

Biogas to liquefied biomethane: Assessment of 3P's–Production, Processing, and Prospects

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Abstract

This review presents a bird-eye assessment of the supply chain (excluding regasification) of major units of liquefied biomethane. The digestion technologies for biogas production are analyzed in terms of their important operating and performance parameters corresponding to optimum digester operation. Further, the cleaning and upgrading technologies are assessed with energy and costs analyses corresponding to their competitive factors. Merits and demerits are also discussed to evaluate the process efficiency of each technology for future applicability and advancement. Low-cost ionic liquids represent a remarkable breakthrough for competitive and energy-efficient absorption-based upgrading of biogas. Resonance radiation effect and novel materials for membrane synthesis will lead to further reduction in the unit cost of membrane-based biogas upgrading. Cryogenic separation is advantageous if the final goal is liquefaction. Since liquefaction itself is an energy- and cost-intensive process, cryogenic separation is synergistic to obtaining upgraded and liquefied biomethane in a single process unit, instead of integrating liquefaction with other upgrading technologies. Furthermore, 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.

Keywords: Biogas; digestion systems; cleaning and upgrading; liquefaction technologies; liquefied biogas; biomethane

Word count (excluding title, author names and affiliations, keywords, abbreviations, table/figure captions, acknowledgments and references) = **9972**

Nomenclature and Abbreviations

kJ	kilo Joule	EDTA	Ethylenediaminetetraacetic acid
NO _x	Nitrogen oxides	KI	Potassium iodide
SO _x	Sulphur oxides	PSA	Pressure swing adsorption
NG	Natural gas	PG/Selexol	Polyethylene glycol
LBM	Liquefied biomethane	DME	Dimethyl ether
LNG	Liquefied natural gas	IL	Ionic liquid
AD	Anaerobic digestion	[bmim][Br]	1-Butyl-3-methylimidazolium bromide
OMs	Organic materials	[Emim][Tf]	1-ethyl-3-methylimidazolium trifluoromethanesulfonate
CSTR	Continuous stirred tank reactor	[Bmim][Tf ₂ N]	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
HRT	Hydraulic retention time	Bmim][PF ₆]	1-butyl-3-methylimidazolium hexafluorophosphate
OLR	Organic loading rates	[Hmim][Tf ₂ N]	1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
MABB	Modified anaerobic baffled bioreactor	ChCl	Choline chloride
FBR	Fluidized bed reactor	[Amim][HCOO]	1-allyl-3-methylimidazolium formate
UASB	Up-flow anaerobic sludge blanket	[BDiMIM][TCM]	1-Butyl-2,3-dimethylimidazolium tricyanomethanide
SRT	Solid retention time	MEA	Monoethanol amine
ABR	Anaerobic baffled reactor	DMEA	Dimethylethanolamine
UASFF	Up-flow anaerobic sludge fixed-film	DGA	Diglycol amine

EGSB	Expanded granular sludge bed	PZ	Piperazine
VFA	Volatile fatty acids	VPSA	Vacuum pressure swing adsorption
IA	Intermediate alkalinity	TSA	Temperature swing adsorption
PA	Partial alkalinity	ESA	Electric swing adsorption
IEA	International energy agency	CPB	Cryogenic packed beds
SMR	Single mixed refrigerant	STP	Standard temperature and pressure
MR	Mixed refrigerant		
DMR	Dual mixed refrigerant		
C3MR	Propane-precooled mixed refrigerant		

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. Figure 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].

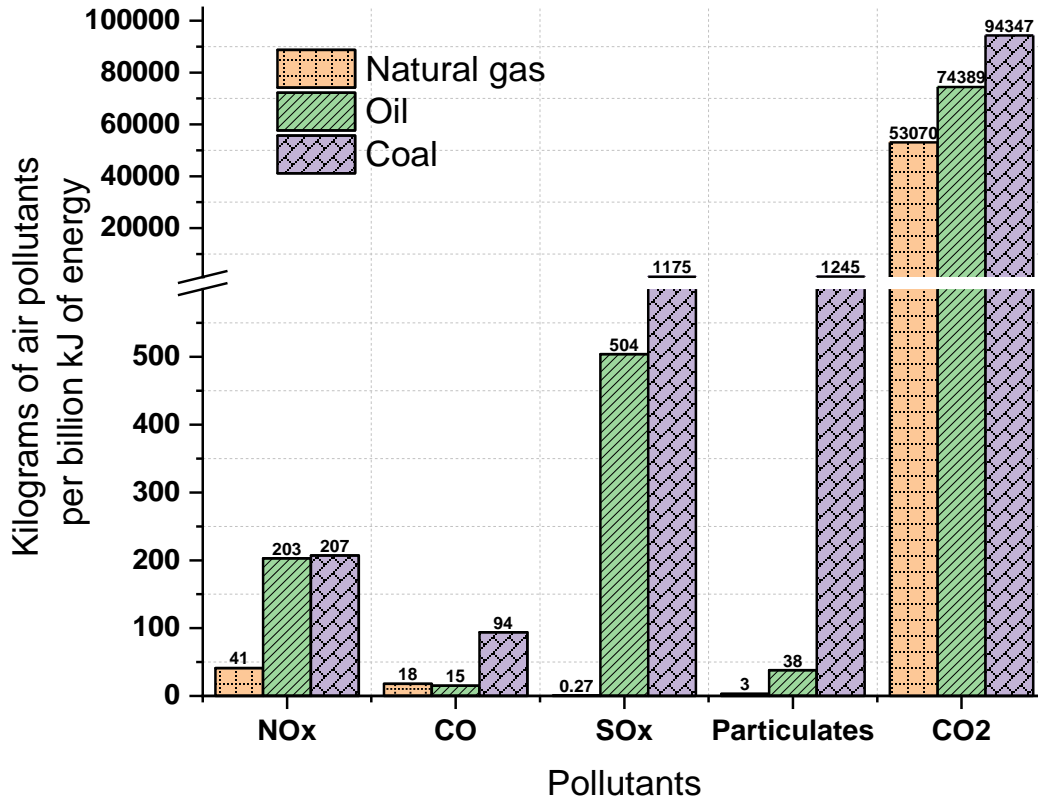


Figure 1. Analysis of air pollutant emissions of fossil-based energy sources [2].

According to Figure 1, all fossil fuels (natural gas, oil, and coal) emit significant amounts of greenhouse gases, such as NO_x , SO_x , and CO_2 , 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 owing 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 (carbohydrate-rich, protein-rich, and fat-rich) materials [10]. Owing to the variety and abundance of its sources, biogas has great potential to serve as a replacement energy source to overcome the dependency on fossil fuels. A biogas mainly consists of methane (50–70%) and carbon dioxide (30–50%), with small fractions of water, hydrogen sulfide, hydrogen, nitrogen, and oxygen [9,11]. The composition of a biogas depends on the type of feedstock, associated technology, environmental conditions, and operating parameters. The use of biogas as a fuel or a main energy source depends totally on its composition.

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 $\geq 97\%$ 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 (CO_2 removal), successful conversion of CO_2 into CH_4 through the well-known

“methanation,” has also been investigated [16–18] to improve the biomethane yield from biogas. A biogas with methane content $\geq 97\%$ [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 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, that is, as liquefied biomethane (LBM), at ~ 600 -times lower volume than its gaseous volume. A simple supply chain of LBM is shown in Figure 2.

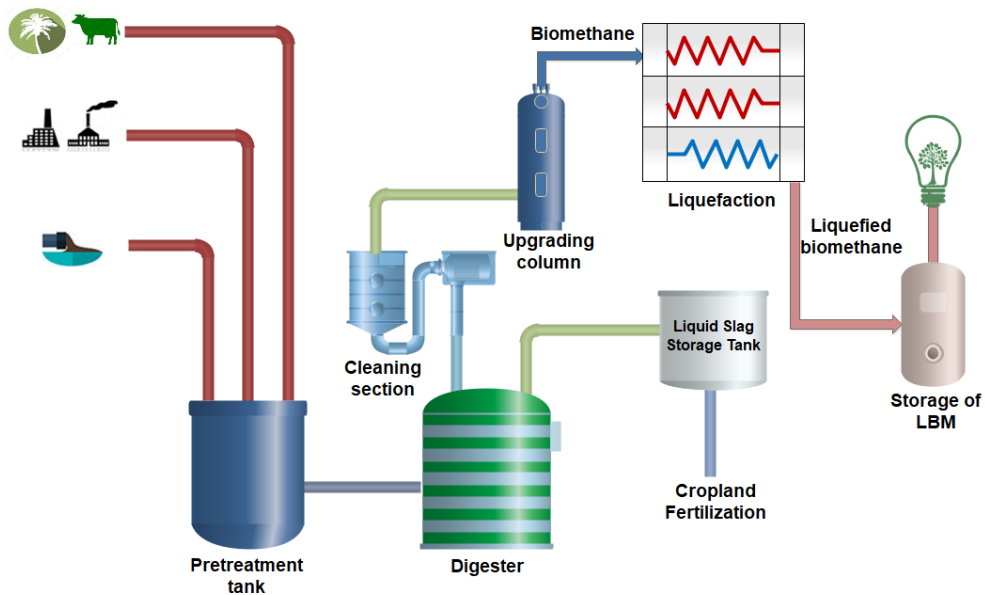


Figure 2. A simple supply chain (excluding regasification) of liquefied biomethane (LBM).

According to Figure 2, 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 open literature regarding the biogas production [10,22], progress and perspective 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 available in open literature. Although, 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, dehydration, mercury removal, acid gas removal, natural gas liquid recovery, followed by liquefaction [28]. However, sustainable scale-up of biomethane to overcome the dependency on fossil natural gas is still not matured, fundamentally owing to its production and availability at a lower pressure (i.e., atmospheric) as compared to that of the conventional natural gas, which is in the pressure range of 40–80.0 bars. This low-pressure production of biomethane makes it less attractive for its scale-up, mainly owing to the high energy requirements for feasible and economical use as a transportation fuel.

However, many technological advancements that can be implemented to design energy- and cost-efficient small- to large-scale schemes to produce LBM have been introduced recently, which are still far away from real-life application, primarily owing to the lack of effective communication between the technical experts, energy policy makers, and the research community. Hence, from a commercial and research viewpoint, a detailed assessment of the biogas production and processing leading to liquefied biomethane is required. In this context, this is a fundamental assessment that specifically aims to offer an overview of the potential of biogas production, cleaning technologies, upgrading technologies, and possible biomethane liquefaction technologies. A comprehensive statistical, economic, and energy analyses of biogas upgrading technologies with their merits and demerits are presented. The aim of this review is to analyze and highlight the potential of biogas as an attractive high-heating-value green fuel, which may potentially reduce our dependency on fossil natural gas. This review also addresses the technical

open issues associated with large-scale adaptation of biomethane, which requires serious attention to enable wider implementation of biomethane to save the environment and public health. Future aspects of the biogas-to-LBM processing are also discussed from the viewpoints of both commercial and academic research. We believe that, the current analysis can aid researchers in better aligning their research directions and goals according to the requirements of renewable and sustainable energy (especially biogas) imposed by policy makers and design engineers.

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]. A simple mechanistic scheme of AD is illustrated in Figure 3, while the complete mechanism of AD is presented in Figure 4 [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 acetogenic 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 (acetic acid and H₂/CO₂) are metabolized by acetoclastic and hydrogenotrophic methanogens to produce biogas [31,34].

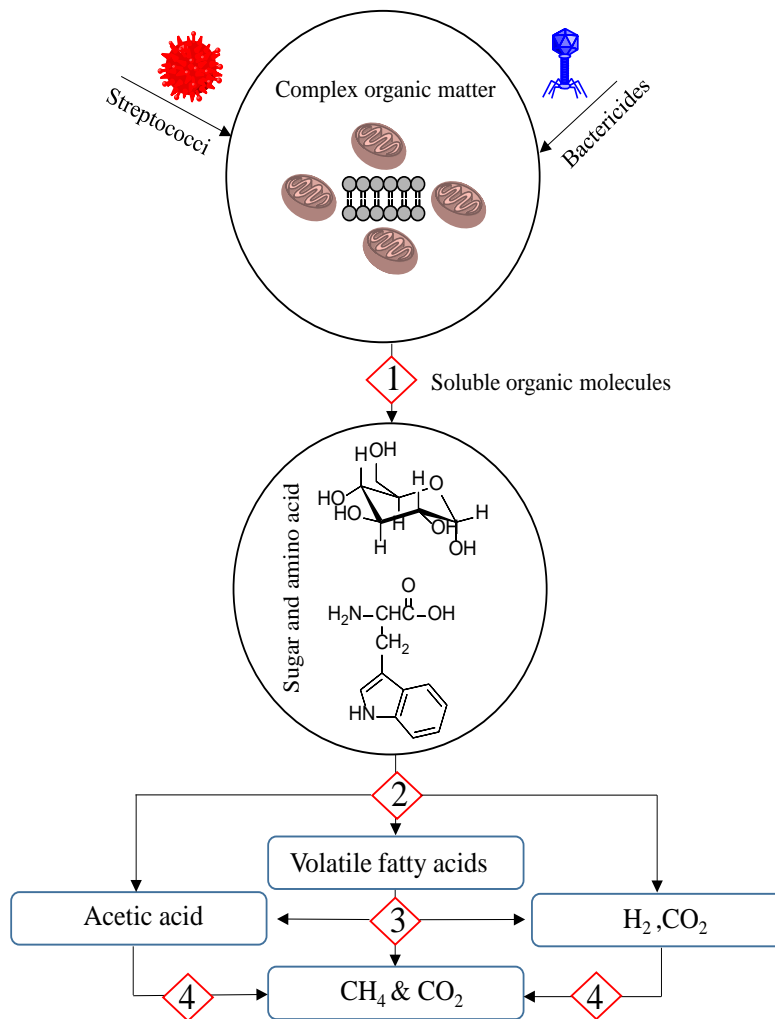


Figure 3. A simple anaerobic digestion mechanism.

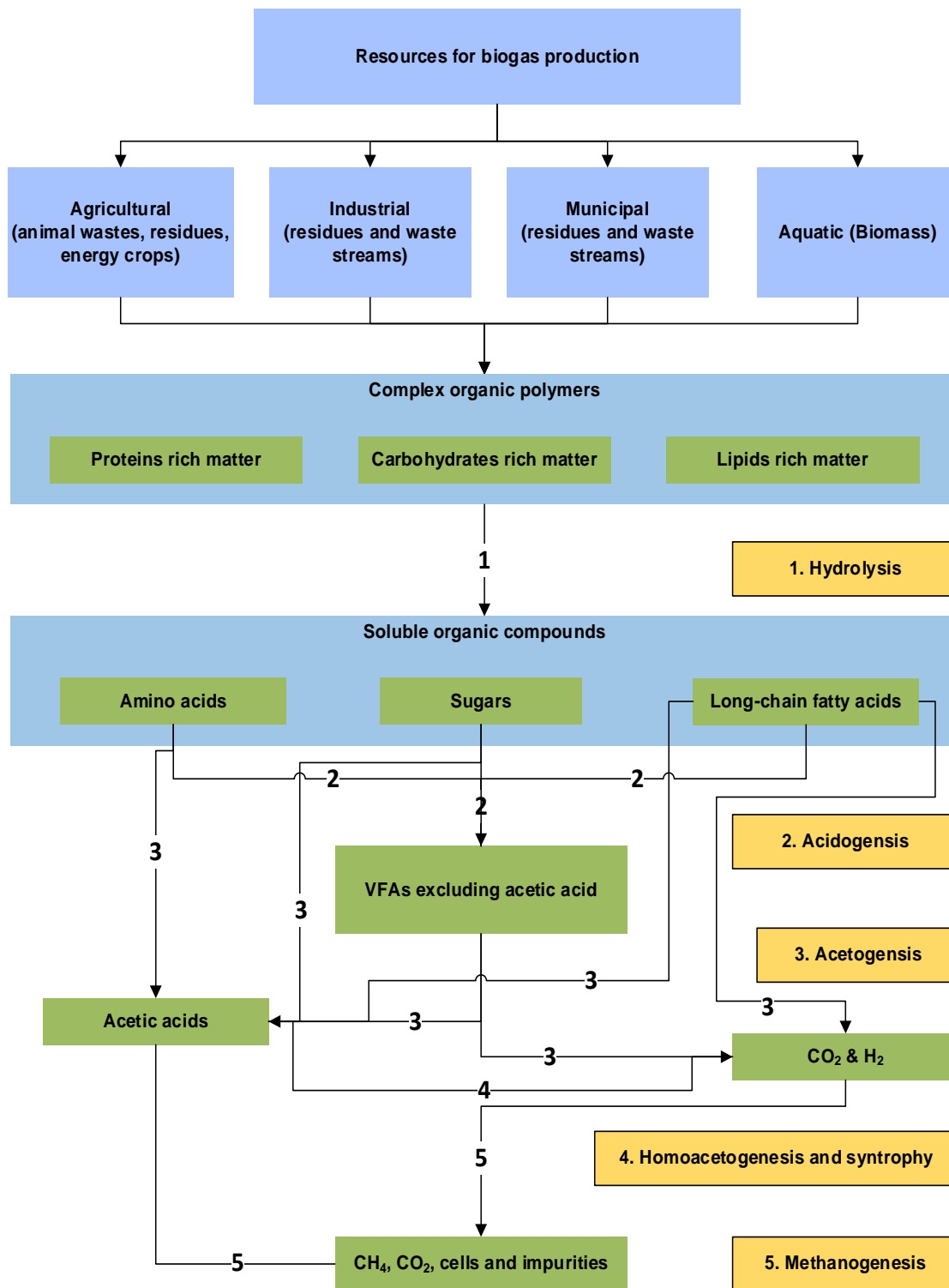


Figure 4. Mechanism of the AD process.

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].

Table 1. A brief sketch of the different digestion systems along with their important parameters

	Digester type	Main components	Advantages	Disadvantages	COD removal efficiency (%)	HRT (days)	OLR (kg COD/m ³ day)	Ref
1	Anaerobic filtration	<ul style="list-style-type: none"> ➤ Vessel (air free) ➤ Digester (completely mixed) ➤ Septic tank ➤ Temperature controller 	<ul style="list-style-type: none"> ➤ Able to handle extensive loads ➤ Cost effective ➤ Volume is small ➤ Efficient for removing suspended solids 	<ul style="list-style-type: none"> ➤ Longer Startup time ➤ Not suitable for highly suspended solids ➤ Continuous water source is mandatory 	94	15	4.5	[43]
2	Continuous stirred tank reactor(CSTR)	<ul style="list-style-type: none"> ➤ Mixer ➤ Mechanical agitator ➤ Digester (closed tank) 	<ul style="list-style-type: none"> ➤ Simple ➤ Cheap ➤ Large biogas production ➤ Provide large heat transfer area ➤ Low maintenance cost 	<ul style="list-style-type: none"> ➤ Biomass retention is lower ➤ Less efficient (at low HRT) ➤ Addition of further reactants can affect the quality 	80	18	3.33	[44,45]
3	Anaerobic digester	<ul style="list-style-type: none"> ➤ Scrapper set ➤ Torque tube ➤ Gear motor ➤ Draft tube 	<ul style="list-style-type: none"> ➤ Low cost (operating, capital and maintenance) ➤ Can handle large range of OLR 	<ul style="list-style-type: none"> ➤ Lower methane emissions ➤ Require large volume ➤ Longer retention times 	70	14	2.43	[46]

4	Modified anaerobic baffled bioreactor (MABB)	<ul style="list-style-type: none"> ➤ Peristaltic pump ➤ Bottle for the collection of effluents and gas ➤ Feed tank ➤ Stirrer (Magnetic) ➤ Water bath 	<ul style="list-style-type: none"> ➤ Able to hold high retention time ➤ Efficient treatment of a variety of feeds 	<ul style="list-style-type: none"> ➤ Less cost-effective ➤ Large area is required ➤ Energy-intensive 	87.4–95.3	3–10	1.60–5.33	[47]
5	Fluidized bed reactor (FBR)	<ul style="list-style-type: none"> ➤ Peristaltic and recycle pump ➤ Separator (for gas-liquid) ➤ Vessel (conical shaped) ➤ Settlement compartment 	<ul style="list-style-type: none"> ➤ Can maintain high biomass concentration (at long SRT) ➤ Have well mixed conditions ➤ Contain large surface area for biomass transfer 	<ul style="list-style-type: none"> ➤ Less energy-efficient ➤ Difficulty in capturing produced biogas ➤ Not suitable for highly suspended solids 	65–75	8	7.31–18.5 2	[48]
6	Up-flow anaerobic sludge blanket (UASB)	<ul style="list-style-type: none"> ➤ Pump (for feeding) ➤ Effluent collector and overflow ➤ Gas outlet and collector ➤ Discharge valve (for gas) ➤ Separator (three-phase) 	<ul style="list-style-type: none"> ➤ Can handle highly suspended solids ➤ Nutrients requirement is less ➤ Provides high CH₄ production ➤ Capable of stabilizing the waste 	<ul style="list-style-type: none"> ➤ Startup time is longer ➤ Biogas quality is low ➤ Relies on sludge concentration 	98.4	4	10.63	[49]

7	Anaerobic baffled reactor (ABR)	<ul style="list-style-type: none"> ➤ Four compartments (containing baffles) ➤ Baffles facilitate the movement (up and down flow) ➤ Sludge blanket ➤ Pipe (for effluent) 	<ul style="list-style-type: none"> ➤ High cell retention time ➤ Simple ➤ Economical ➤ Able to stabilize the waste 	<ul style="list-style-type: none"> ➤ Nutrients stability is compulsory ➤ Recycling is necessary 	90.7	10	1.2	[50]
8	Up-flow anaerobic sludge fixed-film (UASFF)	<ul style="list-style-type: none"> ➤ Pump ➤ Tank (feed and settling) ➤ Gas separator ➤ Combination of UASB and anaerobic filter 	<ul style="list-style-type: none"> ➤ Less chances of clogging ➤ Biomass retention is higher ➤ Methane emission is high ➤ Can bear shock loading 	<ul style="list-style-type: none"> ➤ Poor separation ➤ Pretreatment is needed for suspended solids 	97	3	11.58	[51]
9	Anaerobic contact digestion	<ul style="list-style-type: none"> ➤ Contact process involves a digester and a sedimentation tank pipe (for effluent) ➤ Settlement zone 	<ul style="list-style-type: none"> ➤ High quality of effluents ➤ Steady state is obtained in a short time ➤ Hydraulic retention time is short 	<ul style="list-style-type: none"> ➤ Less stable ➤ Biomass settlement is difficult 	93.3 (BOD)	4.7	3.44	[52,53]
10	Expanded granular sludge bed (EGSB)	<ul style="list-style-type: none"> ➤ Modified form of UASB ➤ Phase separator ➤ Liquid distributor 	<ul style="list-style-type: none"> ➤ Easy sludge separation ➤ Suspended solids can be removed ➤ Effluent can be recirculated' 	<ul style="list-style-type: none"> ➤ For anaerobic sludge, active biomass is required ➤ Can be used mainly for low-strength wastewater ➤ Particulate organic matter is difficult to 	91	2	1.45–17.5	[54]

				remove at high upflow velocity				
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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 Figure 5. 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 (VFA) during the process lowers the pH, while increase in pH is caused by NH_3 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].

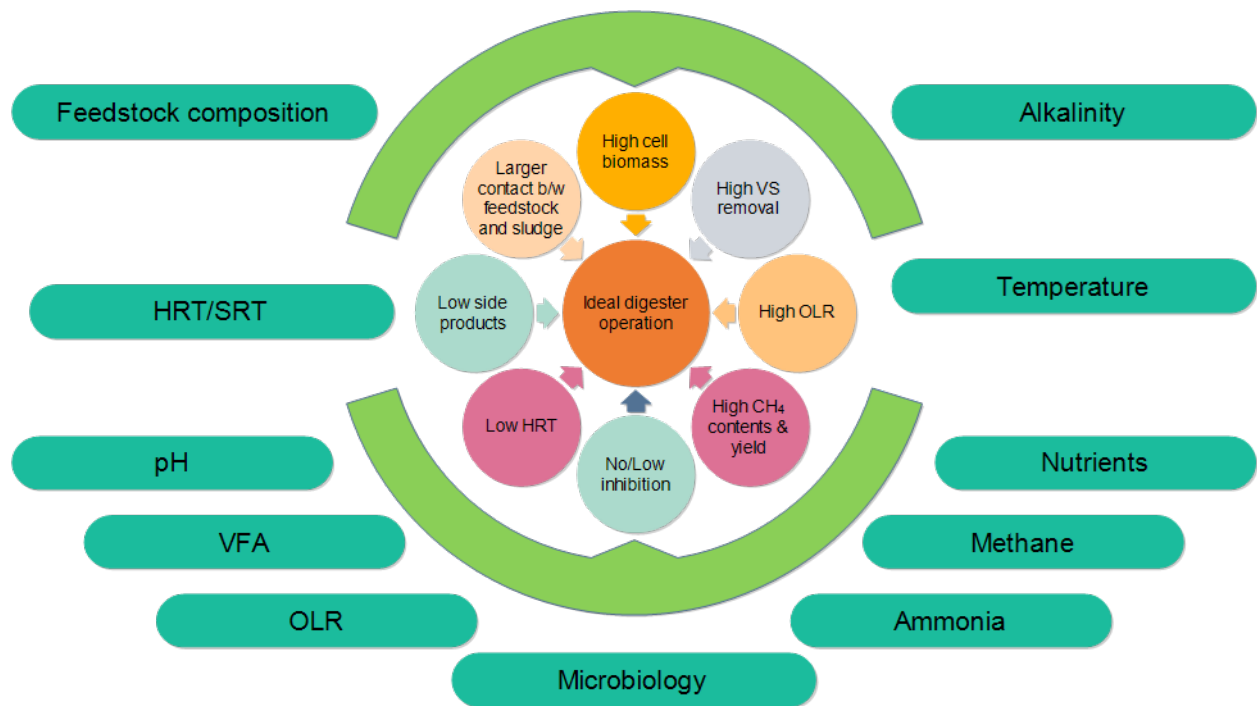


Figure 5. Important parameters and their requirements for an ideal digester operation.

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, so as to use the upgraded biogas as a fuel in transportation or inject it into the natural gas grid [55]. The most commonly used cleaning and upgradation technologies involve membrane separation, absorption (physical and chemical), adsorption, and cryogenic treatment. Figure 6 elucidating the transformation of biogas to biomethane, which will be explained in the forthcoming section.

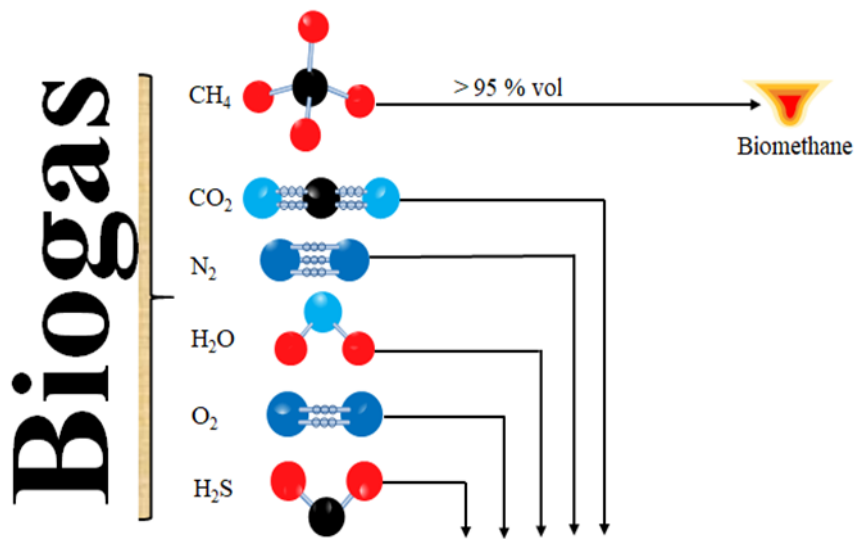


Figure 6. A schematic illustrating the conversion of biogas to biomethane.

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 [11,19,56,57]. These impurities must be removed from the biogas stream, depending on further processing and the subsequent use of biogas [11,57–59]. The permissible limit of impurities for the production of LBM is listed in Table 2.

Table 2. Purity requirements for the LBM [60,61]

Components	Impurity limit in LBM
H ₂ O	< 1 ppmv
H ₂ S	< 4 ppmv
CO ₂	< 25 ppmv

The importance of biogas cleaning becomes more evident for the production of liquefied biomethane, considering that high-purity methane is desired [60,61]. In addition, it can be advantageous to perform biogas cleaning during the upgradation and liquefaction processes to avoid corrosion and other mechanical issues of the equipment [18,19,62]. The impact of impurities is presented in Table 3.

Table 3. Biogas impurities and their impacts to the equipment used in LBM production [18,19,62]

Components	Impacts
H ₂ O	<ul style="list-style-type: none">- corrosion of apparatuses and pipelines due to acid formation- damage of instruments caused by condensation- freezing at high-pressure and low-temperature conditions
H ₂ S	<ul style="list-style-type: none">- corrosion (reaction with H₂O produces sulfuric acid)- SO_x formation as a result of combustion- formation of flammable mixtures (4.5 – 45.0 vol% H₂S in air)
CO ₂	<ul style="list-style-type: none">- corrosion of metallic parts- decrease in the calorific value of biogas
NH ₃	<ul style="list-style-type: none">- corrosion due to base formed when dissolved in H₂O
O ₂ and N ₂	<ul style="list-style-type: none">- Reduce liquefaction rate of biomethane- Cause entropy during liquefaction- decrease the calorific value of biogas
Siloxanes	<ul style="list-style-type: none">- formation of SiO₂ and microcrystalline quartz- abrasion
Dust	<ul style="list-style-type: none">- clogging in compressors, exhausts, and vents
Cl ⁻ and F ⁻	<ul style="list-style-type: none">- corrosion

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, moisture traps, and water traps. Physical drying is often used as a pretreatment 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 SiO_2 , 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 H_2O content, such as a gas for grid injection [19].

3.1.2. Removal of H_2S

Techniques available for the removal of H_2S in the market can be classified into two categories: removal during digestion and removal after digestion [19]. In the digesters, H_2S 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 H_2S is still too high, *i.e.* 100–300 ppm. In the case of removal of H_2S after digestion, desulfurization by reaction with iron oxide or hydroxide, adsorption on activated carbon (often impregnated with KI or H_2SO_4 to increase the reaction rate), and absorption with liquids (*e.g.*, diluted NaOH-solution, FeCl_2 -solution, $\text{Fe}(\text{OH})_3$ -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 H_2S , as well as the combination of physico-chemical processes with biotechnological processes (*e.g.*, Thiopac process [63]). However, when the H_2S 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, [56].

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 [56].

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 [64].

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 (CO₂ removal) the cleaned biogas 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 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) is shown in Figure 7.

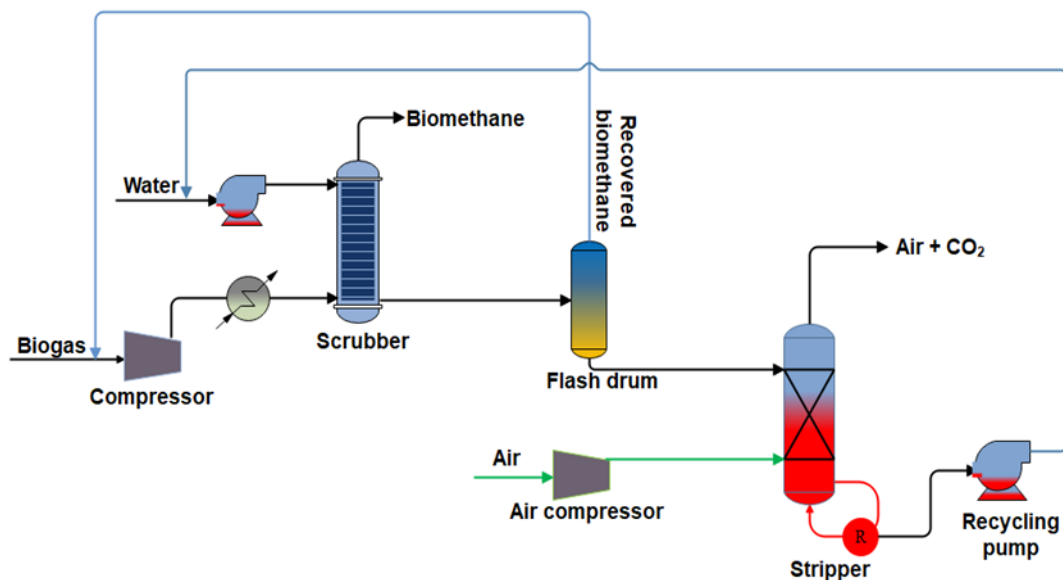


Figure 7. Process flow diagram of a water-based scrubbing unit for biogas upgrading.

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) [65]. At elevated pressures, the solubility of CO₂ increases, but the biomethane loss is estimated to be 3–5% [25]. Biomethane loss up to 1–2% [66] and 18% [67,68] has been reported in water scrubbing methodology. Rimika et al. [69] 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 an organic solvent rather than water is shown in Figure 8.

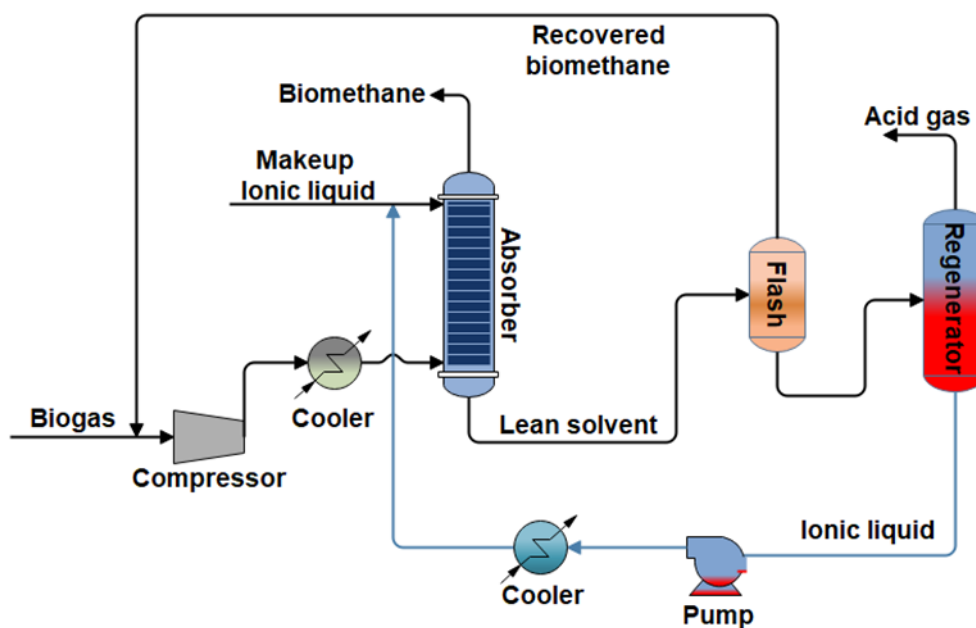


Figure 8. Process flow diagram of a physical absorption unit for biogas upgrading.

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 [70]. 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 [71]. Alternatively, a class of green solvents referred to as ionic liquids (ILs) is introduced in as a replacement for conventional amines and water scrubbing. As discussed

by Yajing et al. [72], 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 [73,74]. Additionally, ILs have gained equal importance in the purification of valuable biochemicals in the biofuel industry [75,76].

Recent studies on ILs are carried out owing to their green and energy-efficient characteristics [73,77,78]. 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 [78–80]. Christian et al. [81] used imidazolium-based IL [bmim][Br], both singly and together with an aqueous amine solution for upgrading biogas. The results indicated that the low volatility and chemical stability of ILs are the leading characteristics, while the absorbing capacity of Br-based ILs is very low as compared to those of the amines, even when the IL is mixed with amine. Manuel et al. [82] reported that [Emim][Tf] 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 [83]. Elena et al. [78] studied the absorbent selection for biogas upgrading applications and showed that ILs provide superior results in terms of absorption and regeneration. Moreover, most of the solvents lose their efficiency after regeneration: for example, amines lose approximately 26–43% of their basic absorption efficiency, while that of IL is very low or negligible [78]. Yujiao et al. [84] studied imidazolium-based ionic liquids and found that the total energy required for scrubbing operation follows the order, [Bmim][Tf₂N]<[Bmim][PF₆]<[Hmim][Tf₂N].

The simulation results reveal that the reduction in energy consumption approaches 29% and 11% upon using ChCl/urea and [Bmim][Tf₂N], respectively, as compared to that of water scrubbing. Recently, advanced ILs such as [Amim][HCOO] [85], [BDiMIM][TCM] [86], ChCl/urea [87], and Cholonium-based IL [88], 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 [89]. In this context, researchers are focusing on blending these emerging ILs with other physical solvents in order to not only to reduce the viscosity but also to enhance the efficiency of the process [77,89–91].

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 Figure 9 [92,93]. Monoethanol amine (MEA), dimethylethanolamine (DMEA), diglycol amine (DGA), and piperazine (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 corrosive nature and degradation of amines [94]. The thermal load can be reduced by adjusting the amine-to-feed ratio by increasing the absorption capacity of the absorbent [95]. It is known that the regeneration of tertiary amines is easier than the regeneration of primary and secondary amines [96]. Recently, Mengna et al. [97] 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.

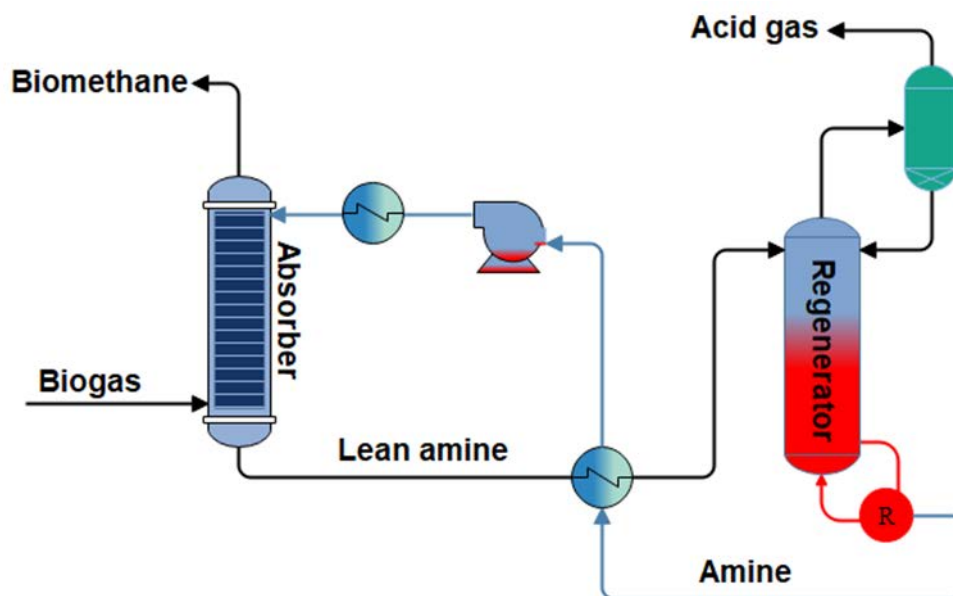


Figure 9. Process flow diagram of a chemical absorption unit for biogas upgrading.

Caustic solvents can also be used as chemical absorbents, instead of amines [98,99]. 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 $\geq 99\%$ purity can also be obtained, owing to the higher selectivity of the solvent towards CO₂ [93,99].

3.2.3. Pressure swing adsorption

In an adsorption process, selected molecules are adsorbed on materials at high pressures and desorbed at low pressures. A general process flow diagram of a PSA process is shown in Figure 10.

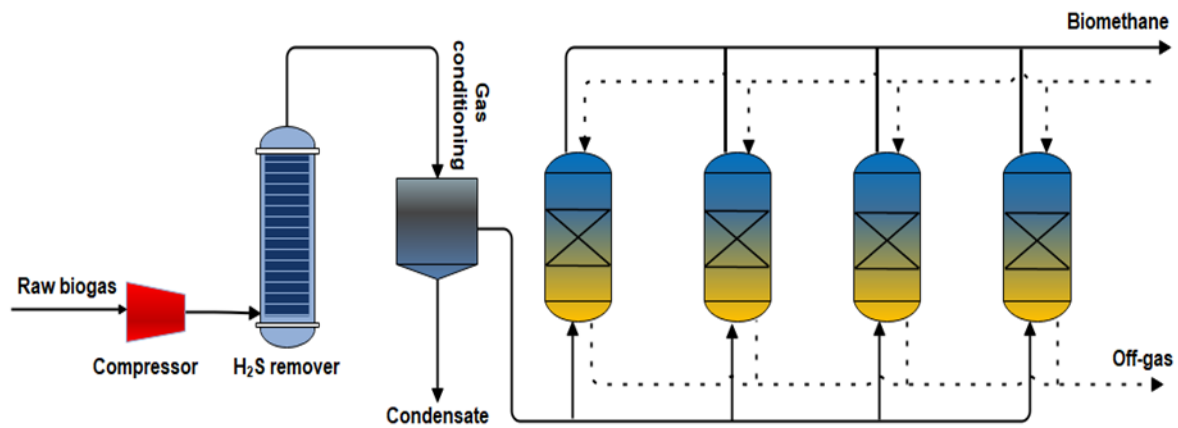


Figure 10. Process flow diagram of pressure swing adsorption for biogas upgrading [19].

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 [100],

- 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 [61]. 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 [101]. This method is also used to upgrade landfill gas [102], and according to Grande [103], 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 [19,104], or six [100] vessels working in parallel are used to emulate a continuous process, and each vessel works on a different stadium of the so-called Skarstrom cycle [61]: 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 [103], respectively, and regeneration pressures are of approximately 100–200 mbar. The cycle typically lasts for ~3–5 min [105].

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 [100]. 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 [61]. 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 demosturization 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 [61]. Similar figures can be found in other literature, 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 [106]. 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 system in which a cooling machine is used [61]. The energy demand

can be higher (probably close to 0.3 kWh/Nm³ [61]) when a catalytic oxidizer is used.

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 [103].

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 [107]. 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 [19,100]. This gas can be dealt with in several ways [61]. 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.

3.2.4. Cryogenic biogas upgrading

Cryogenic biogas upgrading technologies [19,25,61,93,104,108,109] 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 [110]), in cryogenic packed beds (CPB process) [111] or in spray towers, while the latter group relies on low-temperature technologies

mainly used for natural gas purification and based on distillation, as in the Ryan-Holmes process [112] and the dual-pressure low-temperature distillation process DCCDTM [113,114]. A case apart is the CFZTM process [115] 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 [116,117]. However, cryogenic separation technologies based on distillation are not yet used commercially for biogas upgrading [118].

The Cryo Pur process is an integrated process for biogas cleaning, upgrading, and biomethane liquefaction. CO₂ is frosted 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% [119]. 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 300 Nm³/h of biogas to be started mid-2017 in Northern Ireland. Another unit with a larger capacity, *i.e.* 500 Nm³/h of biogas, was planned to be built in 2018 at Doué Métha, Angers, France [119,120].

The GPP[®] processing unit [121] 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 [122]. Two LBM plants (both in Sweden) were operated to produce LBM based on this technology, but both have suffered

several problems [122]. Currently, there is only one smaller demonstration plant situated close to the headquarters of the company [118].

CryoSep [123,124] is a process used by Biofrigas, Sweden to upgrade and liquefy raw gas to LBM in the same plant. In 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 DCCDTM, 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 [57], 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 [114].

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 [125].

For the sake of brevity, only the diagrams of the GPP[®] and DCCDTM processes, as examples of methods based on desublimation and cryogenic distillation, respectively, are shown in Figure 11 and Figure 12, respectively.

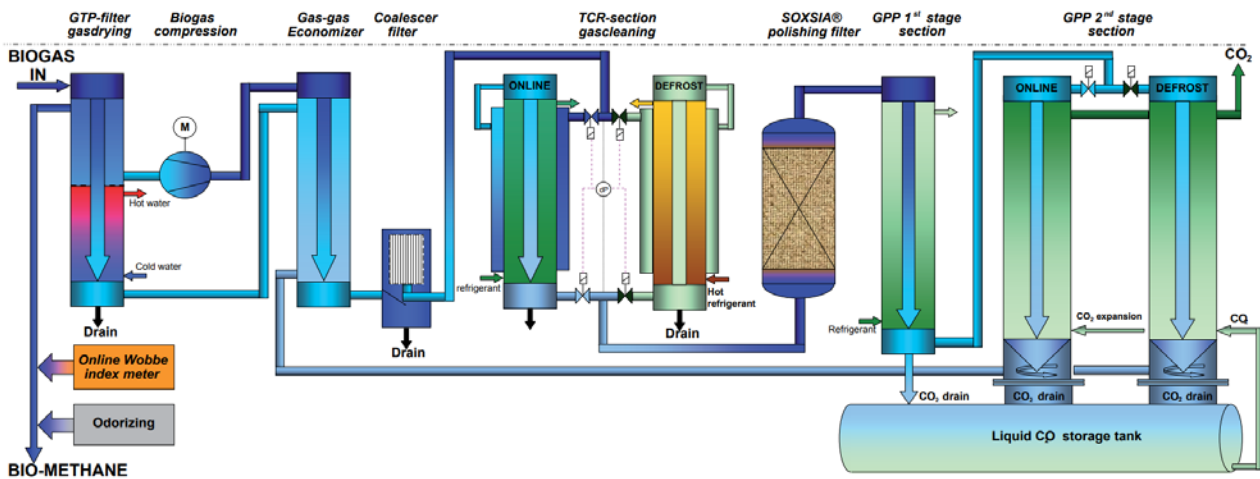


Figure 11. Process flow diagram of the GPP[®] process (Courtesy of GPP[®]) [130].

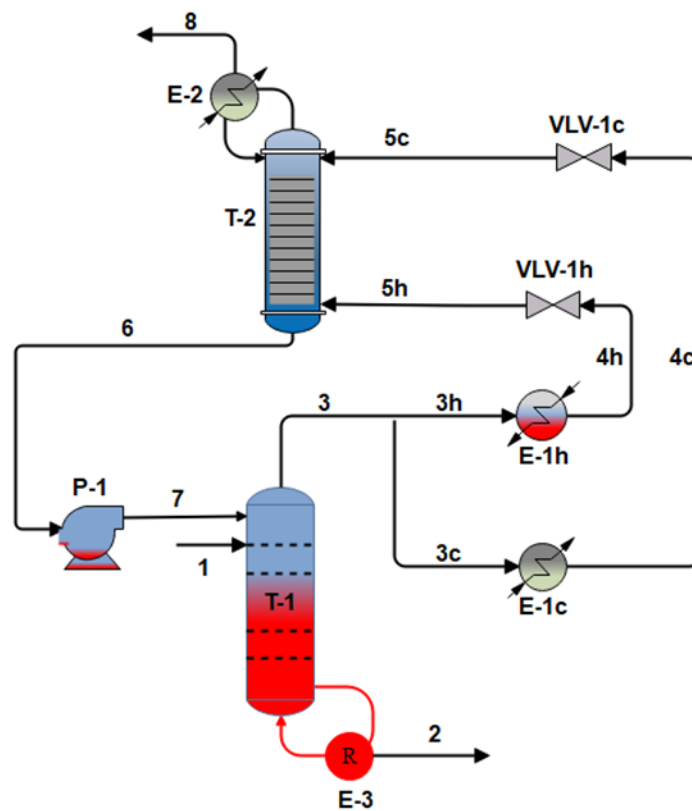


Figure 12. Process flow diagram of the DCCD[™] process [123].

Recent years have seen the development of hybrid technologies that try to exploit the advantages of different upgrading technologies [126].

Pentair [127] has commercialized a hybrid process combining membranes and a cryogenic technology. No further detail on the process lay-out is available.

Terracastus Technologies holds the license of the CO₂Wash[®] process [61], a combination of cryogenic and conventional technologies, developed by the US-based company, Acrion's Technologies. The raw gas stream is cleaned with a liquid carbon dioxide stream, which efficiently absorbs impurities such as siloxanes, halogenated compounds, and non-methane organic compounds ("CO₂Wash"). The CO₂ present in the cleaned gas, ~25%, and any existing O₂ are then separated by a membrane treatment process [60,100].

Table 4 lists the emerging cryogenic separation technologies for biogas upgrading. It includes the information about the development stage of each technology, the inventor, and the location where it is being developed. The performances of these technologies are also summarized in the Table 4.

Cryogenic biogas upgrading processes are emerging technologies with great potential, although they are still under development with only few facilities operating at the commercial scale [93,122]. They produce a methane stream at a high purity level at a low-temperature; they are therefore synergistic with the LBM production [25,104,109,119,122] and are suitable for this application also, because highly purified biomethane can be obtained. Another general advantage of cryogenic upgrading is that no additional fluid is required and very pure CO₂ is produced as a liquid [19].

Table 4. Cryogenic separation technologies for biogas upgrading that are currently available.

Processes	Current development stage	Inventor	Separation methods	Operating condition (reported only for the cryogenic section)
Cryo Pur [110,119,120]	Commercial plant	Cryo Pur, France (2001)	CO ₂ desublimation	T = -90 to -120 °C P = atmospheric pressure (CO ₂ frosting) and 4 - 6 bar (CO ₂ solid melting)
GPP [®] [121,122]	Demonstration plant	Gastreatment Services, Netherlands (2007)	CO ₂ desublimation	T = -50 to -95 °C P = 26 bar
CryoSep [123,124]	Pilot plant	Biofrigas, Sweden (2017)	No information	No information
Cryogenic packed-bed [111]	Simulation study	Eindhoven University of Technology, Netherlands (2012)	CO ₂ desublimation	T = -110 °C P = 5 bar (CO ₂ desublimation) and 1 bar (bed regeneration)
DCCD [™] [113,114]	Pilot plant	Politecnico di Milano, Italy (2014)	Distillation	T = -74 to -88 °C P = 50 bar (stripping section) and 40 bar (enrichment section)
Ryan Holmes [125,128]	Commercial plant for natural gas	Koch Process Systems, Inc., Westborough, Mass., USA (1979)	Distillation	T = -128 to -106 °F at 500 psia with <i>n</i> -butane as entrainer

Pentair Haffmans [127]	Commercial plant	Pentair Haffmans, Netherlands	Membranes permeation and CO ₂ liquefaction	T= -24 °C P= 17.5 bar
CO₂ Wash [60,61,100]	Commercial plant	Terracastus Technologies/Acrion's Technologies	Treatment with liquid CO ₂ and membranes	No information

3.2.5. Membrane technology

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 [129]. 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 CO_2 condense less and pass through the membrane more favorably in comparison to large molecules such as methane [129]. 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: CH_4 , N_2 , H_2S , CO_2 , and H_2O [61,130], as shown in Figure 13.

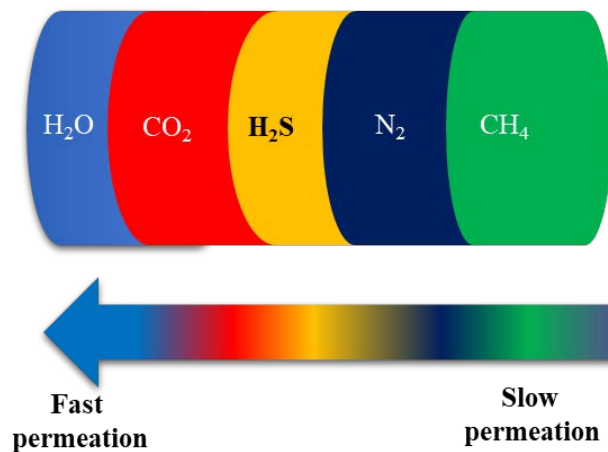


Figure 13. Relative permeation rates of different gases through membranes.

For biogas upgrading, methane is recovered at the inlet side, while H_2S and CO_2 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 Figure 14 [122]. 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. [131] 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 [132]. Membranes of a variety of materials such as organic polymers, inorganic materials, and mixed matrices have been tested for biogas upgrading [133]. However, only polymeric membranes are used at the industrial scale, because of their low cost than those 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 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 [109]. The high permeability difference between CH₄ and CO₂, 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.

Figure 14 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 H₂S is removed with activated carbon because it may not be sufficiently separated by the membranes [59]. 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 [130].

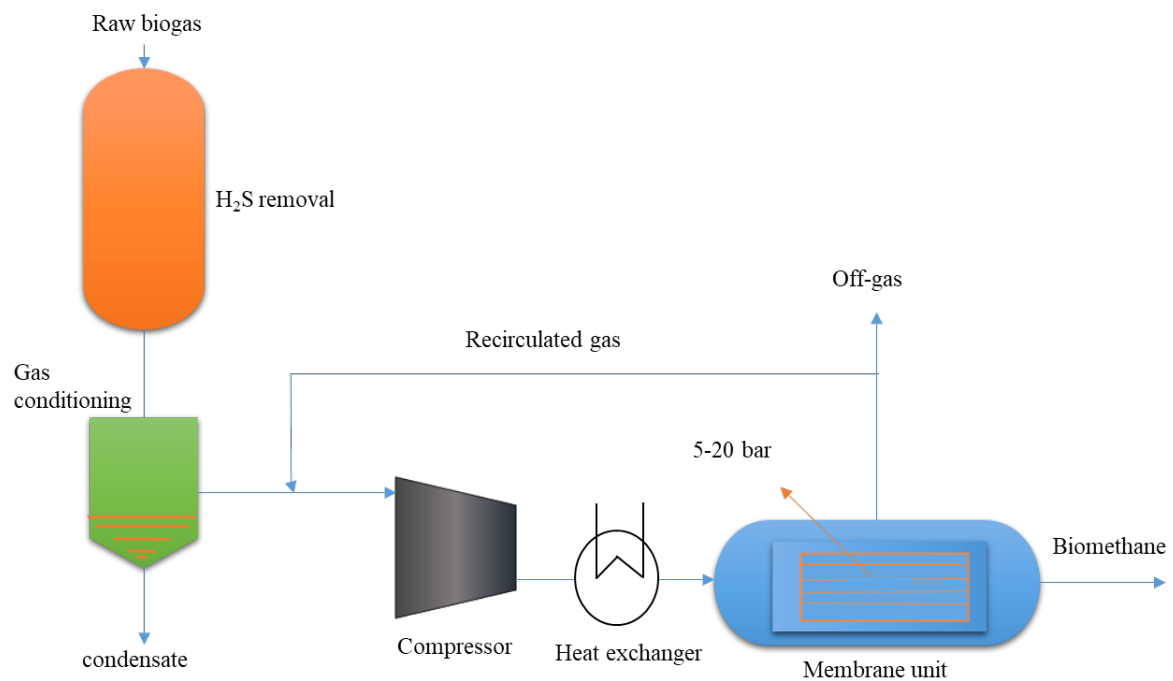


Figure 14. Process flow design of a membrane-based biogas upgrading unit.

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 Figure 15 [134]. There is no need for internal circulation in the first design, which decreases the energy demand. However, the CH₄ 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 [93]. An upgrading plant for biogas employing polyimide membranes was installed for the production of biomethane (100 m³_{STP}/h) to be injected into the gas grid [135]. 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.

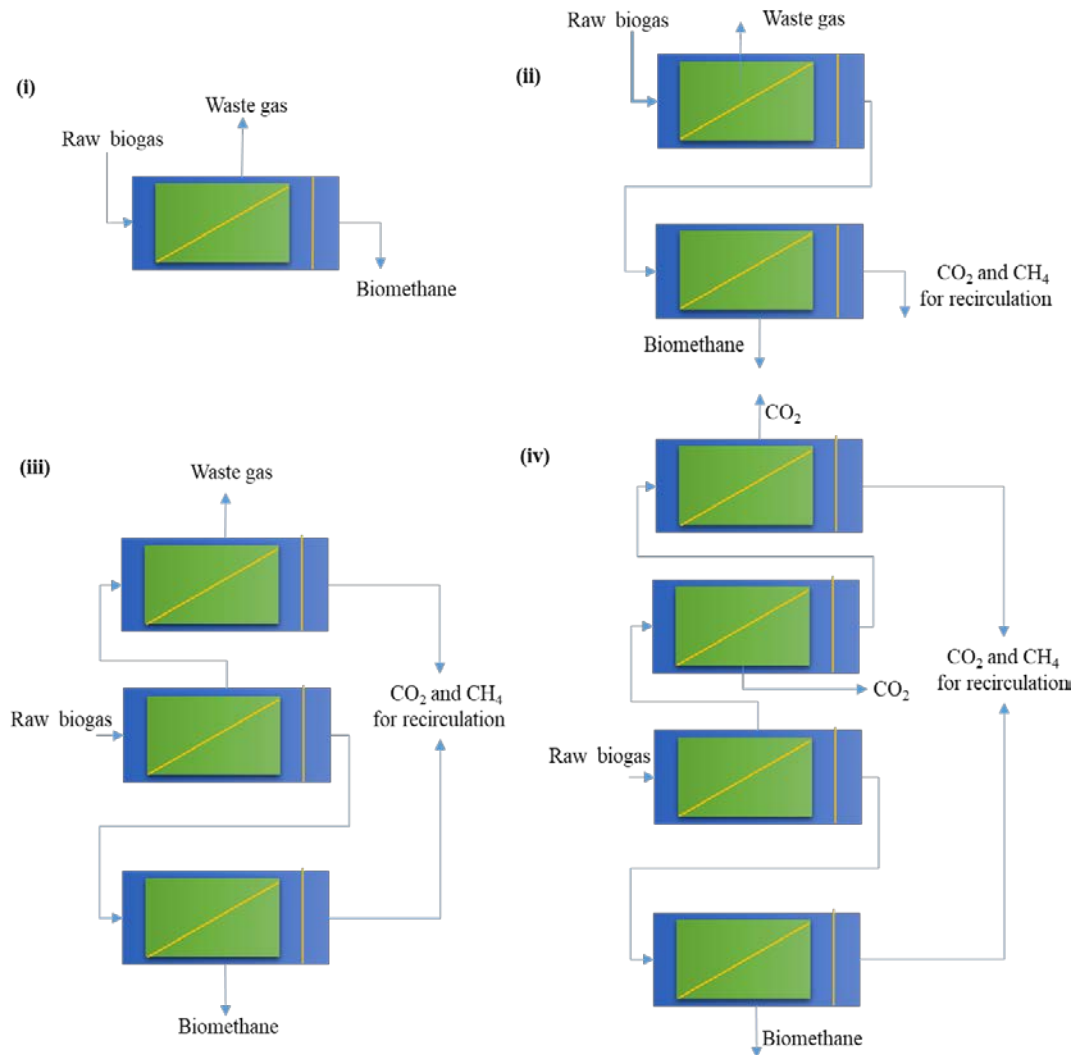


Figure 15. Four different configurations of the membrane technology available in the market.

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 Figure 16. 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.

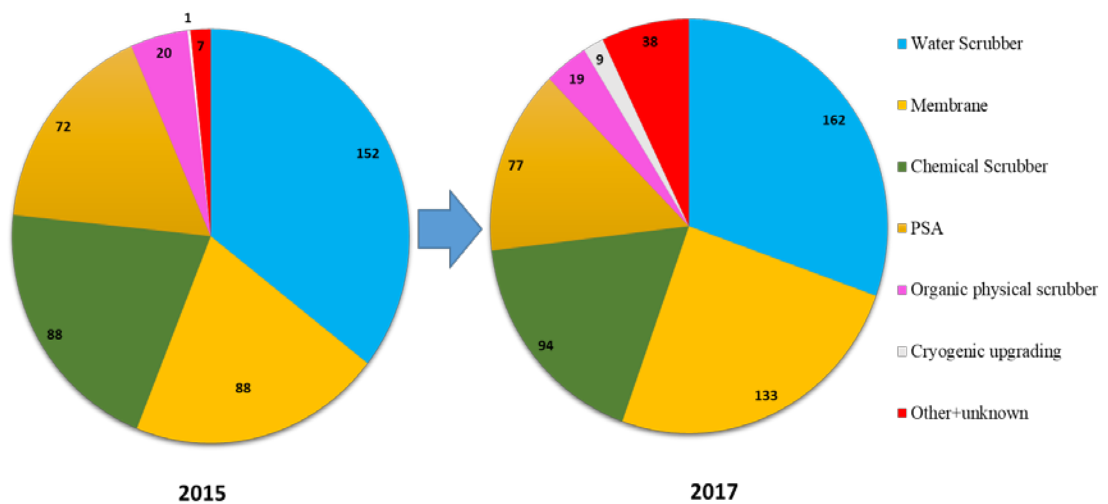


Figure 16. The distribution of the membrane-based upgrading technology as compared with other technologies for the reported biogas upgrading plants in the IEA Bioenergy Task 37 group of countries for 2015 and end of 2017.

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 CO₂ removal, applied pressure, and installed membrane area [126]. 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/Nm³ [61], which is valid for major applications and is independent of the size [126].

4. Comparison of different technologies for biogas upgrading

The processes that are used for the purification of biogas are based on the consistency, purity, and losses of methane. Each technology faces some challenges precluding commercial scale implementation. Among the available technologies, membrane-based separation and pressure swing adsorption offer promising results in terms of purity. 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.

Table 5. Merits and challenges of different technologies for biogas upgrading

Technique	Merits	Challenges
Water scrubbing	-Pre-cleaning is not required	-Excess fresh water requirement
Physical absorption	- Simple operation	- Requirement of chemicals
Chemical absorption	- Cost effective -High biomethane purity - Low methane loss	-Biological contamination -Regeneration is required
PSA	-Dry process -Chemical-free process - Free of microbial contamination	-Pre-treatment is required -Complex -High investment costs
Membranes	- Dry process - Chemical-free process -Compactness -Low mechanical wear	-Pre-treatment is required -Capital intensive -Energy intensive -Unstable over the long term

Cryogenic
separation

-Highest methane purity

-Pre-treatment is required

- Chemicals free process

-Capital and energy intensive

-High-pressure upgrading
facilitates the LBM production

In situ methane
enrichment

-Cheap

- Loss of methane is low

-Simple in operation

-Suitable for small scale

Table 6. Features of typical approaches to upgrade biogas to biomethane

Technology	Mechanism	Investment Cost (€y) for 1000 m ³	CH ₄ Purity (vol %)	CH ₄ loss (%)	P (bar)	T (°C)	Energy consumption (kWh/Nm ³)	Efficiency of the process (%)	Capacity-based economic aspects			Ref.
									Capacity (m ³ /h)	Capital cost (\$/kWh)	Operating and maintenance cost (\$/kWh)	
Water scrubbing + regeneration	Physical absorption	10,00,000	93–98	>2	4–10	-	0.2–0.45	92.7–96.0	100	1339	1.872	[13,25,30,61,136]
Cryogenic separation	Multistage compression and condensation	-	95–99	<0.1	80	-196	0.45–0.76	84.9–96.7	161	1248	6.24	[13,25,30,61,93]
Physical absorption	Physical absorption	10,00,000	95–99	<4	4–8	55–80	0.2–0.3	90–95.5	100	1259.7	1.846	[30,61,136]
Chemical absorption	Chemical absorption	20,00,000	97–99	<0.5	Normal	100–180	0.05–0.18	88.5–97.7	100	1259.7	1.924	[13,30,61,136]
Pressure swing adsorption	Adsorption	17,50,000	95–99	<3	3–10	-	0.23–0.3	84.8–93.6	100	1379.3	1.703	[13,61,136]
Membrane technology	Permeation	20,00,000	80–99	<5	4–6	-	0.18–0.35	82.4–98.0	100	988	1.443–2.119	[13,30,61]

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 [28,137]. 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 [138]. However, the overall integrated cryogenic upgrading and liquefaction process is operated at very low temperatures and uses a refrigeration cycle that is by itself a highly energy-intensive process. 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 [139] use three refrigeration cycles for precooling, liquefaction, and

subcooling with three different MRs. Table 7 [140] 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 sensible and latent heat transfers, 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 [28,141]. A detailed description and analysis of the conventional liquefaction processes (at both large scale and small scale) can be found in the literature [28,142,143].

Table 7. Comparison of LNG processes [140]

Process requirements and specifications	SMR	DMR	Cascade	C3MR	N₂-expander
Heat Exchanger	Precooling (Plate-fin) Liquefaction (Plate-fin)	Precooling (Spoolwound) Liquefaction (Spoolwound)	Precooling (Core-in-kettle) Liquefaction (Core-in-kettle)	Precooling (kettle) Liquefaction (Spoolwound)	Precooling (kettle) Liquefaction (Plate-fin)
Electricity requirement (20 MW turbo generators)	3	3	3	2	3
Production (t/d)	11300	13100	10000	11900	6540
Specific power (kW/(t/d LNG rundown))	14.5	12.5	14.1	12.2	15.6
Fuel efficiency (%)	91.6	92.7	91.2	92.9	90.4
Annual production (MTPA)	7.4	8.7	6.6	7.9	4.3
Specific cost (C3MR = 100)	97	116	119	100	95

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

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. [144,145] 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.

6. Biogas to LBM: Prospects

Considering the environmental and public health issues associated with the 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, the 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. Globally, the generation capacity for biogas reached 16.9 GW in 2017, up from 6.7 GW in 2008 [146,147]. 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 [146,148]. The development of biogas capacity globally is summarized in Table 8 [146,147]. Europe has become a world leader in biogas-based electricity generation with more than 60% of the global capacity for producing electricity from biogas-connected grids [149]. The European Biogas Association reported that, Europe had 6227 biogas plants in 2009 and this number has grown up to 17662 plants in 2016 [150,151]. According to Green Gas Grids [152], 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.

Table 8. Development of biogas capacity globally [MW] [146,147]

Year	World	Africa	Asia	C. America + Caribbean	Eurasia	Europe	Middle East	N. America	Oceania	S. America
2008	6699	14	83	4	34	4474	12	1715	260	103
2009	8241	14	152	4	56	5873	16	1728	267	131
2010	9467	14	261	4	72	6871	24	1793	270	159
2011	11358	16	337	10	91	8471	32	1946	271	184
2012	13137	19	435	10	134	9752	34	2257	275	222
2013	13872	20	585	12	163	10141	39	2425	265	223
2014	14880	20	764	11	205	10770	47	2547	274	243
2015	15482	35	860	19	253	11183	58	2524	278	273
2016	16440	36	978	20	298	11620	58	2610	278	543
2017	16915	40	1115	23	347	12064	58	2634	279	355

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 to 17264 GWh in 2016, as shown in Figure 17 [151].

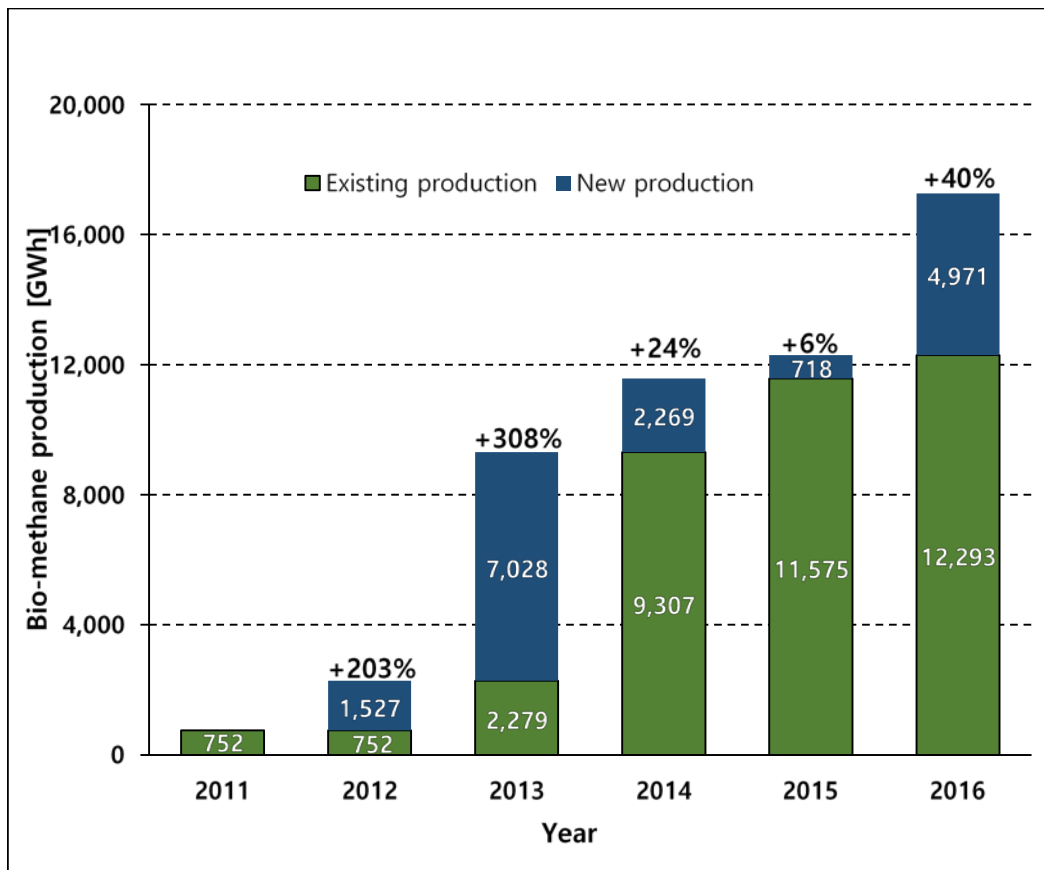


Figure 17. Biomethane production in Europe between 2011 and 2016 [in GWh] [151].

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 [148]. 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 5,570 MW by 2036, while Malaysia's goal is 1,065 MW by 2020, and Indonesia aims to achieve 810 MW by 2025 [153]. Asia Biogas [154] reported that, ten projects were operated in Thailand, Laos, and Indonesia in 2017, from which, 24.2 million Nm³ CH₄ was produced [155,156].

Scarlat et al. [149] 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 feedstock 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 [61,122]. 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 [157]. 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

We successfully analyzed and presented the major units (production, cleaning, upgrading, and liquefaction) involved in the production of liquefied biomethane. We also presented the mechanism of biogas production with a brief sketch of the different digestion systems considering their important performance parameters. The technological trend for cleaning and upgrading biogas was assessed. The economics of each upgrading technology was presented to compare their energy and investment costs. Commercial-scale upgrading units have been highlighted. Liquefaction has been suggested for the feasible and economic transportation of upgraded biogas (biomethane) over long distances. The current trend and future perspectives of the global biogas usage was also presented. 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. Biomethane can also potentially replace-natural gas as a green fuel and feedstock for producing a variety of chemicals.

Declaration

The authors declare no competing financial interest.

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