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Recent progress towards in-situ biogas upgrading technologies

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HIGHLIGHTS

- In-situ biogas upgrading technologies are reviewed.
- H₂-addition technology is the most prominent in-situ technology.
- Hydrogenotrophic methanogens are critical microorganisms in upgrading technologies.
- HFM reactor shows the highest average CH₄ content (92.5%).
- The combination between H₂-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 H₂ 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 H₂-addition technology, with the highest average CH₄ content obtained (HFM: 92.5%) and one of the few full-scale cases reported (Danish GasMix ejector system: 1110 m³). Meanwhile, newly pop-up technology such as HPAD delivers appropriate CH₄ 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 H₂-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 CH₄ content or constraint full-scale application behaviors (disability to operate at high current density). However, its combination with H₂-

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 CH₄.

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Contents

1. Introduction	2
2. Different technologies used for in-situ biogas upgrading	3
2.1. H ₂ addition	3
2.1.1. Mechanism, challenges, and opportunities	3
2.1.2. Existing reactor set-ups for H ₂ -added biogas upgrading	7
2.2. High-pressure anaerobic digestion (HPAD)	10
2.2.1. Mechanism	10
2.2.2. HPAD applications, challenges, and opportunities	10
2.3. Bioelectrochemical system (BES)	14
2.3.1. Mechanism	14
2.3.2. BES applications	14
2.4. Additives	15
2.4.1. Ash	15
2.4.2. Biochar	15
2.4.3. Zero valent iron (ZVI)	15
3. Comparison between different in-situ technologies and predominant methanogens	15
3.1. CH ₄ content and H ₂ conversion	15
3.2. Predominant methanogens in upgrading technologies	18
4. Existing full-scale in-situ applications and future perspectives	18
5. Summary and concluding remarks	19
Funding	19
Declaration of competing interest	19
Acknowledgment	19
Appendix A. Supplementary data	19
References	19

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 CH₄ and 30–50% of CO₂ as well as some trace components such as H₂S, N₂, O₂, CO, and NH₃ (Adnan et al., 2019; Angelidaki et al., 2018; Appels et al., 2011).

Except for CH₄, other gasses in biogas are redundant, as they don't promote energy generation. It is believed that biogas with higher than 90% of CH₄ increases its heating value and enables its quality as natural gas (Table S1) (Bassani et al., 2016). Therefore, high concentrations of

CO₂ and trace contaminants (H₂S, N₂, O₂, water, and NH₃) limit the application of biogas. Thus, during the practical upgrading process, the removal of CO₂ is the primary goal. Meanwhile, such a method is also accompanied by impurities removal (in most cases H₂S and NH₃) 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 ≥ 500 m³ 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 m³ biogas/day (Adnan et al., 2019; Sarker et al., 2018). For medium (500 > Q ≥ 150 m³ biogas/day) and small-scale (150 > Q ≥ 5 m³ 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*, *Methanoculleus* 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) H₂ 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; Dykema et al., 2020). Moreover, the addition of H₂ directly to AD also switches the methanogenic metabolic pathway towards the HM pathway (Table 1). In H₂-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 H₂ and CO₂ to CH₄ (Dahl Jønson et al., 2020).

Table 1
Summary of H₂ 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 Hom, 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%–98%	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	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 ₄ Cl (1 and 7 g NH ₄ ⁺ -N/L)	OLR: 3–8 g VS/L/d 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 was best to gas high CH ₄ content.	<i>Acetanaerobium noterae</i> 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 homoacetogenesis.	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. Pressure increased the H ₂ mass transfer flux.	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		<i>Methanothermobacter thermotrophicus</i>	<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 reactor 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: <i>Methanothermobacter wolfei</i> Two-stage: <i>Coprothermobacter proteolyticus</i> <i>Anaerobaculum hydrogeniformans</i>	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 , CO ₂ 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: <i>Acetobacterium</i> sp., <i>Methanospirillum hungatei</i> 60 °C: <i>Thierricola carboxydiphila</i> ,	-	0.24 mol/mol H ₂	81-92%	(Grimalt-Alemany et al., 2020)

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 ($\text{pH} > 8$), 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):

$$r_t = 22.4k_{\text{La}}(\text{H}_{2\text{gTh}} - \text{H}_{2\text{l}}) \quad (4)$$

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); $\text{H}_{2\text{gTh}}$ is H_2 concentration in the gas phase (mol/L); $\text{H}_{2\text{l}}$ 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
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. ④The efficiency was better at 65 °C than 55 °C. ⑤Reseeding of the process was required as when inoculum ages, efficiencies decreased ⑥Acetate accumulation increased at increasing OLR. ⑦Homoacetogenesis consumed up to 60% of H ₂ at a low CO ₂ level and became less critical after repeated H ₂ injections.	Methanothermobacter sp. 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	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	Batch mode 1.4 L (0.3 L) 38 °C HRT 20 days	①Acetate accumulation increased at increasing OLR. ②Homoacetogenesis 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 mmol/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%	(Dagloglu 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)

UASB	H ₂ :CO ₂ = 4:1	mL) 37 °C, 55 °C, (6.3 L)	①The highest performance achieved by applying gas recycle under thermophilic conditions.	<i>Methanoculleus chikagoensis</i> (37 °C) <i>Methanothermococcus</i> (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.	-	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	③Headspace recirculation improved H ₂ consumption ④High rate methanogenesis was observed without gas-liquid agitation.	<i>Methanosetaeaceae</i> <i>Methanobacteriales</i>	-	<40 v/v/d	<90%	(Savvas et al., 2017)
Ceramic membrane	H ₂ :CO ₂ = 4:1 loading rate 10–30 L H ₂ /m ² /d	Pilot-scale, 60 L 55 °C	⑤More active methanogens existed on biofilm. ⑥Ceramic MBR could efficiently transfer H ₂ to CH ₄ , K _A was 268/h.	<i>Methanothermobacter thermotrophicus</i>	95%	0.22 m ³ CH ₄ /m ³ H ₂	-	(Alfaro et al., 2018)
HFM	H ₂ :CO ₂ = 4:1	40 L (31 L) 55 °C	⑦CH ₄ production rate was 0.18 L/m ³ ; H ₂ transform rate was 95%. ⑧H ₂ mass transfer to the liquid phase was identified as the limiting step for the conversion.	-	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	②Gas sparging through a membrane module can efficiently increase the gas-to-liquid transfer rate. 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%.	<i>Methanoculleus</i> sp. <i>Methanospirillum</i> sp. <i>Methanolinea</i> 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	③Gas recirculation and H ₂ supply through a submerged membrane for biogas upgrading. ①Acetate and ethanol generated by homoacetogen during the upgrading process. ②Increase P _{H2} could help further increase CH ₄ content.	<i>Methanobacterium</i> sp. <i>Clostridium ragsdalei</i> 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	3 L (2 L), CSTR 37 °C, 200 rpm HRT 10 days	The optimum ammonia nitrogen for biogas upgrading was 5.5 g/L	<i>Methanobacterium</i> <i>Methanoseta</i>	91–99%	CH ₄ yield increase 35.2–64%	94.1%	(Li et al., 2020)
HFM	NH ₄ Cl (3.5–6.5 g/L) Coke oven gas (92% H ₂ , 8% CO) Sewage sludge	7.85 L (7 L) 55 °C	①HM and AM existed in the reactor; HM existed in the liquid part, and AM lived on biofilm. ②pH increased after H ₂ addition.	<i>Methanoculleus</i> <i>Methanoseta</i> <i>Treponema</i> (homoacetogenic)	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 submerge 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 physico-chemical 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.

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%	(Diaz 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 Methanoseta Methanoseta concilii Methanobrevibacter	92% (52.4% for control) 88% (64% for control)	(Kim et al., 2021) (J. Zhao et al., 2020; L. Zhao et al., 2020)
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	-	-	(Ceron-Chafia 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	-	-	(Lindeboom et al., 2011)
Single-stage, batch	NaCH ₃ COO·3H ₂ O	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 sequester 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).	Methanoseta concilii; Methanobacterium formicum	-	(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	A mixture of grass and maize	37 °C	The initial pressures didn't significantly influence pressure increase, degradation of organics, and SMY.	-	-	(Lemmer et al., 2017; Merkle et al., 2017a)
Methane filter	silage hydrolysate	10, 20, 30 bar, and 1, 50, 100 bar		-	-	
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	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	①Best performance was 9 bar and 12.5 kg m ⁻³ d ⁻¹ . ②Higher OLR became unstable.	-	74.5%	(Chen et al., 2014b)
Two-stage, Biofilm reactor	Food waste	1.5, 9 bar 37 °C, continuous 3–17 bar	pH decreased from 7.22 to 6.98, and COD removal decreased 93 to 80%, the SMY decreased.	Methanoseta, 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 Thermicola	-	(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)	Sodium acetate, Porous carbon felt, anolyte	CO ₂ , Porous carbon felt, Catholyte, -0.8 V, 1.65 atm CH ₄ produce Graphite felt Substrate: CO ₂ CH ₄ produce -0.85, -0.90, -0.95 V	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 O ₂ produce	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 ₂ SO ₄ solution (anolyte), Indium 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) 35 °C Batch mode 100-2500 mV 35 °C Batch mode	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	420 mL; -600, -800 mV Synthetic gas (55% CH ₄ , 45% CO ₂)	35 °C Batch mode 100-2500 mV 35 °C Batch mode	①Electrode promoted lignocellulose degradation ②Electric polarity was: cathode > anode > blank ③Cathodic micro-voltage was: 250 mV > 500 mV > 100 mV O ₂ diffusion from the anode compartment, which decreased the reactor efficiency.	-	84% (77% control)	(Qu et al., 2014)
Two-chamber + CEM	11-75% (CE)	410 mL H ₂ O as electron donor O ₂ produce	Glucose Carbon felt 0 to -1.2 V	Single-chamber 55 °C, 400 mL (350 mL) Two-chamber 55 °C, 500 mL (350 mL) 0.5 L for each; Continuous; HRT 6.8 h; 23 °C 38 °C, 600 mL (400 mL)	①Single chamber had higher VFAs concentration, especially for propionate. ②Two-chamber reactor had higher CH ₄ content and more stable.	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	Stainless steel mesh Sodium acetate NaHCO ₃ -800 mV	Single-chamber 55 °C, 400 mL (350 mL) Two-chamber 55 °C, 500 mL (350 mL) 0.5 L for each; Continuous; HRT 6.8 h; 23 °C 38 °C, 600 mL (400 mL)	①No significant differences between different inocula for CH ₄ production and CH ₄ recovery efficiency. ②Hydrogenotrophic methanogens were dominated in the biocathode. The CH ₄ yield was enhanced by 48%. The CH ₄ production rate increased 1.65 times.	Methanobrevibacter	83% CH ₄ production rate 0.23 L/m ³ /d	(Cerrillo et al., 2017)
Single-chamber	-	Stainless steel mesh Glucose, xylose, cellulose	Stainless steel mesh Carbon cloth	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 BES + H ₂ injection AD1-MEC-AD2	66.7% (Energy efficiency)	Acetate (10 g/L) Stainless steel 0.4, 1.0 V Carbon cloth	Carbon cloth biogas and H ₂ : CO ₂ = 4:1	180 mL Batch mode AD1, 2.3 L MEC: 2.1 L (0.5–1.5 V) AD2, 0.8 L, 37 °C	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%. ③Combination of MEC with AD improved AD performance. ④H ₂ circulation contributed to the high quality and yield of CH ₄ .	Methanospirillum	98%	(Bo et al., 2014)
BES	6.7–25.4% (CE)	Graphite fabric sheet with multiwall carbon nanotube and Ni		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. The methane-production rate of the reactors showed an applied-voltage dependence.	<i>Methanocorpusculum bavaricum</i>	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		<i>Clostridium quinii</i>	CH ₄ production rate 168 mmol/m ² /d	(Kobayashi et al., 2017)
Two-chamber + PEM	85.2% (CE)	Carbon paper FeSO ₄ ·7H ₂ O	Carbon paper CO ₂	700 mV 0.15 L for each, Batch & Continuous, 37 °C	①This system combined biogas purification, H ₂ S removal, and sulfur recovery. ②Fe ³⁺ could simulate sulfide removal and CH ₄ formation	<i>Methanococcus maripaludis</i> 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 ₂ S and increase CH ₄ content. ②3 V was better for H ₂ S 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 ₂ S) = 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 ₂ S absorption in the alkaline catholyte removed up to 98% of the incoming H ₂ S.	–	>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 ² /d	(Cerrillo et al., 2018)
H-cell reactor	10% (Nitrogen removal efficiency)	titanium mesh drums Wastewater	Steel brushes	<550 mV No membrane Batch mode 0.86 L 0.2, -0.1 V	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)	(Siebert and Tan, 2019)
Two-chamber + AEM	105 mmol/d 85 (CE)	Anolyte Acetate	800 g graphite granules Catholyte CO ₂ N ₂ = 3:7		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%	(Zeppilli et al., 2016)
Two-chamber + PEM	62 mmol/d 53% (CE)						83 meq/Ld 81%	
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 electromethanogenic 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 CH₄ production per unit cathode surface area.^b The volume in parenthesis is the working volume of the reactor.

HPAD to convert the surplus dissolved CO₂ into CH₄ (Kobayashi et al., 2017). Another option is the combination of HPAD and H₂ 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 CO₂ under high pressure could strongly affect the activity (SMY decreased by 30%) and composition of the methanogenic community (50% *Methanosaeta* 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 CO₂ is still a significant bottleneck for the wide distribution of this technique. Conversion of the dissolved CO₂ into CH₄ could be ideal for solving this problem and decreasing CO₂ emissions. Reduction of dissolved CO₂ could be achieved through the direct addition of H₂ 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: $C_xH_yO_zN + (2x-z) H_2O \rightarrow xCO_2 + [y + (2x-z)] [e^- + H^+] + NH_3$ (Eq. (6))), while the reduction of CO₂ to CH₄ 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): H₂ produced at the cathode at the expense of H⁺ reduction, which is catalyzed by extracellular enzymes: $2H^+ + 2e^- \rightleftharpoons H_2$ (Eq. (7)), H₂ can then be captured by hydrogenotrophic methanogens for CO₂ 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, H₂ 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 CO₂ into CH₄ by physical contact on cathode without the intermediate production of H₂. $CO_2 + 8H^+ + 8e^- \rightleftharpoons CH_4 + 2H_2O$ (Eq. (8)) (Cheng et al., 2009; Hagos et al., 2018) (Fig. S2D). 3) Homoacetogenesis plus AM: H₂ and CO₂ are first converted into acetate by homoacetogenic bacteria, and then the formed acetate is degraded by AM to generate CH₄ (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 H₂ injection technologies to a certain extent. In the subsections, factors influencing the efficiency of the conversion of CO₂ into CH₄ (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 CH₄ 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 CH₄ content could exceed 98%, and CH₄ 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 O₂ 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, H₂S, NH₄⁺) 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 NH₄⁺ (136 mV) can be much lower than for the water splitting (1.23 V) with appropriate catalysts in place (Table S2) (Siebert and Tan, 2019). The AD process and BES integration have been tested using real effluents as anodic substrates (Zeppilli et al., 2017), allowing simultaneous N₂ production at the bioanode and CO₂ removal at the biocathode. In another study, Fu et al. (2020) used a single BES reactor to treat synthetic wastewater for simultaneously CO₂ reduction and sulfur recovery. This system comprises a ferrous ion (Fe²⁺) mediated abiotic anode for H₂S oxidation and a methanogen-inoculated biocathode for CO₂ removal. In the anodic chamber, H₂S was removed and selectively converted into elemental sulfur particles. The CH₄ production rate of 20.6 μmol/h and high upgrading level (98.3% CH₄) 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 CH₄ yield (CH₄ yield was enhanced by 40% vs. 10% compared to control), and significantly higher CH₄ 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 CO₂ 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 CO₂ 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 CO₂ electromethanogenesis. Results indicated that carbon stick covered with graphite felt enjoyed the most pronounced CO₂ 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 CO₂ utilization and electron uptake. Likewise, Kim et al. (2017) reported an improved CH₄ content (83%) obtained in a Ni-doped granular activated carbon biocathode than that of the control (73%).

2.3.2.3. Mineral addition for CO₂ sequestration. Besides reactor configurations and cathodic materials, which can promote the conversion rate of CO₂ into CH₄, the implementation of cheap chemicals coupled with BES can be an alternative for further CO₂ reduction and acceptable CH₄ 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-situ CO₂ sequestration by forming calcite precipitates. As a result, they attained the ultimate CH₄ content of 95.9% (control without wollastonite: 90%), followed by an enhancement of CH₄ 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 CH₄ 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 CO₂ sequestration. The gradual addition of ash may not stimulate the hydrolytic and acidifying enzyme activities immediately but favors the action of coenzyme F₄₂₀, 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 CO₂ captured (Yin et al., 2019). After adding the sludge ash to the AD system, the CH₄ yield was improved by up to 26.6%, and the CH₄ content was boosted from 76.1% to 86.6% at thermophilic conditions (Yin et al., 2018). At mesophilic conditions, the CH₄ yield was strengthened by 39.2%, and the CH₄ 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 m²/g), a high ash content (45.2% dry weight), and high concentrations of oxide metals (14.2% K₂O, 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 CO₂ (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 CH₄ 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 CO₂ 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 CaCO₃ 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 CO₂ 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 CO₂ (85.7% CH₄), whereas the CWSB could deduct 51% of the CO₂ (78.9% CH₄) produced from the AD process. In another study, the corn stover biochar-amended digesters produced near pipeline-quality biomethane (>90% CH₄ and <5 ppb H₂S), and CO₂ 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 CH₄ 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 CH₄ production rate (increased by 20–70%) (Wei et al., 2020; Yang et al., 2020; J. Zhang et al., 2020b). Furthermore, keeping CO₂ in the bicarbonate/carbonate form in the aquatic phase encourages CH₄ formation via CO₂ 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 CH₄ 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 CH₄ (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 Fe²⁺ or Fe³⁺) donates electrons that can be used directly for CO₂ reduction by methanogens, or can lead to the formation of H₂, 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 CH₄ content was improved from 58.5% of the control reactor to 68.9%, and CH₄ production was enhanced by 43.5% (Feng et al., 2014). Charalambous and Vyrides (Charalambous and Vyrides, 2021) declared that the CH₄ content was increased to 97% compared to 74% for ZVI-free reactors. Other researchers reported that the total CH₄ production was increased by 123–231% compared to the control system without the ZVI amendment. The content of the headspace CH₄ was around 5 times higher than that of the control (Dykstra and Pavlostathis, 2017a; J. Zhang et al., 2020a). Besides, ZVI could remove H₂S (S²⁻ + Fe²⁺ → FeS ↓) (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 CH₄ content, but the capacity of ash/biochar is limited. The biogas (80–86% CH₄) 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 CH₄ content further.

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

3.1. CH₄ content and H₂ conversion

CH₄ content is the primary indicator in the biogas upgrading technologies, representing the quality of biogas. Fig. 3 summarizes the CH₄

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 mm	Batch: 160 mL Continuous: CSTR	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, conductivity, and alleviated NH ₃ inhibition.	Methanolinea Methanoseta 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	3.67 ND	1.8 L (1.5 L) 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	315.3	0.09	6.5	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				Two-stage	Sludge from WWTP	R1: 37 °C, HRT 12 days R2: 55 °C, HRT 12 days	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	PBC: 310.19 WOB: 296.81	PBC: 0.19 WOB: 0.15	PBC: 5.07 WOB: 4.92	600 mL (550 mL)	Sludge	1.82–3.64 g/g TS 37 °C, 55 °C PBC: 2.49–4.97 g/g DM WOB: 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 mm	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 0.6–1 time. 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 COD 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 H₂ addition has the highest CH₄ content (92.5% on average). While HPAD performs slightly worse, with an average of 87% CH₄ content obtained. UASB + H₂, BES, and additives exhibited a similar CH₄ content (81–83%). Although the highest CH₄ content could increase up to 100% in H₂ with CSTR technology (Treu et al., 2018b), it has the lowest average CH₄ content due to the substrate and H₂ injection methods (NB is not discussed here as only one case is reported regarding H₂ addition). Compared with other technologies, HFM is more stable to produce high-quality biogas.

H₂ conversion efficiency (%) is an essential parameter in H₂ addition upgrading technologies. The HFM reactor has higher H₂ conversion efficiency (97%) than CSTR (83%) and UASB reactors (93%) (Fig. 3B). Presumably, the HFM reactor has higher CH₄ content (>92%) because more CO₂ could combine H₂ to generate CH₄ through the HM pathway. In these H₂ addition technologies, H₂ supplement needs extra equipment and energy (water electrolysis). Thus, using BES alone could be attractive because it combines H₂ 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 CH₄ percentage (%) from various reviewed papers, (B) average CH₄ percentage and H₂ conversion efficiency (%) of different H₂ 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 bio-gas upgrading process. *Methanothermobacter*, *Methanobacterium*, *Methanosaeta*, *Methanoculleus*, and *Methanobrevibacter* are the most predominant methanogens in these reviewed papers (Fig. 3C). Except for *Methanosaeta*, other methanogens could all produce CH₄ through the HM pathway. Therefore, the HM pathway plays a crucial role in the bio-gas upgrading process, especially in H₂ addition technologies. In comparison, the existence of acetoclastic *Methanosaeta* is probably due to homoacetogenic bacteria (e.g., *Treponema*, *Clostridium ragsdalei* P11). In other words, homoacetogenic bacteria use H₂ and CO₂ to produce acetate, and then *Methanosaeta* consumes acetate to produce CH₄ (Wang et al., 2013; L. Zhao et al., 2020). Therefore, in some H₂/CO₂ 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 CO₂ and H₂ as the substrate to produce CH₄ 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 CH₄ production rate and H₂ bioconversion rate in H₂ 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 H₂ addition in-situ technology, Jensen et al. (2018) firstly coupled the venturi-based H₂ injectors (Landia®GasMix) with a full-scale manure-based AD digester (working volume 1110 m³) for in-situ biogas upgrading. They affirmed the positive correlation ($r = 0.95$) between H₂ consumption efficiency (10–26%) and H₂ injection rate (20–65 m³/h). They highlighted the significance of gas-to-liquid mass transfer, which can be improved by a high H₂ injection rate, small gas bubbles, and improved recirculation rate (Jensen et al., 2018). However, they stated that the current H₂ 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 H₂ consumption efficiency (49%), with a maximum CH₄ 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 H₂ 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 m³; pressure: 19–20 bar; H₂ injection rate: 2000 L/d; pH: 6.5–7.5). The output-pressured biogas contains 95% of CH₄ that can be directly injected into the gas grid if the contaminants (H₂S, NH₃) are adequately removed. Furthermore, we will consider producing H₂ 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/m²), 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 H₂ production (water electrolysis) and subsequent biomethanation (H₂ 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, CH₄ production >13,800 Nm³; 2) excellent output gas quality (>97% CH₄ 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	<ul style="list-style-type: none"> High H₂ conversion rate and high CH₄ content. Versatile reactor configurations and can be combined with other in-situ technologies. Applicable at full-scale AD plant. 	<ul style="list-style-type: none"> pH inhibition, pH increases up to >8.5 due to bicarbonate consumption. The limited the gas-to-liquid mass transfer rate. High H₂ level inhibits HM, and acetate accumulates. Require external addition of H₂. High capital and operation costs (e.g., HFM). Automatic system control, safety. A large amount of CO₂ in the liquid phase causes pH decline.
High pressure	<ul style="list-style-type: none"> Efficient removal of gas impurities (CO₂, H₂S, and NH₃). Increase the gas-to-liquid transfer rate. Close to the full-scale application (coupled with H₂ addition) 	
BES	<ul style="list-style-type: none"> H₂ produced within the reactor, with little or no external H₂. Act as surplus renewable energy storage in terms of CH₄. Promotion of hydrolysis, acetogenesis, and methanogenesis. Environmentally-friendly 	<ul style="list-style-type: none"> 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	<ul style="list-style-type: none"> Simple set-up Trace element as cofactors for improved methanogenesis. Carrier for microorganisms to attach and further increase the CH₄ production rate. Increase buffering capacity, conductivity and alleviate NH₃ inhibition. 	<ul style="list-style-type: none"> 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 CO₂ 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 CO₂ 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 H₂ addition technology. Thus, a potential combination between NB and H₂ 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 cheddar whey (29,638 m³/y). Compared with the revenue of conventional AD process (808 €), the introduction of ZVI (50 kg/m³) promoted the CH₄ 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 H₂ is appealing because it can further increase the CH₄ yield and is easy to apply. In addition, the practical application of H₂-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 CH₄ 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, H₂ addition technologies still require extra equipment to produce H₂. In this case, the involvement of BES in H₂ addition technology could be reasonable, which combines H₂ production and CH₄ 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) H₂ addition technologies are currently most suitable for biogas upgrading due to their highest CH₄ content, CH₄ yield, H₂ conversion 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 H₂-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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