Biogas to liquefied biomethane: Assessment of 3P’s–Production, processing, and prospects

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A B S T R A C T

Sustainable scale-up of biomethane to overcome the dependency on fossil energy sources is still not matured, fundamentally owing to its production and availability at a lower pressure (i.e., atmospheric) compared with the conventional natural gas. This is a fundamental assessment that specifically aims to overview the biogas production, cleaning technologies, upgrading technologies, and possible biomethane liquefaction technologies. The digestion technologies for biogas production are analyzed in terms of their important operating and performance parameters corresponding to optimum digester operation. The cleaning and upgrading technologies are assessed corresponding to their competitive factors, merits, and associated challenges. Cryogenic separation relies on different technologies that are based on different mechanisms (anti-sublimation, distillation, etc.). These technologies have been recently studied for CO2 removal from high CO2-content natural gas, showing promising results for application to biogas upgrading, in particular if the final goal is liquefaction. Since liquefaction itself is an energy- and cost-intensive process, cryogenic separation is synergistic in obtaining upgraded and liquefied biomethane in a single process unit, instead of integrating liquefaction with other upgrading technologies. Among all available liquefaction technologies, the nitrogen expander-based liquefaction processes are most promising candidates to produce liquefied biomethane (LBM), mainly due to small investment costs, simple operation, and compact design. This study suggests that there is a need to design energy-efficient small-scale biomethane liquefaction processes following biogas upgrading. Thus, incorporating biogas in the energy mix would result in economic, environmental, and climate benefits, globally.

1. Introduction

Currently, 80% of the global energy demand is fulfilled by the fossil-based energy sources [1], mainly owing to their high heating values, availability, and ease of retrieval. However, the environmental degradation (through greenhouse gas emissions) and public health concerns (air pollutant emissions) are the major issues associated with fossil fuels. Fig. 1 presents a general analysis and comparison between well-known fossil-based energy sources with respect to their air pollutant emissions, corresponding to energy production of 1 billion KJ [2].

According to Fig. 1, all fossil fuels (natural gas, oil, and coal) emit significant amounts of greenhouse gases, such as NOx, SOx, and CO2, which are mainly responsible for climate change and global warming.

Several renewable and sustainable energy sources have been matured to produce bioenergy, with the current contribution corresponding to about 10% of the global energy consumption [1,3]. It has been predicted that the share of bioenergy sources will rise by 10–50% by 2050, mainly due to their green nature [3,4]. Among all renewable and sustainable energy sources, biogas has gained plenty of attention as an important biofuel from energy policy makers, practitioners, and researchers. In general, biogas is produced from farm animal waste [5], livestock [6,7], slaughterhouse waste [6], municipal waste [8], maize [8], sewage treatment plants [8], grass [9], and different organic

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There has been a long history of more than 100 years of household production of biogas and its utilization without any processing or purification treatment [12]. However, there is a mandatory need for biogas processing (cleaning and upgrading), which results in the production of 97% biomethane to make it a more suitable candidate as a gaseous vehicle fuel, power-generation source, and feedstock for the production of value-added chemicals [13–15]. Apart from biogas upgrading (CO₂ removal), successful conversion of CO₂ into CH₄ through the well-known “methanation,” has also been investigated to improve the biomethane yield from biogas [16–18]. Biomethane with a methane content of 97% [19] (also called as biomethane) is the only biofuel that possesses properties superior to those of the fossil fuels, which can reduce the dependency on fossil-based energy sources.

The transportation of conventional natural gas (NG) in liquid form is considered as the most promising approach for long distance (over 3500 km) transportation, in terms of economy and cleanliness [20, 21]. Similar to conventional NG, biomethane may also be transported in its liquid form.e., as liquefied biomethane (LBM), at ~600-times lower volume than its gaseous volume.

The production of LBM is a multistage process involving pretreatment, anaerobic digestion, biogas cleaning, upgrading to biomethane, and liquefaction. Several detailed reviews are available in literature regarding the biogas production [10, 22], progress and perspectives of biogas conversion to transportation fuels [11], biogas processing (in terms of cleaning and upgrading) [19, 23–26], and alternative materials for biogas upgrading technologies [27]. However, to the best of our knowledge, a detailed assessment of the supply chain of liquefied biomethane is not published yet. The supply chain of LBM is simpler compared to that of a conventional LNG value chain, which involves complex processing of natural gas including exploration, production,
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Resources for biogas production

- Agricultural (animal wastes, residues, energy crops)
- Industrial (residues and waste streams)
- Municipal (residues and waste streams)
- Aquatic (Biomass)

Complex organic polymers

- Proteins rich matter
- Carbohydrates rich matter
- Lipids rich matter

1. Hydrolysis

Soluble organic compounds

- Amino acids
- Sugars
- Long-chain fatty acids

2. Acidogenesis

VFAs excluding acetic acid

3. Acetogenesis

CO₂ & H₂

4. Homoacetogenesis and syntrophy

CH₄, CO₂, cells and impurities

5. Methanogenesis

Fig. 2. Mechanism of the AD process.
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products into which. M.A. and monomers to researchers. fermentation, batch scales whereas and digestion and research. hydrolysis, acidogenesis, acetogenesis/dehydrogenation, and methanation. Each step is carried out by the combined action of several groups of microorganisms with unique metabolic activities. These microbial consortia can be grouped into hydrolytic-acidogenic bacteria, syntrophic acetogenic bacteria, and methanogenic archaea. During the hydrolysis step, the hydrolytic and fermentative bacteria break down the complex OM into soluble monomers (sugars, amino acids, and fatty acids) that can pass through the bacterial cell walls and membranes. The newly formed soluble monomers are then converted into short-chain fatty acids, alcohols, H₂, and CO₂ in a process called acidogenesis (fermentation). During fermentation, the short chain fatty acids and alcohols are further converted to acetate in the acetic step. The produced H₂ and CO₂ are also converted to acetate by homoacetogens. The final step involves methanation carried out by the methanogenic archaea, in which the end products of previous reactions (acetate acid and H₂/CO₂) are metabolized by acetoclastic and hydrogenotrophic methanogens to produce biogas.

2. Production of biogas

The biogas production process is divided into various categories: (i) based on the number of stages, it is categorized into a one-stage and two-stage digestion process, (i) on the basis of operation, it is categorized into a batch and continuous digestion process, and (ii) on the basis of configuration, it is categorized into a wet and dry digestion process [29]. Anaerobic digestion (AD) involves anaerobic decomposition of complex organic materials (OMs) (mainly polysaccharides, proteins, and lipids) into a variety of smaller organic components that are further degraded to produce biogas [30]. The mechanism of AD is presented in Fig. 2 [31, 32]. It is a multiple-step process involving four consecutive series and parallel reactions: hydrolysis, acidogenesis, acetogenesis/dehydrogenation, and methanation. Each step is carried out by the combined action of several groups of microorganisms with unique metabolic activities [33]. These microbial consortia can be grouped into hydrolytic-acidogenic bacteria, syntrophic acetogenic bacteria, and methanogenic archaea [33]. During the hydrolysis step, the hydrolytic and fermentative bacteria break down the complex OM into soluble monomers (sugars, amino acids, and fatty acids) that can pass through the bacterial cell walls and membranes. The newly formed soluble monomers are then converted into short-chain fatty acids, alcohols, H₂, and CO₂ in a process called acidogenesis (fermentation). During fermentation, the short chain fatty acids and alcohols are further converted to acetate in the acetic step [34]. The produced H₂ and CO₂ are also converted to acetate by homoacetogens. The final step involves methanation carried out by the methanogenic archaea, in which the end products of previous reactions (acetate acid and H₂/CO₂) are metabolized by acetoclastic and hydrogenotrophic methanogens to produce biogas [31,34].

2.1. Brief sketch of biogas digestion systems

Table 1 gives a brief sketch of the different digestion systems and the corresponding important parameters to be considered for biogas production. In one-stage digestion, anaerobic digestion occurs in one tank, whereas the two-stage digestion involves two phases for the complete microbial process [35,36]. The two-stage process provides an optimized digestion that eventually ensures higher biogas yields [37]. The one-stage digestion is favorable for the industrial scale owing to its operational simplicity, cost effectiveness, and lesser technical issues, whereas the two-stage process is usually conducted at lab and pilot scales [38].

In dry digesters, the feedstock usually consists of 20–40% dry matter, whereas in wet digesters, the feedstock comprises less than 20% of dry matter [35]. In few cases, pretreatments are also necessary when considering wet digesters [39]. Dry digesters are less energy-intensive than the wet digesters. Further, one-stage and dry continuous and batch digesters are considered relatively new digesters and are used for several types of substrates [29,39].

In batch digesters, the loading is done only once for a specific time interval, and the digester is then sealed and left until complete degradation [40]. In continuous digesters, the substrate is fed continuously and regularly, while batch digesters deal only with hybrid batch, one stage and sequential batch [39,41]. More than 90% of the industrial-scale digesters (especially in Europe) employ continuous configuration, whereas, owing to reduced parasitic energy demands, the batch configuration can be advantageous in some cases. For this purpose, more than one batch digester should be used with different startup times to ensure continuous yield of the biogas [42].

The digestion system is influenced by many factors such as pH, re-action temperature, OLR, HRT, microbial activity, pressure, nutrient, chemical equilibrium and many others [43–45]. These factors can be grouped into environmental (e.g. temperature, pH) and internal factors (e.g. HRT, OLR). The pH is a vital parameter that used to show strength of an effluent under anaerobic condition for biogas production. In a typical digestion system, the various metabolic products at each phase of biomethanation are successively transformed into their corresponding output without any major substantial accumulation of intermediate products leading to decline in pH [46]. The decrease in pH is due to hindrance by the methanogenic microorganisms. Most anaerobic bacteria especially methanogens enhance the production of biogas at pH range of 6.5–7.5, and peak at pH of 6.8–7.6 [47]. This suggests that the rate of biogas production may decline at pH lower than 6.5 and higher than 7.6. On the other hand, temperature is another unstable parameter that is often considered during digestion system. Temperature is one parameter that basically designates the efficiency of digestion process probably because it varies with the rates of hydrolysis and methanogenesis [46,47]. Temperature typically plays an essential role in OLRs and HRT during biogas production. Temperature withstand high OLRs and short HRT in the production of more biogas. But, high temperature can also lead to the production of the undissociated form of ammonia, which in turn acts as an inhibitor [48,49]. Therefore, temperature is another important parameter in digestion systems. HRT is typically used to determine time that a certain substrate exist in a bioreactor. The OLR is defined as the amount of organic matter that must be treated by a certain volume of anaerobic digester in a certain period of time [46]. The OLR is frequently shows the relationship with the HRT value. A short HRT yields higher biogas production rate, but less efficient degradation of organic matter. When the OLR increases or HRT decreases, methane production rate is intensified [46,50]. For example as explained in Table 1, the COD removal efficiency for anaerobic filtration is 94% (HRT: 15, OLR: 4) whereas that of up-flow anaerobic sludge blanket (UASB) is 98% (HRT: 4, OLR: 10.63). The methane production rate will be more in UASB in this scenario. It has been reported that high OLR produces high methane gas as compared to low OLR with relative short HRT [50] but this regulation does not apply all the time as the optimization of HRT and OLR depend mainly on the type of configuration. Thereby, technological challenge to improve the digestion system lies in selecting the suitable environmental and internal factors.

2.2. Important operating parameters and optimum digester operation

Important parameters for the AD process and the requirement for an optimum bioreactor operation for biogas production are predicted in Fig. 3. AD process can be operated under mesophilic (35–42 C) and thermophilic conditions (46–60 C), depending on the nature of influent streams [33]. The microbial activity of methanogens depends on temperature of the AD process. Small fluctuations in temperature ( 3 C) under mesophilic conditions will not have a significant effect on the microbial growth; however, slight changes in temperature for thermophiles would significantly affect the growth of methanogenic bacteria. AD operation under thermophilic conditions is usually faster and more efficient (low HRT), but the methanogenic diversity becomes very low [30]. Production of pathogens also reduces at the thermophilic temperature [33]. Moreover, a high temperature may lead to the production of the undissociated form of ammonia, which acts as an inhibitor at concentrations 0.08 g/L or higher [30]. The optimal pH for the AD process is between 6.5 and 7.5 [33]. Increase in the volatile fatty acids
<table>
<thead>
<tr>
<th>Digestor type</th>
<th>Main components</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>COD removal efficiency (%)</th>
<th>HRT (days)</th>
<th>OLR (kg COD/m³ day)</th>
<th>Temp. (°C)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Anaerobic filtration</td>
<td>&gt; Vessel (air free) &lt;br&gt; &gt; Digester (completely mixed) &lt;br&gt; &gt; Septic tank &lt;br&gt; &gt; Temperature controller</td>
<td>&gt; Able to handle extensive loads &lt;br&gt; &gt; Cost effective &lt;br&gt; &gt; Volume is small &lt;br&gt; &gt; Efficient for removing suspended solids</td>
<td>&gt; Longer Startup time &lt;br&gt; &gt; Not suitable for highly suspended solids &lt;br&gt; &gt; Continuous water source is mandatory</td>
<td>94</td>
<td>15</td>
<td>4.5</td>
<td>35</td>
<td>7.2-7.5</td>
</tr>
<tr>
<td>2 Continuous stirred tank reactor (CSTR)</td>
<td>&gt; Mixer &lt;br&gt; &gt; Mechanical agitator &lt;br&gt; &gt; Digester (closed tank)</td>
<td>&gt; Simple &lt;br&gt; &gt; Cheap &lt;br&gt; &gt; Large biogas production &lt;br&gt; &gt; Provide large heat transfer area &lt;br&gt; &gt; Low maintenance cost</td>
<td>&gt; Biomass retention is lower &lt;br&gt; &gt; Less efficient (at low HRT) &lt;br&gt; &gt; Addition of further reactants can affect the quality</td>
<td>80</td>
<td>18</td>
<td>3.33</td>
<td>37</td>
<td>7.1-7.3</td>
</tr>
<tr>
<td>3 Anaerobic digester</td>
<td>&gt; Scraper set &lt;br&gt; &gt; Torque tube &lt;br&gt; &gt; Gear motor &lt;br&gt; &gt; Draft tube</td>
<td>&gt; Low cost (operating, capital and maintenance) &lt;br&gt; &gt; Can handle large range of OLR</td>
<td>&gt; Lower methane emissions &lt;br&gt; &gt; Require large volume &lt;br&gt; &gt; Longer retention times</td>
<td>70</td>
<td>14</td>
<td>2.43</td>
<td>35-45</td>
<td>7.1</td>
</tr>
<tr>
<td>4 Modified anaerobic baffled bioreactor (MABB)</td>
<td>&gt; Peristatic pump &lt;br&gt; &gt; Bottle for the collection of effluents and gas &lt;br&gt; &gt; Feed tank &lt;br&gt; &gt; Stirrer (Magnetic) &lt;br&gt; &gt; Water bath</td>
<td>&gt; Able to hold high retention time &lt;br&gt; &gt; Efficient treatment of a variety of feeds</td>
<td>&gt; Less cost-effective &lt;br&gt; &gt; Large area is required &lt;br&gt; &gt; Energy-intensive</td>
<td>87.4-95.3</td>
<td>3-10</td>
<td>1.60-5.33</td>
<td>–</td>
<td>6.90-7.20</td>
</tr>
<tr>
<td>5 Fluidized bed reactor (FBR)</td>
<td>&gt; Peristatic and recycle pump &lt;br&gt; &gt; Separator (for gas-liquid) &lt;br&gt; &gt; Vessel (conical shaped) &lt;br&gt; &gt; Settlement compartment</td>
<td>&gt; Can maintain high biomass concentration (at long SRT) &lt;br&gt; &gt; Have well mixed conditions &lt;br&gt; &gt; Contain large surface area for biomass transfer</td>
<td>&gt; Less energy-efficient &lt;br&gt; &gt; Difficulty in capturing produced biogas &lt;br&gt; &gt; Not suitable for highly suspended solids</td>
<td>65-75</td>
<td>8</td>
<td>7.31-18.52</td>
<td>25</td>
<td>6.7-7.3</td>
</tr>
<tr>
<td>6 Up-flow anaerobic sludge blanket (UASB)</td>
<td>&gt; Pump (for feeding) &lt;br&gt; &gt; Effluent collector and overflow &lt;br&gt; &gt; Gas outlet and collector &lt;br&gt; &gt; Discharge valve (for gas) &lt;br&gt; &gt; Separator (three-phase)</td>
<td>&gt; Can handle highly suspended solids &lt;br&gt; &gt; Nutrients requirement is less &lt;br&gt; &gt; Provides high CH₄ production &lt;br&gt; &gt; Capable of stabilizing the waste</td>
<td>&gt; Startup time is longer &lt;br&gt; &gt; Biogas quality is lower &lt;br&gt; &gt; Relies on sludge concentration</td>
<td>98.4</td>
<td>4</td>
<td>10.63</td>
<td>35</td>
<td>4.5</td>
</tr>
<tr>
<td>7 Anaerobic baffled reactor (ABR)</td>
<td>&gt; Four compartments (containing baffles) &lt;br&gt; &gt; Baffles facilitate the movement (up and down flow) &lt;br&gt; &gt; Sludge blanket &lt;br&gt; &gt; Pipe (for effluent)</td>
<td>&gt; High cell retention time &lt;br&gt; &gt; Simple &lt;br&gt; &gt; Economical &lt;br&gt; &gt; Able to stabilize the waste</td>
<td>&gt; Nutrients stability is compulsory &lt;br&gt; &gt; Recycling is necessary</td>
<td>90.7</td>
<td>10</td>
<td>1.2</td>
<td>23-31</td>
<td>6.7-7.8</td>
</tr>
<tr>
<td>8 Up-flow anaerobic sludge fixed-film (UASFF)</td>
<td>&gt; Pump &lt;br&gt; &gt; Tank (feed and settling) &lt;br&gt; &gt; Gas separator &lt;br&gt; &gt; Combination of UASB and anaerobic filter</td>
<td>&gt; Less chances of clogging &lt;br&gt; &gt; Biomass retention is higher &lt;br&gt; &gt; Methane emission is high &lt;br&gt; &gt; Can handle shock loading</td>
<td>&gt; Poor separation &lt;br&gt; &gt; Pretreatment is needed for suspended solids</td>
<td>97</td>
<td>3</td>
<td>11.58</td>
<td>38</td>
<td>3.8-4.4</td>
</tr>
<tr>
<td>9 Anaerobic contact digestion</td>
<td>&gt; Contact process involves a digester and a sedimentation tank pipe (for effluent) &lt;br&gt; &gt; Settlement zone</td>
<td>&gt; High quality of effluents &lt;br&gt; &gt; Steady state is obtained in a short time &lt;br&gt; &gt; Hydraulic retention time is short</td>
<td>&gt; Less stable &lt;br&gt; &gt; Biomass settlement is difficult</td>
<td>93.3 (BOD)</td>
<td>4.7</td>
<td>3.44</td>
<td>45</td>
<td>3.4-5.2</td>
</tr>
<tr>
<td>10</td>
<td>&gt;</td>
<td></td>
<td></td>
<td>91</td>
<td>2</td>
<td>1.45-17.5</td>
<td>35</td>
<td>4.8</td>
</tr>
</tbody>
</table>

(continued on next page)
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(VFA) during the process lowers the pH, while increase in pH is caused by NH₃ accumulation. AD operation below pH 6 and above pH 8.5 will be inhibited [30]. Notably, inhibition caused by VFA accumulation is higher for undissociated propionic and butyric acids than for acetic acid [30]. Therefore, it is necessary to maintain a constant temperature and pH over an optimal range to achieve higher microbial growth. In order
to obtain a stable microbial growth, a continuous supply of macro- (C, N, P, and S) and micro-nutrients (Fe, Ni, Co, Se, Mo, and W) is required [30]. The TS content, state (liquid, solid, or semi-solid), and OLR are key parameters for an optimal digester choice. A stable digester operation can be achieved at low OLR, and by maintaining the ratio of intermediate alkalinity (IA) and partial alkalinity (PA) at 0.3 [33].

3. Biogas to LBM: Processing–Cleaning and upgrading

Various technologies are incorporated to bring the biomethane stream concentration close enough to the quality standards (concentration and heating value) set for the conventional natural gas [62]. Certainly, natural gas and biogas are essentially the same type of gas, which mainly consists of methane and other components (minor constituents, except for CO₂, in the case of biogas). In particular, biogas may be considered a natural gas characterized by a relatively high CO₂ content (40–50 mol% on average). However, some differences exist between the two gases. Firstly, the size of the treating plants is different in the two cases (those for natural gas are about two orders of magnitude larger than those used for treating biogas) and, since OPEX and CAPEX of biogas plants are reported to be highly influenced by economy of scale [63], an economic comparison between these two energy sources may be premature at the moment. In addition to that, the concentration of components other than methane is quite different in natural gas and biogas, which makes some technologies more suitable for the treatment of one of the two gases. In this respect, nitrogen can be taken into account, whose concentration in natural gas varies depending on the characteristics of the field and requires a specific section (typically known as Nitrogen Rejection Unit or NRU) for its separation, mainly based on cryogenic distillation due to the high flowrates [64]. On the contrary, nitrogen is removed from biogas (landfill gas) in the cleaning step by means of adsorption.

The most commonly used cleaning and upgrading technologies involve membrane separation, adsorption, absorption, and cryogenic treatment. Fig. 4 elucidates the transformation of biogas to biomethane, which will be explained in the forthcoming section.

3.1. Biogas cleaning

Along with CH₄ and CO₂, biogas can also contain H₂O, H₂S, O₂, N₂, NH₃, siloxanes, and solid particles. The concentration of these substances depends on the substrate from which the gas is produced [11,19,65,66]. These impurities must be removed from the biogas stream, depending on further processing and the subsequent use of biogas [11, 66–68]. The permissible limit of impurities for the production of LBM is listed in Table 2 (some values refer to the LNG importing emission limit for Zeerbrugge LNG terminal in Belgium) [69].

The importance of biogas cleaning becomes more evident for the production of liquefied biomethane, considering that high-purity methane is desired [70,71]. In addition, it can be advantageous to perform biogas cleaning during the upgrading and liquefaction processes to avoid corrosion and other mechanical issues of the equipment [18,19,72]. The impact of impurities is presented in Table 3. Several technologies for biogas cleaning are available in the market. They differ depending on the quality and conditions of the inlet gas, the desired purity level of the produced biogas, the process efficiency, and their operational bottlenecks.

3.1.1. Removal of H₂O

The techniques usually applied for water removal are condensation, adsorption, and absorption. Upon increasing the pressure and/or decreasing the temperature, the water condenses from the biogas, and can thus be removed by means of devices such as demisters, cyclones, moister traps, and water taps. Physical drying is often used as a pre-treatment step before other techniques [19]. Other methods include adsorption and absorption, which are usually applied at elevated pressures to achieve high water removal.

The most common process is adsorption on SiO₂, activated carbon, or molecular sieves [25]. These materials are regenerated by heating and/or by a pressure spring. Adsorption of water with molecular sieves can reduce the water content to less than 1 ppm, which satisfies the water content limit required in the case of LBM production.

Chemical drying technologies involve absorption with glycol solutions or the use of hygroscopic salts. However, these other technologies are only suitable for the production of biogas that meets a less strict specification on the H₂O content, such as a gas for grid injection [19].

3.1.2. Removal of H₂S

Techniques available for the removal of H₂S in the market can be classified into two categories: removal during digestion and removal after digestion [19]. In the digesters, H₂S can be removed by air injection or the addition of iron chlorides. However, these technologies are not suitable for producing LBM, because the concentration of remaining H₂S is still too high, i.e. 100–300 ppm. In the case of removal of H₂S after digestion, desulfurization by reaction with iron oxide or hydroxide, adsorption on activated carbon (often impregnated with KI or H₂SO₄) to increase the reaction rate, and absorption with liquids (e.g., diluted NaOH-solution, FeCl₂-solution, Fe(OH)₃-solution, and Fe(III)-EDTA catalyst solution) have traditionally dominated the market [19].

Increasing attention has been paid to biotechnological methods for the biological degradation of H₂S, as well as the combination of physico-chemical processes with biotechnological processes (e.g., Thiopac process [73]). However, when the H₂S concentration is required to be below 100 ppm, post-treatment or refinement (chemical scrubbing or adsorption with activated carbon) is regularly required after the biological process, [65].

In order to meet the LBM specifications of H₂S concentration (<3 ppm), activated carbon filters are typically used to remove H₂S when the concentration of H₂S in the raw biogas is low. Otherwise, when the concentration of H₂S in the raw biogas is high, alkaline scrubbers are normally used with the integration of regeneration processes at high flows and/or high concentrations [65].

| Table 2 | Purity requirements for the LBM [69–71]. |
| Components | Impurity limit in LBM |
| H₂O | <1 ppmv |
| H₂S | <4 ppmv |
| CO₂ | <25 ppmv |
| O₂ | 10 ppmv |

| Table 3 | Biogas impurities and their impacts to the equipment used in LBM production [18,19,72]. |
| Components | Impacts |
| H₂O | - corrosion of apparatuses and pipelines due to acid formation - damage of instruments caused by condensation - freezing at high-pressure and low-temperature conditions - corrosion (reaction with H₂O produces sulfuric acid) - SO₂ formation as a result of combustion - formation of flammable mixtures (4.5–45.0 vol% H₂S in air) |
| H₂S | - corrosion of metallic parts - decrease in the calorific value of biogas |
| CO₂ | - corrosion due to base formed when dissolved in H₂O |
| NH₃ | - Reduce liquefaction rate of biomethane - Cause entropy during liquefaction - decrease the calorific value of biogas |
| SiO₂ and N₂ | - formation of SiO₂ and microcrystalline quartz - abrasion |
| Dust | - clogging in compressors, exhausts, and vents |
| Cl and F | - corrosion |
3.1.3. Removal of siloxanes, oxygen, nitrogen and ammonia

Siloxanes can be removed from biogas through adsorption on activated carbon, activated aluminum, silica gel, molecular sieves, or polymer pellets [18, 25]. When cryogenic upgrading technologies are used, siloxanes can be removed directly in the upgrading section [19]. Cooling the biogas to 25°C allows 26% removal and cooling to 70°C allows 99% removal [25]. In addition, an absorption process using non-volatile organic solvents has also been reported [74].

Oxygen and nitrogen can be present in landfill gases, if the gas is collected through permeable tubes by applying a slight vacuum [19]. These gases can be removed by adsorption with activated carbon, molecular sieves, or membranes [11, 25]. They can also be removed to some extent during desulfurization processes or during some of the biogas upgrading processes.

The amount of NH3 present in the gas depends on the composition of the substrate and the pH in the digester. Ammonia is usually separated when the gas is dehydrated or upgraded. As a result, an ad hoc cleaning phase is usually not necessary.

3.2. Biogas upgrading

To date, several approaches have been proposed to upgrade the cleaned biogas to biomethane. The upgrading can be accomplished through physical and chemical processing such as physical absorption, chemical absorption, pressure swing adsorption (PSA), and cryogenic separation, and through membrane-based removal technologies. These techniques are briefly illustrated in the upcoming sections.

3.2.1. Physical absorption

CO2 and H2S removal through water or organic solvent scrubbing is the most common approach. The mechanism of physical absorption with water as an absorbing agent (also called water scrubbing [75]) is shown in Fig. 5(a).

The higher absorption rate of CO2 than CH4 in water is due to the solubility difference between both species; the solubility of CO2 in water is approximately 26 times higher than that of CH4 (Henry’s law) [76]. At elevated pressures, the solubility of CO2 increases, while the biomethane loss is estimated to be 3-5% [25]. Biomethane loss up to 1-2% [77] and 18% [78, 79] has been reported in water scrubbing methodology. Rimika et al. [80] reported that higher pressures (10 bar) and high pressure difference between the absorption column and desorption tank are the main reasons of CH4 loss. However, other factors, such as water flow in the scrubbing column, pressure of the desorption vessel, biomethane content in the biogas feed, and water seal in the bottom area of the column, are also responsible for the loss of CH4. Moreover, fresh water make-up is required for the continuity of the process.

The mechanism of physical absorption with any other solvent (e.g., organic solvents or ionic liquids) rather than water is shown in Fig. 5(b). The organic solvent can be polyethylene glycol (Selexol) or dimethyl ether (DME) with remarkable absorption capability, which is 5 times higher than that of water [81]. However, the corrosive nature, the lower solubility of acidic gases, and the huge thermal load requirement in the solvent regeneration step are the main concerns associated with the use of organic solvents [27]. Furthermore, some organic solvents have a solubility tradeoff between H2S and CO2, which ultimately leads to increased cleaning and upgrading cost [82].

Alternatively, a class of green solvents referred as ionic liquids (ILs) is introduced as a replacement of conventional amines and water scrubbing. As discussed by Yajing et al. [83], among water, amine, and IL-based scrubbing, IL showed the highest value of green degree production, energy efficiency, and required lowest make-up during the regeneration process. Numerous designs have been made by considering ILs as absorption solvents to remove undesired components such as H2S, CO2, and SO2 from natural and flue gases [84, 85].

Recent studies on ILs are carried out owing to their green and energy-efficient characteristics [84, 86, 87]. However, absorption using IL is still not mature and needs special attention for commercialization, either in the upgrading of biogas or carbon capture from the natural gas. The salient features of the ionic liquids are their low vapor pressure, higher potential to absorb acidic gases, high thermal stability, easy recovery during regeneration (mainly due to negligible vapor pressure), and environment-friendliness [87–89]. Manuel et al. [90] reported that [Emim][BF4] dissolves CO2 more than water, and presents a higher H2S absorption rate, thus reducing the cost of biogas cleaning. Generally, regeneration under vacuum allows control over the oxygen take-up by the biogas, which solves the common issues arising in biogas purification when air is used as a stripping gas during the regeneration process [91]. Elena et al. [87] studied the absorbent selection for biogas upgrading applications and showed that ILs provide superior results in terms of absorption and regeneration. Recently, advanced ILs such as [Amin][HCOO] [92], [BDIMIM][TCM] [93], CsCl/urea [94], and Cholonium-based IL [95], which present lower viscosity and higher capacity for CO2 adsorption, have been introduced. Despite the merits of ILs, their high viscosity and high cost are the key concerns hindering their application on a commercial scale, so far [96]. In this context, researchers are focusing on blending these emerging ILs with other physical solvents to not only reduce the viscosity but also to enhance the efficiency of the process [86, 96–98].

3.2.2. Chemical absorption

The mechanism of chemical absorption is quite different than that of physical absorption; the absorbent reacts with the acid media of the feed
gas, which is then regenerated in a stripping column, as shown in Fig. 6 [99,100]. Monoethanol amine (MEA), dimethylethanolamine (DMEA), diglycol amine (DGA), and piperazone (PZ) are the most widely used absorbents for chemical scrubbing of biogas. Since the amines are viscous and expensive, suppression of the corrosion potential and economic feasibility are the key concerns of this methodology. In addition, CH₄ is highly selective towards water (used with amines), and excess energy (thermal load) may be required to regenerate the amines. Therefore, the problems and challenges associated with the amine-based removal of CO₂ are the high thermal load in the regeneration step, and the corrosive nature and degradation of amines [101]. The thermal load can be reduced by adjusting the amine-to-feed ratio by increasing the absorption capacity of the absorbent [102]. It is known that the regeneration of tertiary amines is easier than the regeneration of primary and secondary amines [103]. Recently, Mengna et al. [104] utilized non-aqueous phase-changing amines for enhancing the absorption rate. The analysis indicated that, absorption of CO₂ with a mixture of amines and ethanol results in the precipitation of carbamates, which have a decomposition temperature of 90 °C. The heat required for regenerating amine from ethylene diamine-carbamate and PZ-carbamate are lower by 25.6 and 20.5%, respectively, than those of MEA-based carbamates. Owing to the main obstacle in the energy and environmental sustainability, amines are recently recommended to be replaced with novel solvents.

Caustic solvents can also be used as chemical absorbents, instead of amines [105,106]. The main advantage of alkaline absorbents is their higher CO₂ absorption capacity than that of amines. Moreover, solvent loading is reduced by up to 35% as compared to that of MEA during absorption. In comparison to amines, aqueous alkaline solvents are preferred because of their easy availability and low cost. Methane with 99% purity can also be obtained, owing to the higher selectivity of the solvent towards CO₂ [100,106].

The process system engineering (PSE) aspects are the key considerations which undertake the technical, environmental, and economical considerations for the evaluation of process. In case of water scrubbing, the air stripping may cause the generation of elemental Sulphur that can be avoided by the use of steam or inert gas used in the solvent regeneration section. Moreover, the physical separation has weak interaction of solvent and CO₂ as compared to the chemical absorption that needs high amount of water. The overall process aspect reveals that the water scrubbing has expensive investment, low absorptivity, and numerous operational issues such as foaming. Whereas, the physical absorption using organic solvents have high efficiency to recover biomethane, favorable than water regeneration, and low loss of methane. Contrarily, the ILs are impressive in operation, highly efficient, and easy to regenerate. The ecological aspects corresponding to the ILs are far better than conventional amines. The amines have numerous issues associated with PSE aspect such as toxicity, environmental hazard, expensive in regeneration as the bonding is very strong between acid gases and amines, foaming issues that leads to operation problems, poisoning occur by the trace chemicals, high viscosity, and corrosive. Alternatively, the high capital investment and high viscosity are the major issues associated with ILs. These drawbacks of ILs have significant impact on the process economy and operation. However, the energy efficiency is much higher when choosing an IL for the absorption of acid gases from biogas.

3.2.3. Pressure swing adsorption

Several adsorption technologies are commercially available for the removal of CO₂ from biogas, and these differ according to the method used to regenerate the adsorbing material. In particular, they are designated as [107]:

PSA or vacuum PSA (VPSA), Temperature swing adsorption (TSA), Electric swing adsorption (ESA).

The currently most used of these technologies is PSA: in Sweden, of the 55 biogas upgrading units, 8 were using this technology in 2013 [71]. In PSA method, CO₂ is separated from the biogas by means of adsorption on a surface at an elevated pressure; more gas is adsorbed if the operation is carried out at higher pressures [108]. This method is also used to upgrade landfill gas [109], and according to Grande [110], its development is likely to occur in small farms, where a part of the biogas stream can be upgraded to fuel.

The adsorbing material needs to be regenerated, which is accomplished by a sequential decrease in pressure, before the column is loaded again. Thus, an upgrading plant that uses this technology has some vessels that work in parallel, so that the feeding of the raw gas is switched from one vessel, where the adsorbing material is saturated, to another vessel in which the adsorbent has been regenerated. Typically, three, four [19,111], or six [107] vessels working in parallel are used to emulate a continuous process, and each vessel works on a different stage of the so-called Skarstrom cycle [71]: pressurization, adsorption, depressurization, and desorption.

PSA and VPSA are similar adsorption technologies, but VPSA also involves a vacuum pump [19] that allows desorption of the adsorbate under vacuum. Typical adsorption temperatures and pressures are in the range of 50–60 °C and 4–10 bar [110], respectively, and regeneration pressures are of approximately 100–200 mbar. The cycle typically lasts for ~3-5 min [112].

Most of the companies consider a 10-year lifetime for biogas plants involving the PSA technology. The capacities of the installed plants range from 10 to 2000 Nm³ raw biogas/h. However, this upgrading method is reported to be actually suitable starting from 200 Nm³/h [107]. The fact that the PSA technology does not require many resources makes it suitable for many applications. Indeed, it is a dry process that does not involve either water consumption or the production of contaminated waste water [71]. In addition, no heat is required by the process. However, this technology is characterized by a significant electricity demand owing to the relatively high pressures reached in the process. Furthermore, a cooling machine may be needed for gas demoisturization and for cooling the main compressor when no external cooling water is available. According to the producers of PSA systems, the electricity consumption related to biogas upgrading by means of PSA is 0.15–0.3 kWh/Nm³ of raw biogas [71]. Similar figures can be found in other literature works, namely, 0.2 kWh/Nm³ of raw biogas for the upgrading step and an additional 0.17 kWh/Nm³ of product gas for drying and final compression [113]. Process values from PSA units in Sweden show an energy demand of 0.25–0.3 kWh/Nm³, which suggests that the electric energy demand for these units is well verified: the lowest values can be probably reached if external cooling water is available, whereas the somewhat highest values are probable for a
The adsorbent material represents the core of the PSA system. Carbon molecular sieves are widely employed for biogas upgrading, while other adsorbents that are normally utilized are activated carbons and zeolites [110].

When PSA is applied to biogas upgrading, an important fact to be taken into account is the presence of several trace components such as siloxanes, sulfides, and halide, which must certainly be abated before [114]. Further, the presence of H₂S and water in the biogas should be carefully considered. As for H₂S, it adsorbs irreversibly on the adsorbent and poisons it. Therefore, the PSA process requires the removal of H₂S (and other trace components) upstream and a dry gas as a feed stream, depending on the type of the adsorbing material used.

The waste exhaust gas (obtained from the blowdown step), which leaves from the bottom of the PSA unit, includes 2–4% methane and may require gas cleaning, depending on the emission requirements of the country [19,107]. This gas can be dealt with in several ways [71]. One possibility, applicable when the methane content is high enough, is to torch it; otherwise, it can be oxidized in the presence of a catalyst for preventing methane leakages. Other possible ways of dealing with the vent gas are its combustion together with the raw biogas from the digester or its use for heat supply to a local heat demand. PSA has proved to be an efficient technology for biogas upgrading. As an example, the use of the Molecular Gate Technology offered by Guild Associates for digester gas purification has grown in popularity with 7 plants provided [115]. This technology is also an example of the possibility of application of new adsorbent materials, which is one of the area where research can be carried out to trigger PSA development. Indeed, the Molecular Gate Technology is based on the use of narrow pore titanosilicates (ETS-4) that present a unique property of pore contraction when increasing the temperature of activation, which allows pore adjustment to perform complex separations. Another commercial application of PSA to biogas upgrading is represented by the patented PSA process developed inhouse at Carbotech, which is reported to be simple and yet remarkable for its low energy consumption. Most of the biomethane gas to grid projects in Germany are equipped with this system [116].

3.2.4. Cryogenic biogas upgrading

Cryogenic biogas upgrading technologies can be classified into two main groups, depending on whether the formation of solid CO₂ is allowed or not. In the former case, the CO₂ removal is generally accomplished by desublimation, which may occur on appropriately designed exchanger surfaces (as in the Cryo Pur process [118]), in cryogenic packed beds (CPB process) [119] or in spray towers, while the latter group relies on low-temperature technologies mainly used for the purification of high CO₂-content (above 10 mol%) natural gas and based on distillation, as in the Ryan-Holmes process [120] and the dual-pressure low-temperature distillation process DCCDTM [121,122]. A case apart is the CFZ™ process [123] consisting of a distillation column, where solidification is allowed in a dedicated section without blocking the operation of the column.

The most energy-saving cryogenic processes are those based on distillation, and in particular, the dual-pressure low-temperature distillation process DCCDTM [124,125]. However, cryogenic separation technologies based on distillation are not yet used commercially for...
biogas upgrading [126]. In the following, a brief description of each technology is reported.

The Cryo Pur process is an integrated process for biogas cleaning, upgrading, and biomethane liquefaction. CO₂ is frozen as the gas passes through a heat exchanger (temperatures between 90 and 120 °C), which allows the achievement of the methane purity level required for liquefaction, i.e., a drop in the CO₂ content in the gas below 0.3% [127]. As reported in the literature [128], a “Mixed Refrigerant Integrated Cascade” is used to supply the required cooling duty. The Cryo Pur technology was selected in 2013 for the “BioGNVal” project, and a demonstration plant was established. The first commercial contract was signed in 2016 for a unit with a capacity of 300Nm³/h of biogas to be started mid-2017 in Northern Ireland. Another unit with a larger capacity, i.e., 500Nm³/h of biogas, was planned to be built in 2018 at Doue Metha, Angers, France [127,129].

The GPP® processing unit [130] consists of a compression stage and some cleaning stages to remove water, hydrogen sulfide, halogens, siloxanes, and other unwanted components. After the cleaning stages, different vessels at different temperatures allow removal of CO₂ by condensation and solidification (no description of how solidification occurs inside the vessel is found in the literature). After recompression to 48 bar, the biogas is flown into a vessel at 95 °C, where CO₂ is removed further. Then, in the GPP® Plus process, the purified biogas is flashed, thus allowing the removal of nitrogen and oxygen from the biogas and obtaining LBM with >99.5% purity [131]. Two LBM plants (both in Sweden) were operated to produce LBM based on this technology, but both have suffered several problems [131]. Currently, there is only one smaller demonstration plant situated close to the headquarters of the company [126].

CryoSep [132,133] is a process used by Biofrigas, Sweden to upgrade and liquefy raw gas to LBM in the same plant. In the literature, the only information found on the upgrading process is that it is cryogenic and is able to purify biogas to biomethane with a purity of 99%.

In the dual-pressure low-temperature distillation process DCCD™, the purification section consists of two distillation units: the first one operated at high pressure (50 bar) serves as the stripping section, while the second one operated at low pressure (40 bar) serves as the enrichment section. In order to avoid the solidification of CO₂, the gaseous overhead product of the high-pressure column (or part of it), which is enriched in the lightest natural gas component, is heated above its dew point at the working pressure of the low-pressure column. Then, before its entry into the column, the pressure of the stream is reduced while avoiding the occurrence of solid deposition. The produced gas stream at the top of the low-pressure distillation section is methane at the purity specification required for entering the liquefaction train. Unlike conventional upgrading technologies [66], the bottom product from the high-pressure distillation column is a high-pressure, liquid CO₂ stream. Currently, a pilot plant is in operation at Piacenza in Italy [122]. As for the energy requirements, several refrigeration cycles have been studied in the literature [134] and compared on the basis of their Coefficient of Performance (COP).

The Ryan-Holmes process exploits the fact that the addition of a heavier hydrocarbon, usually n-butane, at the top of the distillation column lowers the temperature of the S-L-V equilibrium locus, thus avoiding the formation of solid CO₂. An additional column for the regeneration of n-butane is required, thus increasing the operating expense and capital expense [135].

For the sake of brevity, only the diagrams of the GPP® and DCCD™ processes, as examples of methods based on sublimation and cryogenic distillation, respectively, are shown in Figs. 7and 8, respectively.

Since the application of cryogenic technologies to biogas upgrading is still at an early stage and often very few information is available about the proposed technology, it is not yet possible to compare them. However, a previous literature work [136] presented the results of an energy comparison among some of the technologies mentioned above (namely, the Ryan-Holmes process, the DCCD™ process and the anti-sublimation process) to assess their energy performances with respect to conventional amine scrubbing, on the basis of the “net equivalent methane” approach. It turned out that low-temperature technologies and, in
Membrane technology for biogas upgrading is a competitive alternative to other technologies. Membrane is a selective permeable filter that can separate gases at the molecular level. The basic principle of this technology relies on the selective permeation of biogas components through the membrane, which permits their separation. The permeation across the membrane takes place when a difference in pressure is induced on both the feed and the permeate sides of the membrane module [141]. Gas permeation through polymeric membranes can be explained by the solution diffusion model. The diffusion coefficient decreases with increasing molecules size, and thus, small molecules such as CO₂ condense less and pass through the membrane more favorably in comparison to large molecules such as methane [141]. Different gases in the biogas can permeate at different rates, and they can be arranged in a hierarchical manner according to increasing permeation rate, as follows: CH₄, N₂, H₂S, CO₂, and H₂O [71,142], as shown in Fig. 9.

For biogas upgrading, methane is recovered at the inlet side, while H₂S and CO₂ are collected at the permeate side after passing through the membrane. Some molecules of biomethane can also pass through the pores of the membrane in attempts to achieve a higher purity, leading to a larger methane slip, which is a bottleneck to be overcome in membrane-based upgrading [25].

Yang et al. [11] were amongst the first to apply polymeric membranes to upgrade the biogas in the early 1980s and to report the first scientific study with a synthetic gas mixtures. When raw gas consisting of CH₄, H₂S, and CO₂ is passed through membranes by compressing it at 5–20 bar, it will split into two streams, one rich in CH₄ and the other containing CO₂ and H₂S, as shown in Fig. 10 [131]. Two strategies can be adopted for the removal of H₂S: either pretreatment of the biogas or the permeation of both CO₂ and H₂S through the membrane. The selection of the membrane is a basic factor that determines the efficiency of the system. Basu et al. [143] reviewed commercially applicable membrane-based technologies for biogas upgrading and reported that cellulose acetate and polyimide membranes are the most suitable commercial membranes for this purpose. Conversely, membranes made of cellulose acetate are susceptible to water vapors and are unsuitable for biogas upgrading without pretreatment [144]. Membranes of a variety of materials such as organic polymers, inorganic materials, and mixed matrices have been tested for biogas upgrading [145]. However, only polymeric membranes are used at the industrial scale, because of their cost lower than that of inorganic materials. However, major bottlenecks for the membrane technology are the degradation of membranes with time and change in membrane behavior due to higher partial pressures of carbon dioxide resulting in free volume development within the

![Diagram of a membrane-based biogas upgrading unit.](image)

**Fig. 10.** Process flow design of a membrane-based biogas upgrading unit.
polymer matrix, which leads to membrane swelling. This phenomenon is called plasticization, and it results in increased permeation of methane through the membrane and consequent loss of selectivity [139]. The high permeability difference between CH$_4$ and CO$_2$, as well as high selectivity of the membrane material are required to minimize the biomethane losses and to purify the biogas in an efficient way. Current ongoing studies on membrane-based biogas upgrading are aimed at making plasticization-resistant membrane materials to increase their permeability without compromising the selectivity.

Fig. 10 shows the basic flow sheet of the membrane technology for biogas upgrading along with unit operations. The raw biogas is compressed and fed into the heat exchanger to maintain the temperature required for the membrane system. The raw biogas is usually pretreated to remove water and hydrogen sulfide. The water is removed by cooling and condensation before biogas upgrading to avoid condensation during compression, and H$_2$S is removed with activated carbon because it may not be sufficiently separated by the membranes [68]. In cases where siloxanes, volatile organic carbons, and ammonia are expected, pretreatment is carried out to remove these components before the biogas upgrading. In addition, a particle filter is also installed to protect the compressor and the membranes [142].

Presently, there are four major configurations of membrane technology for biogas upgrading, including the single-stage, two-stage with recirculation, three-stage combined with a sweeping biogas stream, and four-stage integrated with a stream of sweep biogas, as shown in Fig. 11 [146]. There is no need for internal circulation in the first design, which decreases the energy demand. However, the CH$_4$ loss is high; hence, a membrane with a high selectivity is required. In the second design, the permeate is extracted in the first stage, whereas the permeate from the second stage is recirculated to the compressor to decrease the methane loss and enhance its recovery. However, this will increase the energy expenditure. The third and fourth designs provide methane gas with higher than 97% purity [100]. An upgrading plant for biogas employing polyimide membranes was installed for the production of biomethane (100 m$^3$/h) to be injected into the gas grid [147]. This plant employed a two-stage design combined with the recycling of second permeate in the feed and the separation of the permeate from the first stage as an off-gas.

According to the IEA Bioenergy Task 37, the number of membrane technology plants for biogas upgrading under operation has steadily increased in recent years, as shown in Fig. 12. However, researchers are currently focusing on understanding the effect of resonance radiation in
the application of membrane technology for gas mixtures, without the requirement of membrane regeneration, which could reduce the cost involved in the membrane-based upgrading technology.

The energy consumption for a biogas upgrading plant based on permeation through membranes depends on several factors such as the methane slip, concentration of the produced biomethane, the required \( \text{CO}_2 \) removal, applied pressure, and installed membrane area [137]. It is mainly determined by the energy expenditure related to the compressor. A higher pressure is required to achieve a high purity of biomethane, and consequently, the installed membrane area determines the pressure required to treat a specified volume of the biogas [25]. A low pressure is required if a membrane with a larger surface area is installed, because a lower flux can be accepted. The electrical energy requirements for the membrane technology for biogas upgrading can be guaranteed in the range of 0.2–0.3 kWh/Nm\(^3\) [71], which is valid for major applications and is independent of the size [137].

4. Comparison of different technologies for biogas upgrading

The processes that are used for the purification of biogas can be considered on the basis of several aspects, including the purity level of the produced biomethane and its losses. The benefits and challenges associated with each technology are summarized in Table 5, whereas Table 6 summarizes the features of each technology, including the energy requirements and economic performances based on the unit cost. It can be noted from Table 6 that the cryogenic separation requires very high capital and operating cost due to the use of multi-stage compressors as the pressure require for operation is 40–80 bar. Nevertheless, the methane loss is analyzed to be very low as compared to other technologies. Additionally, the product obtained from cryogenic separation is in liquid form and highly pure. Consequently, the other upgrading techniques operated at low pressure conditions with high methane loss compared to cryogenic separation. The major issues and challenges associated with existing technologies especially the liquefaction of biomethane can be better integrated with cryogenic separation process as the process already achieves the liquefaction conditions.

From an economic point of view, the type of different raw materials for biogas production should not affect significantly the cost of its upgrading, since the \( \text{CO}_2 \) concentration does not vary remarkably. According to the outcome of a study previously carried out by some of the
In addition to energy requirements and economic performances, it is also important to take into account environmental issues when dealing with biogas production. Indeed, it is widely acknowledged that biogas is a green fuel due to its lower environmental impacts compared to fossil fuels. To properly assess that, many researchers have applied the method of Life Cycle Assessment (LCA) to biogas production systems. For example, fifteen of these studies carried out on biogas systems from around Europe have been reviewed by Hijazi et al. [148], who have defined three scenarios based on the type of input materials: i) 100% energy crops; ii) 100% manure; iii) a mix of energy crops or and manure or and waste. All scenarios have shown lower specific GHG emissions than their reference systems. Considering, then, AC and EP among the other input categories, biogas from energy crops has turned out to have higher impacts than its reference systems, whereas no significant differences have been found between the second scenario with different types of slurry and the reference one with conventional slurry management. The authors [148] have concluded that the main environmental benefits associated to biogas energy systems in comparison with fossils fuels ones occur in terms of GWP and RC. The interested reader can refer to the literature for further information about this topic.

5. Liquefied biomethane (LBM)

Biomethane can be transported in gaseous form through pipelines or in the liquid form (LBM) through cargo ships. In general, the fossil natural gas is liquefied (by reducing its volume to 1/600th at pressures slightly higher than the atmospheric one) for safe and economic transportation over long distances [28,150]. Similarly, biomethane can also be transported in the liquid form (LBM). Biomethane can either be liquefied using conventional liquefaction cycles (SMR, N₂ expander, etc.) or by coupling the small liquefaction plant with low-temperature upgrading technologies. This latter possibility has certain advantages over the conventional liquefaction processes, owing to the synergy between the low temperatures at which the upgrading process is operated and those that characterize the liquefaction process [136]. The pressure letdown technique can also be considered as one of the liquefaction technologies, but it will not be feasible for biomethane liquefaction owing to the initial compression.

The conventional LNG processes are categorized into two classes, namely, N₂ expander and mixed refrigerant (MR)-based processes. The MR liquefaction processes are further classified on the basis of the involved refrigerants and number of refrigeration cycles. The liquefaction process, which uses only one refrigeration loop with a mixture of nitrogen, methane, ethane, and propane, is referred to as the single mixed refrigerant (SMR) process. Similarly, a process that involves two refrigeration loops with two different mixed refrigerants is referred to as the dual mixed refrigerant (DMR) liquefaction. The propane-precooled mixed refrigerant (C3MR) uses pure propane as a precooling refrigerant in a separate loop. However, cascade processes [134] use three refrigeration cycles for precooling, liquefaction, and subcooling with three different MRs. Table 7 [151] compares the different available commercial liquefaction processes that have been established for the production of LNG. In general, MR-LNG processes have high energy efficiency because of both sensible and latent heats exchange to liquidify the natural gas, which compel to reduce the gap between cold and hot composite curves, but they need high capital investment than that of the N₂ expander-based processes. However, the use of highly flammable hydrocarbons makes MR-liquefaction processes less attractive at a small scale, because of safety and environmental concerns. Comparatively, the
N₂-expander-based process uses N₂ as a refrigerant that is maintained in the gaseous state throughout the process, which makes it safer and simpler, but has high operating costs, which is the major issue so far [20]. However, the selection of the liquefaction process highly depends on the energy efficiency, environmental impact, capacity of the system, and complexity [28,152]. A detailed description and analysis of the conventional liquefaction processes (at both large scale and small scale) can be found in the literature [28,153,154].

Based on the information presented in Table 7, it is possible to conclude that for biomethane liquefaction, N₂-expander liquefaction processes can be the most preferable and feasible candidates owing to smaller investments required and safe and easy implementation of the process technology. Therefore, Fan et al. [155,156] utilized a N₂ expander to liquefy biomethane for evaluating the economic feasibility of the process. The capacity of the process was kept at 5000 Nm³/d with a specific compression power of 0.763 kWh/m³. The outcomes of the process were impressive to overcome the energy crisis and for the development of a sustainable economy in China. Most recently, Haider et al. [157], presented an integrated biogas upgrading and biomethane liquefaction process. They also used nitrogen-methane (N₂–CH₄) expansion liquefaction process for the biomethane liquefaction. They concluded that the biogas upgrading followed by biomethane liquefaction can be an economical and sustainable option to attain liquefied biomethane for long-distance transportation. Furthermore, single mixed refrigerant (SMR) process can also be another promising candidates to produce LBM because of its compactness and simplicity, similar to N₂-expander liquefaction processes. In conclusion, the typical small-scale and offshore LNG processes can also be used to produce LBM, mainly due to the small liquefaction train capacity. However, the major issue associated with small scale liquefaction processes is the high energy consumption. Table 8 [158] lists the available biomethane liquefaction technologies with capacity and specific energy consumption. Table 8 clearly tells that the nitrogen expander-based liquefaction technology has higher specific energy consumption as compared to mixed refrigerant (precooling/without precooling) liquefaction processes.

### 6. Biogas to LBM: Current challenges and future prospects

Considering the environmental and public health issues associated with fossil fuels, the debate over the utilization of fossil fuels has become hot and serious. The policy makers and technical experts are finding satisfactory answers to different questions regarding fossil fuel utilization. For instance:

- Is it right to further use fossil fuels to fulfill the increasing global energy demand?
- How much energy should be obtained from fossil fuels?
- Should we try to cut down their use?
- Which renewable and sustainable energy sources have the potential to completely or partially replace the fossil fuels?

At this stage, it is difficult to provide satisfactory answers to all the above-mentioned questions. However, biogas as one of the potential renewable energy sources has shown rapid growth over the last decade, so as to reduce the dependency on fossil fuels.

#### 6.1. Current status and challenges

Globally, the generation capacity for biogas reached 16.9 GW in 2017, up from 6.7 GW in 2008 [159,160]. Depending on each country’s environment and energy programs, different types of biogas production and processing systems have been developed with different sizes of biogas production units, from small-scale household units to the major ones [159,160]. The development of biogas capacity globally is summarized in Table 9 [159,160], in which data refer to the maximum net generating capacity of power plants and other installations that use biogas to produce electricity and reflect the capacity installed and connected at the end of the calendar year. Europe has become a world leader in biogas-based electricity generation with more than 60% of the

### Table 7
Comparison of typical LNG processes [151].

<table>
<thead>
<tr>
<th>Process requirements and specifications</th>
<th>SMR</th>
<th>DMR</th>
<th>Cascade</th>
<th>C3MR</th>
<th>N₂-expander</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat Exchanger</td>
<td>Precooling (Plate-fin) Liquefaction (Plate-fin)</td>
<td>Precooling (Spoolwound) Liquefaction (Spoolwound)</td>
<td>Precooling (Core-in-kettle) Liquefaction (Core-in-kettle)</td>
<td>Precooling (kettle) Liquefaction (Spoolwound)</td>
<td>Precooling (kettle) Liquefaction (Plate-fin)</td>
</tr>
<tr>
<td>Electricity requirement (20 MW turbo generators)</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Production (t/d)</td>
<td>11,300</td>
<td>13,100</td>
<td>10,000</td>
<td>11,900</td>
<td>6540</td>
</tr>
<tr>
<td>Specific power (KW/t/d LNG rundown)</td>
<td>14.5</td>
<td>12.5</td>
<td>14.1</td>
<td>12.2</td>
<td>15.6</td>
</tr>
<tr>
<td>Fuel efficiency (%)</td>
<td>91.6</td>
<td>92.7</td>
<td>91.2</td>
<td>92.9</td>
<td>90.4</td>
</tr>
<tr>
<td>Capacity (MTPA)</td>
<td>7.4</td>
<td>8.7</td>
<td>6.6</td>
<td>7.9</td>
<td>4.3</td>
</tr>
<tr>
<td>Specific cost (C3MR 100)</td>
<td>97</td>
<td>116</td>
<td>119</td>
<td>100</td>
<td>95</td>
</tr>
</tbody>
</table>

SMR: single mixed refrigerant; DMR: dual mixed refrigerant, C3MR: propane-precooled mixed refrigerant.

### Table 8
Available biomethane liquefaction technologies, capacity, and specific energy requirement.

<table>
<thead>
<tr>
<th>Biomethane liquefaction technology</th>
<th>Capacity (tonne)ἄs/d</th>
<th>Specific energy consumption kWh/kl𝚞m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen recycling plant with single expansion turbine and booster</td>
<td>25-60</td>
<td>0.78</td>
</tr>
<tr>
<td>Nitrogen Brayton cycle with a compressor, composed of 3 intercooled compression stages and single expansion turbine</td>
<td>20-200</td>
<td>0.6-1.1</td>
</tr>
<tr>
<td>Nitrogen Brayton cycle</td>
<td>4.8-43.2</td>
<td>0.87-0.98</td>
</tr>
<tr>
<td>Nitrogen Brayton cycle with double expander, with nitrogen produced from air on-site</td>
<td>30-500</td>
<td>0.35</td>
</tr>
<tr>
<td>Single Mixed Refrigerant (SMR) Rankine cycle with water-glycol precooler</td>
<td>10-25</td>
<td>0.70</td>
</tr>
<tr>
<td>Pre-Cooled Mixed Refrigeration</td>
<td>40-6000</td>
<td>0.48</td>
</tr>
<tr>
<td>Combined process for biogas upgrading and liquefaction (cooling duty for liquefaction provided by refrigeration integrated cascade)</td>
<td>0.6-18.5</td>
<td>1.4-1.77</td>
</tr>
<tr>
<td>Linde cycle with pre-cooling</td>
<td>12-16</td>
<td>0.75-0.84</td>
</tr>
<tr>
<td>Stirling cryocooler</td>
<td>0.15-7</td>
<td>0.31-1.45</td>
</tr>
</tbody>
</table>
global capacity for producing electricity from biogas-connected grids [161]. The European Biogas Association (EBA) reported that Europe had 6227 biogas plants in 2009 and this number has grown up to 17,662 plants in 2016 [162,163] According to Green Gas Grids [164], until 2010, the development of the European biogas industry was mainly in the production of “green” energy for electricity generation. The primary reason is that, in most of the European countries, financial support was provided for generating “green” electricity in the form of guaranteed feed-in-tariffs.

In recent years, biogas upgrading to biomethane has started to gain major attention among European countries. Biomethane production in Europe has greatly increased from 752 GWh in 2011–17,264 GWh in 2016, as shown in Fig. 13 [162].

In 2016 alone, biomethane production in Europe increased by 4971 GWh (40%). The most significant development in biomethane production in 2016 was observed in Germany (900 GWh), France (133 GWh), and Sweden (78 GWh). Currently, Germany has the highest number of operational plants (10,000) that produce 100 TWh of CH₄.

In many other countries, e.g., China and India, biogas is produced at the household level. In China, between 2003 and 2013, 42 million small biogas plants for household use (8–12 m³) were built. There are around 4 million household units in India, while there are many other projects in progress in Asia and Africa [165] The biogas industry in South-east Asian countries like Thailand, Malaysia, and Indonesia is growing according to the country’s bioenergy production targets. Thailand has set a bioenergy capacity target of 5570 MW by 2036, while Malaysia’s goal is 1065 MW by 2020, and Indonesia aims to achieve 810 MW by 2025 [166]. Asia Biogas [167] reported that ten projects were operated in Thailand, Laos, and Indonesia in 2017, from which, 24.2 million Nm³ CH₄ was produced [168,169].

6.2. Policy analysis

The European Union (EU) has established the goal of reaching 80%–95% GHG emissions reduction by 2050 [161]. The share of renewable energy could reach between 55% and 75% of the EU energy consumption in 2050. As an intermediary milestone, a 2020 to 2030 Policy Framework for Climate and Energy is established with the following objectives: (a) a 40% reduction in GHG emissions compared to 1990 levels, at least a 27% share of renewable energy consumption and at least 27% energy savings compared with the business-as-usual scenario [161].

Biogas and biomethane can be a vital renewable energy source by 2030 if supported with sufficient political and financial support. It can be a fundamental tool to achieve the European’s key policy aims, such as energy security, sector integration, sustainable employment and climate-friendly energy. Different strategies, investment programs, support schemes and utilization concepts have been adopted in different countries as reported in the IEA Bioenergy Task 40 and Task 37 joint study [170]. However, according to EBA [171], Europe must implement EU-wide policies to create an internal market for the renewable gas. An integrated policy, including key sectors of the economy (e.g., agriculture, waste, mobility and energy), is necessary to realize the benefits and synergies of biogas and biomethane. EBA also provides several policy recommendations clustered in several topics: trading, grid injection, scalability and applications; transport sectors; cost-competitiveness; agriculture and sustainability; waste management. Within these recommendations, EBA mentioned the importance of incentives for the green gas transition, financial support for alternative technologies such as liquefaction of biomethane, and deployment of liquefied biomethane to gradually replace fossil LNG (e.g., a blending target of 10% of LBM, as in the Netherlands as of 2021, should be introduced EU-wide).

European government is the leader in pursuing policies and promoting mechanisms for the advance application of biogas, i.e., biogas to LBM. On the other hand, countries with small-scale production of biogas from livestock waste to provide fuel and electricity in rural communities are still building on the lessons learned in the European Union to enhance their anaerobic digestion (AD) technologies. According to Ref. [172], several key drivers that shape how countries can leverage policies and incentives to advance anaerobic digestion are creating financial incentives for investments in anaerobic digestion, reducing energy expenses by using power generated by anaerobic digesters, and quantification of the environmental benefits of anaerobic digestion to create market values which can be used, for example, in CO₂ trading. The detailed information on policies and incentives related to anaerobic digestion projects worldwide are discussed in Ref. [172].

![Fig. 13. Biomethane production in Europe between 2011 and 2016 [in GWh] [162].](image-url)
6.3. Practical implications of the study

Currently, Europe leads in the biogas production and utilization for electricity generation, as well as for vehicle fuel. However, Asian countries also have great potential to move on to the biogas-based power generation plants. Biogas can also potentially replace natural gas as a green fuel and feedstock for producing a variety of chemicals. However, as previously pointed out (see section 3), there exist some differences between the two gases that must be taken into account and pose some challenges when considering biogas as a substitute for natural gas. In this respect, one of the main issues is certainly the different plant capacity, which requires additional installations for biogas.

Scarlat et al. [161] reported that biogas production can be increased by utilizing a wider range of raw materials: food waste, crop residues, sewage sludge from waste water treatment, or micro- and macro-algae (freshwater and marine). New techniques for biological digestion (e.g., ultrasonic treatment or enzymatic reactions), use of new enzymes and substrates, use of bacterial strains with a greater tolerance to process changes and foodstock type can also contribute to the advancement in biogas production. The well-established anaerobic digestion is likely to see improvements through developments in biological processes, dry fermentation, and thermophilic processes, which would increase the process efficiency and biogas yield.

The biogas upgrading market will face a harder competition due to the establishment of new upgrading technologies (e.g., cryogenic technologies) and further advancement of the mature ones. The upgrading plants will seek process optimization to minimize the cost and energy requirements, as well as further integration of biogas upgrading with end-user applications [71,131]. Furthermore, to satisfy the global energy demand in an ecological manner, the biomethane in liquid form (LBM) has remarkable properties to compete with the conventional LNG, as well as other available biofuels. In comparison to compressed biomethane, LBM provides improved vehicle efficiency by beating the former by 3 times in energy density and space efficiency [173]. The demand of LBM is expected to increase after the world’s outlook towards renewable and sustainable energy demand and supply changes. However, further developments in energy- and cost-efficient small-scale biomethane liquefaction schemes are required. A tremendous amount of energy (operating cost) required for compression units involved in the liquefaction of biomethane is a major issue so far and demands serious attention in order to obtain clean and green energy globally, in an economic way.

7. Conclusion

The production of LBM is a multistage process involving pretreatment, anaerobic digestion, biogas cleaning, upgrading to biomethane, and liquefaction. Considering the recent interest in the exploitation of biogas and liquefied biomethane, in this paper we successfully analyzed and presented the major units (production, cleaning, upgrading, and liquefaction) involved in the production of liquefied biomethane. The mechanism of biogas production with a brief sketch of the different digestion systems considering their important performance parameters is presented. The technological trend for cleaning and upgrading of biogas is assessed. The economics of each upgrading technology was presented to compare their energy and investment costs. Commercial-scale upgrading units are presented. Liquefaction has been suggested for the feasible and economic transportation of upgraded biogas (biomethane) over long distances. The nitrogen expander-based liquefaction technology has higher specific energy consumption compared with the mixed refrigerant (precooling/without precooling) liquefaction processes. In the end, the current trend and future perspectives of the global biogas usage were presented.

Declaration of competing interest

The authors declare no competing financial interest.

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