Biogas as an energy vector: a review

Ahmad Rafiee[1,2,*], Kaveh R. Khalilpour[3], James Prest[4], Igor Skryabin[5]

[1] Department of Theoretical Foundations of Electrical Engineering, Faculty of Energy, South Ural State University, Chelyabinsk, Russia

[2]DanaCluster Pty Ltd., Sydney, Australia
[3] School of Information, Systems and Modelling, University of Technology Sydney, Australia

[4] ANU College of Law, Fellows Rd, Australian National University, Canberra, Australia

[5] ANU Energy Change Institute, Oliphant Building, Mills Road, Australian National University, Canberra, Australia

Corresponding author email: a.rafiee82@gmail.com

Abstract

Biogas is a sustainable energy vector with diverse input sources (e.g. landfills and anaerobic digestion of waste materials, wastewater treatment sludge, manure from animal production, or energy crops) and diverse applications. The nature of the substrate and the design of the biogas production process determines the composition of raw biogas. All types of biogas must be cleaned and upgraded before delivering to the consumers and in practice, the key challenge of the biogas supply chain is its cleaning and upgrading to consumers quality. The physicochemical technologies used to clean and upgrade the raw biogas are reliable, mature and at high technology readiness levels.

This paper critically reviews the biogas supply chain including feedstock supply, biogas production and upgrading/cleaning processes, potential hazards of biogas contaminants, product specification based on applications, and biogas/biomethane uses. The biogas cleaning and upgrading technologies with emphasis on cost comparison are assessed. In summary, the upgrading technology alternatives and their associated costs are found substantially affected by the project-specific circumstances. For instance, upgrading with chemical scrubbing might be preferred in the availability of cheap on-site thermal energy. If the biomethane is planned to be injected into high-pressure natural gas pipelines, those upgrading methods operating at relatively high pressures (e.g. membranes) would be preferred. If the biomethane injection point to the gas grid is located distant from the production site, the distribution cost will also play a determinative role in the overall biogas supply chain economics. Among all these factors, plant capacity seems to be a pivotal element in the economics of biogas supply chain. Amendments to national and sub-national support schemes are also an important factor affecting investment decisions.

Keywords: biogas upgrading, biomethane, physicochemical, techno-economics, waste-to-energy.

Abbreviations

AD	anaerobic digestion
CCS	CO_2 capture and storage
CHP	combined heat and power
DCM	di-chloro-methane
DEG	di-ethylene glycol
DMC	di-methyl carbonate
DME	di-methyl ether
DMEA	di-methyl ethanolamine
EG	ethylene glycol
EU	European Union
FF	fresh feedstock
FT-GTL	Fischer-Tropsch gas-to-liquid
GHG	greenhouse gas
HRAR	high rate anaerobic reactors
MBR	membrane bioreactors
IPCC	intergovernmental panel on climate change
LF	landfill
MCFC	molten-carbonate fuel cell
MEA	mono-ethanolamine

MSW	municipal solid waste
Mtoe	million tonnes of oil equivalent
O&M	operating and maintenance costs
PAHs	polyaromatic hydrocarbons
PSA	pressure swing adsorption
ppb	part per billion
SOEC	solid oxide electrolysis cell
Syngas	synthesis gas
TEG	tri-ethylene glycol
VOC	volatile organic compounds
WtE	waste-to-energy

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1. Background

Meeting the climate change mitigation targets requires a rapid transition from fossil fuels to renewable electricity and renewable fuels. Increased urbanization rate, growing population, and economic evolution are significantly altering the perspective of national solid waste materials in terms of waste composition, generation pace, and waste treatment processes [1]. Over a few decades of research and industrial actions, today there is general consensus that conversion of the waste to energy is a promising waste management option.

The so-called waste-to-energy (WtE) has multiple advantages. Not only it addresses the waste disposal challenge, but it also offers a good opportunity for energy security, as both the processes for production and consumption of energy can be located in the same geographic location, unlike fossil fuels. WtE can be considered as a semi-renewable source of energy and an alternative (or at least a compliment) to fossil fuels which account for over 80% of the global energy consumption [2]. WtE processes comprise any waste treatment technology that generates any form of energy i.e. heat, electricity, or liquid transport fuels (e.g. diesel, petrol or kerosene) from a waste material feedstock.

Bioenergy refers to power, heat, transport fuels, and gas that is produced from biological sources [3]. It is the third principal source of energy in the world, nearly emission-neutral [4] and can have a positive impact on promoting and balancing existing and future energy systems [5]. Dairy waste, agricultural waste, wastewater treatment plants, urban food waste and garden waste, landfill (LF) gas and municipal solid waste are the principal categories for use.

When an organic waste is decomposed in the absence of oxygen, a blend of gases (primarily methane and CO_2) is released, known as biogas [6]. Some decades ago, biogas was perceived as “poor man’s fuel” [7], but today it has emerged as one of the major options in the international energy planning context. The biogas production process has several advantages including its feedstock flexibility which can also include MSW. In fact, when MSW is dumped in the nature, it goes under biological dissociation and generates biogas the release of which to the atmosphere creates significant environmental impact. The released methane has over 20–times more global warming effects than CO_2 for a 100-year time horizon. But, once the gas is produced in a process, it becomes a potential alternative energy source, especially for rural communities. Regardless of its energy value, biogas even if flared will release CO_2 which has substantially less environmental impact than methane. Last but not least, access to distributed biogas resources supports the energy (gas and electricity) grid decentralization movement and improves the higher uptake of variable renewable technologies such as photovoltaics (PV) and wind. The actual advantage and also necessity would be in the modulation capability of the renewable electricity production in order to compensate for the variability in the PV or wind energy. Other environmental benefits of biogas are:

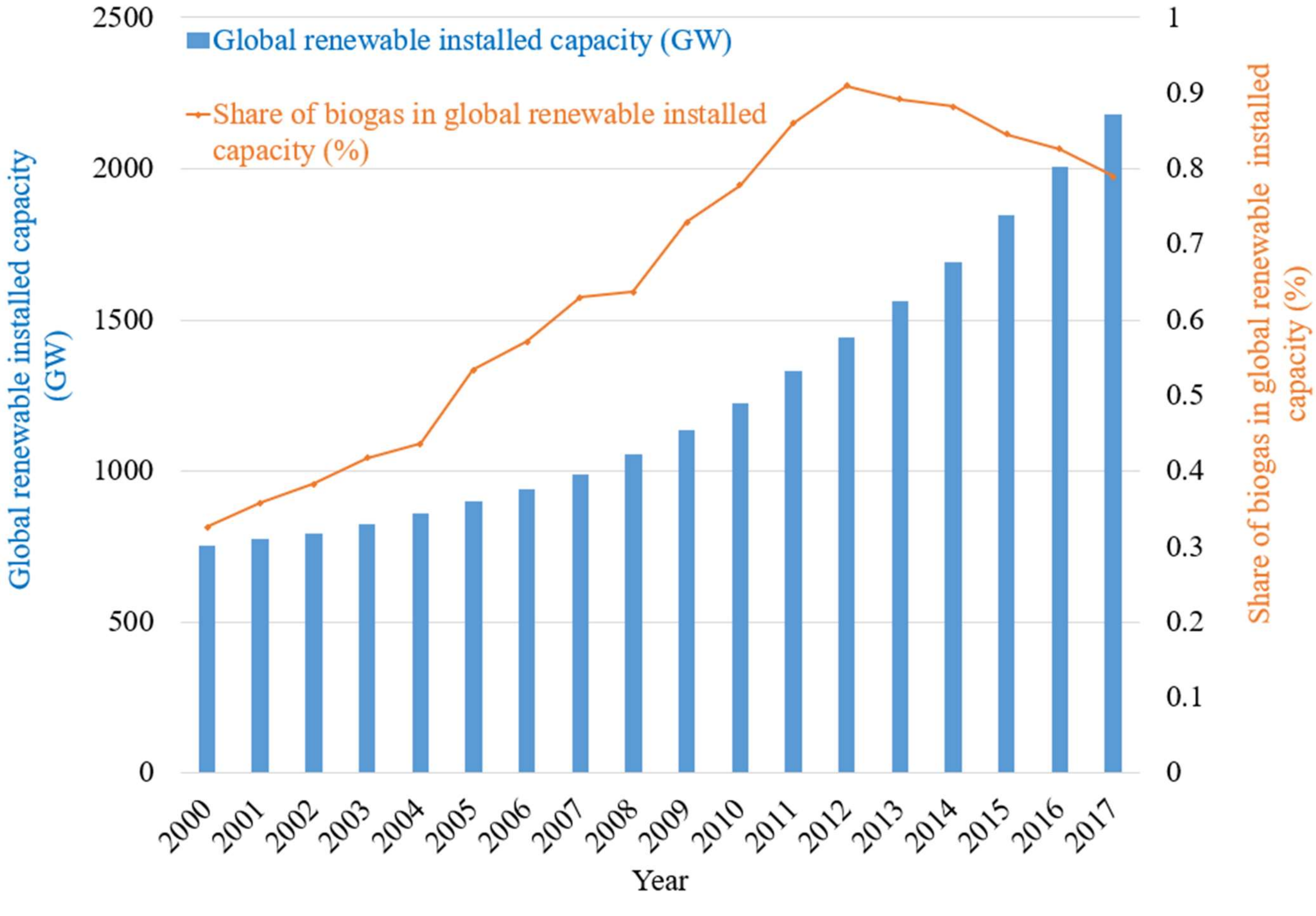
- Protection of the environment by replacing inorganic fertilizer, conservation of forest vegetation, reduction of air & water pollution, and so on [8, 9].
- Green energy production in form of heat, power, vehicle fuel, and trigeneration [10].
- Reduction of greenhouse gas emissions by substituting conventional fossil fuels [9].
- Disposal of organic matters including household wastes, industrial and municipal solid wastes, agricultural residues, etc. [10].
- Supply of base-load energy to the gas and electricity networks.

Full utilization of the sustainable biogas potential can supply nearly 20% of the worldwide natural gas demand. Currently, the sustainable biogas and biomethane potential is 570 and 730 million tonnes of oil equivalent (Mtoe), respectively [11].

Given the increased political prominence of hydrogen and policies and measures to promote it, the contribution of biomethane to energy security and a low emissions future energy mix could be projected. In the search for ‘renewable gas’ the question of the relative economics of biomethane versus renewable hydrogen becomes important. Biomethane has the advantage over hydrogen since natural gas grids and appliances will not require modification, because of the similarity of biomethane to natural gas. The necessary changes of the infrastructure would be rather low up to a H_2 share of around 10% (molar or volumetric concentration) [12]. The mole fractions of hydrogen in non-conventional gas in France is 6%, Austria 4%, Germany 5%, and The Netherlands 12% [13].

Actual biomethane production in 2018 was about 35 Mtoe. Based on the current policies, the biogas consumption in 2030 and 2040 will be around 95, and 150 Mtoe. The sustainable development scenarios are even more optimistic and project biogas consumption to reach nearly 190 and 325 Mtoe in 2030 and 2040, respectively. Currently, most of the biogas is used for onsite power and heat generation. But, as we move in time, the amount of biogas being upgraded to biomethane increases and biomethane production becomes the main biogas-processing pathway, leaving onsite power and heat application as the second.

Figure 1 (a) depicts the evolution of the global renewable installed capacity (bar chart) and the share of biogas (line chart) in the global renewable installed capacity between 2000 and 2017. The installed renewable capacity in 2010 was 754 GW and increased to 2182 GW in 2017. The share of biogas technology in the global renewable installed capacity increased from 0.32% to 0.90% during 2000–2012. Thanks to the fast developments in other renewable technologies such as wind and PV, despite growth in biogas installations, its share in the renewable technology mix showed a little decline reaching 0.79 in 2017. Figure 1 (b) represents the global electricity generation from renewables (bar chart) and the share of electricity generation from biogas (line chart) between 2000 and 2017 [14]. The global electricity generation from renewable resources increased from 2850 TWh in 2000 to 6191 TWh in 2017. This changed the global share of biogas in electricity generation from 0.46% to about 1.42% in this time period.



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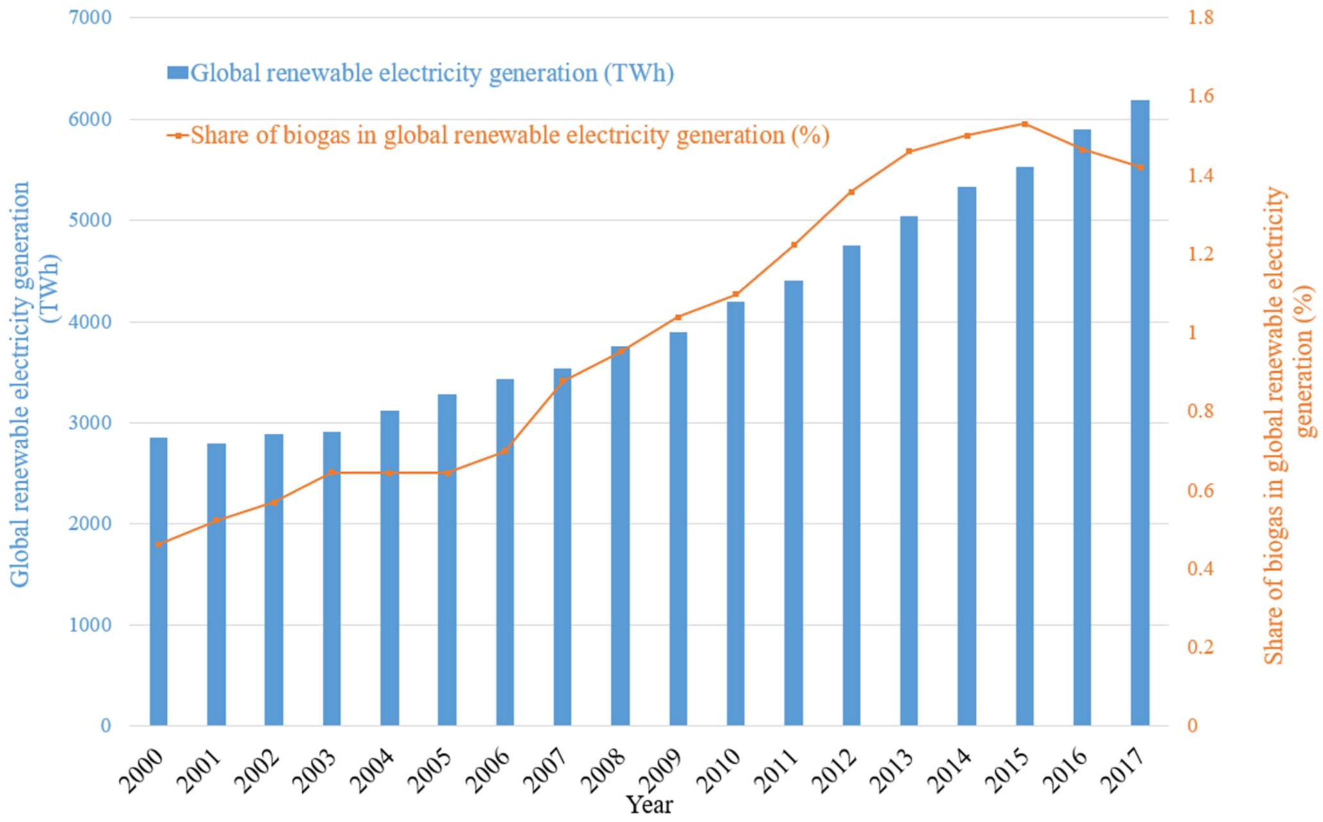


b)

Figure 1: a) Global renewable installed capacity (left axis) and share of biogas installed capacity (right axis) in the total renewable installed capacity during 2000–2017 (data source: [14]). b) Global electricity production from renewable resources (left axis) and share of biogas in renewable electricity generation (right axis) during 2000–2017 (data source: [14]).

Figure 2 shows the installed biogas capacity (MW_{el}) by country as of 2017. Germany with over 6 GW_{el} is on top, followed by the US, UK, Italy, Thailand, China, France, and Turkey.

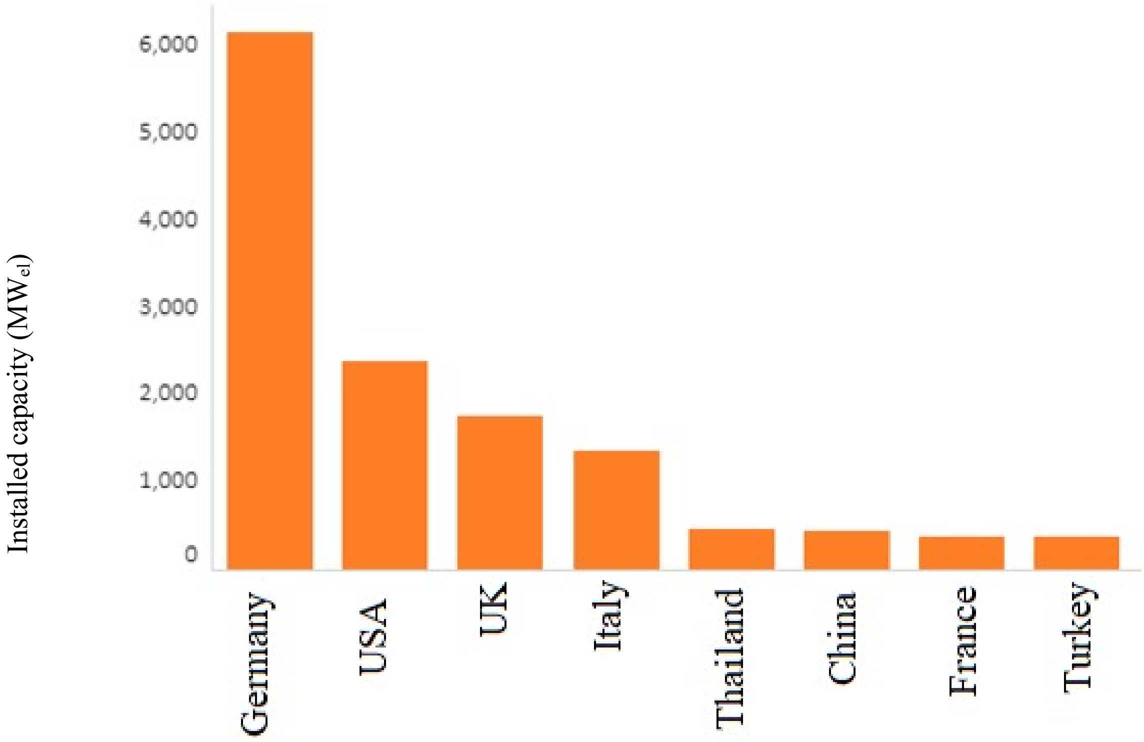


Figure 2: Installed biogas capacity by country as of 2017 (data source: [15])

As also evident from Figure 2, Europe is the world leader in terms of the installed biogas plant capacity and biogas-based power generation [16-18]. In 2017, the total number of biogas plants in Europe was 17783 [16]. At the same year, the number of biomethane plants in Europe was 540 of which 340 were feeding into grid [16]. The majority of the biomethane generation plants were in Germany (195 plants) followed by UK (92 plants) and Sweden (70 plants) [10]. The biogas production in Europe was 18.4 billion Nm^3 (N represents normal conditions i.e. T= 20 °C, P=1 atm) that represented a share of 4 % in natural gas use [16]. It has been anticipated that the biogas production will reach 20 billion Nm^3 by 2020 [19]. A review of biogas upgrading technologies in Europe and share of EU transport sector in 2030 can be found in Ref. [20]. Biogas upgrading technologies are based on pressure swing adsorption, water scrubbing and chemical scrubbing. Biogas upgrading to biomethane will reach 18 billion cubic meter per year in 2030 (about 9.5 times higher than that of 2017). This is equivalent to nearly 10% of the EU's projected natural gas import for 2030. Biomethane will contribute to about 3% of the natural gas consumption of EU countries in 2030 [21]. It is expected that the maritime and road transport customers will use a large share of the produced biomethane in the EU.

In summary, biogas is a sustainable energy vector with several benefits including 1) renewable source of energy, 2) lower discharge of methane to the air in comparison to LFs or traditional manure management, and 3) having a high-quality digestate by-product used as fertilizer [22].

Although the literature is rich on biogas upgrading technologies, there exists growing attention to the investment analysis and operational cost reduction of the upgrading routes. The current study reviews and evaluates the various aspects of biogas as an energy vector such as biogas production pathways, conventional and prospective upgrading technologies (including physical, chemical, and biological [23]) with their basics of operations, advantages/disadvantages, energy needs, methane recovery efficiency, market penetration, biogas markets/applications in addition to economics of various upgrading technologies. The cost of biogas upgrading depends on raw biogas capacity, the concentration of contaminants in the raw biogas, local circumstances, energy and water cost, envisaged lifetime of the investment, and so on. Furthermore, this paper covers the biogas composition for various feedstocks, standard requirements of upgraded biogas for the grid injection, biogas conversion to chemicals, upgraded biogas product specifications, the potential hazards of biogas contaminants during production or upgrading, and final use of the upgraded biogas and CO_2.

The rest of the paper proceeds as follows. Section 2 describes the biogas supply chain including biogas feedstock, biogas production, and the products/by-products (methane, CO_2, chemicals) obtained from biogas. Section 3 addresses the potential hazards of biogas contaminants, final product specification, biogas upgrading processes, in addition to physical/chemical/biological approached for biogas upgrading. Costs of biogas upgrading via various technologies are elaborated in Section 4, followed by conclusions in Section 5.

2. Biogas supply chain

The biogas supply chain is composed of feedstock supply, biogas processing, production and upgrading/purification, in addition to final markets/applications, biogas uses or products (e.g. biomethane injection to gas grid, biomethane conversion to chemicals, etc.). Biogas feedstocks (elaborated in Section 2.1) may be in solid or slurry forms in addition to concentrated and dilute liquid form. Some examples are agricultural residues, livestock manure, organic waste materials, and sewage sludge. The raw biogas must be cleaned and upgraded in various degrees to meet the consumers' gas composition standards (such as mole fractions of H_2, CO_2, O_2, and H_2S in the upgraded biogas). Thereby, the selection of cleaning and upgrading technologies (see Section 3.3 and 3.4) depends on the upgraded biogas demand, the levels of raw biogas contaminants, and project-specific circumstances.

A list of existing production and upgrading plants in Europe and around the world based on various features (such as the feedstock, final application of biogas, upgrading technology, the methane content of the upgraded gas, plant capacity and date of plant commencement) is available in Refs. [24, 25]. In addition, a list of providers of upgrading technologies is available in Ref. [25]. This list includes the manufacturers of PSA units, water/chemical scrubbers, organic physical scrubbing units, membrane modules, cryogenic units, and small-scale biogas upgrading installations. Ref. [25] also gives the number of upgrading units by types in several European countries.

2.1. Biogas feedstock

The content of fats, proteins, and carbohydrates in the substrates has an obvious direct impact on the biogas production system and the subsequent upgrading sequence. Table 1 lists the methane and biogas yield obtained from various feedstocks. It shows that depending on feedstock type, methane yield can vary between 51% and 65%. The range of produced biogas volume is even much wider spanning from 25 to 202 m^3 per tonne of fresh feedstock.

Table 1: Methane and biogas yields of various feedstock materials [26-30]

Feedstock	Methane yield [Vol %]	Biogas yield [Nm^3/tFF] (FF: fresh feedstock)
Distillers grains with solubles	61	40
Grass silage	54	172
Pig manure	60	60
Sweet sorghum	54	108
Cattle manure	60	45
Corn silage	52	202
Liquid pig manure	65	28
Forage beet	51	111
Organic waste	61	100
Beet	53	88
Liquid cattle manure	60	25
Poultry manure	60	80
Whey	15	330
Cattle slurry	12.8	200
Flotation sludge	21.6	540

Subsequently, the actual greenhouse gas (GHG) emissions reduction depends on the substrate source used. Table 2 lists the GHG emissions reduction of some feedstock with maize being the lowest (75%) and manure being the highest (148%).

Table 2: The reduction of GHG emissions of biogas source compared to fossil fuels [31]

Feedstock	GHG reduction vs. fossil fuels [%]
Maize	75
Sugar beet (incl. tops)	85
Grass	86
Organic household waste	103
Waste from the food industry	119
Manure	148

In 2014, the total biomass supply was 59.2 Etta Joule (EJ), i.e. 10.3% of the global energy supply, with annual growth of 2.3% [32]. The key sector for biomass development is the forestry sector with 87% of the supply (fuelwood 67% of the biomass feedstock, followed by charcoal 7%, recovered wood 6%, and wood industry residues 5%). The second sector is the agriculture sector (animal/agricultural by-products and energy crops) with share of 10% to biomass supply. The third one contributes to 3% by generating energy from MSW and landfill gas. In 2015 and in terms of total biogas plants per feedstock in the EU, about 71% of biogas was produced from agriculture sources, followed by 16% from sewage, 9% from LFs and the rest from other sources [19]. Europe has more than 50% of the global agricultural area, and nearly 55% of the global waste to energy conversion [32]. The biomass supply source varies among the continents and for biogas as a renewable energy source, Europe is an evident leader [32].

2.2. Biogas production

Biogas is produced from different routes and environments. Its composition is a function of several factors such as the nature of the substrate used to produce biogas, and the process design [33]. The various routes of biogas production are:

- Anaerobic digestion (AD) is known as the biological conversion process in an oxygen-free environment and is carried out in four steps including hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Figure 3), [34, 35]. Various types of waste materials such as food waste, agricultural and industrial wastes, MSW, wastewater, and crops can be used as feedstock for the AD process [29, 36].

- Anaerobic degradation in LFs (natural decomposition of waste). An LF site is a location dedicated for dumping garbage, rubbish or other sorts of solid wastes. With the growing waste production from homes, offices, hospitals, schools, and markets, landfilling has been the most common disposal approach. LFs are either left to pile in heaps or buried. While LFs are the most cost-efficient method of disposing waste materials, they are associated with environmental risks. Soil, water, and predominantly air are dirtied by the deposition of waste materials in the LFs [37]. In addition, decomposition of organic materials in the oxygen-free environment is slow which in long-term has negative effects on the next generations. There are five distinct types of landfilling including LF as a deposit of inert waste, aerobic, semi-aerobic, hybrid, and anaerobic [38]. To produce biogas from LFs, complex biochemical conversion processes including different phases should be designed.
- Novel AD technologies including high rate anaerobic reactors (HRAR), membrane bioreactors (MBR), and integrated HRAR- MBR, [39].

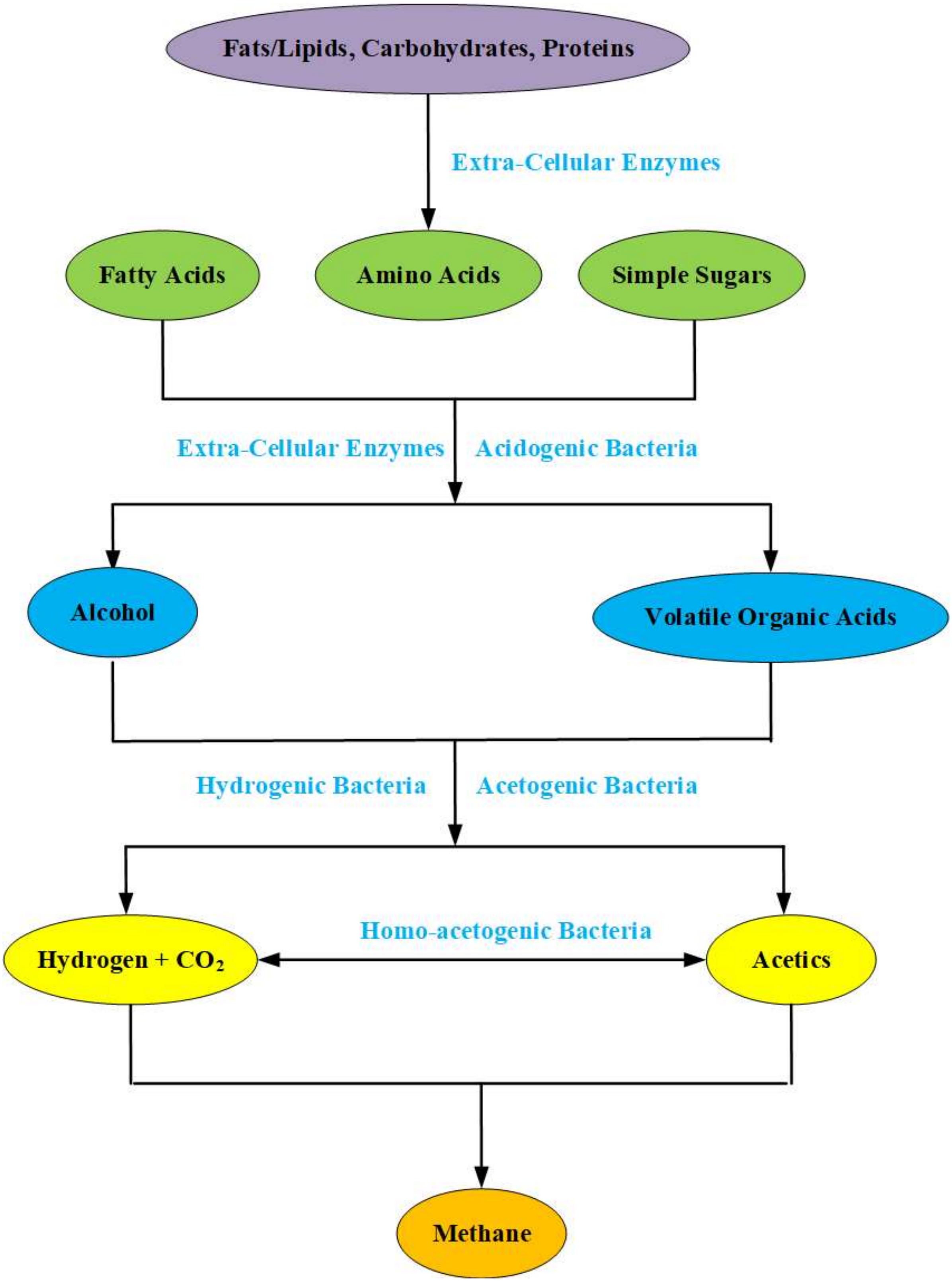


Figure 3: Anaerobic digestion process model [28, 40, 41].

Depending on the source, biogas can contain contaminants including sulphur compounds (H_2S, sulphides, disulphides and thiols), halogenated compounds, nitrogen and organic silicon species.

The biogas obtained from a conventional LF is a complex mixture of compounds [42]. A typical composition of LF gas may contain: methane (35–65%), CO_2 (15–50%), N_2 (5–40%) that seeps into the LF gas during recovery, O_2 (0–5%), H_2 (0–3%), H_2O (0–5%), CO (0–3%), H_2S (0–100 ppm), NH_3 (0–5 ppm), halocarbons (20–200 ppm), volatile organic compounds, VOC (0–4500 mg/m^3), and siloxanes (0–50 mg/m^3). A simpler biogas may be obtained from the degradation of livestock manure in an oxygen-free environment, sewage sludge or agro-industrial wastes which encompasses methane (53–70 %), carbon dioxide (30–47 %), N_2 (0–3 %), O_2 (0–1 %), H_2O (5–10 %), H_2S (0–10 ppm), NH_3 (0–100 ppm), hydrocarbons (0–200 mg/m^3), and siloxanes (0–41 mg/m^3). CO_2, H_2O and N_2 are the main contaminants of biogas. In Ref. [43], the chloride amount in LF gases was reported to be 118–735 and total fluorine amounted 63–256 mg/m^3.

Table 3 represents the biogas properties obtained from digesters and LFs. For the purpose of comparison, the last three rows in Table 3 provide the market natural gas composition in three markets including Denmark, The Netherlands, and the North Sea. The biogas produced in closed digesters shows higher methane content and considerably lower N_2 and O_2 levels than an LF-derived biogas [44].

Table 3: Typical composition of biogas from AD, LF gas and natural gas [45]

Biogas	CH_4 (%)	CO_2 (%)	O_2 (%)	N_2 (%)	H_2 (%)	H_2S (ppm)	Heavy hydrocarbons (%)	Ammonia (ppm)	Other (mg/Nm^3)	Physical properties				Ref.
										Density (kg/m^3)	LHV (MJ/NM$_3$)	Wobbe index (MJ/Nm^3)	Methane number	
LF	35–65 (45)	15–40 (40)	0–5 (1)	5–40 (15)	0–3	0–100 (<100)	0	5	Total chlorine: 20–200	1.3	16	18	>130	[31]
LF	30–60 (45)	15–40 (40)	0–10 (1)	0–50 (15)	0–2 (1.5)	0–1000 (<100) mg/m3		0–5 (5) mg/m3	BTX: 0–500 Total chlorine: 0–800 Total fluorine: 0–800 (10) Siloxanes:0–50	0.8	21	27	144	[13]
LF	47–57	37–43	< 1	< 1–17		36–230			Halogenated compounds: 0.3–1.3 Organic silicon compounds: 0.7–4 Benzene: 0.6–2.3 Toluene: 1.7–5.1					[46]
AD	60–70 (65)	30–40 (35)	0	– (0.2)	0	0–4000 (<500)	0	100	Total chlorine :0–5	1.1	23	27	>135	[31]
AD	50–80 (65)	15–50 (35)	0–1	0–5 (0.2)	0–2	100–10000 (<600) mg/m^3		0–100 (100) mg/m^3	BTX: 0–20 Total chlorine:0–100 Total fluorine: 0–100 (0.5) Siloxanes: 0–50	0.8	22	26	135	[13]
AD	53–70 (63)	30–47 (47)	0	0.2	0	0–1000 (<1000)	0	<100	0–5	1.2	23	27	>135	[44]

AD	55–58	37–38	< 1	< 1–2		32–169			Organic silicon compounds: < 0.4 Benzene: 0.7–1.3 Toluene: 0.2–0.7					[46]
Danish Natural gas	85–92 (90)	0.2–1.5 (0.7)	-	0.3–1 (0.3)	-	1.1–5.9 (3.1)	9	-	-	0.82	39	55	73	[31]
Dutch Natural gas	81	1		14			3.5			0.8	32	44	-	[24, 44]
North Sea natural gas	86.6 – 88.8 (88.8)	1.9 – 2.3 (2.3)	<0.01	0.9 – 1.1 (1.1)		0 – 5 (1.5) mg/m^3	8.3 – 8.5 (8.3)		BTX:0 – 1750	0.7	35	50	76	[13]

2.3. Biogas end-use market

Methane and CO_2 are the major constituents of biogas. In this section, we discuss the various uses of methane and CO_2.

2.3.1. Methane

The typical applications of low/medium/high quality gas obtained from cleaning/upgrading of biogas are represented in Figure 4. Upgraded biogas can be utilized to produce:

- **Heat:** The high quality biogas (biomethane) can be combusted in boilers/stoves. The generated heat can be used for space heating, process heating, and so on. Biogas can also be used in boilers without the need to upgrade it [47]. Chemical absorption upgrading technology is the most suitable way to produce high quality biomethane for domestic stoves [47]. If the purity of the biogas is not of importance, other upgrading technologies can be employed.
- **Heat/Power:** Otto, diesel engines, and gas turbines can be fueled by biogas. About 30–40% of the biogas energy is converted to power while the remaining energy can be extracted as heat. With the exception of the Otto engines, biogas can used in dual-fuel engines. In a dual-fuel engine, biogas and diesel are used to maintain the efficiency of the diesel engine as high as possible. Among the continents, Europe is the main producer of bioelectricity and heat from biogas [32].
- **Fuel for vehicles**: upgraded biogas can fuel light- or heavy-duty vehicles such as cars, buses and trucks. The odorized and pressurized biogas (to nearly 200 bar) is used as fuel in vehicles. A higher H_2 content in biogas is allowed to be used to fuel vehicles. The use of biogas as a vehicle fuel is considered as the best way to reduce fossil fuel consumption [31].

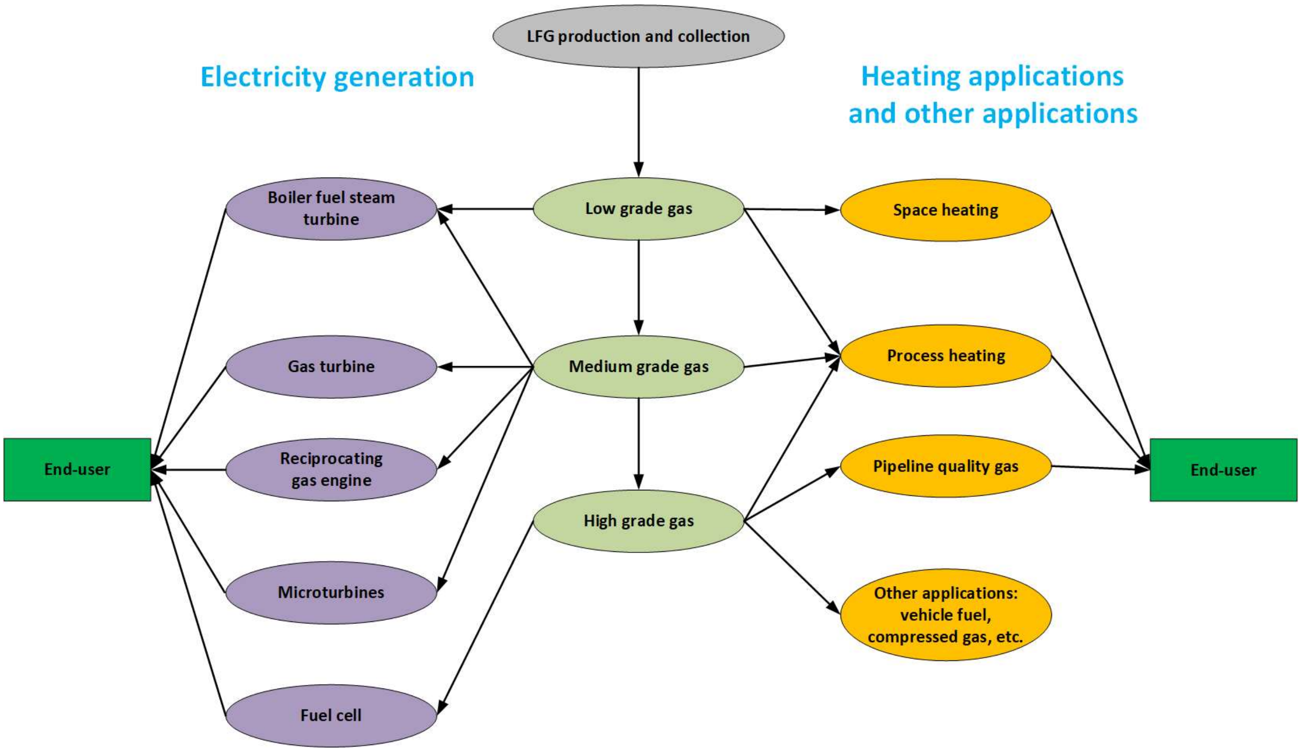


Figure 4: LF gas utilization pathways

- **Injection to gas pipelines**: To inject biogas to the gas transmission networks, it must meet the related standards and requirements listed in Table 4. The injection of a high-quality upgraded biogas (biomethane) to gas grids is the optimal solution to distribute biomethane in the countries with an extensive natural gas network [48]. Injecting biomethane into national gas networks creates new markets and applications. Biomethane and natural gas can be mixed liberally and are wholly interchangeable. Virtual 'green gas' distribution networks are simply implementable to produce green electricity and heat.

Table 4: Standard requirements of upgraded biogas for injecting to gird or fueling vehicles of several countries [13, 24, 31, 34, 49]

Market specifications	**France**		**Germany**		**Sweden***		**Switzerland**		**Austria**	**The Netherlands**
	L Gas	H Gas	L Gas Grid	H Gas Grid	Biogas type A	Biogas type B	Lim. Injection	Unlim. Injection		
CH_4 (%)					97±1	97±2	>50	>96		>80
CO_2 (%)	<2	<2	<6	<6			<6	<6	<2	
O_2 (%)	<0.01	<0.01	<3	♡	<1	<1	<0.5	<0.5	<0.5	<0.5
H_2 (%)	<6	<6	<5	<5			<5	<5	<4	<12
CO_2+O_2+N_2 (%)					<4	<5				
Sulphur (mg/Nm^3)	<100	<100	<30	<30	<23	<23	<30	<30	<5	<45
Water (%)					32 (mg/m^3)	32 (mg/m^3)				
NH_3 (mg/m^3)					20	20				
Water dew point (°C)	<-5	<-5	< ground temp	<ground temp	T*-5	T*-5			<-8 (@40 bars)	-10 (@10 bars)
Wobbe index (MJ/Nm^3)	42.48–46.8	48.24–56.52	37.8–46.8	46.1–56.5	44.7–46.4	43.9–47.3			47.7–56.5	43.46–44.41

*** Biogas type A is used in ´lean-burn´ engines i.e. heavy vehicles such as trucks and buses while type B is used in stoichiometric combustion engines of private cars. ** T = lowest average daily temperature on a monthly basis**

2.3.2. CO_2

CO_2 is one of the key species of the Earth's texture and can be found in its core, crust, as well as in the atmosphere. The increased CO_2 emissions are the main rationale for anthropogenic climate change. CO_2 capture and storage (CCS) has received much attention over the last two decades as one of the main climate change mitigation options. The total CO_2 emitted to the air is nearly 32.2 giga tonnes/annum and the major CO_2 emitter sectors are power/heat production (42.4%), transportation (23%), manufacturing industries and construction (19%), residential (5.8%), services (2.7%), and others (7.1%) [50, 51]. The current global CO_2 utilization amounts up to about 200 million tonnes/annum. Implementing the carbon tax policies make the CO_2 capture inevitable and the CO_2 would be available at a low or even negative price. This may interrupt the current trend of CO_2 valorization and consequently increase the CO_2 utilization in the current and/or new industries. CO_2 can be transported via pipelines from CO_2 sources to the CO_2 demanding industries (CO_2 sinks). The concentration of CO_2 to be transported via pipeline must be above 95% [47]. CO_2 utilization pathways can be divided into chemical and physical. Physical CO_2 utilization routes include use of it in carbonated drinks, fire extinguisher, dry ice, refrigerant, solvent, welding medium, process fluid, algae farms for photosynthesis, enhanced oil/gas recovery, etc. CO_2 can be chemically utilized in the following processes: synthesis gas production, methanol production, di-methyl ether (DME) production, urea synthesis, di-methyl carbonate (DMC) production [52], polyurethane production [53], Fischer-Tropsch gas-to-liquid (FT-GTL) products [54, 55], synthetic methane production [56], chemical looping dry reforming [57], mineralization [58], and so on. A literature review of physical and chemical utilization pathways can be found in Ref. [50]. The CO_2 from the biogas upgrading processes can be used in the CO_2 demanding industries such as for chemicals production [54, 55, 59-66]. CO_2 utilization for production of synthetic methane, methanol, and Fischer-Tropsch derived liquids were addressed by Abdin et al. [59]. Assen and co-workers

[63] studied the direct and indirect utilization of CO_2 in the polyurethane supply chain. The CO_2 utilization for polyols (direct route) is 0.30 kg CO_2 /kg polyurethane while for indirect route is 1.7 kg CO_2 / kg polyurethane. Conversion of CO_2 to synthesis gas (syngas) via catalytic partial oxidation of methane was considered by Chen [64]. The maximum syngas production was reported at CO_2/O_2 ratio of 0.2 when the oxygen to carbon ratio is one. In addition, 10–41% of CO_2 can be consumed for syngas production in the catalytic partial oxidation of methane. Uner et al. reviewed photocatalytic water splitting and CO_2 reduction to produce methane and methanol [65]. Conversion of CO_2 to FT-derived liquid fuels was addressed in Refs. [54, 55, 60]. CO_2 was fed to the reforming section of the GTL process. CO_2 conversion to methanol was investigated in Ref. [66] where the CO_2 stream came from a power-plant CO_2 capture process. Methanol production through CO_2 hydrogenation was studied in Refs. [67, 68]. The methanol production rate of the process with an inlet H_2/CO_2 ratio of 3 is nearly 59 % higher than the process with an inlet H_2/CO_2 ratio of 2 [67]. The profit index of a two-stage reactor system is 2.05% higher than the process with one reactor [68].

2.3.3. Biogas conversion to chemicals

In addition to the separation of CO_2 content of biogas to increase its methane content, there exists another approach to valorize the biogas CO_2 content to commodity fuels and chemicals such as methane [69, 70], methanol, hydrogen [70, 71], etc. In the biogas to methane process, the biogas stream is mixed with additional hydrogen coming from a solid oxide electrolysis cell (SOEC) and then is conveyed to a methanation reactor [69]. Boiling water is used in the methanation reactor as the reactor-cooling medium. Operation of a full-scale methanation reactor under favorable conditions for 1000 hours is possible. To obtain pipeline quality gas, the optimal H_2 to CO_2 ratio to the methanation reactor must be 3.9.

Tamnitra and co-workers [72] simulated methanol production from biogas. In their simulation, biogas is preheated, mixed with steam, and then is conveyed to a reformer. The reformer outflow is sent to a separator and an absorption unit to remove water. The dried syngas is then fed into a methanol reactor. Methanol production via biological conversion of biogas using methane-oxidizing bacteria (methanotrophs) is investigated in Ref. [73].

Hydrogen can be produced via biogas dry reforming. In Ref. [71], the preparation of the catalyst, the optimization of process conditions, types of reactors, and the impact of biogas contaminants were reviewed. A proprietary skid-mounted, small-scale DME production unit that converts biogas (with up to 50% CO_2 content) was developed by Oberon Fuels [74]. The production capacity of the unit is 10,000 gallons/day. Yang et al. [70] reviewed conversion of biogas to hydrogen/syngas, methanol for gasoline production, ethanol and higher alcohols. For biogas conversion to hydrogen/syngas, reforming technologies such as dry reforming, steam reforming, and partial oxidative reforming were discussed. Partial oxidation of methane, photo-catalytic conversion, biological conversion and indirect conversion were addressed for methanol production. For ethanol and higher alcohols production, direct approaches and indirect routes (such as syngas fermentation and catalytic conversion) were elaborated. A novel approach for simultaneous biogas upgrading and co-production of succinic acid and biomethane was addressed by Gunnarsson et al. [75]. Bacterial strain actinobacillus succinogenes 130Z was used to produce high-purity methane.

3. Biogas upgrading

Biogas upgrading is necessary because of two constraints: 1) product safety due to potential hazards caused by contaminants (see Section 3.1 3.2), and 2) product quality enforced by market specifications (see Section 3.13.2).

3.1.Potential hazards of biogas contaminants

Certain actions must be taken to minimize the emissions from AD biogas plants [76]. These actions include the use of flares to avoid methane emissions, enhancing the thermal and electrical efficiency of CHP units, and to avoid leakage to the air [77, 78].

CO_2 release to the air takes place during combustion of biogas, transport and storage of biomass, in addition to digestate use. Poeschl et al. [79] studied the CO_2 release to the environment during the production of biogas from supply system of several feedstocks, biogas plant infrastructure, in addition to digestate management. Biogas production from waste materials (such as pomace, cattle manure, food residues, and slaughter waste) is more sustainable than utilization of energy crops. In addition, management of digestate materials results in higher total emission mitigation when an MSW feedstock is used.

Methane emissions from biogas processes do not have any health issue and there is no evidence of health issue between biological systems and methane [80, 81]. The main release points of methane in the biogas supply chain are biomass storage, incomplete combustion of biogas, and digestate management.

Nitrous oxide emissions from biogas results in a considerable impact on global warming [82].

Biogas production and handling is associated with some safety concerns that should be considered during the biogas production process. The following hazards shall be kept to a minimum level [7, 13]:

- **The health of end-users and employees:** direct toxicity with unburned gas and, indirect toxicity by biogas combustion, chemical products, water and air pollution.
- **Operation of gas facilities and appliances, and gas grids integrity:** some hazards include corrosion and clogging of the grid equipment, clogging as well as the failure of end-user appliances, etc.

In some situations, the treatment processes may suffice to decrease the hazards to acceptable levels. In other occasions, specific treatments of the raw gas may be required. Table 5 indicates the potential hazards of biogas contaminants during the biogas production process, gas treatment equipment, and so on. Water in combination with O_2 or CO_2 can introduce system integrity problems. In addition, H_2S in combination with water and O_2 produces H_2SO_4, that cause corrosion of gas storage tanks, gas pipelines, engines and compressors. The existence of NH_3 and halocarbons corrodes pipelines and engines when biogas is combusted [24].

Table 5: Potential hazards of biogas contaminants and recommended countermeasures [7, 13, 29, 83]

Hazardous Component/agent	**Hazard**	**Countermeasure**
Halocarbons	• Corrosive gases: affect the integrity of the system. • Production of furans and dioxins under combustion conditions: health issues. • Toxic and corrosive combustion species: influence on end-user equipment and health issues.	• Sampling and analysis of halocarbons. • Removal of halocarbons. • Exclusion of materials with high halocarbon content.
High content of CO_2	• Change of combustion properties, which affects the performance and safety of final-user equipment.	• Adding heavier hydrocarbons. • Mixing biogas with natural gas. • Maintaining CO_2 concentration within tolerable limits.
Ammonia	• Corrosive gas: impact on the integrity of the gas network. • Toxic compound: health issues. • Increased NOx emissions after combustion.	• Sampling and analyzing for ammonia. • Removing ammonia from the gas.
Biological agents	• Bio corrosion: affects the integrity of the system. • Health hazard in case of presence of pathogenic agents	• Sterilization of the substrate material. • Filtration. • Increase digester retention time.
Polyaromatic hydrocarbons (PAHs)	• Effect on elastomer and plastic material: system integrity issues. • Carcinogen and toxic: health issues. • Soot formation when PAHs are burnt. • Impact on safety and performance of end-user equipment	• Monitoring and removal.
Siloxanes	Production of silica at combustion conditions which affects the user equipment.	• Sampling and analyzing. • Elimination of materials with high silicon content. • Removing siloxanes from the biomass material or the biogas.
Phosphine (PH_3) and phosgene ($COCl_2$)	• Toxic compounds: health issues. • Corrosive species: Affect the integrity of the system.	• Sampling and analysis. • Removal of phosphine/ phosgene from the biogas. • Exclusion of sources with high phosphine/ phosgene content.

Biogas combustion releases pollutants to the air. For example, CO is the key by-product of biogas incomplete combustion. Sulphur dioxide pollutants depend mainly on the efficiency of desulphurization section of the biogas upgrading plant. NO_x emissions, non-methane volatile organic compounds, and formaldehydes are other key pollutants of the biogas combustion process. The emission factors of the mentioned pollutants are given in Refs. [84, 85].

The storage, management, and treatment of feedstock and digestate materials are the most important steps from the global warming point of view in biogas production processes [76]. Most of nitrous oxide emissions can be avoided when we use closed storage for manure in addition to co-digestion feeding strategy. Outspreading untreated biomass materials on the ground will release large quantities of methane, ammonia, nitrous oxide, volatile hydrocarbons, etc. to the air.

3.2. Requirements for upgraded biogas product specification

Table 6 summarizes the requirements used for biomethane utilization pathways and the associated optional upgrading technologies.

Table 6: Gas quality and technological recommendations regarding biogas utilization [34, 47]

Utilization pathway	CH_4 content (%)	CO_2 content (%)	Contaminants	Cleaning and upgrading technology
Domestic stoves	Heating value comparable to natural gas	-	H_2S < 10ppm	H_2S: iron hydroxide/oxide. CO_2: chemical absorption.
Boiler	-	-	H_2S < 250 ppm	H_2S: biological desulphurization.
Internal combustion engine	>30	-	H_2S: 545–1742 ppm. Halides: 60–491 ppm. Siloxanes: 9–44 ppm. Dew point: T^*-6.7 °C.	H_2S: biological desulphurization.
Stirling engine	>35	-	H_2S < 2800 ppm. Siloxanes: about 0.42 ppm. Halides: 232 ppm. Dew point: T-6.7 °C.	H_2S: biological desulphurization.
Gas turbine/micro turbine	>35	-	H_2S: 10,000 ppm. Siloxanes: around 0.087 ppm (0.005 for micro-turbine). Dew point: T-6.7 °C.	H_2S: biological desulphurization.
Natural gas grid injection	70–98	1.0–8	H_2S: 2–15mg/m^3; N_2: 2–10%. H_2: 0.1–4%. O_2: 0.01–3%.	H_2S: impregnated activated carbon and iron hydroxide/oxide. CO_2: PSA + membrane. When O_2 and N_2 removal is required. Chemical absorption +PSA if high methane purity is needed.
Vehicle fuel	>96	<3	H_2S: 5mg/m^3.	H_2S: impregnated activated carbon along with iron hydroxide/oxide. CO_2: chemical absorption /cryogenic separation.
Fuel cell	SOFC: as much as possible.	SOFC: as little as possible. MCFC: <35	H_2S: 1–5 ppm (MCFC) and 1ppm (SOFC). Siloxanes: few ppm.	H_2S: impregnated activated carbon together with

	MCFC: no specification.		iron hydroxide/oxide.

[*] T: gas temperature, MCFC: molten-carbonate fuel cell, SOFC: solid oxide fuel cell

Gas grids have also certain specifications for the protection of both pipeline assets and end-users. To guarantee the safety, operability and integrity of gas grids, conventional and nonconventional gases should meet the least quality requirements. Each country may have its own standards and requirements for the biomethane grid injection, and vehicle use (see Table 4). Table 7 demonstrates the parameters that are constrained in the US legislation or within the EU directives for cross-border gas transmission.

Table 7: Quality parameters in the proposed harmonized EU H-gas cross-border gas transmission grids [13, 86]

Parameter	**Value**
Wobbe index	13.6 –15.81 KWh/m^3 (25 °C/0 °C)
Relative density	0.555–0.7
Total Sulphur	< 30 mg /m^3
(H_2S + COS)	< 5 mg /m^3
Mercaptans	< 6 mg /m^3
Oxygen	< 10 ppm
Carbon dioxide	< 2.5 % molar
Water dewpoint	< –8°C at 70 bara
Hydrocarbon dewpoint	< –2°C over 1 – 70 bara

Apart from methane and CO_2, biogas may encompass water, H_2S, O_2, N_2, siloxanes, NH_3, and particles. The energy content of biogas is proportional to its methane content, thereby cleaning and upgrading of the biogas (i.e. removing contaminants) rise the calorific value of the gas. In the upgrading methods that CO_2 is separated from the raw biogas, some of the other contaminants are also removed. However, mechanical wear and corrosion of the upgrading equipment is avoided if the biogas is cleaned before the upgrading process for CO_2 removal. The hydrogen sulphide and halogenated compounds present in biogas can cause corrosion to engines. In the presence of water, sulphur compounds corrode gas storage tanks, compressors, and engines. Engine manufacturers may set minimum limits on methane content (energy density) of the fuel to ensure engine performance. Biogas containing organochloride contribute to corrosion in combustion engines or vehicles while under certain combustion conditions, the formation of furans and dioxins is also possible [43].

Depending on the specifications of end-users, the required composition and consequently the type of upgrading technology to be applied is determined. It is also of great importance to minimize methane release from the upgrading process to the air, water leakage from a water scrubber, and any other stream exiting the plant. For instance, in the absorber, some of the methane can be absorbed into the liquid and then be released into the air with the gas stream. The absorption liquid used in the process needs to be treated with other wastewaters.

The techniques used to clean, and upgrade biogas are described below. These technologies are available in standardized and pre-fabricated modules [87].

3.3. Biogas upgrading processes

The market of emerging as well as conventional technologies for biogas upgrading is currently changing because of the stringent composition specifications [88]. Biogas upgrading adds investment and operating costs to the overall process. As such, it is essential to choose the most suitable biogas upgrading method, and to optimize the process with regard to minimum energy consumption and maximum methane concentration of the upgraded gas. Physical or chemical upgrading methods need high energy requirements and/or chemicals. As a result, the development of alternative biogas upgrading technologies (e.g. biological methods, microbial electrochemical) with lower operating costs as well as environmental impacts has been triggered [44]. The upgrading costs of the established methods depend on the selected technology, and most prominently on the size of the plant [24]. There are commercial plants for raw gas capacities below ca. 250 Nm^3/h, and plants larger than about 2000 Nm^3/h are under construction.

New technologies such as cryogenic upgrading [24], in-situ methane enrichment in AD [89, 90] and ecological lung [24] are also being developed. Note that the stage of development of the upgrading routes might be quite different.

The required contaminants concentration of the raw biogas conveyed to upgrading technologies are listed in Table 8 [91]. A detailed process description of the upgrading technologies can be found in Refs. [92-94]. A comparison of different upgrading techniques including PSA, water scrubber, and amine scrubber for different raw gas capacities can be found in Ref. [24].

In Europe and in 2015, water scrubbing method accounted for 34% of the upgrading market, followed by chemical absorption, and pressure swing adsorption (PSA) with 25, and 20%, respectively (see Figure 5) [19]. Other mature technologies such as membrane separation, and physical absorption represent 13, and 8 % of the market share, respectively [19].

Table 8: The required contaminants concentrations in the raw biogas in the various upgrading methods.

Upgrading technology	**H_2S**	**VOC**	**$O_2/N_2/H_2$**	**NH_3**
Chemical scrubbing	Moderate concentrations. Main part goes to CO_2 stream. Polish filter may be needed in upgraded gas.	Moderate concentrations. Main part removed with the CO_2 and condensate streams.	Go to the upgraded gas.	Moderate concentrations. Main part goes to the CO_2 stream.
Water scrubbing	Moderate concentrations. Main part goes to the stripper air.	Moderate concentrations. Main part removed with the condensate and stripper air.	Go to the upgraded gas.	Moderate concentrations. Main part removed with process water.
PSA	Low concentrations	Removal from raw gas is required.	O_2/N_2 go to CO_2 stream, H_2 goes to product gas	Removal from raw gas is required.
Organic physical scrubbing	Moderate concentrations. main part goes to the stripper air.	Moderate concentrations. main part goes to the stripper air.	Go to the upgraded gas.	Moderate concentrations. main part goes to the stripper air.
Membrane separation	Low concentrations. some amount goes to the product gas.	Removal from raw gas is required.	Go to the CO_2 and upgraded gas stream.	Usually removed with condensate during drying the raw biogas.
Cryogenic separation	Moderate concentrations. Removed during first stage refrigeration.	Moderate to high concentrations. Removed during first stage refrigeration.	Go to the upgraded gas.	Moderate to high concentrations. Removed during first stage refrigeration.

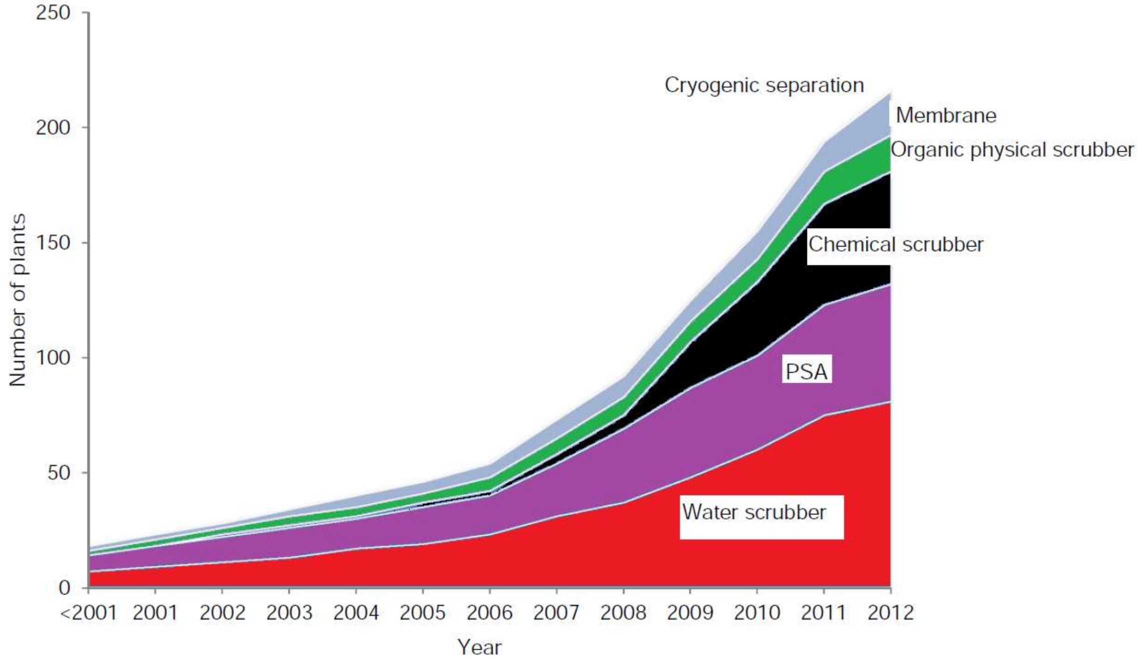


Figure 5: Evolution of the operational biogas upgrading plants in Europe during 2001–2012.

3.3.1. Water scrubbing

CO_2 removal via water scrubbers is a traditional approach in chemical engineering. This process is based on the reality that the water solubility of CO_2 is approximately 26 times (at 25 °C) higher than that of CH_4, [42]. The availability of cheap water supply is a determinative element in the selection of this technology. The CO_2 removal from the biogas produced in wastewater treatment plants can be performed in single-pass water scrubbers operating at 6–10 bar. However, LF biogas can be treated in a sequential water scrubber with tap water coupled to a two-stage desorption column in order to regenerate water. The absorption column is filled with Pall or Raschig rings random packing and counter-current flow of water and gas minimizes the energy consumption and the methane loss [95]. Water flowrate depends on operational pressure. In the desorption column, CO_2 is removed from water by addition of atmospheric air. The regenerated absorbent is then returned to the absorption unit (Figure 6).

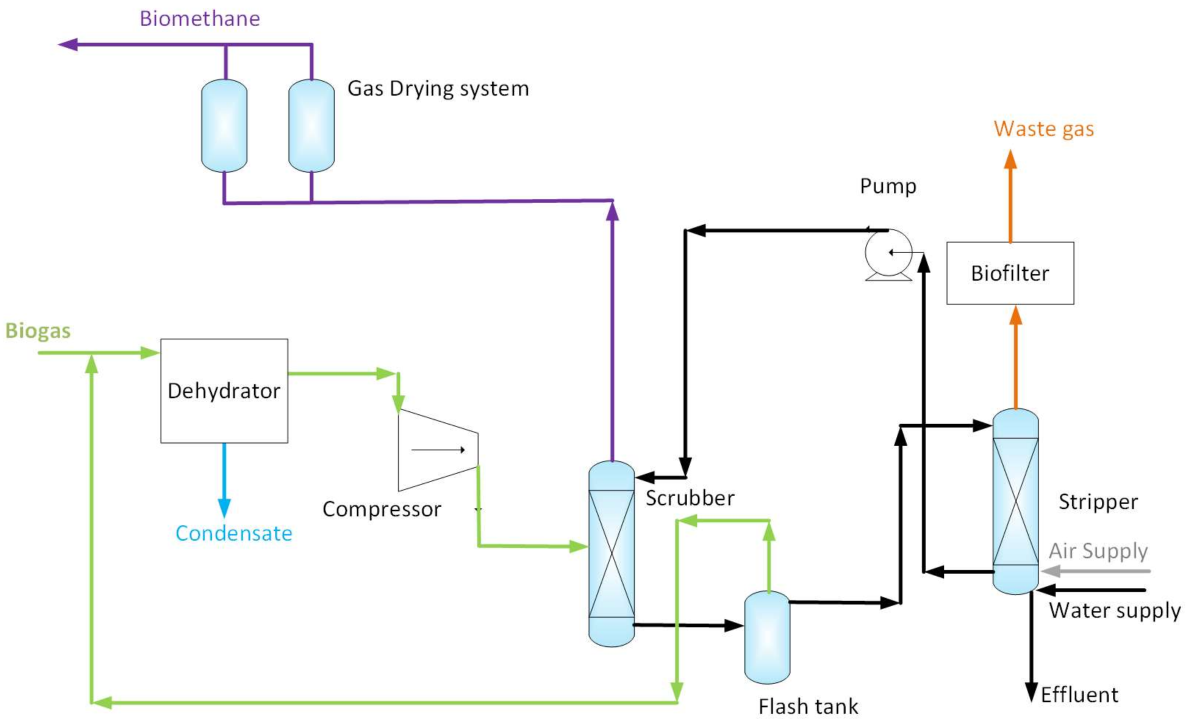


Figure 6: Schematic of biogas upgrading using water scrubber

A typical flow of about 0.1–0.2 m^3 water per Nm^3 of raw biogas is reported for single-pass water scrubbers. The water consumption of process designs with water recycling lies within the range of 0.18–0.23 m^3/Nm^3 of biogas. Higher operating pressures result in lower water flowrates but increases compression, and pumping costs. Off-gas treatment processes such as biofilters, incinerators, or activated carbon filters used to minimize H_2S, and CH_4 emissions from the desorption column entail additional costs to the process.

3.3.2. Organic solvent scrubbing

This upgrading technology is very similar to water scrubbers, except that the use of solvent increases the CO_2 solubility and thus capture. The organic solvent-based scrubbing needs a gas pre-treatment unit (to separate water) and several inter-cooling/-heating stages to guarantee an efficient operation i.e. the solvent is cooled before absorption and heated before desorption (see Figure 7). In addition, CO_2 solubility in Selexol and Genosorb solvents are 5 and 17 times higher than in water. Thereby, the diameters of the scrubbers are smaller than those of water scrubbers, since a lower flowrate of the organic solvent is needed.

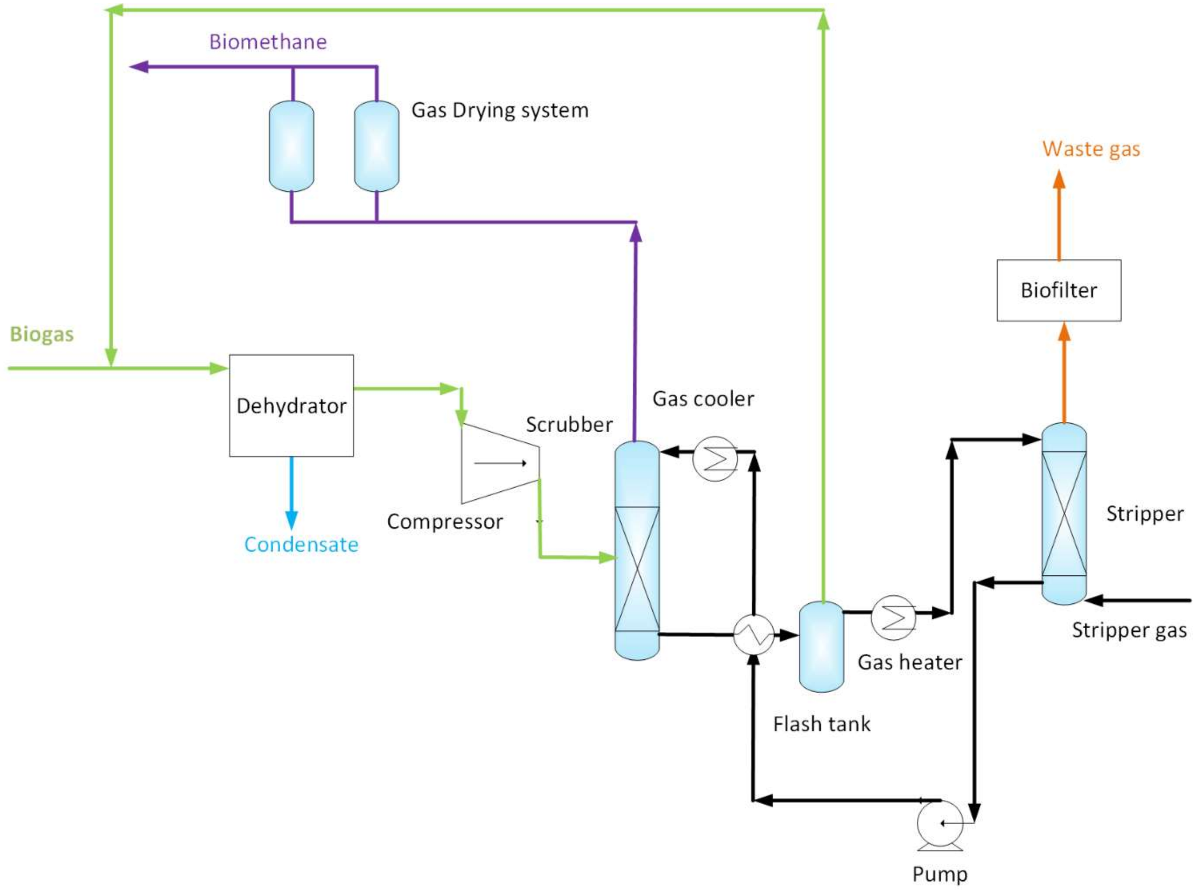


Figure 7: Schematic of biogas upgrading using organic solvent scrubber

3.3.3. Chemical scrubbing

This upgrading process is fundamentally similar to water or organic solvent scrubbing (Figure 8). The process configuration consists of a packed bed (filled with structured or random packings) absorption unit (in which the CO_2 is separated from the biogas) plus a stripper (regenerator) equipped with a reboiler. This process is simpler than water/organic scrubbing due to the enhanced process performance of using CO_2-reactive absorbents such as alkali aqueous solutions or alkanol amines. The CO_2 (and H_2S) of the raw biogas react with the amine.

The absorber operates at 1–2 bar while the operating pressure of the stripper is usually 1.5–3 bar. Steam can be used in the reboiler of the stripper.

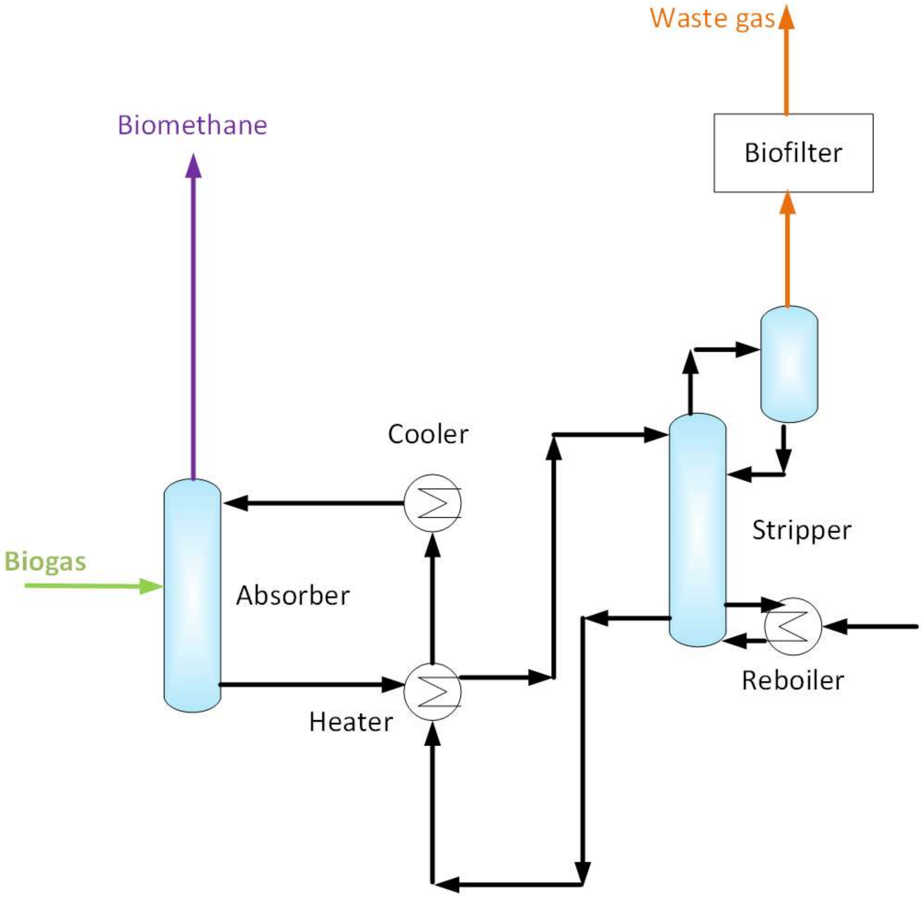


Figure 8: Schematic of biogas upgrading using chemical scrubber

3.3.4. Pressure swing adsorption (PSA)

This technique is a dry method which is based on the selective adsorption of CO_2 over CH_4 onto zeolite and polymeric sorbents, silica-gel, activated alumina, or activated carbon [96]. Packed bed columns operating in parallel under pressurization, feed, blowdown and purge regime. The compressed raw biogas enters the adsorption column where CO_2 is retained and methane flows through the bed. When the adsorbent is saturated with CO_2, the feeding is stopped, the blowdown phase is initiated by decreasing the pressure to release CO_2 which can be directed into an off-gas stream. For continuous operation of the process, four packed bed columns are being closed and opened consecutively (Figure 9).

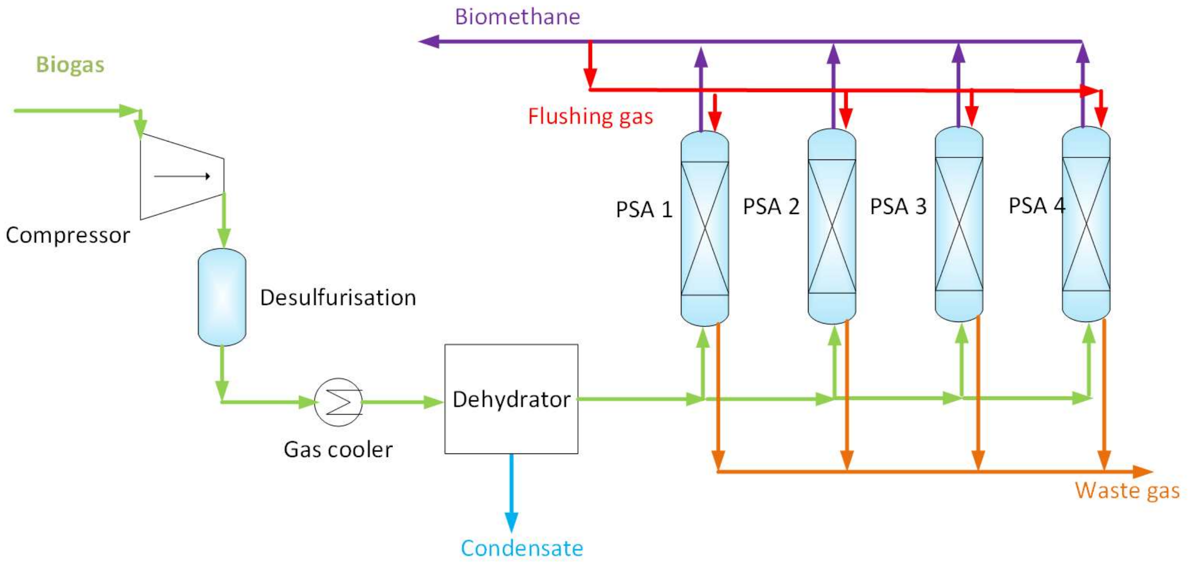


Figure 9: Biogas upgrading using PSA

3.3.5. Membrane separation

This separation technique is based on the selective permeation of gas components flowing through a semi-permeable membrane. Polymeric materials are preferred membranes over non-polymeric materials for upgrading the biogas due to the lower cost, stability at high pressures, easy manufacture, and easy scalability. Most of the methane is retained while most of the CO_2 permeates through the membrane. The biogas is cleaned (to remove particles, H_2O, H_2S, VOCs, NH_3, and siloxanes [97, 98]) to avoid deterioration and clogging of the membrane stages, compressed to 6–20 bar, and then is fed to membrane modules. The process may have several membrane stages.

3.3.6. Cryogenic separation

In this method, contaminants like H_2S and CO_2 are liquefied and separated in three successive stages to remove them and also to optimize the energy recovery [99]. The temperature of the compressed biogas to the first separator is -45 °C, to the second one is -70 °C and to the third separator is -120 °C.

3.3.7. Process configuration

No single technology can remove all contaminants in biogas. Generally, each upgrading technology is capable of removing one or two contaminants. Ultimately, based on the biomethane requirement aspects, a combination of processes is used to build the biogas upgrading plant. The combination of the techniques used for cleaning and upgrading biogas is illustrated in Figure 10.

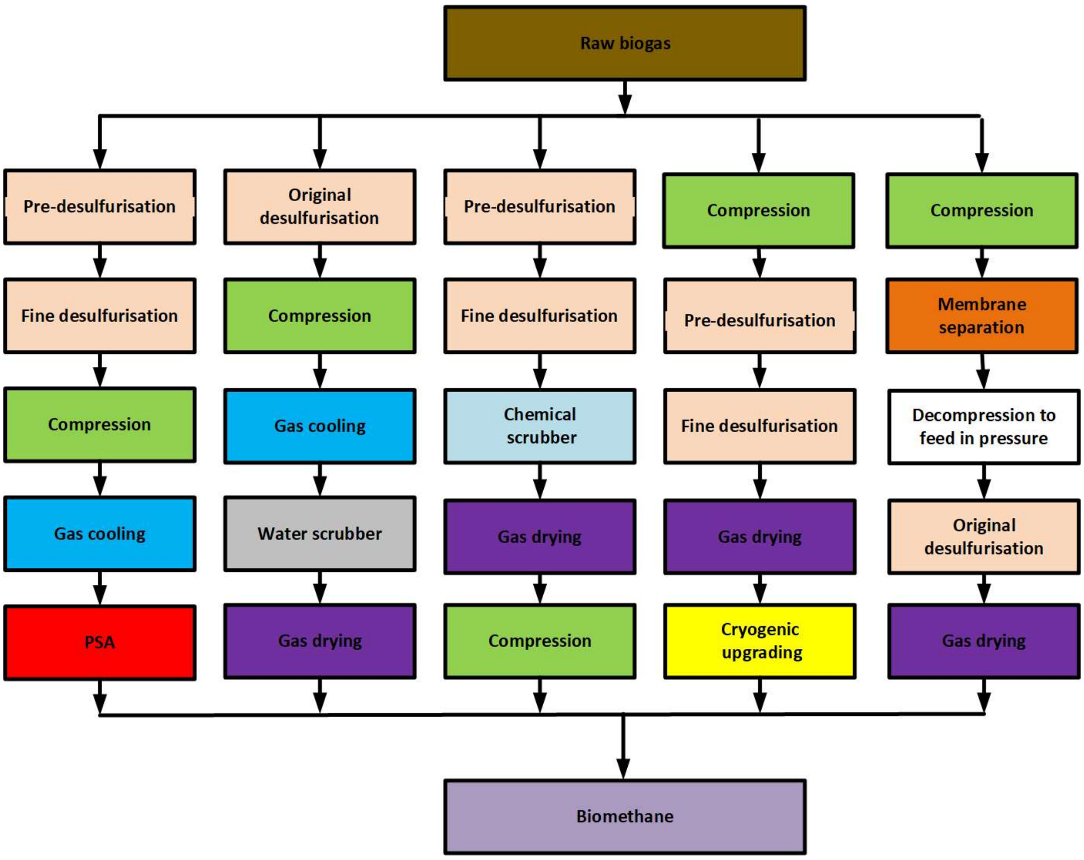


Figure 10: The combinations of biogas cleaning and upgrading processes

The physical/chemical processes used to remove biogas contaminants are described in Section 3.4.

3.4. Physical/Chemical processes for contaminants removal

3.4.1. Water removal

The water content of biogas may condensate or form hydrates in transmission lines and make corrosion and erosion issues [24]. Water can be separated by cooling, compression, adsorption or absorption. By decreasing the temperature or increasing the pressure, water condenses and is then removed, [45]. Water removal by adsorption can be achieved by SiO_2, molecular sieves or activated carbon. The regeneration process can be done by heating or a decrease in pressure. Absorption can be performed in glycol solutions (regenerated by heating) such as ethylene glycol (EG), di-ethylene glycol (DEG), tri-ethylene glycol (TEG) or by the use of hygroscopic salts.

3.4.2. H_2S removal technologies

The H_2S present in the raw biogas can be removed by adsorption onto several materials including activated carbon iron oxide or hydroxide[100], membrane separation, calcium hydroxide $Ca(OH)_2$ [101], ethylenediaminetetraacetic acid Fe-EDTA [102], in-situ precipitation in the digester via iron salt addition, and absorption [103]. The most straightforward method of controlling H_2S concentration in the biogas is the in-situ desulphurization occurring in the biogas digester. It can be done by dosing air/pure oxygen to the digester gas stream or iron hydroxides/chlorides to the digester liquid phase [104, 105]. Use of sodium and calcium hydroxide in the process causes the formation of salts with elemental sulphur which cannot be regenerated.

The H_2S content of biogas can be eliminated by adsorption/oxidation to elemental sulphur or conversion to SO_2 [33]. Mezmur and Bogale used KOH/ NaOH and activated carbon to reduce CO_2- and H_2S- content of biogas by 82 and 99%, respectively [106]. In addition, charcoal and silica gel were employed to remove the moisture. The cleaned biogas was used for power generation.

Membrane-based separation can also be used for the selective H_2S removal from biogas [107]. Polyimide, poly-sulphone and cellulose acetate are commonly used as membrane materials for the biogas upgrading purposes [108]. Significant improvement in the desulphurization efficiency can be achieved if special rubbery polymeric membrane material is used [109].

Table 9 represents the pros and cons of the physical/chemical H_2S removal routes.

Table 9: Pros and cons of physical/chemical H_2S removal technologies

H_2S removal technology	**Advantages**	**Disadvantages**
Adsorption using iron oxide or hydroxide	• Low operating cost. • High H_2S removal efficiency, i.e. >99%.	• Temperature should be controlled. • Regeneration of adsorbent is expensive. • H_2S content of raw gas must be <100 ppm.
Adsorption on activated Carbon	• High H_2S removal Efficiency.	• Activated carbon has a short lifetime. • Carbon regeneration is performed at a high temperature.
Absorption (sodium hydroxide washing)	• Operation under ambient pressure and temperature. • Water can be used as solvent. • High H_2S removal efficiency of 90–100%.	• Low liquid to biogas ratio is needed.
Membrane separation	• High H_2S removal efficiency. • Simultaneous CO_2 removal from the raw gas.	• Concentration of H_2S in the raw gas must be <2%.
In-situ precipitation	• Efficient at high H_2S content of raw gas. • Low investment cost.	• High operating costs. • Not efficient at low H_2S concentrations. • Concentration of H_2S in the raw gas must be >100–150 ppm.

H_2S and CO_2 can also be removed from the raw biogas using cryogenic separation [110]. For large-scale biogas desulfurization, there exist three patented H_2S removal processes i.e. Biopuric®, Thiopaq®, and H_2SPLUS SYSTEM®, [111-113]. In these processes, the combination of bioreactors and chemical scrubbers are used.

3.4.3. Halocarbons, volatile organic compounds (VOC), siloxanes removal technologies

Halogenated compounds contain one or several halogen atoms including chlorine, fluorine, iodine or bromine [114]. Examples of halogenated compounds are carbon chlorobenzene, tetrachloride, tri-fluoromethane and chloroform. Halocarbons are often seen in the LF biogas but rarely found in the AD biogas or from sewage sludge, and organic wastes. Halocarbons are oxidized to corrosive products when biogas is combusted. The corrosive combustion products together with water can cause corrosion issues in downstream pipelines and appliances. In addition, furans (polychlorinated dibenzofurans and polychlorinated dibenzo-p-dioxins), and dioxins can form if the time and temperature of combustion are sufficient. Siloxanes are chemical species that contain a silicon-oxygen bond (Si-O) and are used in shampoos and deodorants. So, siloxanes can be found in raw biogas originated from both sewage sludge treatment plants and LFs. Siloxanes, VOCs and halocarbons can be separated from the biogas by adsorption on activated carbon [42, 105]. Siloxanes can also be removed by cooling the biogas, silica gel/activated aluminum, or absorption in a mixture of liquid hydrocarbons [24]. Siloxanes can also be separated during the H_2S removal process. The adsorption on activated carbon must be run under high pressure with low moisture contents of biogas. There are some technical problems with the regeneration of activated carbon materials. The reported siloxanes removal efficiency via adsorption on activated carbon are 95% [105] and 74–83% [115]. In addition, using cryogenic condensation of siloxanes, a removal efficiency of 25.9 and 99.3% can be obtained when the biomethane temperature is dropped to -25 and -70 °C, respectively [42]. The cryogenic condensation route needs high investment and operating costs [113].

Use of ionic liquids in removing VOC compounds from raw biogas was studied by Privalova et al. [116]. Experimental results suggest that 1-butyl-3-methylimidazolium acetate [BMIM]

[AC] ionic liquid has a better performance compared to aqueous amines solutions as it captures 65 wt% of the identified VOC compounds, whereas amine solutions retain nearby 35 wt% only.

3.4.4. N_2 and O_2 removal technologies

N_2 and O_2 are present at high molar concentrations from LFs when vacuum generation is used to collect the raw biogas as a consequence of air infiltration. The technologies used for both N_2 and O_2 removal are adsorption with activated carbon, molecular sieves, pressure swing adsorption, membrane and cryogenic separation. A fraction of N_2 and O_2 can be separated during the desulphurization processes or via some of the upgrading routes. Removal of both N_2 and O_2 is cumbersome and expensive. The concentration of these species in the upgraded biogas should be too low unless the biogas is used for boilers or CHP units. The corresponding pros and cons of the upgrading process routes used to remove N_2 and O_2 are listed in Table 10.

Table 10: Pros and cons of N_2 and O_2 removal technologies

N_2 and O_2 removal technology	**Advantages**	**Disadvantages**
Membrane separation	• Low energy requirements. • Compact design and light in weight. • Easy operation.	• Complex maintenance. • High purchasing cost of membrane. • Low CH_4 separation efficiency and high CH_4 loss.
PSA	• Low energy demand. • CO_2, N_2 and O_2 can be separated simultaneously.	• Water and H_2S have to be removed before the pressure swing adsorption process. • Periodical regeneration of the adsorbent is required.
Cryogenic separation	• Simultaneous removal of multiple contaminants. • CO_2 is produced as a by-product.	• High capital cost and energy demand.

3.4.5. CO_2 removal technologies

The CO_2 content of biogas is about 25–50% on a volume basis and its removal from biogas is essential to enhance the biogas energy density and heating value, and to mitigate the costs of pipeline/road/rail transportation. Physical/chemical methods used to remove CO_2 from the raw biogas are based on the physical or chemical transfer of the CO_2 to another gas, liquid- or solid-state material. The technologies used for CO_2 removal are PSA, water scrubbing, organic physical/chemical scrubbing, adsorption of gas molecules on adsorbent materials, cryogenic separation, thermo-catalytic methanation, and membranes separation. These technologies are mature and have higher efficiency compared to the biological routes used for CO_2 removal [110]. CH_4 recovery is an important factor from the economic and ecological points of view [117].

The water-scrubbing route is the most popular biogas upgrading process. Commercial water scrubbers from several suppliers can be found in the market for a wide range of gas capacities [24]. In the pressurized water scrubbing process, the raw biogas is compressed and contacted with water counter-currently in a vertical column. In this method, CO_2, some quantities of methane and H_2S of the raw biogas are transferred to the water stream. The regeneration step involves a flash depressurization, to recover methane [70], and a desorption column operating under atmospheric pressure. The water scrubbing process is simple and robust but the existence of nitrogen and oxygen in the desorption column is a drawback. In addition, bacterial growth takes place and cause clogging. Foaming in the scrubbers is another potential operational problem.

Organic physical scrubbing process is extremely similar to water scrubbing technique unless an organic solvent such as polyethylene glycol (with higher solubility for CO_2/H_2S in addition to lower vapor pressure) is used as an alternative to water [118]. Commercial processes using polyethylene glycol (as solvent) are Purisol™, Selexol™, and Genosorb™ [100]. Use of solvents reduce the size of absorption vessels, lessen pumping, and mitigate the solvent loss.

In chemical scrubbing technique, on the other hand, aqueous solutions of several alkanol amines such as mono-ethanolamine (MEA), diethanolamine (DEA), di-glycolamine (DGA), and di-methyl ethanolamine (DMEA) interact with CO_2 that increase the selectivity between CO_2 and methane resulting in a very low absorption of CH_4 s[105]. Most of amine scrubbers operate near atmospheric pressure. The absorption step and chemical reactions are exothermic which heat up the solution by around 25 °C. Note that absorption equilibrium favored by low operating temperatures while chemical reactions favored by high operating temperatures. So, optimal operating temperatures must be found [100]. The solvent leaving the absorber is heated up for regeneration purposes and then is conveyed to the stripper column operating at high temperature. A pre-desulphurization unit is needed to avoid poisoning the alkanol amine solvent. Thermal or oxidative degradation of the solution increases the equipment corrosion potential, chemical consumption, and release of hazardous degradation species [119-121].

Several adsorbent materials such as activated carbon materials, zeolites, titano-silicates, silica gels, etc. can separate CO_2 from methane [122]. Water removal is necessary before the process to prevent the poisoning of the adsorbents. The biogas feed must be pressurized to about 10 bar to have enough driving force in the process. Regeneration process can be carried out in a cycling operation [70]. Two to nine cycling adsorbers are used in parallel arrangement to assure a continuous operation of the process [24]. O_2 and N_2 can be separated simultaneously with CO_2 [47].

Cryogenic separation can be used to remove contaminants from raw biogas. In this approach, ammonia, H_2S are separated and then CO_2 is removed in liquid form. Further cooling causes CO_2 sublimation and its removal in solid form. This technology is very energy intensive [100].

In the thermo-catalytic methanation process, the CO_2 and H_2 content of biogas can be converted to methane on nickel catalyst under 10–20 bar [123, 124]. The mole fraction of methane in the biomethane stream is 96%. Kirchbacher et al. simulated four process configurations to investigate the impact of fermentation setup, recycling of off-gas and multi-stage membrane separation, pressure and gas hourly space velocity [125]. The process configurations are process with no recycle, process with basic recycle, process with recycle + preceding methane removal, in addition to process with recycle + two-stage membrane separation. The results show that a two-stage biogas fermentation is extremely beneficial, as it increases the hydrogen storage capacity by about 70 %. Upgrading of raw biogas obtained from the organic matter of MSW by solar/wind-derived hydrogen was analyzed in Ref. [126]. Two case studies were conducted for UK (high wind availability) and Spain (high solar availability). The results suggest that the cost of biogas upgrading in the UK is lower than in Spain with the current prices.

Membrane separation route is one of the conventional methods used to upgrade the LF gas. The first plants were constructed in the late 1970s. This technology is based on dissimilar solubility and diffusivity of gaseous species in each membrane. The pre-treated raw biogas is pressurized to 5–30 bar and is conveyed to the membrane module [100]. Membrane-based separation is simple to operate, safe and robust, the scale-up flexibility is high, and there is no need of hazardous chemicals [70]. High CO_2 removal efficiency (>95%), as well as low CH_4 loss, are achieved when physicochemical technologies are used for biogas upgrading. Other chemical species can also be captured via physicochemical methods from the raw biogas with CO_2. However, it is recommended to install a biogas pre-treatment process for the partial removal of those compounds prior to CO_2 separation to avoid operational issues.

The highest methane recoveries can be achieved with chemical absorption compared to all other upgrading approaches (Table 11). Employing complex designs with membrane separation can yield methane recovery values of up to 99–99.5% at a higher investment cost

[44]. It is important to note that lower methane loss can be obtained at the expense of higher energy demand.

The fixed capital investment costs of physicochemical CO_2 removal processes depend on the concentration of contaminants and plant size (i.e. the economy of scale). Thereby, the higher the biogas upgrading capacity, the lower the investment cost. The capital costs of membrane separation process rapidly increase as the process is scaled down. The main operating cost of the separation technologies are the cost of electricity needed for mechanical equipment e.g. biogas compression and pre-treatment, liquid pumping, cost of energy for solvent regeneration at high temperatures in case of chemical absorption, etc. The maintenance cost of a membrane-based upgrading route is about 3–4% of the fixed investment costs, while this value is nearly 2 to 3% for absorption and adsorption processes [42].

Table 11: Investment costs, plant capacity, energy use, methane loss and final methane content of the upgraded biogas physical/chemical technologies [42, 44, 47, 127]

CO_2 removal technology	**Working pressure (bar) [24]**	**Operating temperature (°C) [24]**	**Methane loss (%)**	**Methane concentration of the upgraded biogas (%)**	**Power demand consumption (kWh/Nm^3)***	**Heat demand (kWh$_{th}$/m^3 raw biogas) [87]**	**Plant capacity (Nm^3/h), [investment cost (€ h /Nm^3)]** [88]**
Water scrubbing	4–7	No	<2	>96	0.2–0.3	0	100–500–1000 [5500–2500–2000]
Chemical absorption	No pressure	160	0.1–1.2	>99	0.12–0.15	0.6	600–1800 [3200–1500]
PSA***	4–7	No	-	96–98	0.25–0.6	0	600–2000 [2700–1500]
Membrane separation	8	10–30 [128]	-	96–98	0.2–0.38	0	100–400 –1000 [6000–2500–2000]
Physical separation	4–7	55–80	<2	96–98.5	0.2–0.51	0	250–1000 –1500 [4500–2000–1500]

* Electricity consumption can be stated as the amount of energy per volume of cleaned gas, raw gas, ton of CO_2, etc. [47].

** Capital costs, operating and maintenance costs (O&M) of upgrading technologies are available in Ref. [47].

*** H_2S and water needs to be separated before the PSA-column [24].

Acrion Technologies Inc. has built a process named CO_2 Wash® for the upgrading of the LF gas (Figure 11) [129]. This process removes sulphur and halogenated compounds, siloxanes, and non-methane hydrocarbons from the LF biogas. The removed contaminants dissolved in the liquid CO_2 of column bottom stream can be sent to incinerators together with the LF gas. The purified liquid CO_2 with purity of 99.99% and a gas stream comprising mainly methane and CO_2 are the other streams from the CO_2 Wash® process. The siloxanes, chlorinated compounds as well as sulphur contents of the clean methane and CO_2 stream (top stream of the tower) are all below the detection levels of 5, 10 and 100 part per billion (ppb), respectively.

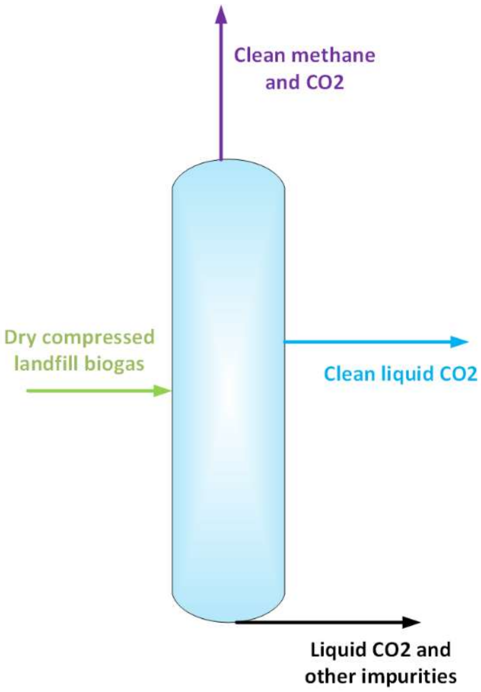


Figure 11: Schematic view of the CO_2 Wash® (Acrion)

3.4.6. Other compounds

Solid particulates, as well as oil-like compounds present in the raw biogas, are separated via dust collectors [114]. Sludge and foam are separated via cyclones. A filter with 2 to 5-micron mesh size is appropriate for most downstream applications of the biogas. Ammonia (NH_3) is removed when the biogas is dried or upgraded and a separate cleaning unit is not required. The methane loss of the upgrading process (i.e. the methane present in the off-gas stream) can be avoided by mixing the off-gas with air to be used for combustion [83]. Methane can be seen in the off-gas of PSA columns, in air/water from water scrubbers with/without water recirculation. Separating methane from the off-gas is done to make the upgrading plant economically viable and to avoid/minimize the methane slip to the environment due to its strong GHG emission.

3.5. Biological biogas upgrading technologies

There are two biological approaches for biogas upgrading: 1) chemoautotrophic, and 2) photosynthetic. Most of these methods are at pilot stage or early stage of full-scale implementation [23].

3.5.1. Chemoautotrophic approaches for CO_2 conversion

The CO_2 content of biogas can be converted to methane by methanation process. Bioconversion of CO_2 to methane is a cutting-edge solution for upgrading a raw biogas [130]. This approach not only reduces the CO_2 concentration but also increases the energy content of the effluent stream by increasing the methane concentration. It is possible to upgrade a raw biogas with CO_2 molar concentration of 60% to biomethane with methane mole fraction of 90% under thermophilic operation at 65 °C [131] and 98% under mesophilic condition (at 37 °C) [132]. In the hydrogenotrophic CO_2 removal route, the CO_2 part of raw biogas is microbiologically upgraded by reduction of CH_4 with H_2 [133]:

$$4H_2+CO_2 \rightarrow CH_4 +2H_2O \tag{1}$$

Microbiological upgrading of CO_2 in biogas to biomethane is performed by each of the following three technologies:

- In-situ (biogas upgrading) by adding H_2 from an external source into anaerobic digester enabling methanogenic Archaea to transform CO_2 (40–60% molar concentration) to methane [134]. In this method, CO_2 can be directly captured from the reactor, it has simple operation, and is an alternative for storing excess renewable electricity [130]. Depending on the optimal temperature, there exist four methanogens, 1) psychrotolerant (about 18 °C), 2) mesophilic (about 37 °C), 3) thermophilic (about 55 °C), and 4) hyperthermophilic (about 65 °C) [130]. The main challenges of the in-situ biological upgrading method are the methanogenesis inhibition at pH values above 8.5, and oxidation of alcohols in addition to volatile fatty acids [23].

- Ex-situ methanation refers to the provision of CO_2 and H_2 in an anaerobic reactor containing hydrogenotrophic to produce methane [23, 135]. The advantages of this approach over in-situ technique are; 1) stability of the process since upgrading operation is taking place in a separate section (unit), 2) simpler biochemical process, 3) it is not dependent on biomass, 4) syngas can be used instead of pure CO_2, and 5) feasibility of supplying power to remote areas. The efficiency of the biogas upgrading process is highly dependent on the reactor type [23]. In addition, the operating temperature is an important factor for the efficiency of the bio-methanation process. The main challenge of this technology is the low mass transfer rate of the present gas and liquid phases.
- Hybrid of in-situ and ex-situ processes: in this method, a fraction of partially upgraded biogas from the in-situ upgrading process is conveyed to an upgrading unit (ex-situ). This technique is less developed compared to the in-situ and ex-situ approaches.

CO_2 removal through microbial electrochemical is an innovative method to upgrade biogas [136, 137]. In microbial electrolysis cells, electrons are released by bacteria and can be combined with protons to produce hydrogen in the cathode [138]. The produced hydrogen can upgrade biogas [139]. The in-situ upgrading approach is more effective than the ex-situ system [136]. The performance of the in-situ method can be further enhanced under continuous mode of operation.

3.5.2. Photoautotrophic approaches for H_2S and CO_2 removal

The photosynthetic CO_2 removal route is an alternative technique that sequester CO_2 to increase the methane concentration. H_2S removal can be achieved by these methods, while over 54% of the raw biogas CO_2 content is consumed [23]. Phototrophic organisms such as algae in enclosed or open photobioreactors can catalyze the process. The advantage of closed systems over open systems are high photosynthetic performance and low land/water needs. The main bottlenecks of closed systems are high energy requirement and cost. An open system needs low resources for its construction and operation.

Photoautotrophic microorganisms such as prokaryotic cyanobacteria and eukaryotic microalgae can convert CO_2 utilizing water, sunlight, and nutrients to produce oxygen, heat and biomass [42]:

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

The produced active biomass for the production of value-added compounds [140] or as a feedstock to produce biogas [141]. Several cyanobacteria or microalga such as Chlorella, Arthrospira and Spirulina have high photosynthetic efficiency and are mostly studied for biogas upgrading.

In the photosynthetic H_2S removal method, biogas is upgraded in algal-bacterial photo-bioreactors [24, 44]. It is a favorable replacement for the concurrent removal of CO_2 and H_2S in a single-step process.

$$2HS^- + O_2 \rightarrow 2S^0 + 2OH^- \qquad (3)$$

$$2HS^- + 4O_2 \rightarrow 2SO_4^{2-} + 2H^+ \qquad (4)$$

$$2HS^- + 2O_2 \rightarrow S_2O_3^{2-} + H_2O \qquad (5)$$

In this technology, H_2S is oxidized to sulphate by sulphur oxidizing bacteria (SOB) using the oxygen which is photo-synthetically produced during bio-fixation of CO_2 via microalgae. This process is described as Eq. (6) [142]:

$$H_2S+CO_2 + \text{nutrients}+O_2 \rightarrow \text{biomass}+ SO_4^{2-}/S + H_2O \tag{6}$$

The H_2S concentration decreases from the range of nearly 3000–5000 ppm to 50–100 ppm [87]. Safety measures and precautions are required to prevent the production of explosive gas mixtures [105]. The dosing of iron hydroxides/chlorides forms and precipitates FeS, which in turn significantly reduce the H_2S concentration in the gas phase.

Biogas can be biologically converted to liquid products such as acetate, ethanol, and butanol [143, 144]. A variety of microorganisms such as acetobacterium woodii, clostridium scatologenes, and the like can convert CO_2 and hydrogen to liquid compounds [145].

3.5.3. Halocarbons, VOC, siloxanes removal technologies

LF biogas halocarbons including 1,1,1-trichloroethane, methylene chloride (di-chloro-methane, DCM), carbon tetrachloride (CCl_4), dichlorodifluoromethane, and tetrachloroethylene are biodegraded at low concentrations under anaerobic, aerobic conditions [146, 147]. The biodegradability of VOC materials present in biogas such as benzene, toluene, volatile fatty acids is reported in Ref. [148].

The removal of hexa-methyl-cyclo-tri-siloxane with a removal efficiency of up to 20% is reported in Ref. [149]. The removal of octamethylcyclotetraxilosane under anaerobic and aerobic conditions was addressed in Ref. [150]. The removal efficiency of 50–60% for aerobic conditions and 15% under anaerobic conditions was reported. In another study, the removal efficiency of 74% for octamethylcyclotetraxilosane was achieved by Li et al. [151].

4. Costs of biogas upgrading

In nations and regions where policies and legislation have been introduced to incentivize the production of renewable gas, or renewable heat, the cost of biogas upgrading can be offset or partially offset by the magnitude of the incentives, depending on their mode of application. For example, in Germany, a Feed-in Tariff is offered for electricity feed-in associated with biogas installations including those involving CHP [152]. In the UK, the Renewable Heat Incentive is offered [153]. If these incentives are withdrawn it will obviously affect the relative economic attractiveness of biogas upgrading. Amendments to national and sub-national support schemes are also important factors affecting investment decisions. There is evidence that investment in biomethane plants has slowed in Germany since amendments to the EEG law in 2018 [10].

Currently, the price gap between natural gas and biomethane varies significantly by region [11]. For example, the price gap in Asian developing counties is the narrowest one while the price gap in the North American counties is the highest one.

The differences in upgrading costs of technologies are very much affected by the project-specific circumstances. For instance, upgrading with chemical scrubbing might be of much interest if cheap heat is available on-site. If the biomethane is injected to the high-pressure natural gas network, those upgrading processes working at relatively high pressure such as membranes would be preferred because the injection costs can be reduced. Biogas production and biomethane consumption may take place at different locations. If the biomethane injection point to the gas grid is located away from the production plant, the distribution cost should be considered.

The investment cost of upgrading technologies to remove CO_2 from the raw gas against the capacity of biogas is presented in Table 11 [88]. By constructing a power law equation for each technology, we find that the chemical adsorption technology has the best economy of scale (when the plant capacity is doubled, the investment cost increases by about 24%). On the other hand, water scrubbing route has the poorer economy of scale (when the plant capacity is doubled, the investment cost increases by about 44%). To remove CO_2 from a raw biogas with flowrate of 50 Nm^3/h, the water scrubbing technology is the cheapest one, while chemical absorption is the most expensive one. At a high biogas flowrate of 2000 Nm^3/h, the cheapest and most expensive technologies for removing CO_2 are respectively physical separation, and chemical absorption.

In Ref. [92], the investment costs of five upgrading routes including PSA, water scrubbing, amine scrubbing, membrane, and Genosorb® scrubbing versus the capacity of raw biogas are presented. All investment costs excluding those for chemical scrubber include the cost of off-gas treatment technology for methane degradation. In addition, the costs of different upgrading technologies were discussed with the following assumptions [92]:

- Investment and maintenance costs were based on the price of technology providers in 2013.
- Plant annual availability of 96%.
- Operating lifetime of plants: 15 years.
- Interest rate: 5%.
- Costs for planning, permission and additional construction was set to 10% of investment costs.
- Insurance costs was assumed to be 0.5% of investment costs.
- Personnel cost for each technology and any plant size was €35 /h.
- Methane recovery rates and energy consumptions (w.r.t 55 and 65% methane content of the raw biogas) were based on warranty values.

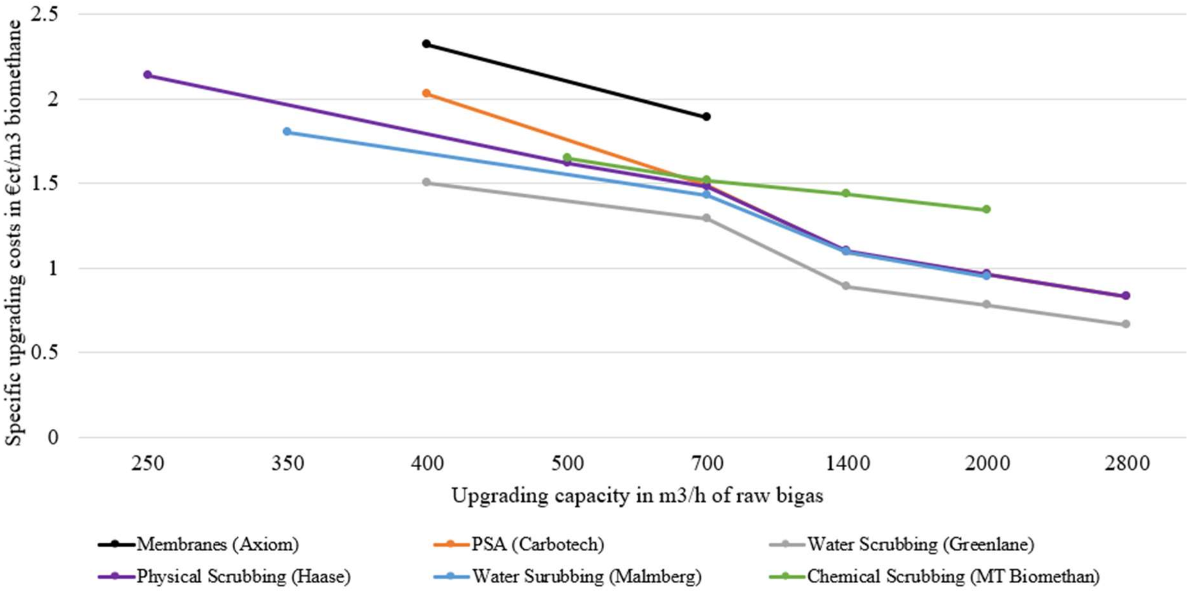
- Desulphurization process (if required): H_2S reduction by 100 ppm, €5/m^3 of raw biogas capacity/year.
- Costs for extra cleaning steps (e.g. NH_3 or siloxanes removal) were not considered.

Methane content of the raw biogas were changing from of 55 to 65%. The heat cost of 3–5 €cent/kWh_{th} and electricity cost of 12–18 €cent/kWh_{el} were assumed.

For the PSA system, the upgrading costs for raw biogas capacities are in the range 350–2800 Nm^3/h. For water scrubbing technology, the raw gas capacities vary between 300–1400 Nm^3/h. The raw gas capacities of amine scrubber system and membrane technology range within 250–2000 Nm^3/h, and 250–750 Nm^3/h, respectively. The comparison of the investment costs of the five upgrading technology suggests that the PSA route has the highest investment cost for upgrading capacities of 250–2800 Nm^3/h. At high upgrading capacities, the Genosorb® scrubbing technology is the cheapest one. On the other hand, at low biogas upgrading capacities, amine scrubbing is the cheapest in most of cases.

Figure 12 illustrates the costs for biogas upgrading (per Nm^3/h of biogas) to biomethane based on a company survey in 2012 [154, 155]. As evident from this figure, the higher the plant capacity the lower the specific investment cost. When the plant capacity is over 250 Nm^3/h, biogas upgrading using membranes results in higher investment costs. On the other hand, for any upgrading capacity, water scrubbers offer the minimum upgrading cost among other technologies [155]. For the cases that the upgrading capacity is 20 Nm^3/h, the specific investment cost based on a rough calculation is about \$1.07/Nm^3 CH_4 while for the upgrading capacity of 200 Nm^3/h, the specific investment cost drops to \$0.25/ Nm^3 CH_4[87].

Miltner and co-workers performed the techno-economic analysis of biogas upgrading (per standard m^3/h of biogas) to biomethane via pressurized water scrubbing, amine scrubbing, PSA, and membrane-based gas permeation [100]. Total upgrading cost comprises fixed investment costs (plant lifetime of 15 years), electricity price of 0.15 €/kWh, annual availability of 98 %, and maintenance costs. At low biogas capacities, membrane-based gas permeation has the lower upgrading cost, while at high plant capacities the pressurized water scrubbing technology is the cheapest technology. Upgrading cost for a plant with a capacity of 250 Sm^3 biogas/h is about 0.25 €/Sm^3 biomethane, and it drops to 0.15 €/Sm^3 biomethane for upgrading capacities above 2000 Sm^3 biogas/h.



Haase: Based on Genosorb® solvent; MT Biomethane: Current name is Hitachi Zosen Inova

Figure 12: Specific costs for biogas upgrading in 2012

For the cases that biomethane is injected to natural gas grid, the most important factors are network pressure, volumetric flow and distance to the gas grid. The highest investment costs are contributed to compressor stations (ca. 60% of the investment [156]), metering/gas quality measurement equipment and pipes construction costs. The major operating costs are the costs of the gas conditioning (heating value adjustment by adding LPG) and power consumption of compressors. The fixed capital investment for connection to a 16 bar (medium pressure) network drops from 12,240 to 2,457 €/Sm^3/h as the biomethane flowrate increases from 125 to 700 Sm^3/h. The operating costs are dominated by the fixed capital costs (up to 350 Sm^3/h biomethane injection). Injection into a distribution network (pressure <1 bar) imposes low investment and operating costs. When the biogas pressure increases from 16 bar to 55 bar (high-pressure pipelines), the compression costs will increase by up to 50%. Table 16.8 and figure 16.4 of Ref. [156] illustrate examples of costs for gas grid connections.

Stürmer et al. [157] compared total cost of biogas upgrading with four technologies including pressurized water scrubbing, PSA, gas permeation, and amine scrubbing for three biomethane production capacities of 80, 150, and 500 Nm^3/h. The scaling factor of the upgrading technologies are pressurized water scrubbing 0.38, PSA 0.49, gas permeation membrane separation 0.61, and amine scrubbing 0.56. The scaling factor of the upgrading technologies + biomethane injection facilities (compression units, transfer station, and gas pipe) are 0.38, 0.46, 0.55, and 0.51, respectively. This means that when the biomethane production capacity is doubled, the increment cost increases of biogas upgrading and injection using water scrubbing is the lowest one. In addition, biogas upgrading via the membrane is the cheapest technology at biomethane production capacities of 80, and 150 Nm^3/h. On the other hand, pressurized water scrubbing becomes the cheapest technology at biomethane production capacity of 500 Nm^3/h. In another study, Paturska and co-workers performed an economic study for biomethane supply based on the Latvian natural gas infrastructure [158]. The authors considered three scenarios and five biogas upgrading technologies including water scrubbing, amine scrubbing, membrane separation, physical scrubbing with organic solvents and PSA. In the first scenario, it was assumed that each biogas plant delivers the produced biomethane via its in-situ upgrading infrastructure to the grid. In the second scenario, it was presumed that the raw biogas of all biogas plants is conveyed to a central biogas upgrading plant for the grid injection. The last scenario states that biomass conversion to biogas, biogas upgrading, and grid injection take place in a central facility. The results indicate that the price of the injected biomethane of Scenario 3 (the most favorable scenario) is nearly 19 % higher than the natural gas.

Figure 13 depicts the biomethane grid injection cost vs. the capacity of the raw biogas. For each capacity, the minimum and maximum costs represent the situations where the injection is to low- and high-pressure gas networks. The economy of scale is mainly attributed to the capital costs. Operational costs are less sensitive to the injection capacity. As illustrated in Figure 13, the difference between the minimum and maximum costs stems from different compression costs of the biomethane. The biomethane injection costs into the gas grid increase considerably when the gas injection capacity is reduced. Further costs for biomethane distribution via the gas network arise as a fee when the gas is transported via the public gas grid. In Germany, for example, the fee varies between from \$0.05–0.26 / Sm^3 methane.

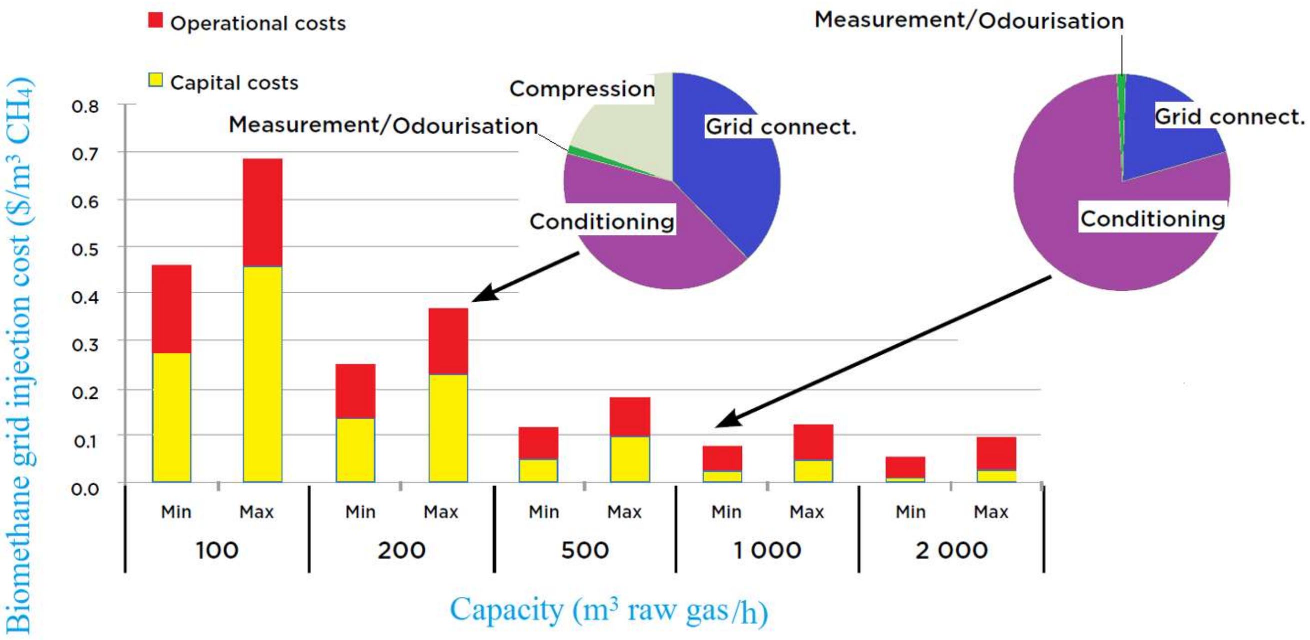


Figure 13: Biomethane grid injection costs based on cost analysis in Germany, 2010

Techno-economic comparison of biogas production from various feedstocks in different countries is presented in Ref. [159]. The total investment of two plants in Sweden with annual capacity of 100 and 20 ktonne of biomethane from pinewood and forest residues in 2014 were estimated to be 65.1, and 60.5 M€, respectively. In addition, the investment cost of a plant in Sweden with capacity of 110,000 m^3 MSW/year + 3500 m^3/day raw biogas in 2012 was 49.2 M$. In Ref. [87], the total production costs of biomethane for vehicle fueling by feedstock and capacity scale ranging from 100–2000 m^3/h is addressed. The feedstock are energy crops, manure and industrial waste. The total production costs include costs of biogas production, cleaning and upgrading, as well as distribution via the gas grid. In another study, the economic feasibility of biogas upgrading of physicochemical upgrading processes (section 3.3) on the market is studied (Figure 14), [91]. In this figure, the lower and upper lines show the low and high fixed capital investment of all existing physicochemical upgrading technologies versus the plant capacity. The lines approach to each other as the capacity of raw biogas increases. Techno-economic analysis of LF biogas upgrading with membranes and utilization for vehicle fuel is addressed in Ref. [160]. The impact of feed composition, feed flow rate and pressure on gas processing cost was investigated. The raw biogas from the LF contains 55% CH_4, 38.9% CO_2, 5% N_2, 0.4% O_2, 0.002% H_2S and 0.66% H_2O.

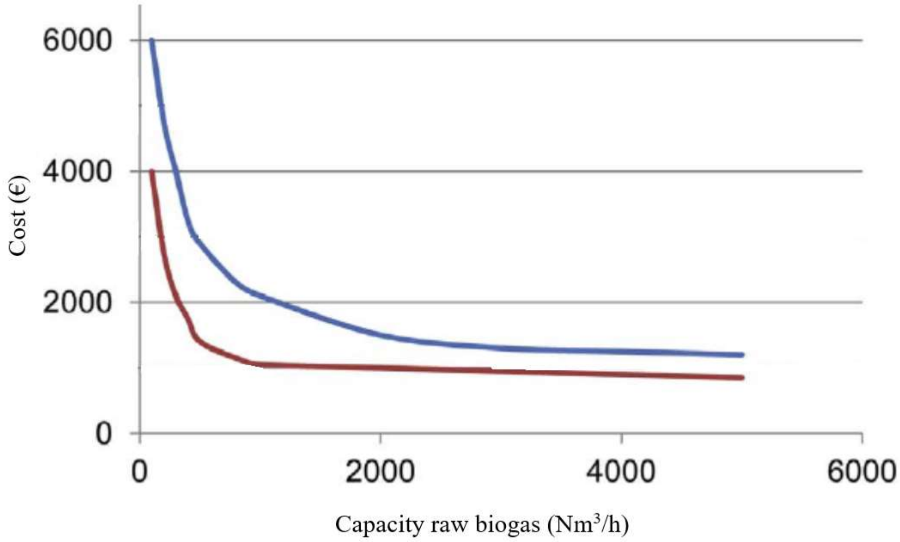


Figure 14: Cost range of physicochemical upgrading technologies versus raw biogas capacity (Note: the lower and upper lines show the low and high fixed capital investment of all existing physicochemical upgrading technologies).

5. Conclusions

Biogas production from waste materials and renewables is a favorable solution to the energy and environmental issues facing communities. Biogas upgrading faces substantial challenges concerning investment costs, energy consumption along with operating costs. The alternatives to biogas upgrading to biomethane are flaring or burning of raw biogas for power production or concurrent heat and power generation. Methane recovery is an important factor from the economic and ecological points of view. The biomethane obtained from biogas upgrading is a replacement of fossil fuels. Biomethane can be used for heating, power and steam generation, as vehicle fuel, in chemical plants, for injections to gas networks, etc. Only if the economic returns from direct injection to grid or sale for use in transport applications are significantly higher (for example if electricity prices are low, and incentives for renewable electricity generation from biogas are low or non-existent), then investment in upgrading for biomethane uses can be made.

This paper addresses the biogas supply chain including feedstock supply, biogas production and upgrading processes (physical, chemical, and biological), requirements for product specification based on applications, upgrading efficiency, methane recovery/loss, capital costs, and biogas/biomethane uses. In addition, the CO_2 utilization in the CO_2 demanding industries is covered.

The cost of biogas upgrading depends on several factors including raw biogas capacity, the concentration of contaminants in the raw biogas, local circumstances, energy and water cost, interest rate, general investment climate, envisaged lifetime of the investment, reliability of the biogas source, other economic risks including the projected cost curves of competitor technologies, and final utilization aspects of the upgraded biogas. Upgrading with chemical scrubbing might be of much interest if cheap heat is available on-site. In case of the grid injection, it will depend on the quality standards (e.g. Wobbe Index, heating value, and other criteria) that is required by the applicable gas safety laws and the gas distribution company in each jurisdiction.

The main findings of this paper are that the biogas upgrading cost depends very much on the raw biogas capacity. For example, a company survey showed that water scrubbing is the cheapest biogas upgrading technology at any biogas capacity. At biogas capacities lower than 750 Nm^3/h, the biogas cleaning via membranes has the highest cost while at capacities higher than 750 Nm^3/h, chemical scrubbing results in higher upgrading costs. Another study in 2013 indicated that among PSA, water scrubbing, amine scrubbing, membrane, and Genosorb® scrubbing, the PSA route has the highest investment cost for almost all raw biogas capacities of 250–2800 Nm^3/h. At high raw biogas capacities, the Genosorb® approach is the cheapest one. On the other hand, at low biogas flowrates, amine scrubbing is the cheapest in most of cases.

For the case that the biogas is upgraded to biomethane for grid injection, the membrane separation is the cheapest technology at low capacities among water scrubbing, PSA, membrane, and amine scrubbing. However, the pressurized water scrubbing is the cheapest technology at high biomethane production capacities. The biomethane injection costs into the gas network increase noticeably with the capacity reduction.

The next step to this research is to develop an economical model for biogas upgrading technologies. The inputs to the model will be biogas composition and capacity, local technical data including electricity, water, gas and utilities price, etc.

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