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Recent trends and advances in biogas upgrading and methanotrophs-based valorization

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ABSTRACT

The global quest for sustainability in industrial activities and waste management has recently boosted biogas production worldwide. However, the rapid decrease in the levelized cost of electricity of renewable energies will soon entail electricity prices from biogas much higher than those from solar or wind power. In this context, the upgrading of biogas into biomethane represents an alternative to on-site biogas combustion. Membrane separation technology is rapidly dominating the biogas upgrading market and displacing scrubbing and adsorption technologies driven by the recent breakthroughs in material science. Similarly, biogas biorefineries have recently emerged as an innovative platform for biogas valorization capable of biotransforming methane into added value products. The limited number of bioproducts naturally synthesized by methanotrophs can be boosted via metabolic engineering of methanotrophs, while novel bioreactor configurations capable of supporting a cost-effective methane mass transfer from the gas phase to the methanotrophic broth are currently under investigation to facilitate the full scale implementation of biogas biorefineries.

1. Introduction

The raw gas derived from the anaerobic digestion (AD) process is known as biogas, which is mainly composed of methane (CH_4, c.a. 50–70%) and carbon dioxide (CO_2, c.a. 30–50%). Biogas is also composed of water vapor, nitrogen (N_2), oxygen (O_2) and other trace constituents such as volatile siloxanes, ammonia (NH_3), hydrogen sulfide (H_2S), volatile organic compounds (VOCs), carbon monoxide (CO) and hydrocarbons [1,2]. Biogas is employed mainly to produce electricity and heat through combined heat and power units. On the other hand, upgraded biogas comprising almost 100% methane is referred to as biomethane, which compared to biogas exhibits a wider applicability in sectors such as industry, transport, power and heating. Biogas can be upgraded to biomethane using a broad portfolio of developing and commercially available (bio)technologies including chemical precipitation, adsorption processes, membrane-based separation, biotrickling filtration, water or chemical scrubbing and pressure swing adsorption, among others [2,3]. According to the most recent statistical report on the state of European biogas and biomethane released in 2021 by the European Biogas Association (EBA), the total number of biogas and biomethane facilities operated in Europe accounted for 18,774 and 880, respectively [4]. Over the last decade, the European biomethane production has increased by 540% and its trend keeps growing at a constant rate, reaching an energy equivalent of 32 TWh in 2020 (23% higher than that in 2019) [4]. Indeed, according to the EBA database it is expected that from 30 to 40% of the total gas consumption in Europe will be covered by biomethane by 2050. In this context, the deployment and development of innovative, sustainable and cost-efficient (bio)technologies for biogas upgrading is crucial towards achieving a mature biomethane industry.

Despite the clear potential of AD-derived biogas as a platform to produce renewable energy from organic waste sources, the economic added value of biogas produced via AD is limited [5]. While the levelized cost of electricity (LCOE) for wind or solar energy has drastically decreased over the past decade from 0.09 to 0.04 USD kWh^{-1} and from 0.38 to 0.06 USD kWh^{-1}, respectively, electricity generation from biogas in combined heat and power units still needs a subsidy of 20 to 50 € MWh^{-1}. The LCOE for biogas in 2019 was estimated at USD

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Table 1
Summary of the main economic and energy indicators, and environmental impacts, of biogas upgrading technologies.

Biogas pollutant	Type of technology	Technology	Capital costs (€/(Nm^3/h)	Operating costs (€/(Nm^3))	Electricity demand (kwh/Nm^3)	Environmental impact	Reference
H_2S	Physical/ Chemical	Precipitation	–	0.024	–	Chemical Consumption	[3]
		Adsorption	3–120	0.0005–0.037	–	Activated Carbon consumption	[3]
	Biological	Biotrickling filtration	–	0.013–0.016	–	Low impact	[3]
		Microaerobic Digestion	–	0.0018–0.0037	–	Low impact	[3]
Siloxanes	Physical/ Chemical	Adsorption	–	0.03	–	Activated Carbon/ Silica consumption	[3]
	Biological	Biotrickling filtration	–	0.013	–	Nitrate consumption	[3]
CO_2	Physical/ Chemical	Water scrubbing, Chemical scrubbing, olvent scrubbing, Adsorption Membrane separation	1800–2000 (> 1000 Nm^3/h) 1500–3200 (> 600 Nm^3/h) 2000 (> 1000 Nm^3/h) 1500–2700 (> 600 Nm^3/h) 2000 (> 1000 Nm^3/h)	0.11–0.15 0.13–0.22	0.2–0.3 0.12–0.15 0.2–0.25 0.25–0.3 0.2–0.38	CO_2 released High energy demand Chemical consumption	[3]
	Biological	Photosynthetic	6000 (> 300 Nm^3/h)	0.03	0.08	CO_2 fixed as microalgae	[15]
		Hydrogenotrophic	–	0.51	–	CO_2 fixed as CH_4	[3]

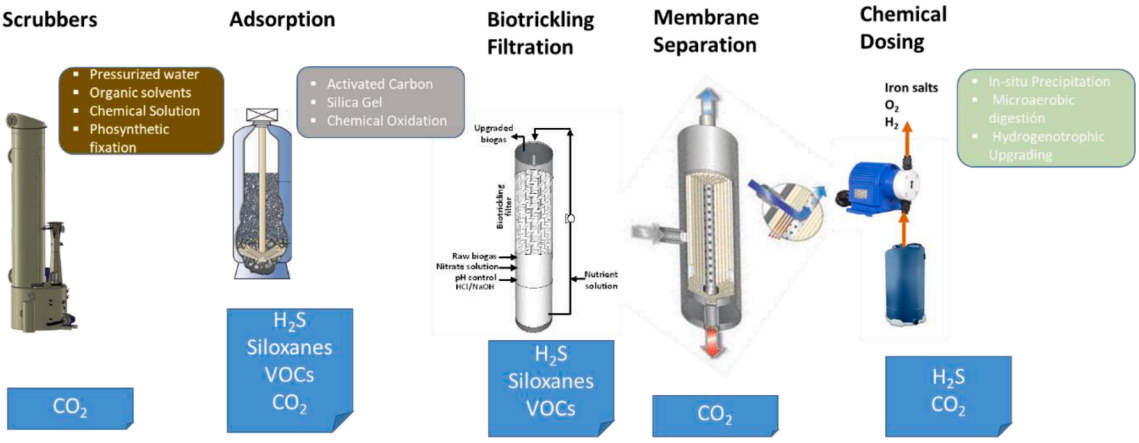

Fig. 1. Summary of the main technologies commercially available or under validation for biogas upgrading into biomethane.

$0.019–0.15 kWh^{-1} while the production of pipeline-quality biomethane is costlier and needs a financial incentive of 15–25 € MWh^{-1} [6,7]. One option to increase the competitiveness of biogas is to develop biogas-based biorefineries driven by specific microorganisms able to metabolize biogas into higher value-added products [8,9]. For instance, biogas can be biotransformed to ectoines, which have commercial application in the cosmetic and pharmaceutic sectors and retain a value of US $1000–1500 kg^{-1} [10]. The portfolio of valuable marketable products that can boost the biogas-based value chain is to date quite limited and includes ectoine [10], bioplastics [11], single cell protein [12], lactic acid [13] and methanol [14], among others. Moreover, biogas biorefineries are still in their infancy, so that further research is needed to move beyond electricity and heat production. The present mini review aims at providing a comprehensive overview of the latest advances in biogas upgrading and valorization. An updated analysis of current and emerging biomethane production (bio)technologies, with a special focus on membrane separation, is provided. Additionally, this review also presents a detailed and updated discussion of recent developments in the metabolic engineering of methanotrophs and in the design of advanced methanotrophic bioreactor configurations.

2. Recent trends in biomethane production

Biomethane production requires an integral cleaning of raw biogas in order to remove H_2S, siloxanes, volatile organic contaminants, water and CO_2, and comply with the standards for injection into natural gas grids or use as gas vehicle fuel [2]. The following subsections summarize the main physical-chemical and biological technologies implemented or investigated for the removal of the main biogas pollutants (Table 1, Fig. 1)

2.1. Biogas desulfurization

H_2S removal is nowadays effectively conducted using physical-chemical technologies via *in-situ* precipitation in anaerobic digesters by dosing costly iron salts (e.g. $FeCL_3$: $2Fe^{3+} + 3S^{2-} \rightarrow 2FeS + S$), or via adsorption into activated carbon or zinc oxide salts packed beds [16]. Among biotechnologies, biotrickling filtration (under aerobic or anoxic conditions) provide similar H_2S removal efficiencies (>98%) at full scale than *in-situ* precipitation or adsorption at similar gas residence times. However, biotrickling filtration exhibits lower operating costs and environmental impacts due to the biocatalytic action of microorganisms, which are able to oxidize H_2S to sulfate at ambient pressure and temperature [3]. The dosing into the digester of small amounts of O_2 to promote the partial biological oxidation of H_2S to elemental sulfur at the digester headspace, in the so-called microaerobic anaerobic digestion, has emerged as a cost-effective biological biogas desulfurization strategy already implemented at commercial scale. Indeed, the operating costs of the above mentioned physical-chemical desulfurization technologies (0.024–0.3 € Nm^{-3}) are significantly higher than the 0.0018–0.016 € Nm^{-3} typically accounted for biotechnologies.

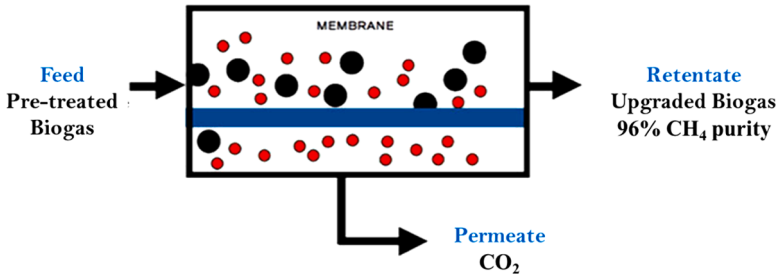

Fig. 2. Membrane configuration scheme the partial pressure difference induces the permeation of CO_2 through the membrane, whereas CH_4 remains at the feed side.

2.2. Siloxane and volatile organic pollutant removal from biogas

Siloxanes and volatile organic contaminants are removed from dry biogas via adsorption onto activated carbon or silica gel at full scale (physical-chemical technologies), with few recent studies showing the emerging potential of biotechnologies for the destruction of these biogas contaminants [17]. Despite exhibiting lower operating costs than adsorption technologies (0.03 € Nm^{-3}), biotechnologies such as biotrickling filtration still support siloxane removal efficiencies lower (40–80%) than those typically reported in activated carbon or silica gel filters (95–99%) [18].

2.3. CO_2 removal from biogas

CO_2 removal is the most expensive step during biogas upgrading and is currently carried out at commercial scale using physical-chemical technologies capable of providing a CH_4 content in the biomethane of 96–98%. Photosynthetic and hydrogenotrophic upgrading based on microalgae and archaea entail lower operating costs and environmental impacts, but require large area and an external hydrogen supply, and are still in validation phase. Pressurized water scrubbing, chemical scrubbing and organic solvent scrubbing are based on the enhanced mass transfer of CO_2 from biogas to a liquid solution (water, chemical solution, organic solvent) followed by solvent regeneration (via solvent decompression, air stripping or heating). These mature technologies exhibit electricity demands of 0.13–0.3 kwh Nm^{-3} and thermal energy requirements of $\approx$ 0.5 kwh Nm^{-3} for chemical/organic solvent regeneration [19]. On the other hand, pressure swing adsorption is based on the sequential operation of 4 adsorbent packed beds undergoing saturation and regeneration cycles, and exhibits similar electricity demands than water scrubbing (0.2–0.3 kwh Nm^{-3}). Cryogenic CO_2 separation is a highly energy demanding technology based on gas condensation at low temperatures, which can eventually provide liquefied CH_4 for transportation uses. Cryogenic processes currently hold a market share $<$ 1%, but the need for massive amounts of biomethane in the transportation sector (road and maritime) will probably boost the implementation of this technology. Membrane-based gas separation is currently the commercial technology with the largest increase in market share in the past 10 years [20]. Hence, membrane technology, which consists of the selective permeation of CO_2 through a membrane (Fig. 2), is a competitive and attractive alternative to conventional upgrading technologies due to its decreasing energy consumption (brought about by the rapid advances in material science), simple and compact engineered modules, and small footprint. Membrane technology is currently undergoing a rapid development thanks to the use of new materials with promising properties and enhanced performance, and is set to play an increasingly important role in reducing the environmental impact and cost of industrial biogas upgrading [1].

Polymeric, inorganic and composite materials based membranes have been extensively investigated for raw biogas upgrading [21]. Inorganic membranes show high selectivity, permeability and resistance to harsh environmental conditions, together with a high chemical and thermal stability. However, these membranes are currently unavailable at commercial scale due to their high cost, difficult processing and poor mechanical properties [22]. Therefore, most membrane materials used today for gas separation are organic polymers as their fabrication cost is lower and they can be easily processed into high surface area modules with a reasonable selective permeation and high mechanical strength. The main polymers used are polycarbonate, cellulose acetate, polysulfone, polyesters, polyetherimide and polyimides. Polycarbonate, polysulfone and polyimides have been widely used for industrial scale applications and several companies such as Air Products, Air Liquide, PermSelect, UBE, Cyanara, GKSS Licensees and Praxair, are currently manufacturing gas separation membranes at commercial scale [23, 24]. However, even though polymeric membranes are currently the best alternative for commercial CO_2 separations, they have low permeabilities and undergo physical aging and plasticization at high pressure or under long-term operation [25–28]. In recent years, emphasis is being given to the synthesis of novel materials with high permeability without compromising selectivity by controlling inter-chain spacing and chain stiffness. This led to the emergence of new classes of microporous polymers with exceptional rigidity that exhibit a superior gas separation performance such as Thermally Rearranged Polymers (TRs) [29] and Polymers of Intrinsic Microporosity (PIMs) [30]. Mixed matrix membranes (MMMs) have also emerged as innovative materials capable of supporting a cost-effective biogas upgrading. MMMs are defined as heterogeneous materials comprising solid fillers uniformly dispersed in a continuous polymer matrix [31], which can also undergo thermal transposition processes [32]. MMMs reveal outstanding properties, exploiting in synergy the advantages of polymers in mechanical stability, selectivity, easy processability and low cost, with the strength of dispersed porous materials in terms of gas separation performance, as they act as molecular sieves enhancing simultaneously gas permeability and selectivity.

3. Biogas as a feedstock in industrial biotechnology

The price of the feedstock (usually glucose in most industrial applications) accounts for around 30% of the total production costs of the chemicals produced using microbial fermentations. According to Comer and co-workers [33], methane is the most cost-efficient carbon source currently available. This conclusion was reached using natural gas prices as a reference. If we consider bio-gas as a by-product of waste treatment, the economic advantage of using methane as a carbon source, would be even higher. Nevertheless, there are two main limitations for methane to be able to substitute glucose as preferred substrate for microbial fermentation. The first limitation is the limited portfolio of chemicals that can actually be produced by methanotrophic organisms. Secondly, methane is a gaseous substrate with low solubility in water, which requires special types of bioreactors.

3.1. Chemicals currently obtainable using methane as a substrate

As it has been mentioned, the current portfolio of products that can be obtained from methane is small [8]. Methanotrophs of the genus Methylocystis accumulate PHB naturally [34] and Methylomicrobium

Table 2
Bioproducts obtained from methanotrophs.

Chemical	Average price ($/kg)	Yield (kg/kgCH_4)	Organism
PHB	9	0.47	*Methylocystis hirsuta*
Ectoine	1200	0.006	*Methylomicrobium alcaliphilum*
Lactic acid	1.5	0.25	*Methylomonas* sp. *DH-1 (engineered)*
2–3-butanediol	600	0.032	*Methylomicrobium alcaliphilum (engineered)*

alcaliphilum produces ectoine, which is an osmoprotector with high market value. In order to further expand the portfolio of products obtainable from methane, methanotrophs should be harnessed as metabolic engineering platforms. Some examples of chemicals obtained using engineered strains are lactic acid produced by an engineered strain of Methylomonas sp.DH-1 [13] and 2–3-butanediol produced by an engineered strain of Methylomicrobium alcaliphilum [35] (Table 2).

3.2. Metabolic models of methanotrophs

The goal of expanding the product portfolio of methanotrophs will be achieved by combining a good understanding of the metabolic capabilities of these bacteria (in the form of the development of Genome Scale Metabolic Models; GSMMs), with the capability to modify their metabolism by introducing heterologous genes (Fig. 3).

GSMMs are comprehensive compilations of all the metabolic reactions taking place in a particular organism. By assuming that the production rate of every internal metabolite equals its consumption (steady state aproximation), these models allow defining a space of feasible metabolic flux distributions. The optimization of one objective function (typically the biomass yield) can be used to compute metabolic flux distributions using linear programing. Gene knockouts or expression of heterologous genes can be modeled by adding or removing reactions from the model. GSMMs were first developed for two species of type I methanotrophs: *Methylomicrobium buryatense* and *Methylomicrobium alcaliphilum* [36,37] (Table 3). These first models allowed to elucidate key questions about the metabolism of methanotrophs. For example, model predictions (for these two organisms) were consistent with the so called mechanism of direct coupling for methane oxidation, according to which the redox co-factor that gets oxidized together with methane, by the methane monooxygenase, is reduced in the following reaction step, which involves the oxidation of methanol to formaldehyde. The GSMM of *Methylomicrobium alcaliphilum* was used for metabolic engineering purposes identifying a set of gene knockouts resulting in an improved production of 2–3-butanediol [35]. To the best of our knowledge, this is the only case in which GSMMs have guided the metabolic engineering of methanotrophs.

GSMMs have been also developed for four species of Type II methanotrophs of the genus *Methylocystis* [38,39]. These models showed that, in contrast to *Methylomicrobium*, these organisms use NADH as co-factor for methane oxidation. Models were also able to predict accurately biomass and PHB production yields on methane, using different nitrogen sources, as well as to elucidate the role of stored PHBs in these organisms, which was shown to be replenishing the serine and TCA cycles with metabolic intermediates in order to support growth (a so called anaplerotic function rather than being used as energy sources) [39]. A GSMM for *M. silvestris* [40] has been used to elucidate the role that the glyoxylate shuttle has in this organism, allowing it to grow on C1 carbon sources, and which is different in other methanotrophs that use the serine cycle. The GSMM of *M. silvestris* also allowed to identify and validate experimentally the existence of two alternative routes for propane utilization in this organism (one of them having lactic acid as an intermediate compound). This finding suggested a possible process for bioconverting propane to lactate. *M. silvestris*, differently from most *Methylocystis,* can be genetically manipulated [41].

3.3. Genetic manipulation of methanotrophs

Genetic manipulation of methanotrophs is very tedious and difficult

Table 3
Summary of the GSMMs reported for methanotrophs.

	Genes	Reactions	Metabolites	Reference
Methylomicrobium alcaliphilum	407	432	422	[37]
Methylococcus capsulatus	730	913	759	[42]
Methylomicrobium buryatense	314	402	403	[3]
Methylocella silvestris	681	1436	1474	[40]
Methylocystis parvus	625	1324	1399	[39]
Methyloscystis hirsuta	650	1350	1428	[38]
M. sp. SC2	879	1449	1435	[38]
M. sp. SB2	643	1337	1451	[38]

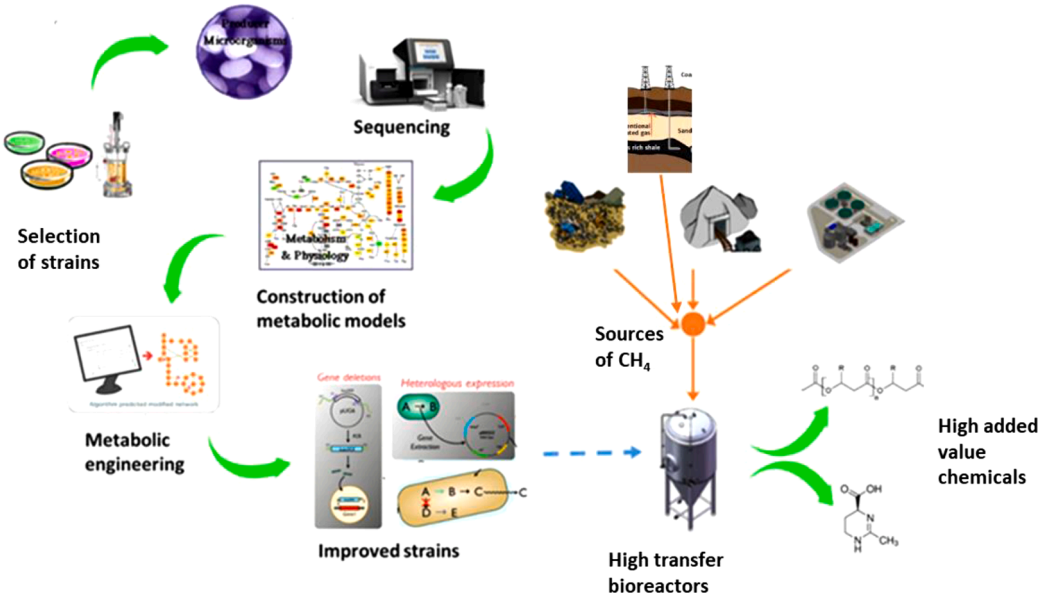

Fig. 3. Steps to follow to create a methanotrophic cell factory and expand the portfolio of chemicals that can be obtained.

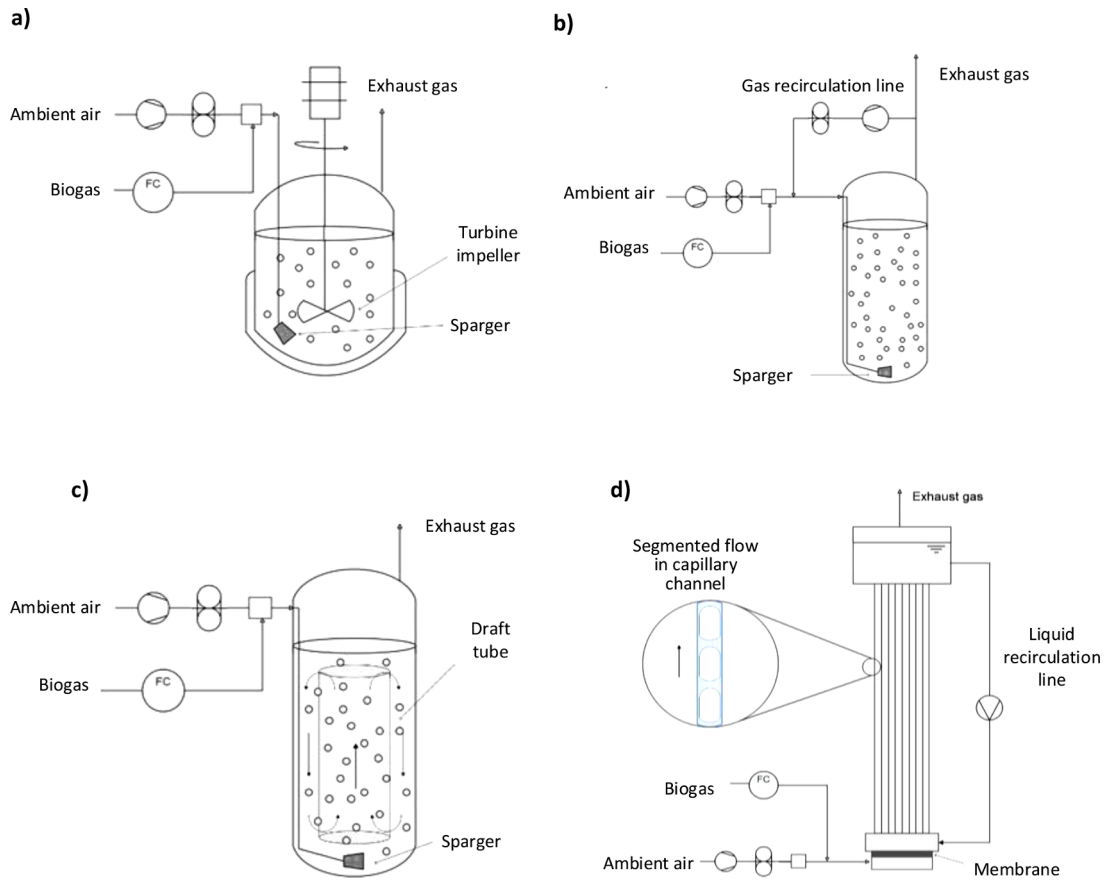

Fig. 4. Schematic representation of conventional and novel suspended growth bioreactors for biogas bioconversion: a) a stirred tank bioreactor; b) a bubble column bioreactor; c) an airlift bioreactor; and d) a capillary bioreactor.

to apply to large numbers of genes. Over the past two decades, it was necessary to develop and validate a tool box of powerful new methods to analyze gene and protein function in methanotrophs. For instance, Baani and Liesack [43] constructed a *Methylocystis* mutant strain defective in *pmoCAB* expression by using an antibiotic resistance marker that replaced the target genes after a double recombination event. The genetic construction comprised an antibiotic-resistance cassette flanked by regions homologous to sequences upstream and downstream of the genes of interest. All these features were contained in a suicide vector for *Methylocystis* sp. strain SC2, which could not replicate in the bacterium. Similarly, Crombie and Murrell [41] described a simple and effective method of genetic manipulation for *Methylocella silvestris* BL2 that relied on the electroporation of a linear DNA fragment to introduce chromosomal gene deletions. The gene of interest was first replaced with an antibiotic-resistance cassette, which was further removed using a Cre-loxP recombinase system, resulting in an unmarked gene deletion. Henard et al. [44] were also able to develop an inducible broad host-range vector for fine-tuned gene expression in *Methylomicrobium buryatense*. The vector (pCAH01) harboured an inducible promoter (i.e. relying in the tetracycline promoter/operator; $tet_{p/o}$), which could be induced using anhydrotetracycline. The authors found that the $tet_{p/o}$ promoter did not show leaky activity in the absence of inducer, which makes this vector a promising tool for conditional gene expression studies in methanotrophic bacteria. In summary, molecular genetic methods in methanotrophs have been limited to the introduction of low and high copy number plasmids by either electroporation, transformation or conjugation [41,45,46], DNA excision by specific recombinase systems (i.e. Cre-lox), gene expression control from conditional promoters ($tet_{p/o}$) and in frame gene deletions by homologous recombination. However, utilization of extrachromosomal elements with a heat sensitive origin of replication, DNA insertions in the chromosome using phage specific integrases, site directed mutagenesis, complex construct modification and CRISPR-cas mutagenesis, among other techniques, need to be yet developed in methanotrophs. Among these methods, CRISPR-Cas systems provide a new direction for both RNA interfering and genome editing approaches. Precise deletions (knock out) or insertions (knock in) can be readily achieved by co-delivering a DNA template that serves as a repair template to guide and budge the host DNA repair pathways. CRISPR-Cas9 platform is concise and self-contained and has the potential to be adapted for different organisms, including those non-model organisms for which genetic engineering methods are not well developed (i.e. methanotrophs).

3.4. Bioreactor for biogas bioconversion

Suspended growth bioreactors are the most common configuration applied for the bioconversion of biogas into added-value byproducts, as they allow for an easy recovery of the biomass and subsequent downstream processing. Mechanically stirred tanks consist of vessels where the liquid broth is mechanically agitated by an impeller and biogas is supplied via a sparger located at the bottom of the reactor. In order to facilitate the mass transfer of CH_4 (a very insoluble gas with a dimensionless Henry's law constant of 29 at 25 °C), intensive mixing is required, thus increasing the energy demand of the process (Fig. 4a) [47]. Despite CH_4 removals up to 60% have been achieved at gas residence times between 4 and 10 min [48], the high power to volume ratios and the excessive shear stress have been identified as main drawbacks of this configuration [49]. An alternative configuration are bubble column bioreactors, where no mechanical agitation of the cultivation broth is necessary since CH_4 mass transfer is promoted either by (i) injecting the

biogas through microporous diffusers that increase the gas-liquid contact area (Fig. 4b), or (ii) installing a concentric draft-tube (riser) to create a density gradient and enhance the turbulence in the so-called airlift bioreactors (Fig. 4c) [47]. However, a poor liquid circulation, the partial CH_4 utilization or bubble coalescence typically limit the removal efficiency of these bubble column bioreactors to 20–30%.

Novel operating strategies have been recently tested in order to improve the cost-effectiveness of biogas conversion in conventional suspended growth bioreactors. For instance, the addition of a non-aqueous phase (NAP) creates a more efficient pathway for the transport of CH_4 from the gas phase to the methanotrophic community (due to the higher affinity of the NAP for CH_4 compared to that of water), together with higher interfacial gas-water and gas-NAP areas. Recent works using silicone oil as NAP in two-phase partitioning stirred tank bioreactors have demonstrated superior CH_4 abatement performance, achieving up to 40% higher removals [48]. These authors attributed the enhanced CH_4 transfer efficiency to the retention of the biocatalytic activity inside the silicone oil. Despite silicone oil is the most studied NAP for gas treatment, other liquid NAPs (2,4,4,6,8,8-heptamethylnonane (HMN), 1,1,1,3,5,5,5-heptamethyltrisiloxane (HMS) or the per-fluorocarbon FC40TM) or solid vectors (polymers such as Desmopan, Kraton or Elvax) could be implemented [50].On the other hand, internal gas recycling allows for the decoupling of the actual gas residence time and turbulence in the microbial broth from the overall gas residence time, thus boosting CH_4 mass transfer without compromising the contact time between the gas and liquid phases [11,47]. This strategy has been tested in a bubble column bioreactor for the bioconversion of CH_4 into PHB, resulting in CH_4 removals of up to 70% and PHB contents of 34% w/w [11].

Capillary bioreactors have been recently proposed to support high CH_4 conversion rates and low energy requirements. Capillary bioreactors are composed of parallel straight microcapillaries (diameter ~1–5 mm), where the gas-liquid hydrodynamics consists of an alternating sequence of gas bubbles and liquid slugs, a flow pattern known as Taylor flow (Fig. 4d). This gas-liquid flow pattern can provide a high gas-liquid interfacial area along with a reduced liquid thickness and high turbulence at the liquid side, thus boosting the mass transfer coefficient with a minimum energy requirement [51]. Although scarcely applied for CH_4 treatment, this configuration has demonstrated promising results, increasing by 50% the removals attained in two-phase partitioning turbulent bioreactors [52].

In brief, methane fermentation will benefit from the global fight against methane emissions, but more research is needed to overcome CH_4 mass transfer limitations at full scale and the limited number of bioproducts. Companies such as Newlight Technologies and Mango Materials have been created (in 2003 and 2010, respectively) with the aim of developing biotechnological processes potentially capable of turning methane into biodegradable materials. After 10 years of research, Newlight Techonologies embarked on its core mission to scale up the technology by opening their first commercial-scale plant. In 2019, the company has expanded its capacity with the construction of a 23 kton $year^{-1}$ plant [53]. Mango Materials currently operates at pilot scale co-located nearby a methane production facility in San Francisco Bay Area (Mango Materials, n.d.). However, the company has recently built a demonstration unit to achieve a material production of 100 kg-PHA per week branded as YOPP+ pellets [54]. In addition, the European Project DEEP PURPLE is currently up-scaling ectoine production up to a 3 m^3 pilot plant. Finally, it should be highlighted that, despite their higher robustness compared to pure cultures, the potential of mixed methanotrophic cultures for biogas bioconversion has been poorly explored.

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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