A review on the state-of-the-art of physical/chemical and biological technologies for biogas upgrading

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Abstract

The lack of tax incentives for biomethane use requires the optimization of both biogas production and upgrading in order to allow the full exploitation of this renewable energy source. The large number of biomethane contaminants present in biogas (CO_2, H_2S, H_2O, N_2, O_2, methyl siloxanes, halocarbons) has resulted in complex sequences of upgrading processes based on conventional physical/chemical technologies capable of providing CH_4 purities of 88-98 % and H_2S, halocarbons and methyl siloxane removals > 99 %. Unfortunately, the high consumption of energy and chemicals limits nowadays the environmental and economic sustainability of conventional biogas upgrading technologies. In this context, biotechnologies can offer a low cost and environmentally friendly alternative to physical/chemical biogas upgrading. Thus, biotechnologies such as H_2-based chemoautrophic CO_2 bioconversion to CH_4, microalgae-based CO_2 fixation, enzymatic CO_2 dissolution, fermentative CO_2 reduction and digestion with in-situ CO_2 desorption have consistently shown CO_2 removals of 80-100 % and CH_4 purities of 88-100 %, while allowing the conversion of CO_2 into valuable bio-products and even a simultaneous H_2S removal. Likewise, H_2S removals >99 % are typically reported in aerobic and anoxic biotrickling filters, algal-bacterial photobioreactors and digesters under microaerophilic conditions. Even, methyl siloxanes and halocarbons are potentially subject to aerobic and anaerobic biodegradation. However, despite these promising results, most biotechnologies still require further optimization and scale-up in order to compete with their physical/chemical counterparts. This review critically presents and discusses the state of the art of biogas upgrading technologies with special emphasis on biotechnologies for CO_2, H_2S, siloxane and halocarbon removal.

Keywords: biomethane, biotechnologies, carbon dioxide removal, hydrogen sulfide removal, siloxane removal, trace biogas contaminants.

1. Introduction.

Biogas represents a renewable energy source based on its high CH_4 content. This CH_4-rich gas is a byproduct from the anaerobic treatment of wastewaters, the organic fraction of municipal solid wastes (OMSW), livestock residues or organic agroindustrial wastes (Rasi, 2009). The composition of biogas is intrinsically determined by the carbon oxidation-reduction state of the organic matter present in the waste and the type of anaerobic digestion process, which in turn depend on the origin of the residue digested (Jönsson *et al*, 2003). For instance, the biogas recovered from conventional landfills is a complex mixture composed of CH_4 (35-65%), CO_2 (15-50%), N_2 (5-40%), H_2O (0-5%), O_2 (0-5%), H_2 (0-3%), CO (0-3%), H_2S (0-100 ppm_v), NH_3 (0-5 ppm_v), halogenated hydrocarbons (20-200 ppm_v Cl^-/F^-), volatile organic contaminants (0-4500 mg m^{-3}) and siloxanes (0-50 mg Si m^{-3}) (Jaffrin *et al*, 2003; Persson *et al*, 2006; Ajhar *et al*, 2010; Bailón and Hinge, 2012). A slightly simpler biogas is typically obtained from the anaerobic degradation of sewage sludge, livestock manure or agroindustrial bio-wastes: CH_4 (53-70%), CO_2 (30-47%), N_2 (0-3%), H_2O (5-10%), O_2 (0-1%), H_2S (0-10.000 ppm_v), NH_3 (0-100 ppm_v), hydrocarbons (0-200 mg m^{-3}) and siloxanes (0-41 mg m^{-3}) (Persson *et al*, 2006; Soreanu *et al*, 2011; Bailón and Hinge, 2012). Carbon dioxide and nitrogen constitute the major contaminants of biogas (N_2 in the particular case of landfills), decreasing its specific calorific value and therefore its Wobbe index (Ryckebosch *et al*, 2011). Large concentrations of O_2 in the biogas can entail explosion hazards, while high levels of H_2S in combination with condensate H_2O causes corrosion in compressors, pipelines, gas storage tanks and engines. Similarly, NH_3 and halogenated hydrocarbons generate corrosive products during combustion, which can severely damage engines and downstream pipelines (Persson *et al*, 2006; Petersson and Wellinger, 2009). Finally, methyl siloxanes combustion generates silicone oxide that deposits in biogas combustion engines and valves, causing their abrasion, overheating and malfunctioning (Abatzoglou and Boivin, 2009).

Biogas is currently used as a fuel for on-site heat, steam and electricity generation in industry, as a substrate in fuel cells, as a substitute of natural gas for domestic and industrial use prior injection into natural gas grids and as a vehicle fuel (Rasi, 2009; Andriani *et al*, 2014; Thrän *et al*, 2014). In this context, biogas production in Europe accounted for 13.4 million tons of oil equivalent (≈10 % increase compared to 2012), which represented 52,3 TWh of electricity produced and net heat sales to heating district networks of 432 megatons of oil equivalent (EurObserv'ER, 2014). In addition, the actual European network of 14.000 anaerobic digesters is expected to increase in order to supply up to 18-20 million m^3 by 2030 (3 % of the European gas consumption) according to the latest European Biogas Association's estimations (European Biogas Association, 2013).

The final use of biogas determines its composition and the type of upgrading process required. Thus, on-site biogas use in boilers for heat generation only requires H_2S removal below 1000 ppm_v and water removal prior to combustion (Bailón and Hinge, 2012). The use of biogas in internal combustion engines for combined heat and power generation (CHP) requires the removal of water, and H_2S, NH_3, siloxanes and halocarbons levels below 200-1000 ppm_v, 32-50 mg m^{-3}, 5-28 mg m^{-3} and 65-100 mg m^{-3}, respectively, depending on the manufacturer. Turbines and micro-turbines for CHP generation require very low contents of siloxane (0.03-0.1 ppm_v) and water (pressurized dew point -6.7 ºC below biogas temperature), but are able to stand high concentrations of H_2S (10000-70000 ppm_v) and halocarbon (200-1500 ppm_v Cl^-/F^-) (Soreanu *et al*, 2011; Bailón and Hinge, 2012). However, the most stringent quality requirements are encountered in biomethane for injection into natural gas grids and as a vehicle fuel, which often demands CH_4

concentrations > 80- 96 %, CO_2 < 2-3%, O_2 < 0.2-0.5 %, H_2S < 5 mg m^{-3}, NH_3 < 3-20 mg m^{-3} and siloxanes < 5-10 mg m^{-3} (Table 1).

With the biogas upgrading market and technologies rapidly evolving, a more frequent evaluation of the state-of-the art technologies available is necessary (Bauer *et al*, 2013b). In this context, most physical/chemical biogas upgrading technologies are still highly energy or chemical intensive, which has triggered the rapid development of biogas upgrading biotechnologies based on their superior economic/environmental sustainability. This paper critically reviews and discusses the state-of-the-art technologies for the removal of CO_2, H_2S, H_2O and trace biogas contaminants such as siloxanes, halocarbons, O_2 and N_2, with a special focus on the potential and limitations of biotechnologies based on the significant technological breakthroughs occurred in this field in the past 10 years.

2. Removal of Carbon dioxide.

CO_2 removal from biogas at industrial scale is nowadays performed by physical/chemical technologies based on their high degree of maturity and commercial availability, while the potential of biotechnologies has been assessed only at lab or pilot scale. However, while most physical/chemical units discharge the separated CO_2 to the atmosphere (prior off-gas post treatment to avoid the release of CH_4), biotechnologies allow for the bioconversion of CO_2 into valuable commercial products, at significantly lower energy costs.

2.1. Physical/chemical CO_2 removal technologies.

Scrubbing with water, organic solvents or chemical solutions, membrane separation, pressure swing adsorption and cryogenic CO_2 separation dominate the biogas upgrading market nowadays. These technologies are discussed below:

2.1.1. Water Scrubbing

CO_2 removal via scrubbing with water as selective absorbent is a classical unit operation in chemical engineering based on the higher aqueous solubility of CO_2 compared to that of CH_4 (26 times higher at 25 ºC) (Sinnott, 2005). Water scrubbing is nowadays a mature technology with accounts for approximately 41 % of the global biogas upgrading market, being considered the upgrading method less sensitive to biogas impurities (Thrän *et al*, 2014). The availability of a low-cost water supply of sufficient quality often determines the water scrubber configuration implemented. For instance, CO_2 removal from biogas produced in wastewater treatment plants (WWTPs) has been performed in single-pass scrubbers using pressurized treated water (6-10 bar), which after absorption is sent back to the main water treatment line (Tynell *et al*, 2007). However, most modern units in landfills or OMSW treatment facilities are constructed based on a sequential pressurized CO_2 absorption in water (tap water quality) coupled to a two-stage stripping, which allows for water regeneration (Beggel *et al*, 2010; Bauer *et al*, 2013). CO_2 absorption is often carried out at 6-10 bar, although pressures in the range of 10-20 bar are also used (Ryckebosch *et al*, 2011). The first flash unit is operated at 2-4 bars, resulting in the emission of a CO_2 rich biogas (80-90% CO_2 and 10-20 % CH_4) that is returned to the absorption unit (Bauer *et al*, 2013b) (Figure 1A). Water decompression to atmospheric pressure in the second stripping unit, often assisted by air injection, results in the final regeneration of the absorbent that is returned to the absorption unit (Kapdi *et al*, 2005; Patterson *et al*, 2011; Ryckebosch *et al*, 2011). The amount of water required (m^3 h^{-1}) depends on the water pressure and temperature, and can be estimated as Q_{biogas} /(H ×P), where Q_{biogas} (kmol h^{-1}) represents the raw molar biogas flow rate, H (M atm^{-1}) the Henry's Law constant and P (atm) the total pressure of operation. Surprisingly, it does not depend on the pH of water or on the CO_2 concentration in the raw biogas. Typical water flow rates of 0.1-0.2 m^3_{water} Nm^{-3}_{biogas} are reported in single-pass scrubbers depending on the operational pressure (Persson, 2003), which are comparable to the 0.18-0.23 m^3_{water} Nm^{-3}_{biogas} in units designed with water recycling (Bauer *et al*, 2013b). Higher operational pressures entail lower water flow rates, but higher pumping and compression costs and a reduced lifetime of the upgrading plant. Despite water recycling significantly reduces water consumption, 20-200 L h^{-1} are continuously purged to avoid the accumulation of detrimental byproducts.

Countercurrent operation is preferred regardless of the scrubbing configuration. Both absorption and desorption units are typically constructed with random packings such as Pall or Raschig rings to support an efficient gas-liquid mass transfer (Ryckebosch *et al*, 2011; Bauer *et al*, 2013). CH_4 and CO_2 concentrations in the upgraded biogas are normally > 96% and < 2%, respectively. CH_4 losses of 1-2 % and technical plant availabilities of 95-96 % are typically reported in technical literature for commercial full-scale facilities (10-10.000 Nm^3 h^{-1}) (Beil, 2009; Rasi, 2009; Patterson *et al*, 2011; Bauer *et al*, 2013b) (Table 2). Despite manufacturers guarantee 2 % methane losses with exhaust gas recirculation, losses of 8-10 % have been measured under regular operation, as a result of the non-optimized operation of the flash tank (Persson, 2003). Elemental sulfur accumulation, corrosion and odour nuisance also rank among the most important operational problems in water scrubbers derived from the simultaneous absorption of H_2S in water. Thus, despite this technology can cope with H_2S concentrations of 300-2500 ppm$_v$ (depending on the manufacturer), H_2S removal is highly recommended prior to water scrubbing (Persson *et al*, 2006; Thrän *et al*, 2014). On the other hand, microbial growth (especially when using treated water in WWTPs) and foam formation in the packed bed constitute additional operational problems of this technology, which result in a limited gas-liquid mass transport and require the use of antifoaming agents (although their cost is marginal) (Bauer *et al*, 2013b).

Investment costs in water scrubbers linearly decrease from 5500 to 2500 € (Nm^3 h^{-1})$^{-1}$ when the design treatment capacity increases from 100 to 500 Nm^3 h^{-1}, and remained relatively constant at 1800-2000 € (Nm^3/h)$^{-1}$ for plant capacities over 1000 Nm^3 h^{-1}. On the other hand, the operating costs range from 0.11-0.15 € Nm^{-3} (200-300 m^3 h^{-1}), which can be attributed to both energy consumption (decreasing from 0.3 kWh Nm^{-3} at 500 Nm^3 h^{-1} to 0.2 kWh Nm^{-3} at 2000 Nm^3 h^{-1}) and annual maintenance costs (2-3 % of the investment costs), since the costs of consumables are often negligible (Urban *et al*, 2009; Patterson *et al*, 2011; Bauer *et al*, 2013b). In this context, the major energy demanding processes are gas compression (0.10-0.15 kWh Nm^{-3} in 6-8 bar modern facilities), water compression (0.05-0.1 kWh Nm^{-3}) and water cooling (0.01-0.05 kWh m^{-3}). The need for an off-gas treatment unit such as incinerators, activated carbon filters or biofilters to abate the H_2S and CH_4 stripped from the desorption tank entail additional costs not considered in the above discussion.

2.1.2. Organic Solvent Scrubbing

This technology, fundamentally similar to water scrubbing, uses polyethylene glycol-based absorbents (commercialized under trade names such as Selexol® or Genosorb®), which exhibit a higher affinity for CO_2 and H_2S than water. For instance, Selexol®, a mixture of polyethylene glycol dimethyl ethers, has a 5 times higher affinity for CO_2 than water (Tock *et al*, 2010). These solvents allow for a decrease in both the absorbent recycling rates and plant sizing, with the subsequent decrease in investment and operating costs (Petersson and Wellinger, 2009; Ryckebosch *et al*, 2011). Unlike water scrubbing, the use of organic solvents requires a gas condition step to remove water and several heating stages to promote an efficient desorption of CO_2 at 40 ºC (Figure 1B). Both biogas and organic solvent are cooled down to 20 ºC prior absorption (Bauer *et al*, 2013b). The anticorrosion nature of the organic solvents does not require the use of stainless steel in the scrubber. Despite the advantages of this mature technology, its share in the biogas upgrading market is only 6% (Thrän *et al*, 2014).

A biomethane with CH_4 contents of 96-98.5 % can be consistently achieved in optimized full scale organic solvents scrubbers with a 96-98 % technical availability (Bauer *et al*, 2013b; Thrän *et al*, 2014). Similarly to water scrubbing, this technology results in CH_4 losses lower than 2 % (Persson *et al*, 2007). When biogas contains high concentrations of H_2S, solvent regeneration is conducted with steam or inert gas in order to avoid a sulfur-mediated solvent deterioration (Ryckebosch *et al*, 2011). However, a complete H_2S removal using activated carbon filters is often recommended prior to organic scrubbing.

The capital costs for implementation of organic scrubbers decrease from ≈ 4500 € $(Nm^3\ h^{-1})^{-1}$ for 250 $Nm^3\ h^{-1}$ plants to 2000 € $(Nm^3\ h^{-1})^{-1}$ for design capacities of 1000 $Nm^3\ h^{-1}$.

Constant capital costs of 1500 € $(Nm^3/h)^{-1}$ correspond to large upgrading plants with treatment capacities over 1500 $Nm^3\ h^{-1}$ (Bauer *et al*, 2013b). Process operating costs mainly derive from the electricity used for biogas compression and liquid pumping (0.2-0.25 kWh Nm^{-3}) and maintenance costs (2-3 % of the investment cost), since the heat required for absorbent regeneration is often obtained from the residual heat of the exhaust gases of the off-gas incineration units (Bauer *et al*, 2013b). Higher energy requirements in the range of 0.4-0.51 kWh Nm^{-3} can be found in technical literature (Berndt, 2006; Günther, 2007; Persson, 2007). On the other hand, the low vapour pressure of polyethylene glycol dimethyl ethers requires a minimum organic solvent make-up.

2.1.3. Chemical Scrubbing

Chemical scrubbing involves similar biogas-liquid mass transfer fundamentals to water/Selexol® scrubbing but a simpler process configuration and an enhanced performance derived from the use of CO_2-reactive absorbents such as alcanol amines (monoethanolamine, diethanolamine, etc.) or alkali aqueous solutions (NaOH, KOH, CaOH, K_2CO_3, etc.) (Andriani *et al*, 2014). According to a recent review of commercial technologies, a mixture of methyldiethanolamine and piperazine (aMDEA) constitutes the most popular amine absorbent nowadays, which is used at aMDEA/CO_2 mol ratios of 4-7 (Bauer *et al*, 2013b). This technology consists of a packed bed absorption unit coupled to a desorption unit equipped with a reboiler, which simplifies process configuration compared to their physical absorption counterparts (Figure 1C). Both structured and random packings are employed since the risk of biomass growth is limited by the high pH of the amine solutions (Bauer *et al*, 2013b). Unlike water/Selexol® scrubbing, the formation of intermediate chemical species (CO_3^{2-}, HCO_3^-) mediated by the exothermic reaction of the absorbed CO_2 with the chemical reagents present in the scrubbing solution results in an enhanced CO_2 absorption capacity and process operation at maximum CO_2 concentration gradients (Ryckebosch *et al*, 2011). This intensification in CO_2 mass transfer from biogas finally results in more compact units and lower absorbent recycling rates (Patterson *et al*, 2011). In addition, process operation at low pressure (1-2 bar in the absorption column and 1.5-3 bar in the stripping column) entails significantly lower energy requirements for biogas compression and absorbent pumping (Patterson *et al*, 2011). However, the high energy requirements for solvent regeneration (carried out at 120-150 ºC) have likely limited the share of this mature technology to 22 % of the global upgrading market (Thrän *et al*, 2014).

Like water scrubbing, chemical scrubbing is operated in a countercurrent flow configuration (Bauer *et al*, 2013b). CH_4 recoveries of 99.5-99.9 % can be achieved at a plant availability of 91-96 % due to the low solubility of CH_4 in alcanol amines (Beil, 2009; Ryckebosch *et al*, 2011; Bauer *et al*, 2013b). On the other hand, H_2S removal (often carried out in activated carbon filters) prior to amine scrubbing is highly recommended to prevent amine poisoning, although some commercial units can cope with biogas containing up to 300 ppm_v of H_2S. Foaming and amine degradation/losses rank among the most important operational problems along with corrosion issues (Bauer *et al*, 2013b).

The investment costs in chemical scrubbing linearly decrease from 3200 € $(Nm^3/h)^{-1}$ for design flow rates of 600 $Nm^3\ h^{-1}$ to 1500 € $(Nm^3/h)^{-1}$ for 1800 $Nm^3\ h^{-1}$ upgrading plants (Bauer *et al*, 2013b). While the costs associated to amine, antifoam and water make-up (3 mg Nm^{-3} for each compound) are marginal and the electricity requirements for gas compression and liquid pumping are moderate (0.12-0.15 kWh Nm^{-3}) (Günther, 2007; Beil, 2009; Bauer *et al*, 2013b), the main operating costs derive from the energy required for amine regeneration (0.55 kWh Nm^{-3}).

2.1.4. Pressure swing adsorption

PSA is based on the selective adsorption of CO_2 over CH_4 onto porous adsorbents with a high specific surface area such as activated carbon, silica-gel, activated alumina, zeolite and polymeric sorbents (Patterson *et al*, 2011; Ryckebosch *et al*, 2011). Molecular size exclusion and adsorption affinity constitute the separation mechanisms of this technology. Molecular sieve adsorbents with average pore size of 3.7 Å are used to retain CO_2 molecules (molecular size of 3.4 Å) inside the pores, while excluding CH_4 molecules (molecular size of 3.8 Å). Hence CH_4 flows unretained through the interstitial spaces of the packed bed under continuous PSA operation, resulting in a CH_4 rich biogas (Patterson *et al*, 2011). Adsorbents such as activated carbon or zeolites base this selective CO_2/CH_4 separation on their higher CO_2 solid-gas partition coefficient compared to that of CH_4. Other adsorbents facilitate a faster diffusion of CO_2 molecules inside the adsorbent pores, kinetically excluding CH_4 retention inside the adsorbent (Bauer *et al*, 2013b). Apart from a high selective adsorption of CO_2, molecular sieves used in PSA must be non-hazardous, readily available, stable under long-term operation and must exhibit a linear adsorption isotherm (Bauer *et al*, 2013b). These adsorbents are often packed in vertical columns operated under a pressurization, feed, blowdown and purge regime, which requires the arrangement of 4 interconnected columns in parallel operating at any of the 4 stages described above (Figure 2). Column pressurization and biogas feeding are often carried out at 4-10 bars to increase CO_2 retention inside the pores. When the column gets saturated with CO_2, the blowdown phase commences by filling the adjacent previously regenerated adsorption column with the exiting gas from the saturated column (in order to reduce the overall energy consumption of the process), which represents the pressurization stage of this new operating adsorption column. The saturated column is finally vented to ambient pressure and purged with upgraded biogas to complete the regeneration of the adsorbent bed. The exhaust gases from column purging are often recirculated to the biogas feed (Bauer *et al*, 2013b). This cycle of adsorption and regeneration (so called Skarstrom cycle) last for 2-10 min (Grande, 2011). PSA, originally developed in the 1960s for the separation of industrial gases, constitutes nowadays a mature technology with a market share of 21 % (Patterson *et al*, 2011; Thrän *et al*, 2014).

Biomethane with a CH_4 purity of 96-98 %, recoveries of ≈98% and technical plant availabilities of 94-96 % are commonly reported in technical literature (Beil, 2009; Bauer *et al*, 2013b). H_2S and siloxanes irreversible adsorb onto the molecular sieves and are often removed using activated carbon filters during the biogas conditioning stage. The moisture content of the biogas is also removed by condensation prior to PSA (Bauer *et al*, 2013b).

Capital costs in PSA linearly decrease from 2700 € $(Nm^3/h)^{-1}$ at design flow rates of 600 $Nm^3\ h^{-1}$ to 1500 € $(Nm^3/h)^{-1}$ for plants with a capacity of 2000 $Nm^3\ h^{-1}$ (Bauer *et al*, 2013b). Electricity requirements for gas compression and biogas demoisturisation in the range of 0.24 to 0.6 kWh Nm^{-3} are typically reported in literature (Günther, 2007; Persson, 2007; Beil, 2009), although a recent cost survey limits electricity needs to 0.25-0.3 kWh Nm^{-3} (including catalytic oxidizers from the abatement of CH_4 off-gas emissions)(Bauer *et* *al*, 2013b). PSA does not entail additional costs derived from water make-up addition or heat for adsorbent regeneration.

2.1.5. Membrane separation

Membrane-based upgrading technologies are based on the principle of selective permeation of biogas components through a semi-permeable membrane (Bauer *et al*, 2013b). Conventional membranes for biogas upgrading retain CH_4 and N_2, and facilitate the preferential permeation of O_2, H_2O, CO_2 and H_2S with CO_2/CH_4 selectivity factors of up to 1000/1 (Ryckebosch *et al*, 2011). Polymeric materials such cellulose acetate are preferred for the manufacture of biogas separating membranes over non-polymeric materials because of their lower cost, easy manufacture, stability at high pressures and easy scalability (Basu *et al*, 2010). Recent breakthroughs in membrane manufacture driven by nanotechnology have increased membrane selectivity factors (and therefore methane recoveries) and renewed the interest in this classical natural gas upgrading technology (Bauer *et al*, 2013b). Membrane separation is in fact a mature technology (with a market share of 10 %) commercialized either in high pressure gas-gas modules or low pressure gas-liquid modules (Patterson *et al*, 2011; Thrän *et al*, 2014). Biogas is pressurized at 20-40 bars in gas-gas systems (although some commercial units also operate in the 6-20 bar range) resulting in a CH_4 rich retentate and a CO_2 rich permeate containing methane and trace levels of H_2S at atmospheric pressure (or negative pressures to increase the purity of the biomethane over 97 %) (Bauer *et al*, 2013b). Gas-gas units are manufactured under different configurations: single-pass membrane unit or multiple stage membrane units with internal recirculations of permeates and retentates (Figure 3). On the other hand, gas-liquid systems are operated at atmospheric pressure (with the associated reduction in construction costs) with biogas and a

CO_2-liquid absorbent separated by a micro porous hydrophobic membrane. Both fluids flow under counter current mode (Ryckebosch *et al*, 2011). Alcanol amines or alkali aqueous solutions are used as CO_2 liquid absorbents.

CH_4 recovery in membrane-based upgrading systems depends on the membrane configuration used. Thus, CH_4 recoveries of 98-99 % can be achieved in gas-liquid units or two-stage gas-gas units with recirculation of the permeate from the second membrane module. Recoveries of 99-99.5 % require more complex designs with recirculation of both the permeate from the second stage and the retentate from the filtration of the permeate of the first module (Benjaminsson, 2006). The technical availability of this mature technology ranges from 95-98% (Beil, 2009; Bauer *et al*, 2013b). CH_4 concentrations of 96-98 % are guaranteed by most membrane manufacturers in gas-liquid or multiple-stage gas-gas units, while single-pass gas-gas units provide a biomethane with CH_4 concentrations of 92-94 % and off-gas permeates with CH_4 concentrations of 10-25 % that need to be further treated (Ryckebosch *et al*, 2011; Andriani *et al*, 2014). Higher pressures or higher membrane areas would be required to further increase the CH_4 concentration in the final biomethane. Biogas pre-treatment involving the removal of particles, H_2S, H_2O, VOCs, NH_3 and siloxanes by condensation and activated carbon filtration is highly recommended prior to membrane separation to avoid a rapid deterioration and clogging of the membrane (Patterson *et al*, 2011; Bauer *et al*, 2013b).

The investment costs of gas-gas membrane units rapidly increase from 2500 € $(Nm^3/h)^{-1}$ for design flow rates of 400 $Nm^3\ h^{-1}$ to 6000 € $(Nm^3/h)^{-1}$ when scaling down the process to 100 $Nm^3\ h^{-1}$ (Bauer *et al*, 2013b), remaining approximately constant at 2000 € $(Nm^3/h)^{-1}$ for plants with capacities over 1000 Nm^3 h^{-1}. The operating costs of this technology are mainly determined by membrane replacement (5-10 years lifetime), biogas compression cost (0.2-0.38 kWh Nm^{-3}) and the cost associated to biogas pre-treatment (activated carbon replacement plus energy for condensation) (Benjaminsson, 2006; Beil, 2009; Bauer *et al*, 2013b). Costs in the range of 0.13-0.22 € Nm^{-3} are typically reported in literature (Hullu *et al*, 2008). Membrane-based upgrading exhibits slightly higher maintenance cost (3-4 % of the initial investment costs) compared to their physical chemical counterparts (2-3 %).

2.1.6. Cryogenic separation

The different liquefaction/solidification temperatures of the biogas components allow for a selective separation of H_2O, H_2S, CO_2 and CH_4 if the temperature of biogas is stepwise decreased, which even allows for the generation of a liquefied biomethane (free of O_2 and N_2) at temperatures between -162 and -182 ºC (Bauer *et al*, 2013b). Cryogenic biogas upgrading can be conducted at constant pressure (10 bar) using a sequential temperature decrease to -25 ºC (where water, H_2S, siloxanes and halogens are removed in liquid phase), to -55 ºC (where most CO_2 is liquefied to facilitate its withdrawal from the upgrading unit and further commercialization) and finally to -85 ºC as polishing step (where the remaining CO_2 solidifies) (Ryckebosch *et al*, 2011). Process operation at high pressure avoids the sudden solidification of CO_2 below -78 ºC, which prevents operational problems derived from clogging of pipelines and heat exchanges (Bauer *et al*, 2013b). The most common operational procedure involves a preliminary biogas drying followed by a multistage compression (with intermediate cooling) up to 80 bar (Patterson *et al*, 2011; Ryckebosch *et al*, 2011). The pressurized biogas is stepwise cooled to -45 ºC and -55 ºC to promote the liquefaction of most CO_2, and finally expanded to 8-10 bar in a flash tank (-110 ºC) to facilitate biomethane purification via CO_2 solidification. Despite its synergies with the process of biomethane liquefaction, this technology is still not reliably commercialized at full scale and represents only 0.4 % of the upgrading market at a global level (Bauer *et al*, 2013; Bauer *et al*, 2013b; Thrän *et al*, 2014).

Cryogenic upgrading can provide a biomethane with a purity over 97 %, with methane losses lower than 2 % (Beil, 2009; Andriani *et al*, 2014). The emerging nature of this technology, with few operating plants in the United States, Sweden and The Netherlands, does not allow yet an accurate determination of its technical availability (Petersson and Wellinger, 2009; Bauer *et al*, 2013b). Water, H_2S, siloxanes and halogens must be removed prior to CO_2 removal to avoid operational problems such as pipe or heat exchanger clogging (Bauer *et al*, 2013b). On the other hand, no reliable data for investment and operating costs of cryogenic upgrading plants is available, with the only estimation reported by Hullu *et al* (2008) to 0.4 € Nm^{-3}. There is also a large uncertainty on the estimations of the energy needs for this process, with values ranging from 0.42 to 1 kWh/Nm^{-3} (Benjaminsson, 2006; Bauer *et al*, 2013b).

2.2 Biological CO_2 removal technologies

CO_2 mass transfer from the biogas to a microbial or enzymatic broth followed by a CO_2 biological reduction constitutes the basis of most biotechnologies currently under research. Of them, H_2-assisted CO_2 bioconversion, microalgae-based CO_2 fixation, enzymatic CO_2 dissolution, fermentative CO_2 reduction and in-situ CO_2 desorption are discussed below:

2.2.1. Chemoautotrophic biogas upgrading

The chemoautotrophic microbial conversion of CO_2 to CH_4 is based on the action of hydrogenotrophic methanogens capable of using CO_2 as their carbon source and electron acceptor, and H_2 as electron donor in the energy-yielding reaction described by equation 1 (Strevett *et al*, 1995):

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \ (\Delta G_0 = -131 \text{ KJ}) \qquad (1)$$

The bioconversion of CO_2 to CH_4 using an external H_2 injection has been used both in the upgrading of biogas to biomethane and in the reduction of CO_2 emissions from the electronic industry using the on-site hydrogen produced from the electrochemical treatment of its fluorhydric acid-containing wastewaters (Ju *et al*, 2008; Kim *et al*, 2013). Even syngas from coal or biomass gasification processes containing CO, H_2 and CO_2 can be upgraded to CH_4 based on the ability of some methanogens to convert CO to CH_4 and CO_2 ($4CO + 2H_2O \rightarrow CH_4 + 3CO_2$). Microorganisms from the Archaeal domain such as *Methanobacterium* sp., *Methanococcus* sp., *Methanothermobacter* sp., *Methanosarcina* sp., *Methanosaeta* sp., *Methanospirillum* sp. and *Methanoculleus* sp. have been consistently found in stand-alone bioreactors or anaerobic digesters upgrading CO_2 to CH_4 via H_2 injection (Strevett *et al*, 1995; Luo *et al*, 2012b; Kim *et al*, 2013; Luo and Angelidaki, 2013; Wang *et al*, 2013). These autotrophic methanogens often exhibit an optimum pH interval of 6.5-8 under both mesophilic and thermophilic conditions, and can even remove part of the H_2S present in the biogas by assimilation into biomass. However, while thermophilic methanogens (55-88 ºC) exhibit higher bioconversion rates than their mesophilic counterparts (30-40 ºC), the latter can achieve a more complete conversion of

CO_2 (Strevett *et al*, 1995). In addition, thermophilic methanogens often present lower growth yields (commonly defined as grams of biomass per mole of CH_4 formed), which ideally should be lower than 1 to promote the conversion of CO_2 to CH_4 rather than the formation of biomass. In this context, chemical compounds such as cyanide or alkylhalides have been shown to uncouple archaeal anabolism and catabolism, thus maximizing biomethane production (Strevett *et al*, 1995).

Most CO_2 bioconversion studies using H_2 as electron donor have been carried out at lab scale (0.05-100L) under mesophilic or thermophilic conditions in stirred tank, bubble column, packed bed or membrane bioreactors with synthetic mixtures of CO_2 and H_2 supplied at stoichiometric ratios (1:4) (Table 3) (Kim *et al*, 2013). The extremely poor aqueous solubility of H_2 (dimensionless gas-water Henry's law constant of 52) always limited the gas-water H_2 mass transfer rates and therefore the bioconversion of CO_2 to CH_4, which is known to occur in the aqueous phase containing the methanogenic community. In this regard, process operation under H_2 mass transfer limitation is known to decrease the efficiency of CH_4 production at the expenses of an enhanced biomass formation (Strevett *et al*, 1995). This resulted in the need to operate the process at extremely high gas residence times (1-208 h) in order to achieve CH_4 concentrations in the upgraded biogas over 90 %, but entailed low volumetric CH_4 productivities ranging from 0.65 to 5.3 L CH_4/L_r d (Table 3). The few bioreactors reporting volumetric CH_4 production capacities sufficiently high to support a cost-efficient CO_2 bioconversion (54-470 L CH_4/L_r d) were operated during short periods of time at low gas residence times (0.02-0.13 h) but yielded CH_4 concentrations (30-50%) not suitable for injection in natural gas grids or direct use as autogas. In this context, the implementation of this bioconversion in high-mass-transfer gas phase bioreactors such as two-phase partitioning or Taylor Flow bioreactors could support an increase in the volumetric CH_4 productivities of up to 1 order of magnitude, as reported during the treatment of volatile organic contaminants (Kreutzer *et al*, 2005).

On the other hand, the studies evaluating the performance of the direct H_2 injection in the anaerobic digester are scarce (Luo *et al*, 2012b; Luo and Angelidaki, 2013). This process configuration can avoid the use of an additional external bioreactor for biogas upgrading (estimated to require 1/10 of the digester volume), and made the anaerobic digestion of cattle manure and acidic whey more robust towards sudden increases in organic loading rates, unexpectedly preventing the accumulation of Volatile Fatty Acids (VFA) likely due to its associated pH increase (Luo and Angelidaki, 2013). Indeed, the addition of H_2 into the above described digester did not decrease the activity of the acetate kinase, a key enzyme in the bioconversion of VFA to acetate, and increased the activity of the coenzyme F420 (involved in hydrogenotrophic and acetoclastic methanogenesis). Likewise, the injection of H_2 into the digester also resulted in a significantly higher microbial activity, as shown by the twice higher specific ATP content of the H_2 supplemented biomass compared to the mixed liquor of a similar digester deprived of H_2 (Luo and Angelidaki, 2013). The main limitation of this process configuration arises from the fact that anaerobic digesters are not designed to maximize the gas-liquid mass transfer (excessive mixing might damage the structure and functionality of anaerobic flocs), which might limit the performance of this in-situ approach of CO_2 bioconversion at large scale. Even small scale (0.6 L) stirred tank digesters provided with fine bubble diffusers only achieved a biomethane composition of 75%/6.6%/18.4% $CH_4/CO_2/H_2$. In addition, the consumption of CO_2 in the digester can mediate inhibitory pH increases if the alkalinity of the organic fed is not properly controlled, as reported by Luo *et al* (2012b) during the anaerobic digestion of cattle manure.

The use of H_2 to upgrade biogas entails a significant loss in energy efficiency and requires the enforcement of severe safety operating procedures in anaerobic digestion plants as a result of the high flammability of hydrogen. However, the use of CH_4 as a fuel gas benefits from both the exiting gas distribution infrastructure and well established combustion technology, which represents the main reason to promote the production of CH_4 over H_2 (Wang *et al*, 2013). Water electrolysis from renewable energy sources (e.g. wind and solar power) represents nowadays the only environmentally friendly (large-scale) method to obtain H_2 for bioconversion of CO_2 to CH_4. In this context, it must be highlighted that the low density of H_2 often requires high storage volumes, while the technology for H_2 transportation and direct utilization is still under development. Therefore, H_2 transformation to biomethane, which can be injected into natural gas grids or employed as autogas, constitutes a very attractive alternative to chemically store an energy that would be otherwise lost. Finally, for chemoautotrophic biogas upgrading to be a sustainable and low cost technology, H_2 must be produced from water electrolysis using excess of electricity (typically during the night) or as a byproduct in a nearby facility (Kim *et al*, 2013).

2.2.2. Photosynthetic biogas upgrading

Photosynthetic biogas upgrading relies on the ability of eukaryotic microalgae and prokaryotic cyanobacteria (commonly referred to as microalgae) to bioconvert the CO_2 present in the biogas into microalgae biomass using the electrons released during water photolysis (López *et al*, 2013). This redox CO_2 reduction process, namely oxygenic photosynthesis, can be represented by the overall equation 2:

$$CO_2 + H_2O + \text{photons} + \text{nutrients} \rightarrow O_2 + CH_{1.63}N_{0.14}O_{0.43}P_{0.006}S_{0.005} + \text{waste heat} \quad (2)$$

Such process requires the initial transport of the CO_2 from the biogas to a microalgae-containing aqueous phase. Likewise, approximately 1.8 g CO_2 are required per gram of microalgae produced. The low affinity for CO_2 of the enzyme RubisCO in microalgae ($K_M \approx$ 1-8 mg CO_2 L^{-1}) does not entail however any technical limitation during photosynthetic biogas upgrading as a result of both the relatively high levels of CO_2 allowed in most European biomethane legislations (3-6 %) and the presence of inorganic carbon-concentrating mechanisms in most microalgae (Raven *et al*, 2008). Despite any microalgae could eventually support photosynthetic biogas upgrading, *Chlorella*, *Arthrospira* and *Spirulina* species have been preferentially used in the lab and pilot scale studies conducted up-to-date, based on their tolerance to high CO_2 and pH levels (Table 4). In this context, while CO_2 gas concentrations of 5 % were traditionally considered inhibitory for microalgae growth, the intense research efforts conducted over the past 10 years in the field of CO_2-biomitigation from flue gases have resulted in the isolation of species tolerant to CO_2 concentrations of up to 60 % (Miyairi, 1995; Wang *et al*, 2008). The presence of H_2S in the biogas can inhibit microalgae growth, with H_2S concentrations over 100 ppm_v exhibiting inhibitory effects on *Chlorella* sp. growth (Kao *et al*, 2012). However, the synergistic occurrence of H_2S oxidizing bacteria and the chemical oxidation of H_2S in biogas upgrading photobioreactors (operating under non-sterile conditions at high dissolved oxygen concentrations) rapidly oxidizes this toxic sulfur compound into sulphate, which eventually prevents any H_2S-mediated microalgae inhibition in real applications (Bahr *et al*, 2014). On the other hand, methane does not exert any significant inhibitory effect on microalgae growth in the concentration range of 20-80%, likely due to its low aqueous solubility and reactivity (Kao *et al*, 2012).

Provided a sufficient CO_2 mass transport from the biogas to the microalgal cultivation broth, the rate of CO_2 fixation, which itself determines the maximum biogas loading rate to be applied to the upgrading unit, is governed by environmental factors such as light availability, temperature, pH and dissolved O_2 concentration in the cultivation medium. Thus, the photosynthetic CO_2 fixation rate linearly increases when increasing light intensity up to a critical species-dependent saturation radiation (200-400 μE m^{-2} s^{-1}), remaining constant afterwards up to a critical photoinhibition value and deteriorating subsequently as a result of the damage in the microalgal photosystem II at high light intensities (Tredici, 2009). At this point it should be highlighted that light availability does not depend exclusively on the impinging light irradiation at the microalgae cultivation surface, but also on the biomass density and photobioreactor configuration (Muñoz and Guieysse, 2006). Most microalgae exhibit an optimum growth temperature in the range of 15 to 25ºC, although some species such as *Chlorella* can grow optimally at 30-35ºC, which are temperatures typically encountered in outdoor environments. On the other hand, while most microalgae present an optimum activity at pH 7-8, process operation at pH of 9-10 (optimal for cyanobacterial species such as *Spirulina platensis*) is desirable to maximize CO_2 mass transport from the biogas due to the acidic nature of this gas (Bahr *et al*, 2014; De Godos *et al*, 2014). Finally, high dissolved oxygen concentrations in the cultivation broth can mediate a competitive inhibition in the enzyme RubisCO (which also exhibits oxygenase activity) and oxidative damage in the photosynthetic apparatus of microalgae due to the formation of oxygen radicals.

The physical and biological mechanisms underlying CO_2 removal from biogas in photobioreactors are similar to those governing CO_2 capture from exhaust flue gases (Yan and Zheng, 2013; De Godos *et al*, 2014). Both processes have been implemented in open and closed photobioreactors (Table 4), which are designed to maximize light distribution, pH control, CO_2 supply and O_2 evacuation (Morweiser *et al*, 2010). Raceways, which constitute the most common configuration of open photobioreactors, are characterized by a simple construction and operation, and lower capital (2-20 € m^{-2}) and energy requirements (2-10 W m^{-3}) than their closed counterparts (Tredici, 2009; Craggs *et al*, 2012). However, raceways entail a poor light utilization efficiency (≈ 2 %), a high water footprint by evaporation (≈ 6 L m^{-2} d^{-1}) and large land requirements (López *et al*, 2013; De Godos *et al*, 2014). The higher photosynthetic efficiency of enclosed photobioreactors (4-6%), supported by their higher illuminated surface-volume ratio and turbulence, results in microalgae productivities of 0.4-1 g l^{-1} d^{-1}, but at the expenses of significantly higher energy consumptions (50-100 W m^{-3}) and investment costs (500-3000 € m^{-2}) (Acién *et al*, 2012). The number of studies evaluating the potential of microalgae-based biogas upgrading in photobioreactors is scarce, most of them being conducted indoors under artificial illumination and ambient temperatures (20-30 ºC) (Table 4). Bubble column and horizontal tubular photobioreactors, and raceways constructed with additional biogas scrubbing units rank among the preferred photobioreactor configurations evaluated. Most experimental units were capable of removing CO_2 with efficiencies higher than 80 %, providing a biomethane with CH_4 concentrations of ≈ 90% (Table 4). The gas residence times in the absorption units ranged from 0.03-0.3 h in outdoors photobioreactors to 0.7-96 h in indoor set-ups, which suggests that photosynthetic activity rather than CO_2 mass transfer limits the biogas upgrading capacity of photobioreactors. In this context, high biogas residence times in the absorption unit or a direct scrubbing in the photobioreactor entails high O_2 concentrations in the upgraded biomethane (5-25 %). This constitutes one of the main limitations to be overcome in this novel biotechnology, due to its associated explosion hazards and to the fact that most biomethane regulations require O_2 levels below 0.5 % (Mandeno *et al*, 2005). In this context, the use of a 2-stage process based on biogas scrubbing in an external column interconnected to the photobioreactor via a variable microalgae broth recycling has been shown to support a satisfactory biogas upgrading with O_2 concentrations below 1 % (Bahr *et al*, 2014) (Figure 4). Nitrogen gas stripping from the cultivation broth, which results in N_2 concentration of 6-9% in the upgraded biomethane, has been also identified as a technical limitation to be overcome. Thus, the removal of N_2 from biomethane would be required in order to comply with biomethane regulations of some European countries such as Sweden, Spain or Austria that require CH_4 contents over 95 % (Persson *et al*, 2006; Huguen and Le Saux, 2010; Serejo *et al*, 2015). Finally, the CH_4 losses derived from the mass transfer of CH_4 from biogas to the recycling microalgal cultivation broth and its subsequent oxidation by the methanotrophs present in this aqueous medium were recently estimated to be <1% as a result of the low aqueous solubility of methane (Serejo *et al*, 2015).

Unlike most physical/chemical CO_2 absorption technologies, where CO_2 is separated from the biogas and discharged to the atmosphere, photosynthetic biogas upgrading allows the valorization of this CO_2 in the form of a valuable algal biomass. This microalgal biomass could be used as a feedstock for the production of biofuels (biogas, bioethanol or biodiesel) or high-added-value products (Alcántara *et al*, 2013). In this context, health-promoting molecules from *Chlorella* sp., β-carotenes from *Dunaliella salina*, pharmaceuticals, cosmetics and phycobiliproteins from *Spirulina platensis* or eicosapentaenoic acid from *Nannochloropsi*s sp. are already commercially available (Spolaore *et al*, 2006; Raja *et al*, 2008). An additional advantage of photosynthetic biogas upgrading is the possibility of simultaneously removing the H_2S present in the biogas based on its much higher solubility and rapid bacterial oxidation kinetics at the typically high dissolved oxygen concentrations present in photobioreactors (Bahr *et al*, 2014). Finally, the fact that residual nutrients from the anaerobic digester can support microalgae growth brings an added environmental benefit to the process in term of biomitigation of the eutrophication potential of anaerobic digestion.

2.2.3 Other biological CO_2 removal methods

Fundamental studies on the use of the immobilized enzyme carbonic anhydrase resulted in a 99% pure biomethane (Mattiasson, 2005). This enzyme catalyses the reaction of CO_2 dissolution to bicarbonate in the blood and the reverse bioreaction of bicarbonate to CO_2 in the lungs (equation 3):

$$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^- \qquad (3)$$

This technology was recently patented by CO_2 Solution Inc. (CO2 solutions, 2014) and marketed for the removal of CO_2 from flue gases. However, the high production costs and low lifetime of the enzyme can limit the economic viability of this innovative biotechnology (Petersson and Wellinger, 2009). The CO_2 reduction needed for biological biogas upgrading can be also accomplished by using the CO_2 present in the biogas as a carbon source during the anaerobic fermentation of sugars to succinic acid (Gunnarsson *et al*, 2014). Bacterial species such as *Actinobacillus succinogenes*, *Mannheimia succiniciproducens*, *Anaerobiospirillum succiniciproducens*, *Corynebacterium glutamicum* and some recombinant *Escherichia coli* can use glucose, xylose, arabinose, galactose, maltose, fructose, sucrose, lactose, mannitol, arabitol, sorbitol, or glycerol to produce succinic acid, which requires the fixation of 1 mol of CO_2 per mol of succinic acid produced. In a recent investigation, Gunnarson et al. (2014) achieved an upgrading of biogas from 60% CH_4 to 95.4 % in a pressurized (1.4 bar) lab-scale stirred tank reactor inoculated with *Actinobacillus succinogenes* using glucose as a carbon and energy source.

2.2.4. CO_2 removal by in-situ desorption

Biogas upgrading by *in-situ* desorption of CO_2 is based on the higher aqueous solubility of CO_2 compared with CH_4. This technology has been implemented on a novel anaerobic digester configuration (Figure 5) consisting of an external desorption unit, interconnected with the anaerobic digester. The anaerobic mixed liquor is continuously recycled to an aerated desorption unit, operated in countercurrent mode. The dissolved CH_4, H_2S and CO_2 are easily stripped out from the recycling sludge, which results in an overall decrease in the H_2S and CO_2 content in the biogas. However, the methane yield is lower as a result of CH_4 losses (Lindberg and Rasmuson, 2006; Nordberg *et al*, 2012). The higher content of CO_2 in the mixed anaerobic liquor (mainly present as bicarbonate) compared to that of CH_4 support the quasi-selective separation of CO_2 in the desorption unit. Lindberg and Rasmuson (2006) identified the air flow rate in the desorption unit as a key operational variable during the evaluation of the performance of this innovative biogas upgrading configuration, using a bubble column as external desorption unit. The higher the air flow rate, the lower the CO_2 and H_2S content in the upgraded biogas but the higher the CH_4 losses and the redox potential of the mixed liquor, which surprisingly did not cause any negative effect on the activity of the digester. Longer (but high enough to bring CH_4 concentration to the set point) sludge residence times in the desorption unit are recommended to maximize CO_2 removal from biogas while minimizing methane losses and the N_2 content in the biogas. Maximum CH_4 concentrations of 87% with associated CH_4 losses of 8 % and biogas N_2 concentrations of 2% (the main biogas pollutant being CO_2) were obtained by Nordberg *et al* (2012) in a pilot scale (15-19 m^3) digesters interconnected to 90-140 L desorption units. Likewise, an external hollow fiber membrane (where degassing was driven by vacuum) was interconnected to a lab scale UASB reactor via mixed liquor recycling in a recent study by Luo and co-workers (2014), which resulted in a biomethane with CH_4 concentrations of ≈94 % and no disturbance on the COD removal or biogas yield.

Finally, it should be stressed that the fact that most biological CO_2 removal technologies are still in a lab or pilot scale limited the availability of both investment and operating cost data for the technologies discussed in section 2.2.

3. Removal of Hydrogen Sulfide

Unlike CO_2 removal, biotechnologies for biogas desulfurization are nowadays implemented at full scale due to their similar efficiencies and lower operating costs when compared to their physical/chemical counterparts. The following section reviews the most commonly used technologies for H_2S removal from biogas nowadays.

3.1. Physical/Chemical H_2S removal Technologies

Most physical/chemical technologies available nowadays for biogas desulfurization are conventional unit operations adapted from chemical engineering, which also support the removal of other sulfur biogas contaminants such as mercaptans. *In-situ* chemical precipitation, adsorption, absorption and membrane separation constitute the most commonly used technologies for H_2S removal from biogas.

3.1.1 In-situ H_2S precipitation

The addition of Fe^{2+} or Fe^{3+} in the form of $FeCl_2$, $FeCl_3$ and $FeSO_4^2$ into the digester or to the organic feed can efficiently control H_2S concentrations in the biogas by *in-situ* reacting with the H_2S in the anaerobic mixed liquor, generating the insoluble salt FeS (equations 4, 5) (Petersson and Wellinger, 2009; Ryckebosch *et al*, 2011):

$$Fe^{2+} + S^{2-} \rightarrow FeS \qquad (4)$$

$$2Fe^{3+} + 3S^{2-} \rightarrow 2FeS + S \qquad (5)$$

This technology is suitable to *in-situ* remove the H_2S biologically produced in the digester at high H_2S concentrations, but cannot cost-efficiently reduce H_2S levels in the biogas below 100-150 ppm_v (Persson *et al*, 2006). While this technology requires only an iron salt storage tank and a dosing pump as major investment, the high operating costs derived from the purchase of the chemical reagents (≈0.13-0.33 € kg $FeCl_3^{-1}$) represent the main disadvantage of this simple H_2S control approach. Thus, operating costs as high as 0.024 € m^{-3} of biogas have been reported in literature using a $FeCl_3$ dose of 0.035 kg $FeCl_3$/ kg of total sludge solids (Tomàs *et al*, 2009).

3.1.2 Adsorption

This classical unit operation is based on two parallel adsorbent modules (packed with either Fe_2O_3, $Fe(OH)_3$, ZnO or activated carbon) operated in an adsorption-regeneration (or alternatively adsorbent replacement) configuration. The high cost associated to the regeneration and replacement of the adsorbent material limits its application to small-medium scale digesters (Abatzoglou and Boivin, 2009).

Chemical adsorption of H_2S into Fe_2O_3, $Fe(OH)_3$ and ZnO-based filters has become a popular technology based on its simplicity, high efficiency (e.g. ZnO can provide H_2S biomethane levels down to 1 ppm_v), fast oxidation kinetics (Petersson and Wellinger, 2009; Ryckebosch *et al*, 2011). The oxidation of H_2S and further regeneration of this adsorbent material can be stoichiometrically described as follows (equations 6,7,8):

$$Fe_2O_3 + 3H_2S \rightarrow Fe_2S_3 + 3H_2O \quad (6)$$

$$2Fe(OH)_3 + 3H_2S \rightarrow Fe_2S_3 + 6H_2O \quad (7)$$

$$2Fe_2S_3 + 3O_2 \rightarrow 2Fe_2O_3 + 6S \quad (8)$$

These chemical reagents are often immobilized onto wood chips or red mud (a waste from aluminum manufacture) in order to increase the superficial area of the adsorbent, which significantly decreases as a result of aggregation due to biogas water condensation (Persson *et al*, 2006). The process is operated at gas residence times ranging from 1- 15 min using breakthrough threshold H_2S concentrations of ≈ 100 ppm_v. Adsorbent regeneration is a very exothermic process which can result in wood chip auto-ignition if temperature is not properly controlled, and can be conducted only 1-2 times based on an empirical loss of adsorption capacity of 33 % per regeneration (Abatzoglou and Boivin, 2009). Commercial adsorbents exhibit an adsorption capacity of 0.2 g H_2S per gram of iron wood chips or 1.8-2.5 g H_2S g $Fe_2O_3^{-1}$ under continuous operation with air supplementation (2-3 %) to allow an in-situ adsorbent revivification (Kohl and Neilsen, 1997; McKinsey, 2003; Kapdi *et al*, 2005). The cost of these adsorbents varies from 0.6 to 1.7 € kg^{-1} (Abatzoglou and Boivin, 2009). The high adsorbent costs and replacement frequency, together with the hazardous nature of the saturated material, entail very high operating costs (0.021-0.037 € m^3, considering 5 year capital amortization), which constitutes one of the main disadvantage of this technology. On the other hand, the investment costs (only considering the adsorption unit) largely depend on the commercial brand (SulfaTreat®, Sulfur-Rite®, Media-G2®, etc), ranging from 120 to 640 € $(m^3/h)^{-1}$.

H_2S removal can be also carried out using adsorption into non-impregnated, catalytic-impregnated, and impregnated activated carbons, the two latter catalyzing H_2S oxidation to elemental sulfur (which indeed is the element adsorbed onto the activated carbon) at higher rates (Persson *et al*, 2006; Abatzoglou and Boivin, 2009). Catalytic impregnation is conducted by treating the carbon with a nitrogen containing reagent such as urea or ammonia, while regular impregnation requires mixing of the carbon (before, during or after activation) with $NaHCO_3$, Na_2CO_3, NaOH, KOH, KI or $KMnO_4$. H_2S adsorption is performed at high pressure (7-8 bar) and temperature (50-70ºC) with addition of air to the biogas at 4-6 % in order to support the partial oxidation of H_2S (equation 9) (Ryckebosch *et al*, 2011):

$$2H_2S + O_2 \rightarrow 2S + 2H_2O \qquad (9)$$

Only KI or $KMnO_4$ impregnation supports the partial oxidation of H_2S in the absence of O_2. Carbon impregnated with these compounds is the preferred option for desulfurization when biomethane is to be injected in natural gas grids or used as a vehicle fuel (Petersson and Wellinger, 2009). Despite the elemental sulfur adsorbed can be desorbed at high temperatures, in most cases the saturated activated carbon bed is replaced rather than regenerated (Rutledge, 2005). Catalytic, impregnated and non-impregnated carbons exhibit maximum adsorption capacities of 0.1, 0.15 and 0.2 g H_2S g carbon^{-1}, respectively. The mechanisms underlying H_2S oxidation are highly sensitive to the chemical properties of the activated carbon surface, with acidic surfaces promoting H_2S oxidation to SO_2 and H_2SO_4, and alkaline surfaces boosting the production of elemental sulfur (Bandosz, 2002). In addition, the presence of water in the biogas severely deteriorates the performance of H_2S removal since this biogas component reacts with CO_2, forming carbonates, and promotes the formation of sulfurous acid, which can deactivate the active catalytic sites. Finally, while the operating costs of activated carbon adsorption range from 0.0005 to 0.037 € m^3_s

(with an average impregnated activated carbon cost of ≈ 4 € kg^{-1}), the capital cost of this technology accounts for 3-120 € $(m^3/h)^{-1}$ (Abatzoglou and Boivin, 2009).

3.1.3 Membrane separation

This process is based on the selective permeability of certain membranes to H_2S and the corresponding retention of CH_4 on the other side of the membrane. Gas-liquid membranes using alkaline liquids on the other side of microporous hydrophobic membranes can support H_2S removal efficiencies of 98% during the desulfurization of biomethane containing H_2S at 2% (Ryckebosch *et al*, 2011). This technology is similar to that described in section 2.1.5 for CO_2 removal. H_2S removal efficiencies of 58-94% have been recently reported by Iovane *et al* (2014) using a Polymeric polyetheretherketone Hollow fiber membrane (150 ×1210 mm) at biogas operating pressures of 25-41 bar.

3.1.4 H_2S absorption

The absorption of H_2S from biogas in conventional gas-liquid contactors (spray or packed bed towers) can be carried out using either water or organic solvents in a process purely based on physical absorption, or using aqueous chemical solutions with a conversion of H_2S to elemental sulfur or metal sulfides (Wellinger and Lindberg, 1999). While H_2S absorption in water can be implemented in both single pass and absorption-desorption configurations, absorption in organic solvents such as Selexol (which entails lower liquid flow rates than water scrubbing as a result of its higher affinity for H_2S) requires solvent regeneration based on their high cost (Ryckebosch *et al,* 2011). Absorption-desorption configurations for H_2S removal are similar to Figure 1C. Both water and organic solvent scrubbing are suitable for the removal of low concentrations of H_2S, and only competitive when combined with the simultaneous removal of CO_2 (Wellinger and Lindberg, 1999; Kapdi *et al*, 2005).

The addition to the scrubbing process of chemical reagents such as NaOH, $FeCl_2$, $Fe(OH)_3$, Fe^{3+}/MgO, $Fe^{3+}/CuSO_4$ and Fe^{3+}/EDTA can support a maximum H_2S concentration gradient between the biogas and the aqueous phase, thus reducing the liquid to biogas ratio needed for an efficient H_2S mass transfer (Abatzoglou and Boivin, 2009; Ryckebosch *et al*, 2011). The soluble salts sodium sulfide and sodium hydrogen sulfide are the end-products during water scrubbing with NaOH solutions, hindering the regeneration of the NaOH solution (Persson *et al*, 2006). However, this process is only applied for the upgrading of high H_2S concentrations or large biomethane flow rates based on the harsh operational conditions imposed by the high concentrations of NaOH required (Petersson and Wellinger, 2009). In addition, the presence of CO_2 in the biomethane significantly increases chemical requirements. Likewise, Fe^{3+}-based scrubbing was originally developed (and patented under trademarks such as SulFerox® or LO-CAT®) for the desulfurization of sour gases from oil and coal industry, and therefore only cost-effective for the upgrading of high biogas flow rates with high H_2S concentrations (>200 kgS d^{-1}). This technology is highly efficient, supporting final H_2S biomethane concentrations of 1-10 ppm_v, with an almost complete regeneration of the oxidizing agent Fe^{3+} via aeration in a separate stage (Abatzoglou and Boivin, 2009; Petersson and Wellinger, 2009). The chelated iron Fe^{3+}/EDTA (typically present at 0.2 mol L^{-1}) is one of the most popular catalyst used for H_2S capture since the elemental S produced during the reduction of Fe^{3+} to Fe^{2+} according to equation 10 (a first order reaction on iron and sulfur) can be easily recovered by sedimentation prior to the regeneration of the Fe^{3+}/EDTA solution by oxidation with air according to equation 11 (Neumann and Lynn, 1984; Demmink and Beenackers, 1998):

$$2Fe^{3+} + S^{2-} \rightarrow 2Fe^{2+} + S \quad (10)$$

$$2Fe^{2+} + 0.5O_2 + H_2O \rightarrow 2Fe^{3+} + 2OH^- \quad (11)$$

This process can be operated at ambient pressure and temperature using gas residence times (≈ 1 min) comparable to those used by their chemical adsorption counterparts (Horikawa *et al*, 2004). Chelated iron based technologies can also remove 50-90 % of the mercaptans present in the biomethane, without a significant reduction in CO_2 concentration, at operation costs of 0.24-0.3 € kgS^{-1} (Abatzoglou and Boivin, 2009).

On the other hand, the use of $FeCl_2$ and $Fe(OH)_3$ solutions result in the formation of the insoluble salts FeS and Fe_2S_3 (Ryckebosch *et al*, 2011). Another process based on the formation of intermediate insoluble metallic sulfides was originally developed by Broekhuis *et al* (1992) for sour gas desulfurization using solutions of $CuSO_4$ supplemented with Fe^{3+} in a process operated at 60 ºC and gas residence times of 16-22 s. In this process, H_2S is transformed in a venture scrubber into CuS as described by equation 12, which is further converted to elemental sulfur using Fe^{3+} as electron donor according to equation 13. The electron donor is subsequently regenerated with air in a bubble column (equation 14):

$$Cu^{2+} + H_2S + 2SO_4^{2-} \rightarrow CuS + 2HSO_4^- \quad (12)$$

$$CuS + 2Fe^{3+} \rightarrow Cu^{2+} + Fe^{2+} + S \quad (13)$$

$$2Fe^{2+} + 0.5O_2 + 2HSO_4^- \rightarrow 2Fe^{3+} + H_2O + 2SO_4^{2-} \quad (14)$$

Finally, a full scale chemical scrubber using NaOH and H_2O_2 (as oxidizing agent) supported H_2S removal of 90-100 % at a plant availability of 95 % and operating cost of 0.03 € m^{-3} biogas (Miltner *et al*, 2012).

3.2 Biological H_2S removal technologies

The ability of naturally occurring sulfur oxidizing bacteria (SOBs) has been used in conventional biofiltration units, algal-bacterial photobioreactors and at the headspace of anaerobic digesters to desulfurize biogas.

3.2.1 Biofiltration of H_2S

The ability of lithoautotrophic bacteria to use H_2S as electron donor and CO_2 as carbon source has supported the development of end-of-the pipe biotechnologies for biogas upgrading (Montebello, 2013). Unfortunately, the removal of CO_2 from biogas in this particular technology is marginal compared to that of H_2S (> 99% if properly designed) due to the significantly lower H_2S concentrations compared to CO_2 and to the low biomass yields of SOBs ($Y_{X/S} \approx 0.3$ g VSS g S^{-1}) (Mora *et al*, 2014). Oxidation of H_2S using O_2 as the electron acceptor provides the energy required for lithotroph growth according to equations 15 and 16.

$$H_2S + 0.5O_2 \rightarrow S + H_2O \qquad (15)$$

$$H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^+ \qquad (16)$$

The biological oxidation of H_2S can be also carried out using NO_3^- (or NO_2^-) as electron acceptors, which would avoid the contamination of biogas with O_2 in the biofiltration unit, via the denitrification reactions described by equations 17 and 18 (Soreanu *et al*, 2008):

$$3H_2S + NO_3^- \rightarrow 3S + 0.5\ N_2 + 3H_2O \qquad (17)$$

$$3H_2S + 4NO_3^- \rightarrow 3SO_4^{2-} + 2N_2 + 6H^+ \qquad (18)$$

Thus, low O_2/S and NO_3^-/S ratios result in the preferential production of elemental sulfur. Bacteria belonging to the genera *Thiobacillus, Paracoccus, Thiomonas, Acidithiobacillus, Halothiobacillus* or *Sulfurimonas*, which are either strictly aerobes or facultative anaerobes are capable of performing these H_2S bioconversions. These microorganisms present optimum growth temperatures in the range of 28-35 ºC. In addition, while most SOBs exhibit an optimum activity at pH 6-8, extremophile species such as *Acidithiobacillus ferrooxidans* or *Acidithiobacillus thioxidans*, present an optimum biocatalytic activity in the low pH range (2-4) (Montebello, 2013). Strains of *Acidithiobacillus thioxidans* with maximum sulfide oxidation rates of 21 g S g TSS^{-1} d^{-1} and tolerant to pH values as low as 0.2 and sulfate concentrations as high as 74 g L^{-1} have been reported in literature (Lee *et al*, 2006).

This end-of-the-pipe biotechnology has been mainly implemented in biotrickling filters (BTF) due to their cost effectiveness, efficient gas-liquid mass transfer and easy control of operational variables such as pH, temperature or nutrient supply (Estrada *et al*, 2012). Desulfurization BTFs are packed bed columns (pall rings, HD-QPAC or polyurethane foam as packing material supporting biofilm growth) operated with a recirculating aqueous phase (at rates of 1-20 m h^{-1}) containing the nutrients needed for SOB growth under pH controlled conditions in the neutral (6-7.5) or acidic (2-3) range (Fortuny *et al*, 2011) (Table 5). This bioreactor configuration has been successfully operated at laboratory and full scale using both O_2 (supplied via aeration) and NO_3^- as electron acceptors for the treatment of H_2S concentrations ranging from 500-10000 ppm_v with efficiencies of 80-100 %, H_2S being totally depleted at concentrations below 2000 ppm_v (Table 5). The high concentrations of H_2S present in biogas entail the operation of desulfurization BTFs at gas residence times ranging from 2-16 min, which are 2 orders of magnitude larger than those typically encountered in BTFs treating H_2S malodorous emissions in WWTPs (Gabriel and Deshusses, 2003). In this context, mass transfer limitations were recorded in desulfurization BTFs operated below 120 s at a H_2S concentration of 2000 ppm_v (Fortuny *et al*, 2011). The high H_2S loading rate applied to these biological units, together with their satisfactory desulfurization efficiency, result in ECs ranging from 40-220 gS m^{-3} h^{-1}. Air is typically used as O_2 source based on its free availability, but results in the dilution or contamination of biogas with N_2 and O_2 (the transfer of the latter to the liquid phase hindered by its high Henry law constant). O_2/H_2S ratios of 2-41 have been implemented, the higher ratios promoting a full oxidation of H_2S to SO_4^{2-} but a higher dilution of the biomethane, which can limit its further applications. On the other hand, no significant differences on the desulfurization performance were observed in anoxic BTFs using $Ca(NO_3)_2$, KNO_3 and $NaNO_3$, although a concern exist on the potential accumulation of calcium salts (Fernández *et al*, 2014).

H_2S biofiltration exhibits a surprisingly high robustness (e.g recovery of steady state H_2S removal efficiencies within 4 h after a 5-days biogas supply shutdown) and lower operating costs than physical/chemical technologies (Fortuny *et al*, 2011). Thus, operating costs of 0.013 and 0.016 € m^{-3} of biogas treated were estimated by Fernandez *et al* (2014) and Tomàs *et al* (2009) for aerobic and anoxic biotrickling filtration, respectively, which are significantly lower than the costs associated to $FeCl_3$-mediated H_2S chemical precipitation or H_2S chemical scrubbing (0.024 and 0.03 € m^{-3}, respectively) (Tomàs *et al*, 2009; Miltner *et al*, 2012). Packing media clogging, entailing higher operating costs derived from the increase in pressure drop and the need for packing media cleaning or replacement, as a result of elemental sulfur accumulation constitutes the main operational limitations of this technology (Montebello *et al*, 2014). However, S accumulation can be minimized by either the natural presence of mercaptans in biogas (as a result of the chemical reaction of mercaptans with the accumulated S and the further biological oxidation of the DMDS formed) or the implementation of operational strategies based on the oxygenation of the packed bed in the absence of biogas supply (which has been shown to remove 80 % of the accumulated S within a week) (Montebello *et al*, 2012; Montebello *et al*, 2014).

3.2.2 In-situ microaerobic H_2S removal

Microaerobic H_2S removal in the headspace of anaerobic digesters relies on the action of SOBs able to grow lithoautotrophically on H_2S while producing S^0 under O_2-limited conditions according to equation 15 (Madigan *et al*, 2009). SOBs show diverse morphological, physiological and ecological characteristics and employ primarily O_2 as the terminal electron acceptor, since many sulfur chemolithotrophs are aerobic (Tang *et al*, 2009). While *in-situ* microaerobic H_2S removal has been traditionally used in anaerobic digesters treating agricultural wastes based on the economic benefits of on-site biogas exploitation (Schneider *et al*, 2002), recent research has extended its application to anaerobic reactors treating industrial wastewaters (Rodríguez *et al*, 2012), WWTP sludge or cow manure (Jenicek *et al*, 2008; Kobayashi *et al*, 2012). In this particular technology, the headspace of anaerobic digesters acts as a H_2S abatement unit where different microaerophilic SOBs such as *Acidithiobacillus* sp., *Arcobacter* sp., *Sulfuricuvum* sp., *Sulfurimonas* sp., *Thiobacillus* sp., *Thiofaba* sp. and *Thiomonas* sp. developed when a limited amount of O_2 is supplied (Díaz *et al*, 2011b; Kobayashi *et al*, 2012; Rodríguez *et al*, 2012). SOBs grow over the headspace walls and ceiling due to the lack of any specific biomass support, thus creating superimposed laminas of S^0 that act as a support material (with a high specific surface area which facilitates both O_2 transfer and further microbial growth) (Díaz *et al*, 2011b; Kobayashi *et al*, 2012). The main advantage of *in-situ* H_2S removal is that additional end-of-pipe units for desulfurization are avoided. However, an excessive S^0 deposition in the digester's headspace might impair the removal performance over the time by reducing the residence time of biogas and, accordingly, the O_2 transfer rate to the microorganisms. This ultimately requires a periodical cleaning to maintain the H_2S removal efficiency.

Research studies on *in-situ* microaerobic H_2S removal have been performed in Upflow Anaerobic Sludge Blanket bioreactors, Expanded Granular Sludge Bed bioreactors and fully mixed digesters under a wide range of biogas flow rates (7L d^{-1}-250m^3 h^{-1}), H_2S concentrations (2500- 67000 ppm_v) and operational conditions affecting O_2 mass transfer rate in the headspace (Table 6). The biogas residence time in the headspace was found to be a key parameter determining the desulfurization efficiency. Hence, H_2S removal efficiencies over 97 % are typically encountered when operating at biogas residence times over 5 h. Empirical observations also pointed out that higher O_2 to H_2S molar ratios are required to maintain a H_2S removal efficiency over 99%, when decreasing the biogas residence time in the headspace. In this context, the O_2 (or equivalent air) supply rate can be adjusted to 0.3%-3% of the biogas production rate depending on the H_2S concentration and the aforementioned biogas residence time. However, a variable O_2/air dosing is often required in most digesters in order to minimize the residual O_2 in the upgraded biogas as a result of the variable biogas production rates. Hence, a residual O_2 concentration of 1-1.8% in the biogas can be reached by controlling the ORP in the anaerobic mixed liquor, while a 0.3-0.5% residual O_2 concentrations were recorded when employing biogas production as the control variable, despite both operational approaches supported H_2S removal efficiencies larger than 99% (Ramos and Fdz-Polanco, 2014). O_2 can be supplied to the liquid recirculation or directly to the headspace of the anaerobic digester. In this regard, similar H_2S removal efficiencies at equivalent O_2 dosing rates were found since microaerophilic SOBs seem to be favored under O_2 limiting conditions (Díaz *et al*, 2011b; Kobayashi *et al*, 2012; Ramos *et al*, 2014). In contrast, mixing conditions can be manipulated to control the amount of O_2 supplied and the removal of dissolved sulfide (Figure 6). Thus, when anaerobic mixed liquor mixing provides a low contact between the biogas and mixed liquor, i.e. by using liquid recirculation or low speed mechanical agitation, H_2S is removed from the biogas without altering the concentration of total dissolved sulfide. On the other hand, when biogas recirculation is employed and the contact between phases is larger, both H_2S in the biogas and dissolved sulfide are oxidized (Díaz *et al*, 2011b). Besides, a higher O_2/H_2S ratio was necessary to achieve satisfactory H_2S removals with biogas recirculation when compared to sludge recirculation, and the concentration of more oxidized sulfur species such as $S_2O_3^{2-}$ increased presumably as a result of the higher O_2 mass transfer rate (Díaz *et al*, 2011a).

In this particular technology, the low O_2 supply rates required do not significantly compromise the performance of organic matter removal or CH_4 productivity (Díaz *et al*, 2010; Rodríguez *et al*, 2012). On the contrary, enhanced organic matter hydrolysis and methanogenic activity as a result of the suppression of sulfide toxicity have been reported (Jenicek *et al*, 2010; Jenicek *et al*, 2011). Air supply is often the less costly alternative, but CH_4 dilution by nitrogen can eventually reduce the combustion engine efficiency. In fact, a recent economic evaluation of the *in-situ* H_2S treatment of 550 m^3/h of biogas in full-scale WWTP sludge digesters showed that the total cost of H_2S removal using a PSA O_2 generator (92-98% O_2) was lower than process operation with air or pure O_2. Thus, the utilization of an oxygen generator showed the lowest operational costs (0.82 € kg-S^{-1} or 0.0018 € m^{-3} of biogas treated) compared to air and pure O_2 supply (1.18 € kg-S^{-1} or 0.0026 € 100^3 and 1.72 € kg-S^{-1} or 0.0037 € 100^{-3}, respectively). Conversely, the investment cost on the equipment for e-donor supply accounted for 10000 € for pure O_2, 19000 € for air supply and 30000 € for concentrated O_2 (Díaz *et al*, 2015).

3.2.3 Microalgae-based H_2S removal

Algal-bacterial symbiosis in photobioreactors can support the simultaneous removal of H_2S and CO_2 in a single process (Bahr *et al*, 2014). Thus, the O_2 supplied by microalgal photosynthesis during CO_2 biofixation is used by SOBs to fully convert H_2S to sulfate based on the high dissolved O_2 concentration typically encountered in microalgal photobioreactors. In this process, the higher aqueous solubility of H_2S compared to CO_2, along with the rapid H_2S microbial oxidation kinetics, always render CO_2 removal as the limiting step during biogas upgrading in algal-bacterial systems (entailing biogas residence times in the absorption column of 1-2 h). Indeed, most studies evaluating H_2S removal in photobioreactors reported efficiencies of 100 % regardless of the use of stand-alone photobioreactors with in-situ biogas sparging or two-stage absorption column-photobioreactor configurations (Figure 4) (Mann *et al*, 2009; Bahr *et al*, 2014; Serejo *et al*, 2015).

Most of the technologies developed and implemented at pilot and full scale use O_2 as an electron acceptor for H_2S removal, however promising results have been obtained at lab and pilot scale using NO_3^- as an electron acceptor. In this context, biogas desulfurization by lithotrophic denitrification is a very promising field of research that would support the simultaneous removal of sulphide from biogas and nitrogen from wastewater in WWTPs, especially in processes using anaerobic digestion as a core WWT technology (Dolej et al. 2015; Deng et al. 2009).

4. Removal of H_2O

Water is nowadays removed from biogas only by physical/chemical technologies such as adsorption, absorption or condensation (Rutledge, 2005). Water adsorption can decrease the biomethane's dewpoint down to -40 ºC and is carried out in pressurized columns (6-10 bar) packed with silica, alumina, magnesium oxide or activated carbon. This technology requires two adsorption columns in parallel operated sequentially: while one column is in operation until saturation, the other is being regenerated at low pressure (Persson *et al*, 2006). Despite its lower operating costs, water adsorption requires high investment cost and a previous removal of dust and oil particles. On the other hand, water absorption in glycols operates in a similar way as CO_2 scrubbing in organic solvents, and can decrease the biomethane`s dewpoint down to -15 ºC, requiring solvent regeneration at 200ºC. This technology supports the simultaneous removal of oil and dust particles during the absorption of water. However, it entails high operating and investment costs due to the energy intensive solvent regeneration and its moderately high operating pressures. In addition, a minimum biomethane flow rate of 500 m^3 h^{-1} is often required to guarantee the economic viability of glycol-based absorption (Ryckebosch *et al*, 2011). Water absorption in hygroscopic salts is also a very efficient process but carried out batchwise, since the absorbent material is often replaced upon saturation rather than *in-situ* regenerated (Persson *et al*, 2006). Finally, biogas cooling at atmospheric pressure, and the subsequent separation of the condensed water droplets by deminsters, cyclones or water traps, represents the simplest but less efficient water separation process since it can only decrease the biomethane dewpoint to 0.5 ºC, due to operational problems caused by water freezing at the surface of the heat exchanger. Lower dewpoints down to -18 ºC require the compression of the biomethane prior to cooling (Ryckebosch *et al*, 2011). Biogas cooling is nowadays performed using electric coolers or underground pipelines provided with water traps as a exchanger (Petersson and Wellinger, 2009).

5. Removal of other trace pollutants

5.1 Removal of O_2 and N_2

Despite the N_2 content of biomethane is not directly regulated in most European legislations, the minimum CH_4 levels required for biomethane injection in natural gas grids demand a strict control of this biogas pollutant. Likewise, the low admissible levels of O_2 in biomethane (typically < 0.5%) entail the need for cost-effective strategies for the control of air intrusion in anaerobic digesters or in the biogas extraction system of landfills since the end-of-pipe removal of these two air compounds from biomethane is extremely costly (Petersson and Wellinger, 2009). In this context, both compounds can be removed using low temperature PSA (using activated carbon or molecular sieves as adsorbents) or membrane separation (Persson *et al*, 2006; Ryckebosch *et al*, 2011).

5.2 Removal of halogenated compounds

Activated carbon filtration using two packed bed modules operated in parallel in an adsorption-regeneration configuration is often used for the removal of halocarbons (Ryckebosch *et al*, 2011). To the best of our knowledge, no end-of-pipe biotechnology has been tested for the removal of these trace halogenated contaminants from biogas despite halocarbons typically found in landfill biogas such as 1,1,1-trichloroethane, 1,1-dichloroethane, 1,2-dichloroethane, tetrachloroethylene, 1,1,1-trichloroethane, tetrachloromethane, dichloromethane, dichlorodifluoromethane and 1,1,2-trichlorotrifluoroethane can be biologically degraded under aerobic and anaerobic conditions (Deipser and Stegmann, 1997; Lollar *et al*, 2010; Schmidt *et al*, 2010).

5.3 Removal of siloxanes

Adsorption constitutes the only technology commercially available for methyl siloxane removal, exhibiting moderate to high operating costs as a result of process operation at high pressure, and the need for regeneration or replacement of the adsorbent material (Ryckebosch *et al*, 2011; Soreanu *et al*, 2011). A preliminary adsorbent screening is often recommended since the efficiency of this classical unit operation is determined by the type of siloxane present in the raw biogas (Schweigkofler and Niessner, 2001). Activated carbon adsorption can support siloxane removals of up to 95 % when treating dry biomethane, since the presence of water significantly deteriorates its adsorption potential by competition for the active sites (Ryckebosch *et al*, 2011). Unfortunately, the regeneration of siloxane-saturated activated carbon at high temperatures has been proven not cost-effective (Persson *et al*, 2006; Abatzoglou and Boivin, 2009). Other adsorbents such as silicagel, despite being also limited by high moisture contents, have shown a superior performance, with siloxane removal efficiencies of up to 99 %, adsorption capacities of 0.1 g siloxanes $g_{silicagel}^{-1}$ and an easy regeneration (95 % adsorption capacity recovery at 250ºC for 20 min). Zeolites and activated alumina have been also successfully tested, and even patented, for siloxane removal from biomethane (Higgins, 2007). The few economic data available on siloxane removal by activated carbon filtration estimates operating costs ranging from 0.003 to 0.023 € kWh^{-1} of energy produced from biogas (Ajhar *et al*, 2010). On the other hand, the cryogenic condensation of siloxanes can support satisfactory removals (99.3 %) only when decreasing biomethane temperature down to -70 ºC (Hagmann *et al*, 2001). However, and despite the absence of costly/hazardous reagents and the simultaneous drying of the biomethane during cryogenic siloxane separation, the high investment and operating costs still hinder the scale-up of this technology (Soreanu *et al*, 2011). Siloxane absorption into organic solvents such as tetradecane or Selexol in spray or packed bed towers can provide siloxane removal efficiencies of 97-99 % at the expenses of high operating costs (mainly derived from solvent regeneration). Similarly, reactive absorption using concentrated HNO_3 (65%) and H_2SO_4 (48%) aqueous solutions at 60ºC can support siloxane removals of 95 %, although the sustainability of this technology (from an environmental and techno-economic perspective) has limited its widespread implementation (Schweigkofler and Niessner, 2001).

Despite the general belief that methyl siloxanes are non-biodegradable (Abatzoglou and Boivin, 2009), microorganisms from the genus *Pseudomonas* are capable of biodegrading hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane (Accettola *et al*, 2008). Unfortunately, there is no experimental study evaluating the potential of biotechnologies to abate methyl siloxanes in biogas. The only two works reported in this topic use a siloxane-laden air as a model emission. Popat and Deshusses (2008) recorded removal efficiencies of 50-60 % in a 0.4 L biotrickling filter packed with cattle bone porcelite treating an air emission containing 45 mg m^{-3} of octamethylcyclotetrasiloxane, at a gas residence time of 30-40 min. Removal efficiencies of 15 % were also observed by the authors in a similar experimental set-up operated under anaerobic conditions, at a gas residence time of 4 min using a octamethylcyclotetrasiloxane-laden emission. Likewise, Acettola *et al* (2008) reported removal efficiencies of 20% in 1.9 L biotrickling filter packed with Pall rings during the treatment of an air emission containing 46 mg m^{-3} of hexamethylcyclotrisiloxane, at a gas residence time of 2.1 min. Both studies explained the low siloxane elimination capacities recorded as a result of the strong mass transfer limitations mediated by the extremely low aqueous solubility of this type of biogas pollutants, although the recalcitrant nature of methyl siloxanes is widely accepted. In this context, high mass transfer bioprocesses such as two-phase partitioning or Taylor flow bioreactors are expected to support higher methyl siloxane removal efficiencies at significantly lower gas residence times in order to make biotechnologies competitive with state-of-the-art adsorption technologies (Kreutzer *et al*, 2005).

6. Conclusions

Physical/chemical technologies for biogas upgrading based on absorption, adsorption, chemical reaction, membrane separation or cryogenic separation are nowadays mature technologies capable of providing a biomethane suitable for injection into natural gas grids or use as autogas, with a limited room for technical and economic optimization (with the exception of membrane or cryogenic separation). However, their high energy and chemical requirements impose a severe limitation to the exploitation of the full potential of biogas as a renewable energy source. In this context, biotechnologies such as algal-bacterial photobioreactors can provide a simultaneous CO_2 and H_2S removal in a single process, while bioconverting CO_2 into a valuable feedstock for the production of bioenergy or high added value products. The conversion of the electricity grid excess during the night into H_2, and its use as electron donor in chemolitotroph-based bioreactors can bioconvert the CO_2 from biogas into CH_4. Both technologies have been so far evaluated at lab and pilot scale, industrial scale testing and optimization being still necessary to show their full potential for biogas upgrading. Mass transfer limitations of CO_2 and H_2 have been identified as the main bottlenecks of algal-bacterial photobioreactor and chemolitotrophs-based bioreactors, respectively. Similarly, biotechnologies such as aerobic or anoxic biotrickling filtration and anaerobic digestion under microaerophilic conditions have been consistently shown to support H_2S removal efficiencies > 99 % at significantly lower operating costs than *in-situ* chemical precipitation, adsorption or chemical scrubbing. These biotechnologies have undergone a rapid development over the past 20 years and are nowadays commercially available and implemented in full scale facilities. However, both biotechnologies don't allow for a significant CO_2 removal, contaminate the biomethane with O_2 and N_2 and still suffer from operational problems derive from elemental sulfur accumulation in the digester's headspace or in the packed bed. Finally, the high catabolic potential of microorganisms allows for the biodegradation of both methyl siloxanes and halocarbons from biogas. Little research, and only restricted to lab scale feasibility tests, has been conducted in this particular field, with methyl siloxane mass transfer from the gas phase to the microorganisms being identified as the main process limitation. Based on their high biogas pollutant removal efficiencies and robustness, research on innovative biogas-microbial community mass transfer strategies and process scale-up constitute the road map to the development of cost-efficient and sustainable biotechnological process for an integral upgrading of biogas.

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Figure 1. Biogas upgrading by liquid absorption. A) Water scrubbing; B) Organic solvent scrubbing; C) Chemical scrubbing. Adapted from Bauer *et al* (2013b).

Figure 2. Biogas upgrading by Pressure Swing Adsorption (PSA). Adapted from Bauer *et al* (2013b).

Figure 3. Biogas upgrading by membrane separation. Different configurations of gas-gas units: I) single-pass membrane unit, II) multiple stage membrane units with internal recirculation of permeate and III) internal recirculation of retentates. Adapted from Bauer *et al* (2013b).

Figure 4. Biogas upgrading using microalgae cultures. Adapted from Bahr *et al* (2014).

Figure 5. CO_2 removal by *in-situ* desorption in the anaerobic digester.

Figure 6. Evolution of sulfur species under anaerobic/microaerobic conditions and the effect of mixing conditions.

Figure 1
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Figure 1.

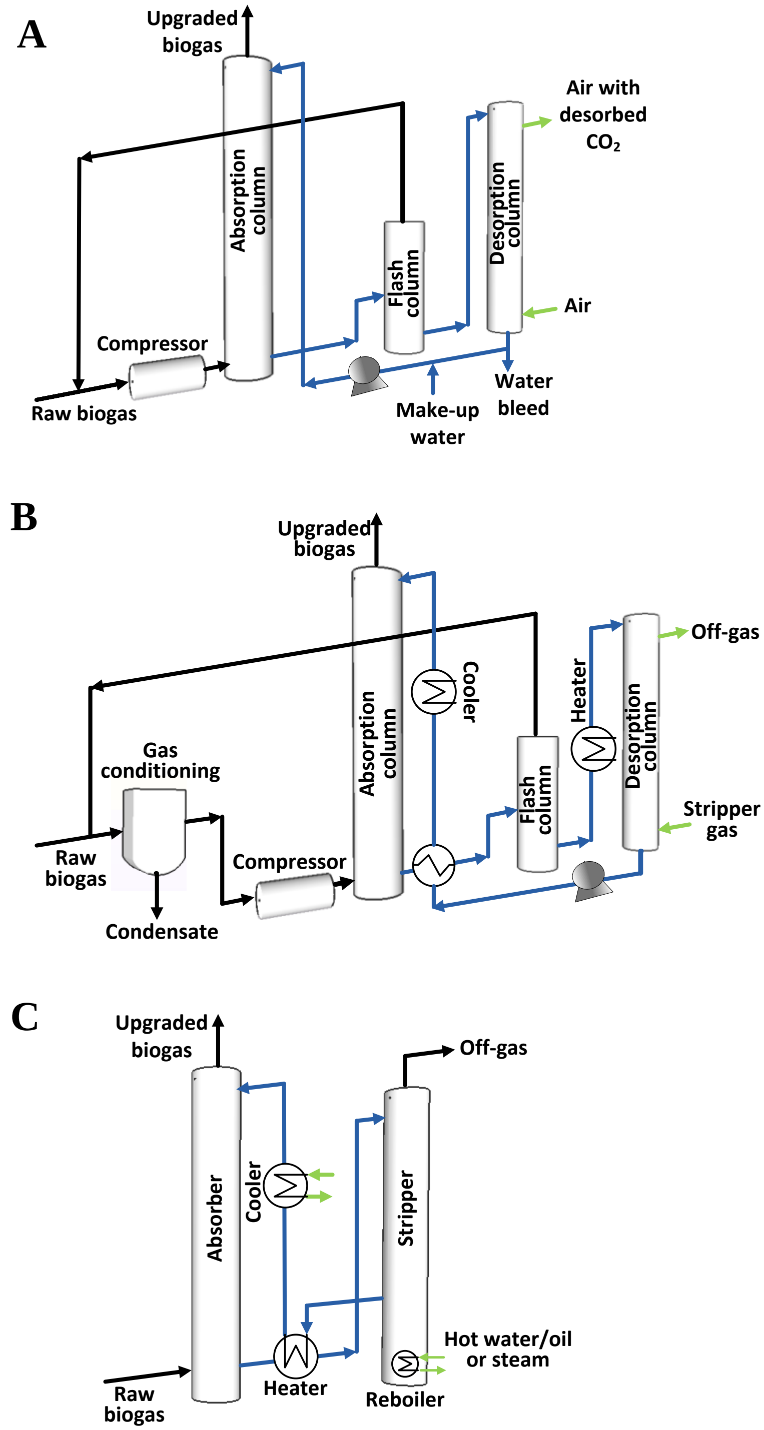

Figure 1. Biogas upgrading by liquid absorption. A) Water scrubbing; B) Organic solvent scrubbing; C) Chemical scrubbing. Adapted from Bauer *et al* (2013b).

Figure 2
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Figure 2.

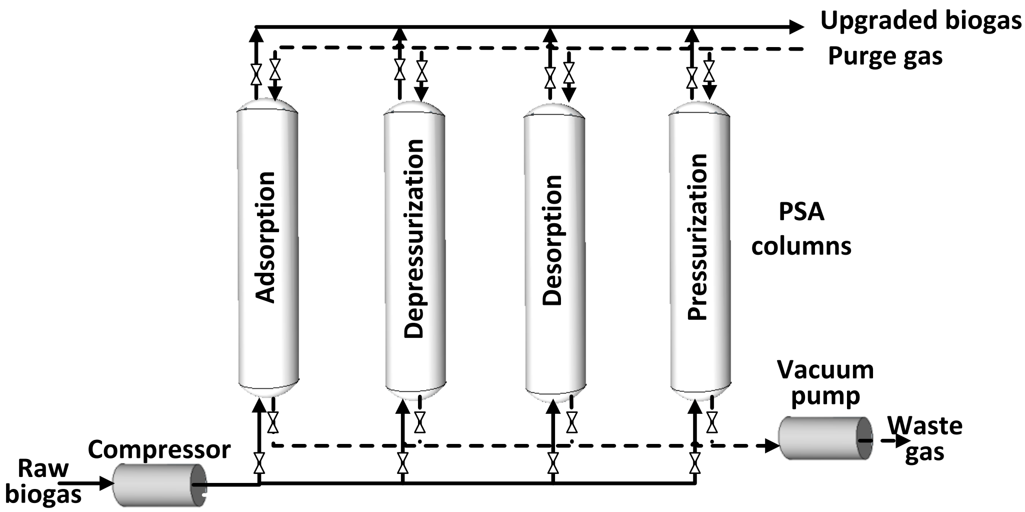

Figure 2. Biogas upgrading by Pressure Swing Adsorption (PSA). Adapted from Bauer *et al* (2013b).

Figure 3
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Figure 3.

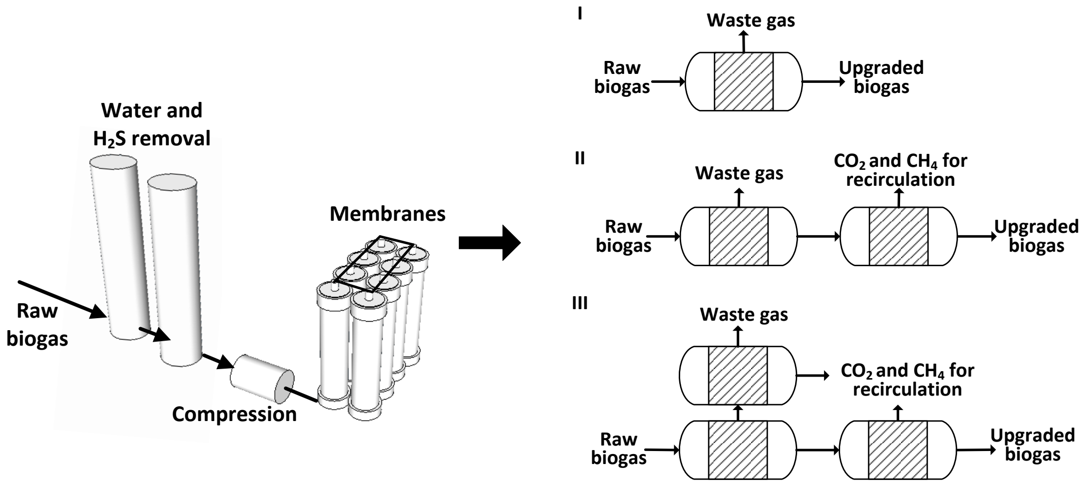

Figure 3. Biogas upgrading by membrane separation. Different configurations of gas-gas units: I) single-pass membrane unit, II) multiple stage membrane units with internal recirculation of permeate and III) internal recirculation of retentates. Adapted from Bauer *et al* (2013b).

Figure 4
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Figure 4.

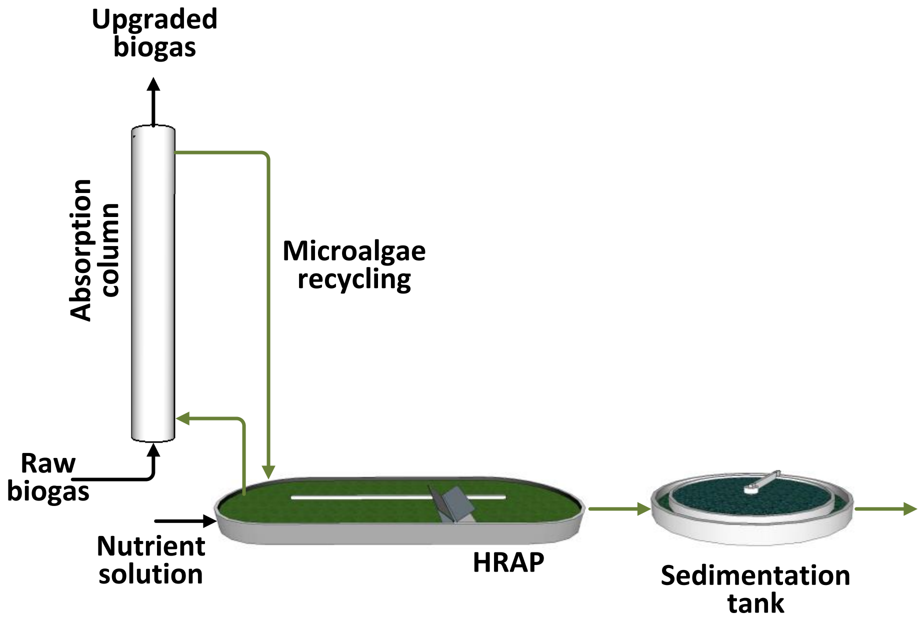

Figure 4. Biogas upgrading using microalgae cultures. Adapted from Bahr *et al* (2014).

Figure 5
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Figure 5.

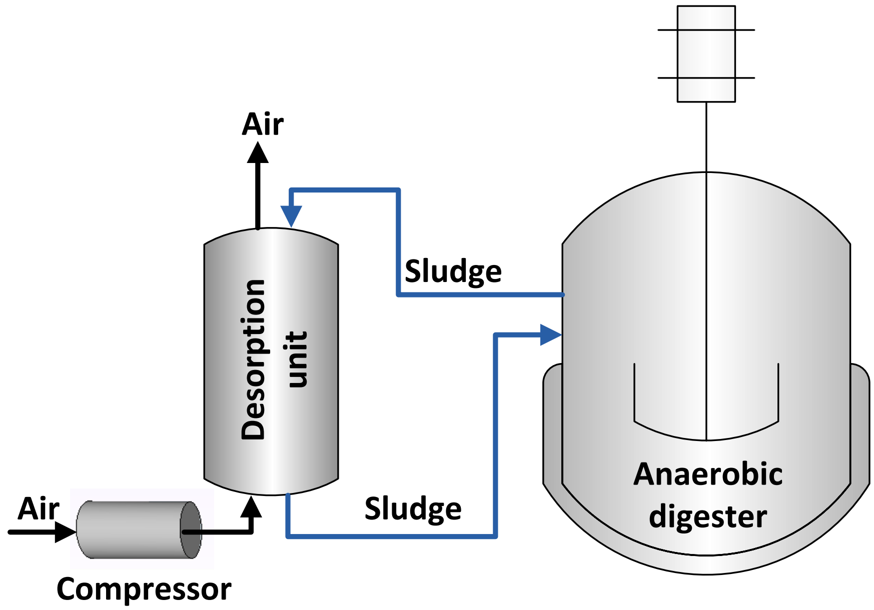

Figure 5. CO_2 removal by *in-situ* desorption in the anaerobic digester.

Figure 6

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Figure 6.

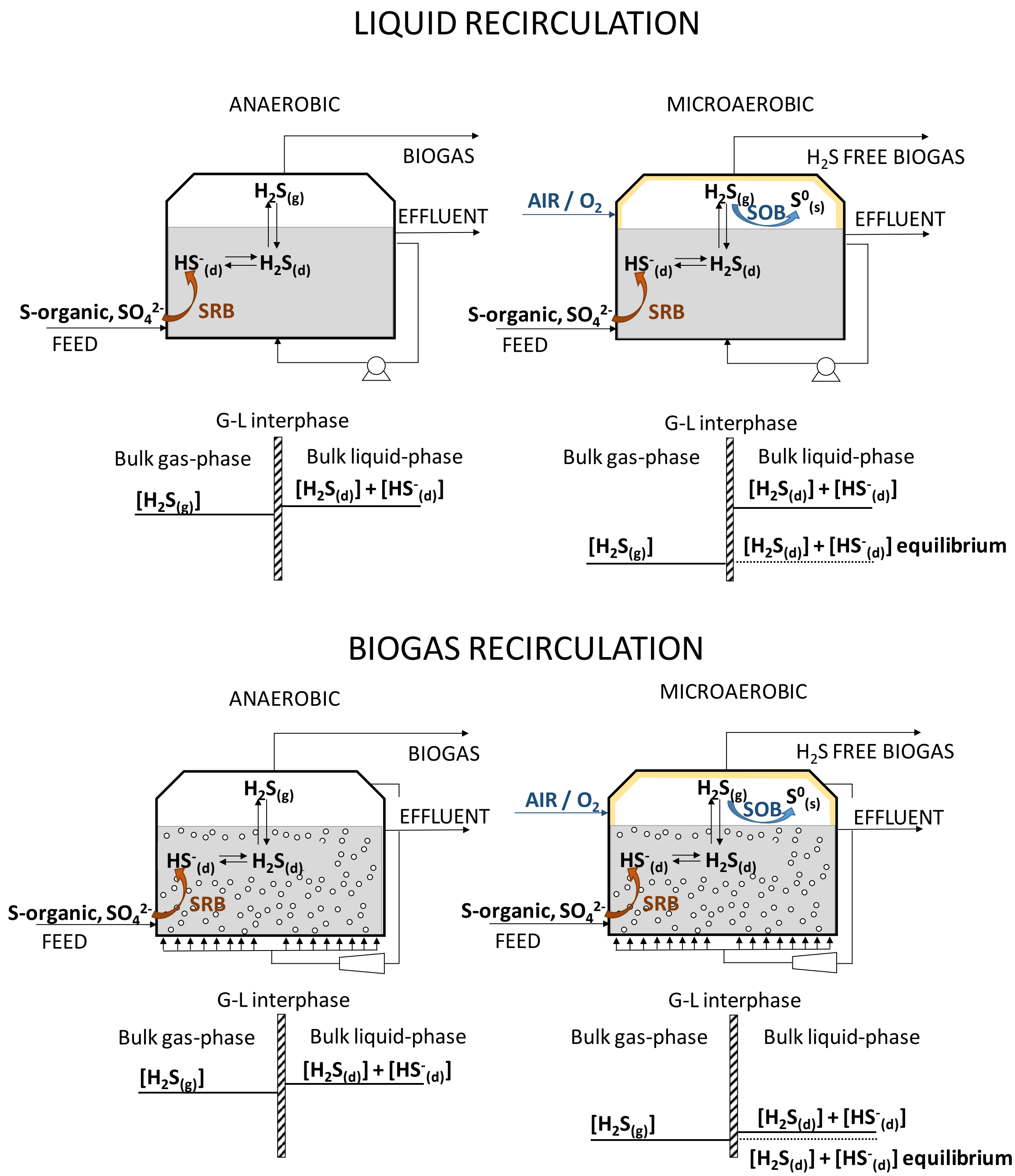

Figure 6. Evolution of sulfur species under anaerobic/microaerobic conditions and the effect of mixing conditions.

Table 1
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Table 1

Table 1. Technical specifications for injection of biogas in natural gas grid and use as a vehicle fuel (Marcogaz, 2006; Persson *et al*, 2006; Huguen and Le Saux, 2010; INN, 2010; Bailón and Hinge, 2012; BOE, 2013).

Country	Sweden	Switzerland	Germany	France	Austria	Netherlands	Spain	Belgium	Czech Rep	California U.S.	Chile
CH_4 content (%)	97±1 (Type A)(1) 97±2 (Type B)	> 96(2) > 50(3)			> 96	> 80	> 95	> 85	> 95		> 88
Wobbe index (MJ Nm^{-3})	44.7–46.4 (Type A)(1) 43.9–47.3 (Type B)	47.9 - 56.5 (unlimited injection)	46.1 - 56.5(4) 37.8 - 46.8(5)	48.2 - 56.5(4) 42.5 - 46.8(5)	47.7 - 56.5	43.46 - 44.41	13.40-16.06 kWh m^{-3} (48.25-57.81 MJ m^{-3})			47.6–51.6	47.28 – 52.72
Water dew point (°C)	< t(6)–5 < -9 (at 200 bar)	-8 at MOP	Ground temp.	< -5 at MOP	< -8 (40 bar)	< -10 (8 bar)	2°C at 7 bar		< -10°C		
Water content max. (mg Nm^{-3})	< 32					< 32					
CO_2 (%)	< 3	< 4 (2) < 6 (3)	< 6	< 2.5(7)	< 2	< 6 (< 10–10.3 for regional grid)	2.5	< 2.5	< 5	3	
O_2 (%)	< 1	< 0.5	< 3	< 0.01(7)	< 0.5	< 0.5	0.01 (0.3(8))		< 0.5	< 0.2	< 1
CO_2+O_2+N_2 (%)	< 4 (Type A)(1) < 5 (Type B)										1.5 – 4.5 (CO_2+N_2)
H_2S (mg Nm^{-3})	< 15.2	< 5	< 5	< 5 (H_2S+COS)	< 5	< 5	15 (H_2S+COS)	< 5 (H_2S+COS)	< 7	88	-
Total sulfur (mg Nm^{-3})	< 23	< 30	< 30	< 30	< 10	< 45	50	< 30	< 30	265	< 35
Mercaptans (mg m^{-3})		< 5	< 6	< 6	< 6	< 10	17	< 6	< 5	106	

NH_3 (mg/Nm^3)	< 20	< 20	< 20	< 3	Technically free	< 3	< 3	< 3		< 0.001 % mol	-
Siloxanes					< 10 total silicon mg m^{-3}	< 5 ppm_v	< 10mg m^{-3}		< 6 mgSi $^{m-3}$	Commercia l free or < 0.1 mgSi m^{-3}	
Halogenated compounds		< 1 mgCl m^{-3}	< 1 mgCl m^{-3}	< 1 mg m^{-3} (9) < 10mg m^{-3} (10)		< 50 mg m^{-3} (9) < 25 mg m^{-3} (10)	< 1 mg m^{-3} (9) < 10mg m^{-3} (10)	< 1 mg m^{-3} (9) < 10mg m^{-3} (10)	< 1.5 mg m^{-3} (Cl + F)	< 0.1 ppm_v	

(1) Type A: biogas as vehicle fuel – Engines without lambda control, type B: biogas as vehicle fuel – Engines with lambda control. (2) Unlimited gas injection in Switzerland; (3) Limited gas injection in Switzerland; (4) High calorific gas; (5) Low calorific gas; (6) Ambient temperature; (7). France allows some flexibility on parameters, O_2 and CO_2 content may be increased to 3 % and 11.3 %, respectively, under some conditions; (8) possible if the following conditions concur in the injection point: CO_2 < 2%, water dew point < -8°C, biogas injection flow rate into the main transport network never exceeds 5000 m^3h^{-1} (Possibility to inject higher flow rates are studied on a case by case basis); (9) Chlorine compounds; (10) Fluorine compounds.

Table 2
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Table 2.

Table 2. Commercial upgrading technologies

	Technology	CH_4 (%)	CO_2 (%)	H_2S (%)	Methane loss	Costs	Power consumption	Examples	References
High pressure water scrubbing	**DMT Carborex®PWS** P= 8-10 bar CO_2 and H_2S removal Solvent regeneration: Flash tank in two steps:1) 2-4 bar; 2) 1 bar. Air stripping unit and Biotrickling Filter.	> 97%	< 2%	< 2 ppm_v	< 2%	0.105 € m^{-3} (250 Nm^3 h^{-1}) 0.052 € m^{-3} (2000 Nm^3 h^{-1})	0.4-0.5 kWh m^{-3} produced gas	1) Zalaegerszeg, HU, Okoprotec (50-85 Nm^3 h^{-1}; WWTP) 2) Zwolle, NL, Nature Gas Overijssel (520 Nm^3 h^{-1}; green waste and other garbage) 3) Wijster, NL (1500 Nm^3 h^{-1}; Landfill)	DMT (2014)
	Malmberg COMPACT® CO_2 and H_2S removal Capacity: 100-3000 Nm^3 h^{-1} Methane emissions are avoided by thermal oxidation in the process air.	> 97%	1-2%		< 1%	2 ct kWh^{-1} (250 Nm^3 h^{-1}) 1 ct kWh^{-1} (2000 Nm^3 h^{-1})		1) Stockholm Vatten, Henriksdal (1400 Nm^3 h^{-1}; WWTP) 2) Jönköping Municipality, Sweden (150 Nm^3 h^{-1}; sludge digestion)	Malmberg (2014)
Chemical scrubbing	**OASEgreen™ Process (Bilfinger EMS GmbH)** Chemisorption with PuraTreat™ solvent CO_2 and H_2S removal Atmospheric pressure T° solvent regeneration: 106-110°C Capacity: 600- 10.000 Nm^3 h^{-1}	> 99%	< 1%	< 4 ppm_v	< 0.05%	< 0.01 € kWh^{-1} of raw biogas		1) BUP´s Verbio (2 separate plants Schwedt and Zörbig; 6000 Nm^3 h^{-1}) 2) BUP Weltec (Arneburg; 1450 Nm^3 h^{-1})	Bilfinger EMS GmbH (2014)
	LP Cooab-technique (Cirmac) Absorption by amines CO_2 removal Atmospheric pressure Exhaust-gas treatment is not necessary	99.5%			< 0.1%		0.05 - 0.12 kWe Nm^{-3} raw gas	Gasslosa biogas plant in Boras, Sweden	Energy Transition–Creative Energy (2014)

	CApure™ process (Purac Puregas) Absorption by amines CO_2 removal Atmospheric pressure 100 - 3000 raw biogas $Nm^3\ h^{-1}$	99%	0.20%	< 0.5 ppm_v	< 0.1%		0.23 - 0.26 kWh Nm^{-3} raw gas (with heat recovery system)		Purac Puregas (2014)
Organic physical scrubbing	**Schwelm Biogas treatment plant** Capacity: 200-1600 $Nm^3\ h^{-1}$ Absorption by polyethylene glycol.	98%			< 1%		0.21 kWh Nm^{-3} of raw gas		Schwelm Anlagentechnik GmbH (2014)
Pressure Swing adsorption	**Xebec PSA** P= 8-11 bar 9 vessel system with a patented rotary valve Previous H_2S removal Regeneration under vacuum pressure (typically 0.5 bar) Capacity: 100-10000 $Nm^3\ h^{-1}$ Removal CO_2 and water vapour	98%	1-2%					1)Scenic View Dairy, Fennville, Michigan (animal waste; 225$Nm^3\ h^{-1}$) 2)Rumpke Landfill Cincinnati,Ohio (7000 $Nm^3\ h^{-1}$)	Xebec (2014)
Membrane separation	**DMT Carborex® MS** Previous H_2S and water vapour removal P= 10 bar The off-gas contains over 99.5% CO_2. Removal CO_2 Gas/gas membrane	97-99%	1-3%		<0.5%	50 $Nm^3\ h^{-1}$ (0.432 ct Nm^{-3}); 200 $Nm^3\ h^{-1}$ (0.211 ct Nm^{-3})	< 0.22 kWh Nm^{-3}		DMT (2014b)
	Biopower plant P = 16 bar Hollow fiber membrane Removal CO_2 Gas/gas membrane	96%			<1%			Biopower plant in Pratteln, Switzerland (210 $Nm^3\ h^{-1}$;high solids digestion, biowaste, yard waste)	Eisenmann (2014)

Table 3
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Table 3. Experimental studies on the chemoautotrophic CO_2 conversion to CH_4

Bioreactor configuration	**CO_2:H_2** (mol mol^{-1})	**Gas Residence Time** (h)	**Maximum CH_4 production**	**CH_4** (%)	**Reference**
Mesophilic sewage sludge STR digester (2 L) stirred at 200 rpm supplied with in-situ coke gas addition (92 %H_2/8% CO) via bubbleless membranes	0.11-0.24	13-22	1.45 L CH_4 gVS^{-1} d^{-1} 0.65 L CH_4 L_r^{-1} d^{-1}	90-99	Wang *et al* (2013)
Mesophilic biotrickling filter (27 L) with random packing and internal gas recycling supplied with synthetic CO_2:H_2 mixtures. Batchwise operation	0.25	2-10	1.17 NL CH_4 L_r^{-1} d^{-1}	94-98	Burkhardt and Busch (2013)
Mesophilic STR (100L) stirred at 70 rpm with sparging of residual H_2 and CO_2 gases	0.125-0.5 (0.2)*	42-208	4.1 L CH_4 L_r^{-1} d^{-1}	92	Kim *et al* (2013)
Thermophilic manure-whey STR digester (0.6 L) stirred at 150-300 rpm with in-situ H_2 supply via ceramic and column diffusers.	0.25	14	0.88 L CH_4 L_r^{-1} d^{-1}	75	Luo and Angelidaki (2013)
Thermophilic STR (0.6L) stirred 500-800 rpm with sparging of synthetic mixture of H_2:CH_4:CO_2 (60:25:15)	0.25	1-8	5.3 L CH_4 L_r^{-1} d^{-1}	90-95	Luo and Angelidaki (2012a)
Mesophilic STR (0.5 L) supplied with synthetic CO_2:H_2 mixtures	0.25	1	0.24 L CH_4 gVS^{-1} d^{-1} 2.4 L CH_4 L_r^{-1} d^{-1}	-	Ako *et al* (2008)
Mesophilic packed bed filter (7.8L) supplied with synthetic CO_2:H_2 mixtures	0.125-0.5 (0.2)*	3.8-6.5	1.34 L CH_4 L_r^{-1} d^{-1}	100	Lee *et al* (2012)

Mesophilic Hollow Fiber biofilm membrane bioreactor (0.195 L) supplied with synthetic CO_2:H_2 mixtures	0.25	1.2	4.6 L CH_4 L_r^{-1} d^{-1}	80-90	Ju *et al* (2008)
Thermophilic STR (2L) with sparging via membrane diffusion of synthetic biogas mixtures and H_2	0.27	0.13	-	96	Strevett *et al* (1995)
Thermophilic column packed bed reactor (0.2L) sparged with synthetic CO_2:H_2 mixtures	0.25	-	54 L CH_4 L_r^{-1} d^{-1}	-	Bugante *et al* (1989)
Thermophilic packed bed column (0.105 L) supplied downwards with a synthetic CO_2:H_2 mixture	0.25	0.033	105 L CH_4 L_r^{-1} d^{-1}	40-50	Jee *et al* (1988)
Thermophilic STR (1.5L) stirred at 320-1015 rpm supplied via sparging with a synthetic CO_2:H_2 mixture (batch and continuous)	0.25	0.012	76 L CH_4 L_r^{-1} d^{-1} (continuous) 470 L CH_4 L_r^{-1} d^{-1} (batch)	50%	Peillex *et al* (1988)
Thermophilic packed bed column (0.05 L) supplied downwards with a synthetic CO_2:H_2 mixture	0.25	0.02	144 L CH_4 L_r^{-1} d^{-1}	30	Jee *et al* (1987)

*- Optimum value

Table 4.

Table 4. Experimental studies on biogas upgrading and CO_2 removal from flue gas in microalgal photobioreactors

Photobioreactor and absorption unit configuration	**Gas Residence Time*** (h)	**CO_2-RE** (%)	**Microalgae productivity** (g l^{-1} d^{-1})	**O_2** (%)	**N_2** (%)	**CH_4** (%)	**Reference**
Indoor 180 L raceway inoculated with a microalgae consortium and interconnected to a 2.5 L bubble column (1.65 m height) via algal-broth recirculation at a liquid to biogas ratio of 1:10. Synthetic Biogas (30%/69.5%/0.5% CO_2/CH_4/H_2S) supplied via porous diffuser.	1.4	82±2	0.079	1	6	88	Serejo *et al* (2015)
Indoor 180 L raceway inoculated with *Spirulina platensis* and interconnected to a 0.8 L bubble column (0.6 m height) via algal-broth recirculation at a liquid to biogas ratio of 1:1. Simulated biogas (30%/69.5%/0.5% CO_2/N_2/H_2S) supplied via porous diffuser.	0.7	86±5	-	0.2	-	-	Bahr *et al* (2014)
Indoor 1 L column photobioreactor stirred at 100 rpm supplied with real biogas (CH_4 70-72%, CO_2 17-19%) and inoculated with *Arthrospira platensis*.	96	100	0.041	10-24	-	-	Converti *et al* (2009)
Indoor 0.45 L enclosed tubular photobioreactor supplied with biogas (41%/57.5%/0.05% CO_2/CH_4/H_2S) inoculated with *Chlorella vulgaris*.	-	98	-	18-23	-	50-53	Mann *et al* (2009)

Indoor 15 L algal ponds inoculated with *Chlorella vulgaris* using a biolift absorption unit inside the pond and supplied with real biogas (CH_4 55-71%, CO_2 44-48%, H_2S 1 %).	-	74-95	-	-	-	88-97	Conde *et al* (1993)
Outdoor pilot raceway supplied with simulated biogas (40%/60% CO_2/N_2) using a countercurrent absorption sump (1 m deep) using a mixed microalgae population	-	>85	-	5.2-6	-	-	Mandeno *et al*. (2005)
Indoor 0.4-6 L bubble column photobioreactor inoculated with *Chlorella vulgaris* supplied with real biogas (CH_4-38-80%, CO_2-19-62%, H_2S-0.2 %).	0.16	-	2.6-3.8	3.5 <	-	-	Douskova *et al* (2010)
Outdoors 50 L bubble column photobioreactor (3 m height) inoculated with a mutant *Chlorella* strain supplied with biogas (20%/69%/0.005% $CO_2/CH_4/H_2S$) using intermittent biogas/air cycles (30 min/30 min)	0.06-0.3	74-85	0.3-0.32	-	-	86-91	Kao *et al* (2012)
Outdoor 100 m^2 raceway constructed with a 0.65 m^3 absorption sump (1 m deep) operated at a liquid recirculation rate of 0.22 m s^{-1} supplemented with flue gas (10.6 % CO_2) via membrane diffuser	0.2	96	0.088	>15	-	-	De godos *et al* (2014)
Outdoor 420 L raceway interconnected to a 1.4 L bubble column (3.1 m height) via water recycling from the HRAP. Abiotic experiment at pH 9-10	0.025	82-83	-	-	-	-	Putt *et al* (2011)

Indoor 75 L open photobioreactor inoculated with *Nannochloropsis gaditana* and interconnected to a 0.7 L bubble column (2.2 m height) by continuous recirculation of microalgae culture at a liquid to biogas ratio of 1.8:1. Real biogas (72±2% CH_4; 28±2% CO_2) was supplied.	0.2	93	0.03	1.2	-	-	Meier *et al* (2015)

*Gas Residence Time estimated based on the volume of the absorption unit

Table 5
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Table 5.

Table 5. Design and operation parameters of H_2S biofiltration units under anoxic and aerobic conditions during biogas upgrading.

Biofiltration Unit	**$[H_2S]$** (ppm_v)	**Gas Residence Time** (min)	**H_2S-RE** (%)	**Elimination Capacity** ($g\ H_2S\ m^{-3}\ h^{-1}$)	**Reference**
Aerobic biotrickling filter (5.15 m^3) packed with plastic pall rings and operated with an aeration rate of 5.6 $m^3\ h^{-1}$ at a pH of 1.7 controlled by WWTP effluent addition	2107 ±151	3.8-5.9	99±2	54±13	Rodríguez *et al* (2014)
Aerobic unit with metal wire, plastic tubing and paper strips, inoculated with 1 L of anaerobic sludge and supplemented with real biogas and O_2/H_2S ratios of 2-18	2800-3700	61-100	96	40-100	Ramos *et al* (2013)
Aerobic biotrickling filter (2 L) packed with HD-QPAC supplied with H_2S/N_2 synthetic mixtures simulating biogas and operated at O_2/H_2S ratios of 23.6	2000	3	99	55	Maestre *et al* (2010)
Aerobic biotrickling filter (2L) packed with metallic pall rings, fed with $H_2S/N_2/CH_3SH$ synthetic mixtures and operated at O_2/H_2S ratios of 39, at a pH of 6-6.5 with air sparged at the bottom of the BTF	2000	3	99	52	Montebello *et al* (2012)
Aerobic biotrickling filter (2 L) packed with HD-QPAC supplied with H_2S/N_2 synthetic mixtures simulating biogas and operated at O_2/H_2S ratios of 23.6 and a pH of 6-6.5	2000	2-3	98	55-82	Fortuny *et al* (2011)
Aerobic biotrickling filter (2.4 L) packed with metallic pall rings, fed with H_2S/N_2 mixtures simulating biogas and operated at a pH of 2.5 and O_2/H_2S ratios of 8.2-41.2	2000-10000	2.1	80-100	52-223	Montebello *et al* (2014)

Aerobic biotrickling filter (12 m^3) packed with plastic pall rings, fed with real biogas (69% CH_4, 29% CO_2, 1% N_2) and operated at a pH of 2.7	1250-4750	1.9-9.7	99	50*	Tomàs *et al* (2009)
Anoxic biotrickling filter (2.3L) packed with polyurethane foam, fed with $H_2S/CH_4/CO_2/CH_3SH$ synthetic mixtures and operated at a pH 7.5. NO_3^- was used as e^- donor	2000	2.7	99	59	Montebello *et al* (2012)
Anoxic biotrickling filter (2.4L) packed with polyurethane foam, fed with real biogas (68% CH_4/ 26% CO_2) supplemented with H_2S and operated at a pH 7.5. $Ca(NO_3)_2$, KNO_3 and $NaNO_3$ were used as e^- acceptor.	-	2.4-3.4	99	99.8-130	Fernández *et al* (2014)
Anoxic biotrickling filters (6.7 L) packed with polyester fibers and lava rock, supplied with synthetic biogas (65% CH_4/ 35% CO_2) using NO_3^- supplemented SBR effluent at a pH of 6.5.	500-1500	5-16	93-96	177-182	Soreanu *et al* (2009)

*- Average elimination capacity

Table 6
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Table 6.

Table 6. Experimental studies on *in-situ* microaerobic H_2S removal

Bioreactor configuration	**Biogas** ($m^3\ m^{-3}{}_R d^{-1}$)	**Biogas Residence Time in headspace** (h)	**[H_2S]** (ppm_v)	**Residual [H_2S]** (ppm_v)	**H_2S RE** (%)	**O_2/H_2S** (mol mol^{-1})	**Reactive Rate** %	**Residual [O_2]** %	**Reference**
Mesophilic digester of agricultural wastes	250 m^3/h	2.5	2500	< 300	> 88	1.3 -1.7	1.5 - 2 % air	-	Schneider *et al* (2002)
Mesophilic digesters (2 × 1500 m^3) of WWTP sludge	0.41	-	3300	30	99	3.7	5.4% air	-	Jenicek *et al* (2008)
Mesophilic digester (2100 m^3) of WWTP sludge	0.40	-	5600	54	99	5.5	14% air	-	Jenicek *et al* (2008)
Mesophilic digester (200 L) of WWTP sludge	0.95	6.3	13000	< 50	> 98	1.1	1.4% O_2	0.6	Díaz *et al* (2011b)
Mesophilic digester (200 L) of WWTP sludge	1.07	5.3	10000	260	> 97	1	4.7% air	0.7	Diaz *et al* (2010)
Mesophilic digester (5 m^3) of WWTP sludge	1.00	9.6	2500 – 4900	< 72	> 99	0.9 - 2	0.5% (92-98% O_2)	< 0.1	Ramos *et al* (2014)
Mesophilic digester (200 L) of WWTP	0.75	8	3300 – 5000	< 10	99	1	0.3-0.5% O_2	< 0.1	Ramos and Fdz-Polanco

sludge									(2014)
Mesophilic digester (338 m^3) of cow manure	1.6 - 2	1.36	2000 – 4000	1100	68	1.8 – 4.4	3.3 – 4.2% air	-	Kobayashi *et al* (2012)
Mesophilic EGSB (3.8L) treating synthetic vinasse	2.50	2.4	25000	7000	72	1,8	4.7% O_2	4,1	Rodríguez *et al* (2012)
Mesophilic UASB (2.7L) treating synthetic brewery wastewater	3.20	n/a	67000	16000	73	0.5*	12% air	< 0.1	Krayzelova *et al* (2014)
Mesophilic digester (50 L) of WWTP sludge	0.73	13	6000	< 30	> 99	-	-	1-1.8%	Nghiem *et al* (2014)

*- Related to S content in feed