pH (alkaline pH) in the biochar-added digesters, which converts excess CO_2 to bicarbonate/carbonate. The reaction would contribute to the accelerated carbonation reaction and high alkalinity. Linville et al. (2017) stated that biochar addition increased alkalinity as $CaCO_3$ increased from 2800 mg/L to 4800-6800 mg/L, providing process stability for AD of food waste. Besides, the material for biochar affects the CO_2 adsorption capacity. Linville et al. (2017) believed that fine walnut shell biochar (FWSB) had higher adsorption capacity than coarse walnut shell biochar (CWSB) due to the increased surface and ash content. The FWSB could remove 61% of the CO_2 (85.7% CH_4), whereas the CWSB could deduct 51% of the CO_2 (78.9% CH_4) produced from the AD process. In another study, the corn stover biochar-amended digesters produced near pipeline-quality biomethane (>90% CH_4 and <5 ppb H_2S), and CO_2 removal by up to 86.3% (Shen et al., 2015); Shen et al. (2017) and Wei et al. (2020) also introduced corn stover biochar to upgrade biogas and raised the CH_4 content to 95% and 87.3%, which were much higher than previously reported results. However, the negative effect of high dosages of biochar was unveiled due to high concentrations of mono- and divalent cations released from biochar into the digester. Another function of biochar is that it could act as a kind of carrier material for immobilized functional bacterial/methanogens (*Clostridia*, *Methanothermobacter*) and further increase the CH_4 production rate (increased by 20-70%) (Wei et al., 2020; Yang et al., 2020; J. Zhang et al., 2020b). Furthermore, keeping CO_2 in the bicarbonate/carbonate form in the aquatic phase encourages CH_4 formation via CO_2 reduction by hydrogenotrophic methanogens (Yang et al., 2020).

2.4.3. Zero valent iron (ZVI)

ZVI is another additive used in the AD system to upgrade biogas and increase CH_4 yield, which could provide Fe element as a cofactor of enzymes and promote the DIET pathway (both conductive material and indirectly provide conductive pili/cytochromes) (Fig. S2), thus enhancing more conversion of VFAs to CH_4 (Romero-Güiza et al., 2016; J. Zhang et al., 2020a, 2020b; L. Zhang et al., 2020a, 2020b; Y. Zhang et al., 2020). The anaerobic corrosion of ZVI (oxidized to Fe^{2+} or Fe^{3+}) donates electrons that can be used directly for CO_2 reduction by methanogens, or can lead to the formation of H_2, enhancing the abundance and activity of hydrogenotrophic methanogens. Additionally, its reductive character also decreases the oxidation-reduction potential, inducing a more favorable environment for the activity of anaerobic microorganisms (J. Zhang et al., 2020a, 2020b; L. Zhang et al., 2020a, 2020b; Y. Zhang et al., 2020). For instance, Feng et al. (Feng et al., 2014) claimed that the addition of ZVI effectively enhanced protein and cellulose decomposition. The CH_4 content was improved from 58.5% of the control reactor to 68.9%, and CH_4 production was enhanced by 43.5% (Feng et al., 2014). Charalambous and Vyrides (Charalambous and Vyrides, 2021) declared that the CH_4 content was increased to 97% compared to 74% for ZVI-free reactors. Other researchers reported that the total CH_4 production was increased by 123-231% compared to the control system without the ZVI amendment. The content of the headspace CH_4 was around 5 times higher than that of the control (Dykstra and Pavlostathis, 2017a; J. Zhang et al., 2020a). Besides, ZVI could remove H_2S ($S^{2-} + Fe^{2+} \rightarrow FeS \downarrow$) (J. Zhang et al., 2020a, 2020b; L. Zhang et al., 2020a, 2020b; Y. Zhang et al., 2020).

As mentioned above, ash, biochar, and ZVI all could increase CH_4 content, but the capacity of ash/biochar is limited. The biogas (80-86% CH_4) produced from the ash addition reaction still cannot meet the applications' requirements. Thus, ash, biochar, or ZVI could be a kind of additive used in other reactors (e.g., BES) to increase the CH_4 content further.

3. Comparison between different in-situ technologies and predominant methanogens

3.1. CH_4 content and H_2 conversion

CH_4 content is the primary indicator in the biogas upgrading technologies, representing the quality of biogas. Fig. 3 summarizes the CH_4

Table 4
Additives used for biogas upgrading.

Additives	Surface (m^2/g)	Pore volume (cm^3/g)	Diameter of pores (nm)	Reactor type	Substrate	Operation condition	Function of additives	Microbes	CH_4 (%)	Reference
Sludge incineration ash	14.2	0.047	Particle size: 0.1-0.3 mm	2 L (1.5 L) 100 rpm	Waste activated sludge	1.5 g/g DM 55 °C	① Stepwise addition of ash enhanced CH_4 production by 35.8% and facilitated CO_2 sequestration as calcite sediment ② Relative activity of coenzyme F_{420} was improved by 43.8% in stepwise addition.	Methanomassiliicoccus	79.4% (69.1% for control)	(Yin et al., 2019)
Sludge incineration ash	14.2	0.047	Particle size: 0.1-0.3 mm	Batch mode 2 L (1.5 L)	sludge	0.6-1.5 g/g DM 55 °C	① Optimal AD performance was achieved at ash dosage of 0.9 g/g DM. ② CH_4 production increased by up to 26.6%. ③ Ash accelerated sludge hydrolysis and fermentation. ④ CO_2 sequestration was linearly correlated with ashes dosage.	-	55-90%	(Yin et al., 2018)
Ash (thermal power plant)	–	–	Particle size: 0.8-2.36 mm	Batch 250 mL (200 mL)	Primary sludge and secondary sludge	35 °C	① Particle size of 1-1.4 mm had the highest degradation of organic matter and highest CH_4 production	-	28-96%	(Montalvo et al., 2017)
Corn stover biochar	302.6	0.11	5.9	Batch: 160 mL Continuous: CSTR 1.8 L(1.5 L)	Primary sludge	Biochar:1.82-3.06 g/g TS 55 °C HRT 15 days	① Accelerated primary sludge hydrolysis and enhanced CH_4 production (8.6-17.8%). ② Increased buffering capacity, conductively, and alleviated NH_3 inhibition.	Methanolinea Methanosaeta Rgodobacter Paludibacter Proteinclasticum	81.3-87.3% (67.5% for control)	(Wei et al., 2020)
Walnut shell biochar (WSB)	Fine WSB: 86.5 Coarse WSM: 792.7	Fine WSB: 0.16 Coarse WSM: 0.11	Fine WSB: 7.06 Coarse WSM: 3.67	Bench-scale 650 mL (550 mL)	Food waste	Biochar: 0.96-3.83 g/gVS 37 °C, 55 °C	① Increased alkalinity from 2800 to 4800-6800 mg/L ② The FWSB had a better CO_2 adsorption capacity of 61%	-	77.5-98.1%	(Linville et al., 2017)
Corn stover biochar	ND	ND	ND	0.5 L CSTR Two-stage	Sludge from WWTP	0.25-1.0 g/day R1: 37 °C, R2: 55 °C HRT 5-15 days	① Biochar addition increased CH_4 production rate by up to 25-37%. ② Increased fertilizer value of the digestate ③ CO_2 removal by up to 86.3%.	Methanosarcina Clostridia	95%(max)	(Shen et al., 2017)
Corn stover biochar	315.3	0.09	6.5	Two-stage	Sludge from WWTP	R1: 37 °C, HRT 1.2 days R2: 55 °C, HRT 12 days 1.82-3.64 g/g TS	① Biochar addition sequestered CO_2 and enhanced CH_4 yield. ② Biochar addition increased alkalinity and mitigated NH_3 inhibition.	-	>90%	(Shen et al., 2015)
Woody biochar Pinewood (PBC) White oak biochar (WOBC)	PBC: 310.19 WOBC: 296.81	PBC: 0.19 WOBC: 0.15	PBC: 5.07 WOBC: 4.92	600 mL (550 mL)	Sludge	37 °C, 55 °C PBC: 2.49-4.97 g/g DM WOBC: 2.2-4.4 g/g DM	① CO_2 sequestration by up to 32.4-66.2%. ② Biochar addition increased alkalinity, and alleviated free ammonia by up to 10.5%	-	79-92.3%	(Shen et al., 2016)
Digestate biochar(DB) and corn straw biochar (CSB)	DB: 334.91 CSB: 279.93	DB: 0.02-0.13 CSB: 0.02-0.11	2-50	Batch mode 300 mL	H_2:CO_2:N_2 = 4:1:1	3.0 g 37 °C 120 rpm	① Biochar as a carrier material for immobilized HM. ② CH_4 production increased by 20-70%	Methanobacterium Spirochaetes	-	(Yang et al., 2020)
ZVI	0.05	ND	Particle size: 0.2 mm	Two-stage 250 mL working volume	Alkaline-pretreated Waste activated sludge	35 °C, 120 rpm ZVI: 1, 4, 20 g/L	① ZVI effectively enhanced the decomposition of protein and cellulose. ② The activities of key enzymes increased 0.6-1time. ③ CH_4 production raised by 43.5%, and the sludge reduction ratio increased by 12.2%.	HM Homoacetogens	68.9% (58.5% for control)	(Feng et al., 2014)
ZVI (powder and scrap type)	–	–	–	Batch mode 250 mL (100 mL)	Cheese whey	36 °C, 100 rpm 25, 50, 100 g/L	① Addition of powder ZVI (25 g/L) or scrap ZVI (50 g/L) enhanced production and SCOD removal, resulting in the substantial conversion of VFAs. ② 50 g/L scrap ZVI was most cost-effective than 25 g/L powder ZVI.	-	97% (74% for control)	(Charalambous and Vyrides, 2021)

Note: '-' not mentioned; DM: dry matter.

content from the reviewed papers and is classified by different upgrading technologies. HFM combined with H_2 addition has the highest CH_4 content (92.5% on average). While HPAD performs slightly worse, with an average of 87% CH_4 content obtained. UASB $+H_2$, BES, and additives exhibited a similar CH_4 content (81-83%). Although the highest CH_4 content could increase up to 100% in H_2 with CSTR technology (Treu et al., 2018b), it has the lowest average CH_4 content due to the substrate and H_2 injection methods (NB is not discussed here as only one case is reported regarding H_2 addition). Compared with other technologies, HFM is more stable to produce high-quality biogas.

H_2 conversion efficiency (%) is an essential parameter in H_2 addition upgrading technologies. The HFM reactor has higher H_2 conversion efficiency (97%) than CSTR (83%) and UASB reactors (93%) (Fig. 3B). Presumably, the HFM reactor has higher CH_4 content (>92%) because more CO_2 could combine H_2 to generate CH_4 through the HM pathway. In these H_2 addition technologies, H_2 supplement needs extra equipment and energy (water electrolysis). Thus, using BES alone could be attractive because it combines H_2 production and biogas upgrading in one system. Or, BES coupled with pressure should be highlighted as it solves the gas-to-liquid transfer problem if the dominant pathway in BES is IET instead of DET (Kobayashi et al., 2017).

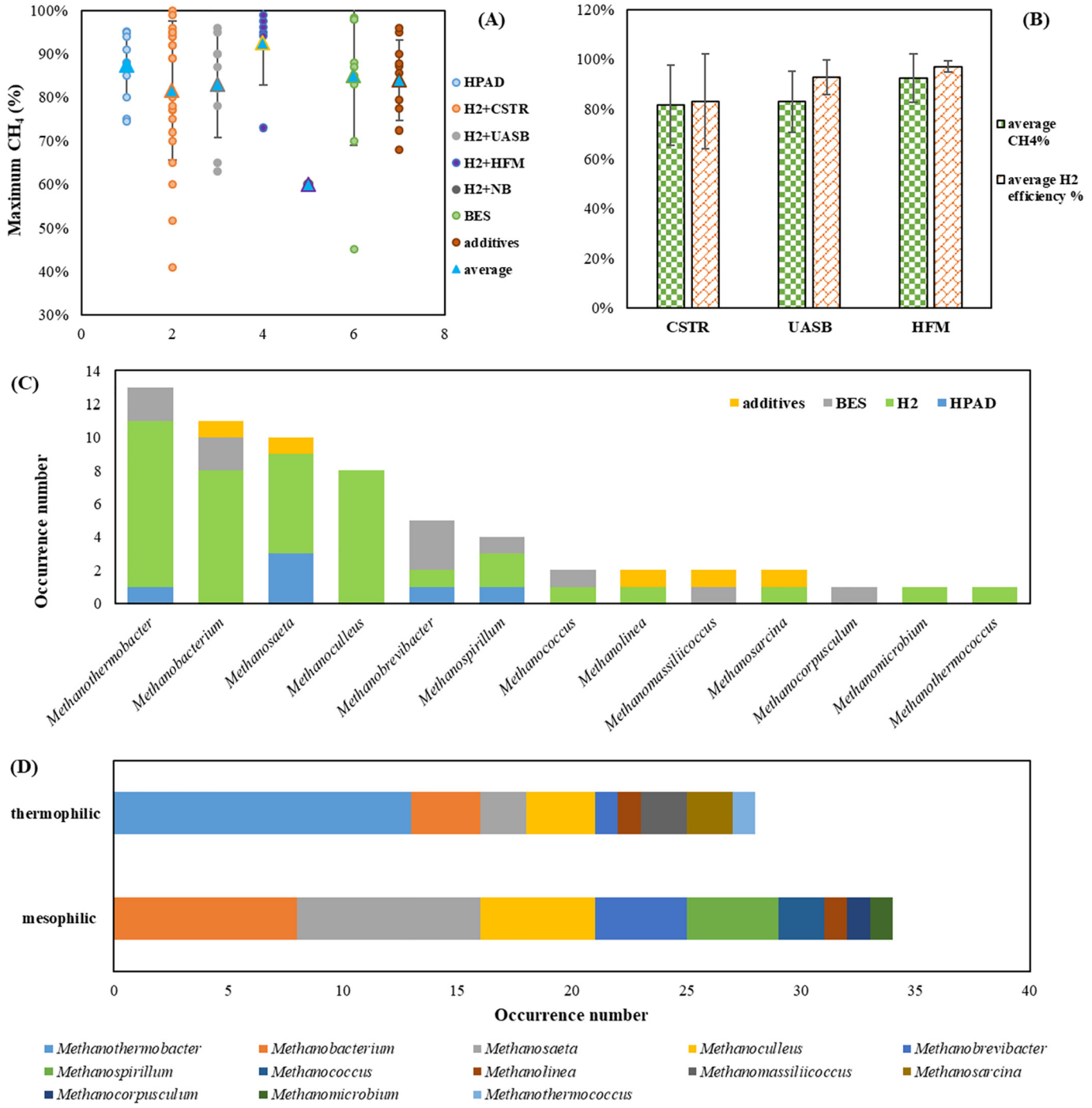

Fig. 3. Comparison of different in-situ upgrading technologies (A) Maximum CH_4 percentage (%) from various reviewed papers, (B) average CH_4 percentage and H_2 conversion efficiency (%) of different H_2 addition technologies, (C) the show-up frequency of methanogens (occurrence number, y-axis) among these reviewed papers, (D) The influence of operating temperature on the show-up frequency (occurrence number, x-axis) of methanogens under mesophilic and thermophilic condition, respectively among the reviewed papers).

3.2. Predominant methanogens in upgrading technologies

Microorganisms, especially methanogens, are key players in the biogas upgrading process. *Methanothermobacter*, *Methanobacterium*, *Methanosaeta*, *Methanculleus*, and *Methanobrevibacter* are the most predominant methanogens in these reviewed papers (Fig. 3C). Except for *Methanosaeta*, other methanogens could all produce CH_4 through the HM pathway. Therefore, the HM pathway plays a crucial role in the biogas upgrading process, especially in H_2 addition technologies. In comparison, the existence of acetoclastic *Methanosaeta* is probably due to homoacetogenic bacteria (e.g., *Treponeme*, *Clostridium ragsdalei P11*). In other words, homoacetogenic bacteria use H_2 and CO_2 to produce acetate, and then *Methanosaeta* consumes acetate to produce CH_4 (Wang et al., 2013; L. Zhao et al., 2020). Therefore, in some H_2/CO_2 addition reactors, acetate can also be identified (Omar et al., 2018; Omar et al., 2019; Sarker et al., 2020).

Methanothermobacter is a thermophilic methanogen that uses CO_2 and H_2 as the substrate to produce CH_4 and grows best at a temperature between 55 °C and 65 °C. In thermophilic reactors, *Methanothermobacter* can make up to 50% of the biomass. It is noteworthy that HM has a higher proportion in thermophilic reactors (20 cases reported) than in mesophilic ones (17 cases reported) (Fig. 3D). Some researchers reported that thermophilic conditions presented a higher CH_4 production rate and H_2 bioconversion rate in H_2 addition reactors (Figeac et al., 2020; Grimalt-Alemany et al., 2020; Luo and Angelidaki, 2012; Yun et al., 2017; Zhu et al., 2019b). In BES, *Methanobacterium* and *Methanobrevibacter* prevailed (Geppert et al., 2016).

4. Existing full-scale in-situ applications and future perspectives

Compared with a thorough investigation of large-scale ex-situ technologies, relevant examination of in-situ technologies, mainly technical and economic feasibility analysis, is scarce for the moment. However, some researchers/companies have devoted themselves to bridge the gap between lab-scale in-situ trials and corresponding large-scale installations.

For H_2 addition in-situ technology, Jensen et al. (2018) firstly coupled the venturi-based H_2 injectors (Landia®GasMix) with a full-scale manure-based AD digester (working volume 1110 m^3) for in-situ biogas upgrading. They affirmed the positive correlation ($r = 0.95$) between H_2 consumption efficiency (10-26%) and H_2 injection rate (20-65 m^3/h). They highlighted the significance of gas-to-liquid mass transfer, which can be improved by a high H_2 injection rate, small gas bubbles, and improved recirculation rate (Jensen et al., 2018). However, they stated that the current H_2 consumption rate disabled venturi-based technology to constitute a stand-alone in-situ upgrading system, requiring substantial improvement. The same group modified the gas injectors into the GasMix ejector system and attained a pronounced H_2 consumption efficiency (49%), with a maximum CH_4 content of 65% (Jensen et al., 2021). Concomitantly, the reaction heat of the upgrading process entailed significant savings regarding the heat of the biogas reactor. Despite those merits, the incomplete H_2 transfer implied a necessity for a subsequent ex-situ technology for final biogas upgrading. Researchers should examine whether or not such in-situ technology could serve as a low-cost first step in the biogas upgrading system to reduce the necessary capacity of subsequent ex-situ upgrading technologies in the future.

For HPAD, our group is currently collaborating with a Dutch company (BAREAU; https://bareau.nl/en/for-professionals/) on the establishment of a medium-scale HPAD in a wastewater treatment plant for simultaneous biogas upgrading and nitrogen removal (by annomax) (Basic information of HPAD: volume: 1 m^3; pressure: 19-20 bar; H_2 injection rate: 2000 L/d; pH: 6.5-7.5). The output-pressured biogas contains 95% of CH_4 that can be directly injected into the gas grid if the contaminants (H_2S, NH_3) are adequately removed. Furthermore, we will consider producing H_2 from the electrolysis of AD effluent or wastewater via BES. Relevant technical and economic assessment is in progress to see if these two compatible technologies can make HPAD competitive in the market.

For BES, sole large-scale BES has not yet been reported, probably due to its technical incompetence to make the process economically feasible. According to the estimated capital costs of BES (reactor type: single-cell; current density: 1000 A/m^3), the capital costs (€/kg COD) of a BES is 8, which is significantly higher than the product revenue (0.2 €/kg COD) (Rozendal et al., 2008). Such a considerable gap requires a breakthrough in reactor configurations, anode and cathode materials, solution conductivity, and screening of efficient electroactive microorganisms. Despite the obstacles confronted by BES, a combination of BES for H_2 production (water electrolysis) and subsequent biomethanation (H_2 addition technology) might be a viable effort. Under such circumstances, Cambrian Innovation (http://cambrianinnovation.com/resources/) and Electrochaea (http://www.electrochaea.com/) are two leading companies that made progress by developing industrially applicable, bioelectrically enhanced anaerobic treatment systems. One commercial project (with a basis for the design of 1 MW) in Solothurn, Switzerland established by Electrochaea has accomplished several goals: 1) stable operation of >1200 h, CH_4 production >13,800 Nm^3; 2) excellent output gas quality (>97% CH_4 in product gas) that exceeds standards for grid injection; 3) Load factor tests: 0%-100% capacity testing achieved. These achievements will inspire the corresponding efforts for more efficient development of BES systems, at either lab-scale principle analysis or large-scale application. The larger plants built by these companies will be crucial for a techno-economic assessment of the technology, especially when the electricity is readily available from renewable energy facilities (windmill, photovoltaic, tidy, etc.). Moreover, an

Table 5
The merits and challenges of different types of biogas upgrading technologies.

Technologies	Merits	Challenges
H_2 injection	• High H_2 conversion rate and high CH_4 content. • Versatile reactor configurations and can be combined with other in-situ technologies. • Applicable at full-scale AD plant.	• pH inhibition, pH increases up to >8.5 due to bicarbonate consumption. • The limited the gas-to-liquid mass transfer rate. • High H_2 level inhibits HM, and acetate accumulates. • Require external addition of H_2. • High capital and operation costs (e.g., HFM).
High pressure	• Efficient removal of gas impurities (CO_2, H_2S, and NH_3). • Increase the gas-to-liquid transfer rate. • Close to the full-scale application (coupled with H_2 addition)	• Automatic system control, safety. • A large amount of CO_2 in the liquid phase causes pH decline.
BES	• H_2 produced within the reactor, with little or no external H_2. • Act as surplus renewable energy storage in terms of CH_4. • Promotion of hydrolysis, acetogenesis, and methanogenesis. • Environmentally-friendly	• Limited gas-to-liquid mass transfer rate. • Limited to lab-scale (can't be operated at high-current density yet). • Not economically feasible yet.
Additives	• Simple set-up • Trace element as cofactors for improved methanogenesis. • Carrier for microorganisms to attach and further increase the CH_4 production rate. • Increase buffering capacity, conductivity and alleviate NH_3 inhibition.	• A large quantity of heavy metals is present in the reactors, which may adversely affect methanogenesis. • Need cost-effective and environmental-friendly additives.

investment screening on the spatial deployment of two types of PtG biogas upgrading installations (biogas upgrading and CO_2 methanation) has been carried out on a national scale in Danish (Nielsen and Skov, 2019). They concluded that biogas upgrade paths had the lowest costs of the two approaches (3.1 M€ for biogas upgrade vs. 7.0 M€ for CO_2 methanation) at the current cost level. More importantly, the method could be an excellent reference for other countries, given the availability of the same type of data.

Unfortunately, a relevant large-scale sample of NB technology has not been documented yet. But such upgrading holds great promise as it may fix the frustrating gas-to-liquid problem in H_2 addition technology. Thus, a potential combination between NB and H_2 addition technology would be appealing in large-scale applications. For example, NB can be used in Jensen's research, as mentioned above.

For additives applied in biogas upgrading, Charalambous and Vyrides (Charalambous and Vyrides, 2021) proposed a simulated economic calculation of ZVI-mediated biogas upgrading process treating chasse whey (29,638 m^3/y). Compared with the revenue of conventional AD process (808 €), the introduction of ZVI (50 kg/m^3) promoted the CH_4 content (95%), thus contributing to annual revenue of 28,376 €. Such in-situ technology will gain more interest since the source of ZVI is readily available (for example, waste iron powder from an iron factory).

5. Summary and concluding remarks

A list of merits and challenges among the available biogas in-situ upgrading technologies is presented in Table 5. Adding extra H_2 is appealing because it can further increase the CH_4 yield and is easy to apply. In addition, the practical application of H_2-added technology exists, as discussed above. For HPAD, its utilization is promising, and its future full-scale application is approachable (Table 5). We suggest combining additives and other in-situ technologies for additives technology since additives alone may not present admirable CH_4 content (Fig. 3B). While for BES, temporarily, it can't act as a stand-alone in-situ technology due to its practical limitation (such as operating at high current density). Noticeably, H_2 addition technologies still require extra equipment to produce H_2. In this case, the involvement of BES in H_2 addition technology could be reasonable, which combines H_2 production and CH_4 production in one system.

Concluding remarks are summarized as follows:

(1) pH and alkalinity are critical chemical parameters in upgrading technologies.
(2) Hydrogenotrophic methanogens are vital archaea in in-situ biogas upgrading technologies.
(3) H_2 addition technologies are currently most suitable for biogas upgrading due to their highest CH_4 content, CH_4 yield, H_2 conversation rate, and ready-to-apply potential.
(4) Currently, individual HPAD or BES can't stand out for biogas upgrading, especially for industrial applications.
(5) The combo between H_2-addition technology and HPAD/BES deserves more investigations.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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