applied sciences

MDPI

Review

From Biogas to Biomethane: An In-Depth Review of Upgrading Technologies That Enhance Sustainability and Reduce Greenhouse Gas Emissions

Ahinara Francisco López, Telma Lago Rodríguez, Shoeib Faraji Abdolmaleki, Marta Galera Martínez and Pastora M. Bello Bugallo *

TECH-NASE Research Group, Department of Chemical Engineering, Universidade de Santiago de Compostela, Av. Lope Gómez de Marzoa, s/n, Campus Vida, E-15782 Santiago de Compostela, Spain; ahinara.francisco@rai.usc.es (A.F.L.); telma.lago.rodriguez@gmail.com (T.L.R.); shoeib.faraji@rai.usc.es (S.F.A.); marta.galeram@gmail.com (M.G.M.)

* Correspondence: pastora.bello.bugallo@usc.es

Abstract: Renewable energies present an opportunity to enhance energy security, reduce dependence on imports, and lower greenhouse gas emissions. Natural gas, viewed as a transitional fuel from coal to renewables, lacks reliable environmental sustainability and does not contribute to EU energy independence. Recently, biomethane has been gaining attention as an alternative to natural gas. Obtained from purified or "upgraded" biogas, it offers environmental and economic advantages. Several developed technologies, including absorption, adsorption, membrane separation, and cryogenic separation, are commercially available. However, those are energy- and resource-intensive. In this context, this review aims to examine the recent advancements in biogas upgrading, particularly in physical, chemical, and biological pathways. It focuses on CO_2 removal and/or conversion to methane, offering an updated overview for future studies. The technologies are classified based on the separation method (by phase addition, by solid agent, by phase creation, and by biological process), and an analysis of each category is conducted. The discussion covers the economic and environmental characteristics, process complexity, and future research prospects in sustainable technologies. This review highlights the potential of biogas upgrading technologies in contributing to sustainable development, increasing energy security, and achieving greenhouse gas reduction goals that are aligned with EU targets.

Keywords: energy security; biogas upgrading; biomethane; clean technology; bioenergy

Citation: Francisco López, A.; Lago Rodríguez, T.; Faraji Abdolmaleki, S.; Galera Martínez, M.; Bello Bugallo, P.M. From Biogas to Biomethane: An In-Depth Review of Upgrading Technologies That Enhance Sustainability and Reduce Greenhouse Gas Emissions. *Appl. Sci.* **2024**, *14*, 2342. https://doi.org/10.3390/app14062342

Academic Editor: Francisco Jesús Fernández Morales

Received: 31 January 2024
Revised: 4 March 2024
Accepted: 6 March 2024
Published: 11 March 2024

1. Introduction

The European Green Deal solidifies ambitions for a green transition, encompassing climate targets that aim for net zero by 2050 [1]. Additionally, it emphasizes the need for cutting-edge technologies in key industrial sectors by 2030, with priority areas including alternative fuels and energy storage [2]. The European Union's reliance on external energy supplies has hindered energy security and resulted in increased energy costs for households and industries, with Russia and Norway being the top two suppliers [3]. Growing concerns about securing the energy supply led the European Energy Security Strategy and the Energy Union to focus on reducing energy dependency from abroad [4,5]. This external dependency entails economic, social, ecological, and physical risks [6]. The tension in energy markets due to geopolitical uncertainty is escalating. Wars are reshaping the global energy system, prompting governments to bolster energy security. In 2021, a quarter of the EU's energy came from Russia, underscoring the importance of investing in robust gas network infrastructure to better integrate regional markets [7]. The EU is committed to reducing its dependence on imported gas, accelerating the production and integration of renewable energies to mitigate climate change, and fostering energy and agroecological

transitions, in addition to embracing the circular economy [8]. The REPowerEU plan exemplifies the proactive measures taken by policymakers to enhance internal energy security following the 2022 crisis and advance towards climate objectives, promoting the sustainable production of biomethane to 35 billion cubic meters by 2030 as a cost-effective means of reducing natural gas (NG) imports from Russia [9].

The security of the energy supply encompasses two dimensions: an external one and an internal one [4]. In the internal dimension of securing energy, efforts are made to reduce the energy demand, increase renewable energy sources, and create a common energy market. Therefore, the security of the energy supply is closely related to the EU's climate strategies and targets, which aim to progressively reduce greenhouse gas (GHG) emissions up to 2050 and achieve the transformation towards a low-carbon economy [10]. Facing this energy transition, NG will play a key role in the EU's energy mix [11] (it is promoted as a transition fuel from coal to renewable resources), but it is necessary to diversify imports by country and by route to increasingly interconnect domestic gas networks in order to overcome supply disruptions [5,11]. Additionally, there is a lack of reliable data regarding its real sustainability due to methane emissions into the atmosphere throughout its lifecycle [12]. This variability is influenced by factors such as the method of extraction, mode of transport, and distance, among others [13,14]. Methane is the second most significant greenhouse gas, after carbon dioxide, with an even greater capacity for retaining heat in the atmosphere. On a 100-year timescale, methane exhibits a global warming potential 28 times greater than that of carbon dioxide, and its potency increases to 84 times on a 20-year scale [15]. However, considerable uncertainties surround the total emissions, and results vary significantly among studies, consistently demonstrating that methane emissions are likely to be significantly underestimated [13,16]. Therefore, they remain a significant challenge in key sectors [17].

Anaerobic digestion (AD) is recognized both as a technology for treating organic waste and as a renewable source of biogas; it is composed predominantly of methane (CH_4) and carbon dioxide (CO_2). It is notable that the presence of CO_2 significantly diminishes the heating value of the biogas, which typically consists of 55–65% methane (CH_4) and 35–45% carbon dioxide (CO_2) [18]. Raw biogas may also contain trace amounts of H_2S, water vapor, NH_3, and siloxane. Therefore, biogas must undergo pretreatment to remove CO_2 and other trace gases in a process known as biogas upgrading in order to produce biomethane.

The extensive infrastructure available for the transport and use of NG in Europe suggests that the purification of biogas, also known as upgrading, can achieve a composition similar to that of NG [19]. High CH_4 purity is required for NG grid injection and vehicle fuel, meeting criteria such as high energy content, gas transportation, storage, and technical restrictions [20]. Biomethane is a biofuel that can serve as a renewable alternative to NG. It can be used as a transport fuel, to produce electricity, as feedstock in chemical processes, and for household consumption [21,22]. Additionally, it is fully compatible with the existing gas infrastructure [21]. It is a local renewable alternative that can contribute to reducing the EU's energy dependence and GHG emissions [23].

When focusing on sustainable production, biomethane should be produced from organic waste, forest residues, and agricultural residues to avoid implications for land use and food security [9], thus promoting the goals outlined in the Circular Economy Action Plan [24]. Biomethane can be produced from different feedstocks and conversion technologies, namely (Figure 1) through the following approaches [25]:

- By upgrading biogas from the AD of biodegradable organic matter;
- Via the thermochemical conversion of biomass (gasification), followed by syngas methanation;
- Via the methanation of hydrogen, produced through water electrolysis, and a biogenic CO_2 source stream, also called "Power-to-Gas" or, more specifically, "Power-to-Methane" (PtM).

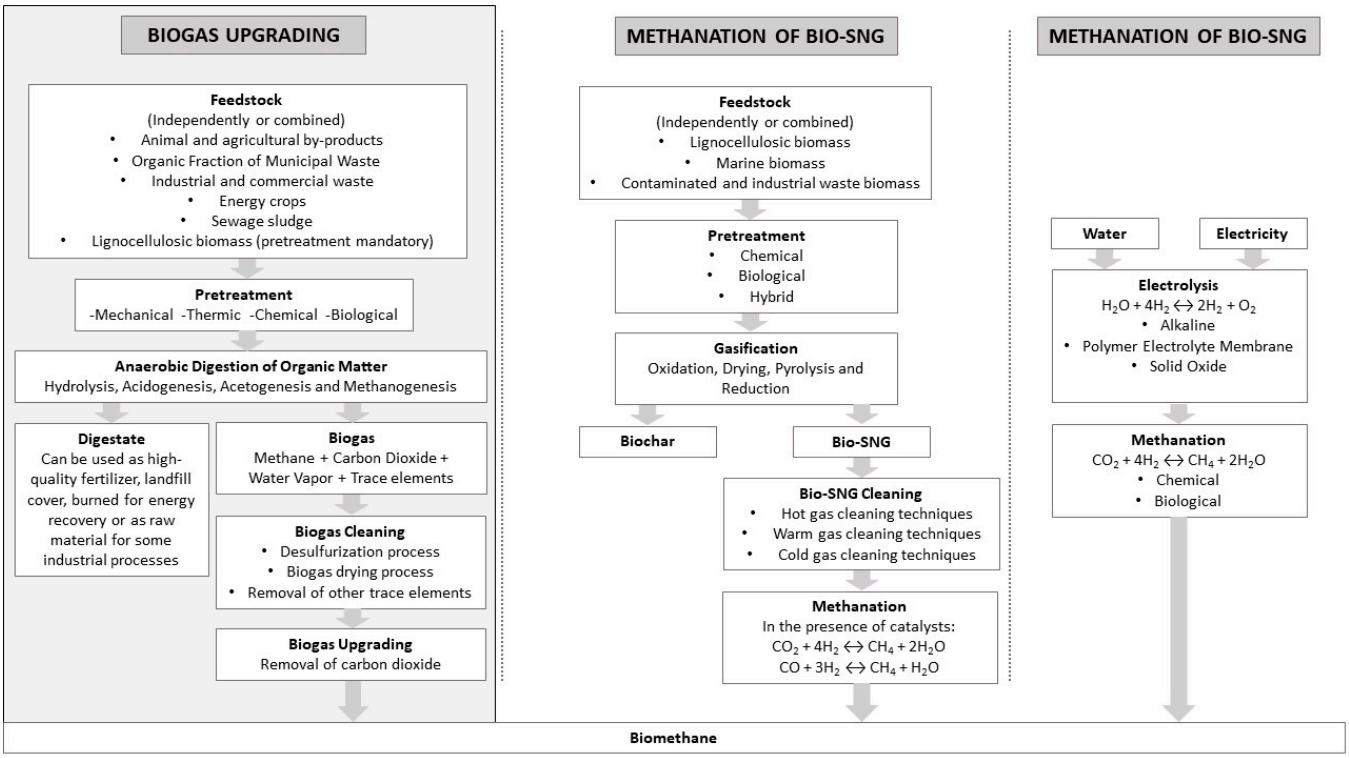

Figure 1. Biomethane production pathways [21,22,26–38].

Biogas production is increasing in Europe. As a result, the only established way of producing biomethane is via biogas upgrading (the two others are under development). Europe reached a total of 1322 biomethane-producing facilities by April 2023 [39] (Figure 2).

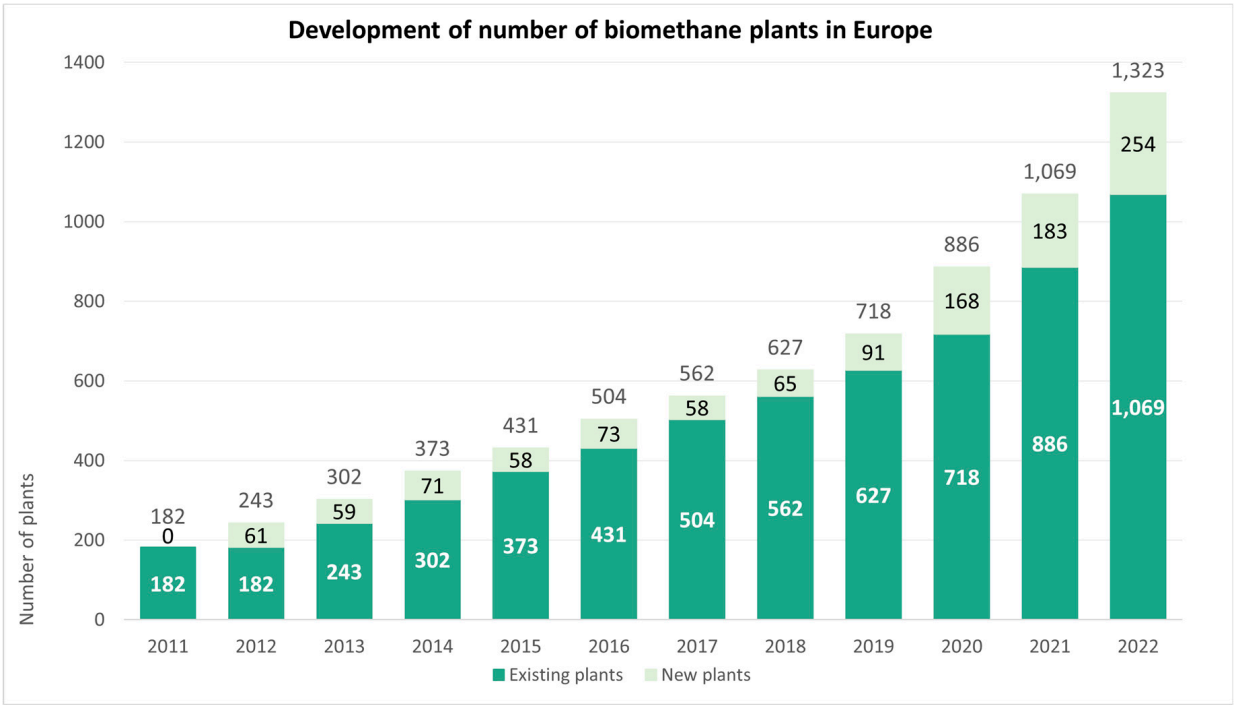

Figure 2. Development of number of biomethane plants in Europe. Adapted from EBA [39].

Combined biogas and biomethane production in 2021 amounted to 196 TWh of energy [8], and 2020 saw biomethane production in Europe of 31 TWh. This figure grew to 37 TWh in 2021, representing an increase of 20% [8]. Biomethane production doubled from 2018 to 2022 (Figure 3), with France, Italy, Denmark, and the UK being the fastest-growing countries [39].

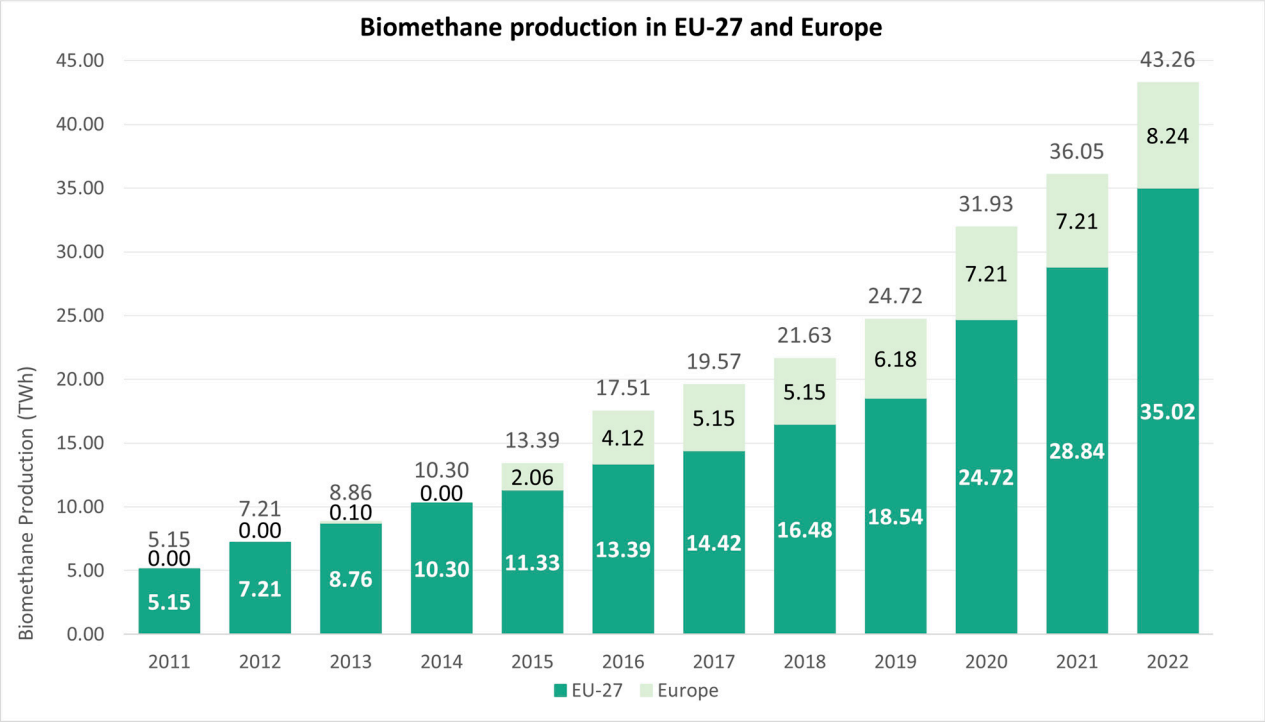

Figure 3. European biomethane production in EU-27 and Europe. Adapted from EBA [39].

By 2050, the annual consumption of biogases (biogas and biomethane) in the union is projected to increase to approximately between 628 TWh and 836 TWh, up from approximately 198 TWh in 2017 [17]. However, as shown in Table 1, the potential of biomethane production via biogas upgrading in Europe is higher than the current production. Furthermore, the International Energy Agency estimates that, if the full potential of biogas and biomethane were utilized, it could cover around 20% of the current global gas demand [40].

Table 1. Potential of biomethane production.

Biomethane Production Pathway	Production in 2020 (TWh/y)	Production in 2030 (TWh/y)	Production in 2050 (TWh/y)	Total Existing Potential (TWh/y)
Biogas upgrading	24.7–79.4 [1] [41] 510.67 [1,2,3] [42] 221.11–278.89 [1] [43]	148.3–369.4 [1] [41] 334.94–467.6 (1) [43]	1088.9 [1] [44]	865.6 [1,3] [42] 500 [1,4] [45]
Gasification with methanation	-	885 [1,5] [46]	-	-
PtM	-	5.9–13.9 [1] [41]	266.7 [1] [44]	-
Biogas upgrading and gasification with methanation	88.61 [1] [47]	200–222.2 [1] [47]	-	1521.4–2467.8 [1] [47]

[1] Converted to TWh according to [48]. [2] This is the total production accumulated between 2010 and 2020. [3] Considers only agriculture by-products and waste as feedstock. [4] Considers only waste as feedstock. [5] Does not consider the competition in the biomass market, biofuels, or new biochemical production pathways.

The EU's 2050 long-term strategy includes clear indications about the potential future role of low-carbon gaseous fuels in the EU energy system. It is projected that the share of NG in gaseous fuels will be reduced to 20% or less, with the majority of the remaining 80% of gaseous fuels being of renewable origin (i.e., hydrogen, biogas, biomethane, or synthetic methane) [24]. The upgrading of biogas is essential for using the excess gas as domestic and transportation fuel [20].

Amidst the current energy crisis, driven by conflicts, soaring prices, and energy dependence, biomethane emerges as an essential renewable energy source. Its rapid expansion highlights its importance in the European and global energy discourse, emphasizing the significance of this study in the current European context. The field of biogas enhancement technologies is vast and continually evolving, influenced by numerous factors. This comprehensive review aims to encompass a wide range of contributions to understand these technologies more thoroughly.

This work stands out in providing a comprehensive overview of advances in innovative enhancement technologies. The main objective is to examine and conduct an analysis of the recent advancements in physical, chemical, and biological biogas upgrading technologies, with a specific focus on processes for carbon dioxide removal and/or its conversion into methane. The currently available commercial technologies are also summarized. Furthermore, the review aims to provide a comprehensive overview of current biogas production processes and upgrading technologies in this field, thus discussing and evaluating different options to provide a basis for future studies.

2. Biogas Cleaning and Upgrading

Depending on the final utilization of biogas, its composition must be adjusted accordingly. It is necessary to clean and upgrade biogas when biomethane is desired. Cleaning and upgrading are usually carried out separately, but sometimes, they are accomplished simultaneously for certain pollutants.

H_2S is formed during the microbiological reduction of compounds that contain sulfur, and it can lead to corrosion problems [49]. The existing methods for H_2S removal are as follows: in situ precipitation [50], adsorption (using iron oxides/hydroxides or activated carbon) [51], physical and chemical absorption [51], membrane separation (MS) [50], biofiltration [51], in situ microaerobic removal [52], micro-algae-based removal [52], and the combined biological method [53]. The emerging technologies for H_2S removal are FlashH_2S [54] and a novel electrochemical process [55].

Oxygen and nitrogen are not detected in a properly conducted AD process [56]. The proportions of impurities vary, depending on the substrate and digestion conditions, and they are removed through adsorption or MS [50]. Water and ammonia are removed via gas cooling, compression, adsorption, or absorption [49]. Siloxanes and Volatile Methylsiloxanes (VMSs) are removed via commercially available techniques such as adsorption [57], absorption, or cryogenic separation (CS) [52], while biological methods are in the preliminary research stage [53]. Particles can be removed from biogas through mechanical filters (installed at the biogas outlet of the digester and before the biogas enters the upgrading unit) [40,49]. However, due to the humidity content of biogas, wet dedusting systems, such as electrostatic precipitators and wet scrubbers, are primarily employed for particle removal [58]. Halogenated compounds are usually removed simultaneously with CO_2 [59].

Biogas upgrading involves refining biogas by reducing or removing the CO_2 from biogas (although other compounds can be separated, too) to obtain biomethane with the needed quality for its utilization as a renewable substitute for NG [51]. The existing biogas upgrading technologies are divided into developed technologies that are commercially available and established and emerging technologies that are still at a laboratory or pilot scale. The processes used for biogas upgrading can be classified according to the separation methods: phase addition, a solid agent, a barrier, phase creation, and a force field or gradient [60].

3. Developed Biogas Upgrading Technologies

The developed technologies for biogas upgrading include adsorption, absorption (chemical and physical), MS, and CS (Figure 4) [61].

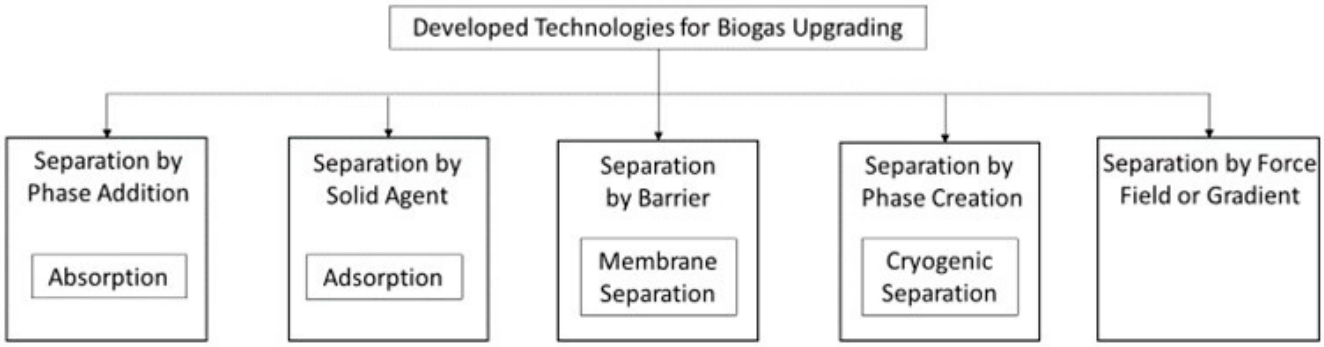

Figure 4. Developed technologies for biogas upgrading [60,61].

Adsorption technologies employ an adsorbent that selectively captures CO_2 from biogas, allowing methane to exit the system. According to how the adsorbent is regenerated, three different technologies exist: Pressure Swing Adsorption (PSA) (with Vacuum Swing Adsorption (VSA) being a special type), Temperature Swing Adsorption (TSA), and Electrical Swing Adsorption (ESA) [62].

Absorption technologies are divided into physical and chemical types [63]. Physical absorption is based on the different solubility values for the gases in a liquid solution [51]. There are two types: Water Scrubbing (WS) and Organic Physical Scrubbing (OPS). WS is the most-used technology for biogas upgrading [64]. In WS, the water absorbs the CO_2 since its solubility in water at 25 °C is 26 times higher than methane's [65]. WS is a simple process in comparison to other technologies. Its major drawback is a high water volume requirement [20]. In OPS, the scrubbing liquid is an organic solvent, such as methanol, N-methyl pyrrolidone [61], or dimethyl ethers of polyethylene glycol [66]. Their affinity for CO_2 and H_2S is five times higher than water's, requiring smaller flows of the scrubbing liquid compared to WS [67]. Chemical absorption (referred to as amine scrubbing directly by some authors) is similar to physical absorption, but there is a reversible chemical reaction between the absorbed substances and the solvent [68]. There are two types: amine scrubbing (AS) and inorganic solvent scrubbing (ISS), with ISS still in the developing phase.

MS takes advantage of membranes to separate the components of biogas, allowing the CO_2 to pass through while retaining the methane [69]. There are two types: gas–gas separation (gas phase on both sides of the membrane) and gas–liquid separation (a liquid absorbs the molecules that pass through) [51]. The fibrous membrane materials used in the gas separation technique can be categorized as inorganic membranes, polymeric membranes, and mixed-composition membranes [70]. The membranes used in biogas upgrading are high-cost, thus requiring research to optimize both the economy and efficiency of the process.

CS is the least established among the developed technologies, but since several facilities are in operation and it is commercially available, it cannot be considered an emerging technology. It consists of physically removing the CO_2 and other contaminants by taking advantage of their different condensation temperatures [71]. For the substances to be separated individually, cooling and compression are performed in different steps [72]. The main advantage of CS is the possibility of obtaining liquefied biomethane, which is equivalent to liquefied NG [51]. The frozen CO_2 generated during the upgrading process has industrial applications, and by liquefying the biomethane at 15 bars and −125 °C, energy consumption can be minimized [73]. However, the high cost of separating carbon dioxide remains a disadvantage compared to other techniques [74]. The raw biogas contains approximately 35% CO_2, which can be used to produce dry ice at a temperature of −78.5 °C. Dry ice is

an attractive alternative to conventional ice in many industrial applications, and it can generate additional revenue [20].

Some characteristics of each developed biogas upgrading technology are presented in Tables 2 and 3. CS is also included, but, since it is not as mature as the other technologies [75], its reported characteristics differ more among references, and a fair comparison cannot be assessed. There is not a single best technical solution valid for every case; each technology presents advantages and disadvantages. The selection of the upgrading technology must be site-specific and case-sensitive, depending on local circumstances and regulations [66].

Table 2. Comparison of developed biogas upgrading technologies. Note: OPS data from [65] are valid only for Genosorb solvent.

Characteristics	Adsorption	Absorption			MS	CS
	PSA	WS	OPS	AS		
Compounds that must be pre-removed	H_2S and H_2O [51,61,63,69]	H_2S (if the concentration is high) [61,63,65]	H_2S (recommended) [61,63]	H_2S (if the concentration is high) [61,63] O_2 [68]	H_2S and H_2O [61,63]	H_2S and H_2O [52,61]
Technology separates N_2 and O_2	Yes [51,54,66,69]	No [65,66]	Yes [61] No [65,66]	No [65,66]	Partly separates O_2 but not N_2 [65]	Possible if LBM is obtained [51,55]
Methane content in upgraded gas (%vol CH_4)	95–99 [54,61,63] >96 [69] 98 [52,76] 96–98 [77]	>97 [52,61] 95–99 [63] 95–98 [77]	>97 [61,65] 96–98.5 [51] 98 [52] 95–99 [63] 93–98 [77]	99 [61] 97–99 [66] >99 [52,63] >98 [77]	91 [61] 92 [78] 98 [51,65] 99 [54] 95–99 [63] 90–99 [77]	98 [61] 97–99 [54,66] >97 [52] 99 [77]
Water demand (dm^3/Nm^3 biogas) [65]	0	0.4–4	0	0.03	0	0
Heat demand (kWh/Nm^3 biogas)	0 [65,69,78]	0 [65,69,78]	<0.2 [78] 0.10–0.15 [69]	0.55 [65] 0.50–0.75 [78] 0.4–0.8 [69]	0 [65,69,78]	0 [69,78]
Electricity consumption (kWh/Nm^3 biogas)	0.15–0.30 [65] 0.23–0.30 [78] 0.16–0.35 [69] 0.16–0.43 [77]	0.20–0.30 [65,69] 0.3 [78] <0.25 [78] 0.2–0.5 [77]	0.20–0.29 [65] 0.2–0.3 [78] 0.23–0.33 [69] 0.10–0.33 [77]	0.12–0.14 [65] 0.10–0.15 [78] 0.06–0.17 [69] 0.05–0.18 [77]	0.20–0.30 [65] 0.18–0.21 [78] 0.18–0.35 [69,77]	0.20–0.28 [78] 0.72 [78] 1.05 [78] 0.18–0.25 [69,77] 0.4–1.0 [52]
Other consumables [65]	Lubricant oil for compressors	Anti-foaming agents (in some cases) and lubricant oil for compressors	Organic solvent addition once a year and lubricant oil for compressors	Anti-foaming agents, make-up of amine, and lubricant oil for compressors	Membrane replacement (5–10 years) and lubricant oil for compressors	Lubricant oil for compressors
Methane losses (%)	<2 [63,65] 2–4 [66] 10–12 [66] 1.5–10.0 [69] <3 [77]	<2 [52,54,61,77] 3–5 [66] 0.5–2 [69] 2 [63] 1 [65]	1–4 [65] <2 [51] <1 [52] <4 [63,66,77]	<0.1 [52,65,69] 0.04 [63] <0.5 [77] 4 [51]	<0.5 [54,65] 1–15 [69] <1 [52] 0.5–20 [63] <5 [77]	<1 [51,61] <2 [52,65] 0.1–2.0 [69] <0.1 [77]

Table 3. Comparison of developed upgrading technologies regarding capital expenditure (CAPEX), maintenance costs, availability, and number of working plants; 1 k USD = 810 €.

Parameters		PSA	WS	OPS	AS	MS	CS
Specific CAPEX for different flows (€/(Nm^3/h))	1000 Nm^3/h biogas	1750 [77] 1782 [61] 2000 [65,66]	1000 [77] 1620 [61] 1700 [65] 1800 [66]	1000 [77] 1944 [61] 2000 [65] 2200 [66]	2000 [77] 2106 [61] 2500 [65] 2400 [66]	1782 [61] 2000 [65,77] 1300–2400 [66]	-
	500 Nm^3/h biogas	2592 [61] 2800 [65] 2900 [66] 3700 [62]	2187 [61] 2700 [65] 2500 [66] 3500 [62]	3078 [61] 3300 [65] 3500 [62]	2916 [61] 3300 [66] 3500 [62]	2750 [65] 3500–3700 [62]	600 Nm^3/h: 2300 [66]
	250 Nm^3/h biogas	4455 [61] 5400 [62,66]	4000 [65] 5500 [62]	3890 [61] 4500 [65] 4400 [66] 5000 [62,66]	4455 [61] 5000 [62]	3000–3500 [65] 4700–4900 [62,66]	-
	100 Nm^3/h biogas	3000 [79]	5000 [66,79]	-	-	5000 [79] 6000 [52,66]	-
Maintenance costs (% of CAPEX) [65]		-	2–3	2–3	3	3–4	-
Maintenance costs for 1000 m^3/h biogas (m€/y) [61]		56	15	39	59	25	-
Availability (%)		94 [61,78] 94–96 [52]	96 [61,78] 95–96 [65]	96 [61,78] 96–98 [65]	91 [61,78] 96 [65]	98 [61,78] 95–98 [65]	-
Number of plants in Europe (2019) [80]		79	175 1 (WS + PSA)	17	103	173 1 (MS + PSA)	10 (MS + CS)

4. Emerging Biogas Upgrading Technologies

As stated, several upgrading units exist nowadays and are commercially established. However, there is still significant ongoing research concerning biogas upgrading technologies. Research focuses on developing unconventional upgrading techniques and improving mature technologies to reduce their capital and operational costs, increase efficiency, and decrease their associated environmental impact [51,61], especially for membranes and CS [52,81].

The emerging biogas upgrading technologies can be classified according to different separation methods. Apart from these, biological technologies for biogas upgrading are also being studied. They are not separation methods in the strict sense, as they do not yield two separated output flows; rather, they convert CO_2 into other valuable compounds. Also, a combination of different technologies is possible.

A proposal for the classification of emerging biogas upgrading technologies can be found in Figure 5.

4.1. Separation via Phase Addition

Separation via phase addition consists of introducing a second phase into the system that selectively dissolves some of the species from the mixture [60].

4.1.1. Inorganic Solvent Scrubbing

ISS is a type of chemical absorption still in the development phase for biogas upgrading, but it is mature for CO_2 capture and removal in post-combustion gas flows [68]. The used solvents are an aqueous solution of alkaline salts such as NaOH, KOH, $Ca(OH)_2$, and NH_4OH [61,68]. The main advantage of inorganic solvents compared to chemical absorption using amines is that they are usually cheaper and widely available [68,82]. Furthermore, NaOH and NH_4OH have a higher theoretical CO_2 capture capacity compared

to MEA [68,82]. KOH is more expensive than NaOH, but K_2CO_3 is formed, which is a compound with many industrial applications (e.g., the crystal industry, special glass production, potassium salts, inks and pigments, detergents, the food industry, and waste gas treatment) [68,83]. NH_4OH is less corrosive than MEA and requires less energy for its regeneration [82,84], but it is highly volatile, and some traces can be present in the upgraded gas [85].

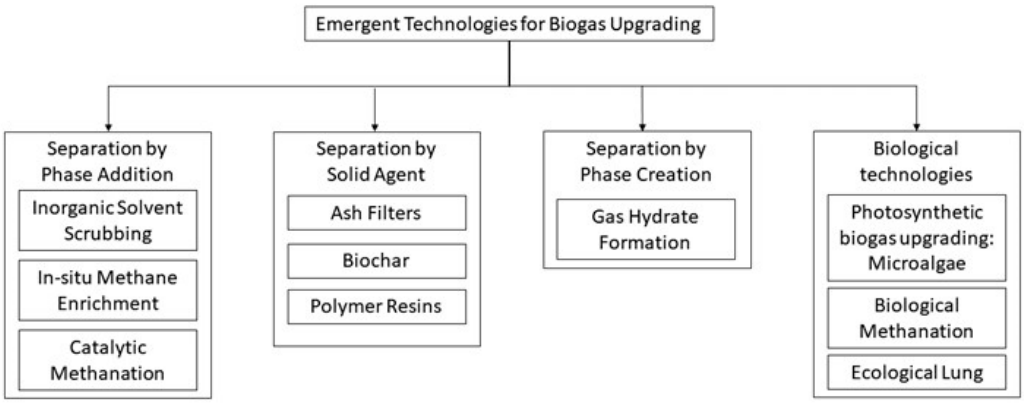

Figure 5. Classification of emerging biogas upgrading technologies.

The process includes, like regular chemical absorption, a first step in which the CO_2 from the biogas is chemically removed via the alkali compound in an absorption column. The chemical reactions with CO_2 for the alkali solvents are shown in Equations (1)–(4) [68,82]. Afterwards, regeneration or replacement of the solvent takes place.

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \quad (1)$$

$$2KOH + CO_2 \rightarrow K_2CO_3 + H_2O \quad (2)$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad (3)$$

$$NH_4OH + CO_2 \rightarrow (NH_4)\,HCO_3 \quad (4)$$

Table 4 summarizes the results from experiments conducted by different researchers (except for case 5, for which the data are theoretical concerning the concentration of the upgraded biogas but experimental for the other parameters). Although the obtained results indicate that alkali compounds could be effectively used for biogas upgrading or as a pretreatment for CO_2 removal, the critical point for their implementation is their poor regeneration [86]. The identified procedures for the regeneration of the described alkaline compounds are a thermic process, lime treating, and regeneration or carbon storage with waste material [68].

The thermic process consists of applying high temperatures to decompose the formed carbonate. During this process, CO_2 is released, and the sorbent is regenerated. For NaOH regeneration, the reaction that takes place is the inverse of Equation (1). The working temperature of this process is around 800 °C [87]. $Ca(OH)_2$ regeneration is described in Equations (6) and (7), and it is also the process used for solvent regeneration via lime treatment. NH_4OH regeneration can also be performed via heat addition with the advantage that it has lower energy requirements. In a CO_2 absorption process from combustion gases, J. T. Yeh et al. (2005) found a reduction of 62% in energy demand for ammonia regeneration compared to MEA [88].

Table 4. Experimental results for ISS biogas upgrading.

Solvent and Concentration	Apparatus	Operating Conditions	Biogas Composition (% Vol)	Product Purity (Highest CH_4, Lowest CO_2)	Loading Capacity (kg CO_2/kg Solvent Solution)	Comments	Case/ Reference
1.5 M NaOH	Glass cylinder (H = 54 cm; D = 5 cm)	Ambient T	65.79% CH_4 34.2% CO_2	96.23% CH_4 3.76% CO_2	0.29	Saturation after 12 min	1/[86] (lab-scale tests)
1.5 M KOH				92.1% CH_4 7.89% CO_2	0.18		
0.5 M $Ca(OH)_2$				85.99% CH_4 14% CO_2	0.36		
NH_4OH (10% aqueous sol.)				97.44% CH_4 2.55% CO_2	0.27		
12% vol NaOH	Packed column (H = 2 m; D = 0.1 m) Packing: plastic bioballs	p = 0.1 MPa T= 298 K Liquid flow: 72 kg/h Gas flow: 6 kg/h	59.8% CH_4 40.1% CO_2	85.9% CH_4 10.8% CO_2 3.3% H_2O	-	NH_4 scrubbing can be improved by adding a WS process afterwards to reduce NH_3 concentration	2/[85] (lab-scale tests)
5% vol NH_3				76.0% CH_4 8.9% CO_2 3.4% H_2O 7.2% NH_3			
10% NaOH	Packed column (H = 1.8 m; D = 0.3 m) Packing: polyethylene balls	p = 0.1 MPa T = 303 K	60.59% CH_4 36.03% CO_2	93.62% CH_4 2.05% CO_2	-	Saturation after 6 h and cleaning of the system for corrosion after 3 h	3/[72] (pilot-scale tests)
0.1 M NaOH	Glass cylinder (H = 1 m; D = 0.07 m) Packing: plastic bioballs	p = 0.1 MPa T = 303 K	53.1% CH_4 46.8% CO_2 2150 ppm H_2S	95.5% CH_4 3.2% CO_2 0 ppm H_2S	0.22	Saturation after 100 min	4/[89] (lab-scale tests)
0.1 M $Ca(OH)_2$				95.0% CH_4 4.0% CO_2 0 ppm H_2S	0.18	Saturation after 50 min	

Table 4. *Cont.*

Solvent and Concentration	Apparatus	Operating Conditions	Biogas Composition (% Vol)	Product Purity (Highest CH_4, Lowest CO_2)	Loading Capacity (kg CO_2/kg Solvent Solution)	Comments	Case/ Reference
Pig manure: 1 g NH_4+/L	Lab-scale stirrer bath	p = 0.1 Mpa T = 313 K	70% CH_4 30% CO_2	-	0.0031	Saturation after 15 min; fertilizer rich in N and C	5/[90] (lab-scale tests)
Effluent from a digester treating pig manure: 1.1 g NH_4+/L				87.5% CH_4 12.5% CO_2 (theoretical)	0.0045		
53% mass concentration KOH	Column filled with laboratory packing (H = 0.99 m; D = 0.08 m)	p = 0.1 Mpa T (KOH) = 313–318 K T (gas) = 288–293 K	60% CH_4 40% CO_2 (landfill gas)	97% CH_4 2% CO_2	-	-	6/[83] (pilot-scale tests)
0.2 M $Ca(OH)_2$	-	Biogas flow: 5 L/min Solution flow: 30 L/min	51% CH_4 39.36% CO_2 0.21% O_2 2940.61 ppm H_2S	89.3% CH_4	-	-	7/[91] (lab-scale tests)

The process of solvent regeneration through lime ($Ca(OH)_2$ solution) treatment is called causticization. The product from NaOH's reaction with CO_2 is Na_2CO_3 (Equation (1)), which can react with $Ca(OH)_2$, according to Equation (5). The solvent is regenerated and can be recirculated to the absorption column, but now $Ca(OH)_2$ has to be regenerated (Equations (6) and (7)). The formation of CaO and CO_2 from $CaCO_3$ occurs under high temperatures, making this process very energy-extensive, even higher than MEA regeneration [85]. Similar reactions for KOH, $Ca(OH)_2$, and NH_4OH regeneration take place [68,92]. Since raw lime production is environmentally costly (it releases CO_2), several efforts have been made to find other lime sources. It has been stated that waste material rich in calcium can regenerate the alkaline solvent or even permanently store CO_2 [68].

$$Na_2CO_3 + Ca(OH)_2 \rightleftharpoons 2NaOH + CaCO_3 \quad (5)$$

$$CaCO_3 \rightleftharpoons CaO + CO_2 \quad (6)$$

$$CaO + H_2O \rightleftharpoons Ca(OH)_2 \quad (7)$$

The regeneration of alkali compounds using waste material has been studied by Baciocchi and co-authors [93–95]. They have implemented a process through which NaOH and KOH are used for biogas upgrading, and regeneration is achieved with treated Air Pollution Control (APC) residues from Waste-to-Energy plants. These residues originate from cleaning flue gas before it is released to the atmosphere [96], and apart from calcium and potassium hydroxide, they also contain VOCs, dioxins, sulfates, and other contaminants; for this reason, they are considered a hazardous waste [97]. For CO_2 absorption, the reactions that take place are described in Equations (1) and (2). APC residues are rich in $Ca(OH)_2$, which reacts with Na_2CO_3 and K_2CO_3, as stated in Equation (5). After that, the alkali compound is recirculated to the absorption column, and $CaCO_3$ is removed as a solid. The main advantages of this regeneration process are that the captured CO_2 is permanently stored and that it is accomplished using waste material. The mentioned researchers have called this method Alkali Absorption with Regeneration (AwR).

Huang and co-authors have studied an innovative solution to regenerating ammonia for the capture of CO_2 in flue gases from combustion processes [82]. The method consists of using a weakly basic ion-exchange resin that contains amine-functional groups. This resin can regenerate, at ambient temperature, the ammonia from the ammonia carbonate, which is the compound that is formed during CO_2 absorption (Equation (4)). When the resin is saturated, it must be regenerated. This can be done via heating with water at a temperature of 50 °C or higher (higher efficiency is achieved at higher temperatures). Chemical formulas for ammonia and resin regeneration can be found in Equations (8) and (9), where *Ra* is the ion-exchange resin.

$$(NH_4)\,HCO_3 + Ra \rightleftharpoons Ra{\cdot}H_2CO_3 + NH_3 \quad (8)$$

$$Ra{\cdot}H_2CO_3 \rightleftharpoons Ra + CO_2 + H_2O \quad (9)$$

4.1.2. In Situ Methane Enrichment

In situ methane enrichment aims to increase methane's proportion in the biogas inside a digester. Although the first approach to this technology was performed more than 20 years ago, it is still under development at a pilot scale [66,98]. However, the limitations of this technology could be addressed by combining two or more methods to create a hybrid system [98]. Its main advantages are its lower CAPEX and operational expenditure (OPEX) compared to developed upgrading technologies [99].

It consists of continuously stripping CO_2 from digester sludge [99]. Since CO_2 is soluble in water, it is present in the liquid phase of the digester sludge. Sludge is circulated to a desorption column, where the CO_2 is desorbed, and the sludge is reconducted back to the digester. This causes a shift in the carbonic equilibrium in the digester towards the liquid phase, resulting in an increase in methane proportion in the biogas leaving the digester [49]. The desorption of CO_2 from the sludge can be achieved by pumping

a counter-flow of air or nitrogen to the sludge or applying a vacuum (0.4 bar) in the desorption column [66,100]. In some cases, organic acids can be added to the desorption column to enhance CO_2 removal [100]. In addition to CO_2, H_2S and NH_3 can also be removed with this technology [66,100].

The results and obtained biogas purity vary among the references, as different substrates lead to different results, and it is difficult to optimize the operation parameters (Table 5) [100]. The results of a simulation show that methane purity of 95% and methane losses of 2% can be achieved, but the obtained experimental results from the simulated facility show purity of 87% and losses of 8% [49,100]. The results obtained from another simulation with other characteristics show an increase in the methane concentration from 58% to 69% and methane losses of 1.3% [100]. The Swedish Institute of Agricultural and Environmental Engineering (*JTI*) has conducted further research and obtained other data for a pilot plant using manure as a substrate. The results show an increase from 60% to 81% of methane in the biogas, a reduction of H_2S from 1100–1500 ppm to 150–300 ppm, and methane losses of 1,8%. Also, nitrogen from the was reduced by 11–21% [101]. When using N_2 in the desorption step, values of 95% and 87% methane concentration have been obtained at the laboratory and pilot scales, respectively; however, methane losses of 8% have been reported [66]. These results show that, although in situ methane enrichment significantly increases the methane content of biogas, it does not reach sufficient purity. Therefore, it can be used as a pretreatment step or in combination with other upgrading technologies.

Table 5. Results from different experiments for in situ methane enrichment.

Substrate Type	Desorption Compound	Biogas Composition (%vol CH_4)	CH_4 in Upgraded Gas (%vol)	CH_4 Losses (%)	Comments	Case/Reference
Sludges	Air	-	87	8	-	1/[49] (best performance from different experiments)
Sewage sludge	Air	58	69	1.3	Low sludge flow rate and high gas flow rate lead to higher CH_4 concentration and lower CH_4 losses	2/[100] (computer simulations)
Nitrogen-rich substrate	Air	69	66	-	Bad performance due to ammonia inhibition and pH increase	3/[100] (lab-based platform)
	Vacuum (40 kPa)		63	-		
Substrate mixture with less N than 3/	Air	55	64	-	Addition of organic acids to air stripping may achieve better results	4/[100] (lab-based platform)
	Vacuum (40 kPa)	60	62	-		
	Vacuum (40 kPa) with organic acids	49	61	-		
Manure	-	60	81	1.8	H_2S reduction from 1100–1500 ppm to 150–300 ppm and reduction of nitrogen by 11–21%	5/[101] (pilot plant)
Chicken manure	Air	55	60–70	3.7–10.3	Up to 60% H_2S removal	6/[99] (lab-based platform)

4.1.3. Catalytic Methanation

Methanation consists of converting the CO_2 present in the biogas into methane by continuously adding H_2 to the process, thereby increasing carbon utilization [54]. There are two different types of methanation: catalytic and biological. They are based on the Sabatier reaction (Equation (10)), in which CO_2 reacts with H_2 to produce CH_4 [102] through a very exothermic reaction:

$$CO_2 + 4\,H_2 \rightleftharpoons CH_4 + 2H_2O \quad (10)$$

Catalysts that have been widely reported include noble metal-based catalysts and non-noble metal-based catalysts [103]. Ruthenium (Ru) is highly reactive for methanation, but its effectiveness and selectivity depend on the chosen support, the dispersion of metallic Ru on the support, and the inclusion of promoters that enhance Ru activity [104]. Nickel (Ni) is extensively investigated as a metal for CO_2 methanation, given its relatively high activity, outstanding CH_4 selectivity, and lower cost compared to noble metals [105] (catalyst at 250–350 °C and 10–20 bar) [79]. CO_2 can be separated from the CH_4 in raw biogas, but the latest research shows that feeding the reactor with pre-treated biogas (CH_4 and CO_2 after the removal of H_2S and other pollutants) allows better thermic control of the reactor [106].

Hydrogen is obtained via water electrolysis using surplus energy from renewable sources [52,78]. For this reason, water electrolysis to obtain hydrogen is studied as a form of energy storage because of the fluctuation in electricity production from renewable sources, creating a new technology called Power-to-Gas [75,102]. However, this process requires a high energy demand, while trace compounds from the biogas degenerate the catalyst, resulting in a need for periodical replacement, and the costs are high, especially those derived from hydrogen production [75,107]. There are several demonstration plants in Europe to prove the viability of the technology, and it is forecasted that catalytic methanation will be very interesting for biogas plants in the medium-term future [79].

Balzarotti et al. [108] prepared a $NiRh/CeO_2$ catalyst. This was tested in a simulated biogas methanation reaction, achieving CO_2 conversion values as high as 70%. The effect of the H_2/CO_2 molar ratio on the simulated biogas feed was evaluated, demonstrating that substoichiometric H_2/CO_2 molar ratios are suitable for obtaining high-quality upgraded biogas. CO_2 conversion ranged between 62.5 and 66.7% at a reaction temperature of 500–600 °C.

The carbon emissions associated with producing synthetic NG via the catalytic methanation of biogas were assessed [109]. This method is considered viable for a partial reduction of carbon emissions in gas network infrastructure. As a result, synthetic NG can facilitate the intermittent integration of renewable sources by enabling seasonal storage and offering a gas alternative with lower carbon emissions. The resulting gas from catalytic methanation may achieve high CH_4 content (up to 99%) with nearly 100% conversion of CO_2 [110].

4.2. Separation via a Solid Agent

In this method, a solid acts as an inert support for a layer of adsorbent, or it chemically reacts directly with certain compounds from the feed [60].

4.2.1. Ash Filters

Mineral carbonation is a process for CO_2 sequestration that happens spontaneously in nature [90]. In this process, CO_2 reacts with CaO and forms $CaCO_3$ [68], according to Equation (11). It is a slow process at ambient temperature and pressure, but the rate of reaction can be increased by running the process at the best liquid-to-solid ratio (the aqueous mineral carbonation of limestone) and by increasing both the temperature and the pressure [68]. This process is called accelerated carbonation:

$$CaO + CO_2 \rightleftharpoons CaCO_3. \quad (11)$$

New sustainable filter materials, such as ash filters, can also be used in biomethane technologies [111]. A source of calcium can be found in ash from different processes, and it can be used to react with the CO_2 present in raw biogas. Also, ash is rich in other compounds that can contribute to the separation of H_2S [90]. Andersson [112] used a wood ash filter and obtained a concentration of 0% for both CO_2 and H_2S in the outlet gas. The loading capacity of the ash was 0.1–0.2 g CO_2/g of dry ash. Another experiment using ash from mussel shell found a loading capacity of only 1.4 g CO_2/kg of ash and a saturation time of 30 min (defined as the time that the concentration of CO_2 in the outlet gas was below 5%), while ash from a biomass incineration plant had a capacity of 15.4 g CO_2/kg of ash and a saturation time of 300 min [90]. Mostbauer et al., [113] used bottom ash (BA) from municipal solid waste incineration (MSWI) for biogas upgrading. They called this process BABIU, standing for BA for Biogas Upgrading. The maximum obtained purity of the upgraded biogas, in a pilot-scale test, was 99% methane for an inlet concentration of 58%, obtaining a capacity of 13.9 kg CO_2/t of BA. Also, the content of H_2S decreased from 95 ppm in the inlet to 1.4 ppm. Capacity values of 23 kg CO_2/t of BA were obtained in a test with an inlet concentration of 54.7% methane and an outlet of 95% but using less BA than what was used to achieve the previous results [113]. Other wastes that have been studied as a source of calcium are fly ash from coal burning, slag from ground steel (derived from the steel manufacturing process, it is an industrial by-product that constitutes a calcium-rich waste material [114,115]), dust from a cement kiln, waste combustion residues, BA from municipal solid waste incinerator, and paper mill effluent [68]. Table 6 presents some results concerning the use of ash filters.

Table 6. Results of different experiments that upgrade biogas via ash filters.

Ash Filter Type	Biogas Composition (%Vol)	Upgraded Gas Composition (%vol)	Loading Capacity (kg CO_2/t Ash)	Comments	Case/Reference
BA from MSWI	58% CH_4 95 ppm H_2S	99% CH_4 1.4 ppm H_2S	13.9	This process is called BABIU (Bottom Ash for Biogas Upgrading)	1/[113] (pilot plant)
	54.7% CH_4	95% CH_4	23 (less BA than in the previous result)		
Ash from a biomass incineration plant	Gas rich in CO_2	-	15.4	Saturation time * of 300 min	2/[90] (lab-scale tests)
Mussel shell ash		-	1.4	Saturation time * of 30 min	3/[90] (lab-scale tests)
Wood chip ash	65% CH_4 35% CO_2	98% CH_4	0.14 (dry ash)	Two serial reactors utilize the ash's total CO_2 capacity; the pH of the ash (approx. 13) was reduced by 2–3 units	4/[116] (lab-scale tests)
Wood pellet ash		99% CH_4	0.2 (dry ash)		
Mixture of fly ash (10%) and BA (90%) from a biomass incineration plant	65% CH_4 35% CO_2 100–600 ppm H_2S	Almost 100% CH_4 and 0 ppm H_2S	35–135 (wet ash) 0.56–1.25 kg H_2S/t wet ash	Pure CH_4 was achieved for a few hours, while H_2S removal was longer-lasting	5/[117] (pilot plant)
Basic Oxygen Furnace (BOF) slags	68.4% CH_4 31.2% CO_2 250 ppm H_2S	95% CH_4 5% CO_2 <2 ppm H_2S	48	Saturation time * of 42 min and 300–350 kg of BOF to produce bio-compressed NG to fill up one vehicle	6/[118] (lab-scale tests)

* Saturation time is the time at which the concentration of CO_2 in the biomethane is below 5%.

4.2.2. Biochar

Biochar was recently proposed for its utilization in AD due to its capacity to improve the methane yield and increase methane content in biogas while reducing H_2S concentrations [119]. Moreover, biochar derived from biomass pyrolysis has been shown to enhance AD performance by providing microbial habitats, reinforcing buffering capabilities, and promoting bioelectrical connections between fermentative bacteria and methanogens [120]. The use of an appropriate amount of biochar reduces the lag phase, accelerating the AD process and improving methane production. CO_2 can be separated from CH_4 through adsorption, employing a porous solid with a high specific surface area. Biochar is considered a promising, environmentally friendly alternative in this context [121]. The high porosity and extensive specific surface area of biochar favor the effective capture of CO_2; likewise, the presence of a slightly alkaline pH facilitates the conversion of CO_2 into bicarbonate or carbonate [106]. Biochar is a pyrogenic material rich in carbon generated from carbon-neutral sources [122]. It can be obtained from several biomass feedstocks, and its effects will vary accordingly. Biogas extracted from sludge anaerobic digestion typically comprises 50–70% CH_4, 30–50% CO_2, and small quantities of H_2S, NH_3, siloxanes, H_2, N_2, and O_2. Utilizing biogas on-site for combined heat and power (CHP) generation necessitates purification and enhancement (e.g., removing CO_2, H_2S, water, and other impurities) to achieve high-quality biomethane suitable for pipeline distribution (with CH_4 content > 96% and a heating value > 37 MJ/m^3) [49]. Additionally, corn stover biochar serves as a supplementary nutrient source, offering calcium, magnesium, and iron for the anaerobic digestion process of sludge [49].

Some results are shown in Table 7. For example, a study performed by Shen et al. [123], using corn stover biochar inside a digester with WWTP sludge as its feedstock, obtained biomethane with a concentration of more than 90% methane and less than 5 ppb H_2S. When using pine biochar, methane content of up to 92.3% and 79% was obtained during AD at mesophilic and thermophilic temperatures, respectively; meanwhile, for white oak biochar, those values were 89.8% and 78.5% [119]. Biochar can also be used in a separated unit from a digester for H_2S removal; Sahota and co-authors used leaf waste biochar and obtained a reduction in H_2S concentration of 84% (from 1254 ppm to 201 ppm) [124]. An extra advantage of using biochar in a digester is that the obtained digestate is enriched with nutrients, such as K, Ca, Mg, Fe, and S (the concentration depends on the biochar and biogas feedstock) [119,123].

Table 7. Results of biochar utilization inside a biodigester.

Biochar Type	Biogas Composition (%Vol CH_4)	Case/(Reference)
Corn stover	90 <5 ppb H_2S	1/[123]
Pine	92.3 (mesophilic T) 79 (thermophilic T)	2/[119]
White oak	89.8 (mesophilic T) 78.5 (thermophilic T)	3/[119]
Walnut shell	77.5–98.1	4/[125]

4.2.3. Polymer Resins

Polymer resins are studied as a novel technique for upgrading biogas. The polymer resins used consist of beads of about 0.6 mm in diameter, which are functionalized with CO_2 selective groups and used in bulk [126]. The polymer resins are impregnated with amino functional groups, which selectively adsorb the CO_2 from the biogas [127]. For their regeneration, heat and/or a purge gas are used [126,128]. It is expected that this technique will entail reduced energy demand, lower CAPEX, and lower OPEX compared to conventional technologies [126]. Final methane concentrations of 98–99% were achieved with continuous lab-scale units [126,127].

Polymer resins with a higher capacity and lower adsorption enthalpies should be analyzed to achieve longer cycles and reduce energy demand [126].

4.3. Separation via Phase Creation

The separation via phase creation method consists of creating a second phase by transferring energy to or from the process or by reducing pressure.

Gas Hydrate Formation

Gas hydrate formation (also called clathrate hydrates of gases), as a novel technique for biogas upgrading, takes advantage of the capability of water to spontaneously organize itself around a gas molecule, forming a solid structure under certain conditions of temperature and pressure [129]. These "cages" are stabilized via the existing van der Waals forces between the water and the gas molecules [130]. Furthermore, it is possible to improve the hydrate formation rate using chemical additives (promoters), although they can reduce the hydrate's stability and the separation selectivity of the process [130,131].

Gas hydrates were discovered because they caused plugging problems in NG transport via pipelines [129]. NG hydrates are also very common on the sea floor, where NG finds adequate conditions for hydrate formation. It is estimated that the quantity of existing NG hydrates in nature is more than twice the reserve of the other fossil fuels [129]. The captured CO_2 and impurities can then be stored in geological deposits of NG hydrates (NGH), leading to an exchange of in situ CH_4 hydrate for a CO_2-dominated hydrate and a simultaneous release of CH_4 from these extensive natural energy deposits in permafrost sediments [132]. Thus, they can be considered an unconventional energy source [129]. The next step in gas hydrates' investigation focused on their applicability to gas storage and transport since they are safer and their formation occurs under mild temperature and pressure conditions, thus reducing the energy requirements of the process [131]. Lastly, efforts were made concerning their use for gas separation and purification [129]. It is also necessary to understand well the effects of associated gas impurities, such as SO_2 (from landfill gas), H_2S, N_2, and H_2, in hydrate-based biogas purification [132].

For biogas upgrading, two different methods using gas hydrates (a clathrate compound, which is an ice-like solid that consists of methane that is trapped within the crystal structure of water; it has the formula of $CO_2 \cdot 5.75H_2O$ or $4CH_4 \cdot 23H_2O$ [133]) have been described: carbon dioxide hydrates and biogas hydrates [129]. The first consists of forming CO_2 hydrates selectively from biogas. This is possible since CO_2 forms hydrates at lighter conditions than methane [129]. Also, H_2S is removed simultaneously with CO_2. This way, the upgraded biogas is obtained, and then the hydrate phase is dissociated to recover CO_2 [130]. The second method, biogas hydrates, forms hydrates of CO_2 and methane, and then it releases the components selectively: first the CO_2 and then methane [129]. This process requires more energy than forming only CO_2 hydrates, but the external energy required can be minimized using proper process integration [129]. H_2S cannot be removed with this method since it will remain trapped along with the methane, so its pre-removal is highly recommended. This can be used, in addition to biogas upgrading, for biomethane storage, as gas hydrates are characterized by high storage capacity. Theoretically, a given volume of gas hydrates contains more than 150 times the same volume of gas at a standard temperature and atmospheric pressure [134].

The results obtained from different experiments are summarized in Table 8. The collected data correspond to the experiment with better results for each reference. The upgraded biogas does not reach enough purity with this method, so it can be used as a pretreatment step or in combination with other upgrading technologies. Apart from not reaching high methane concentrations, the methane losses are high [66]. However, research is still ongoing regarding hydrate formation selectivity, multi-stage hydrate production in order to reach higher purities, the reduction of methane losses, and decreasing energy consumption [51,130].

Table 8. Experimental results for biogas upgrading via hydrate formation.

Method	Operating Conditions		Promoter	Biogas Composition (%vol)	CH_4 in Upgraded Gas (%Vol)	CO_2 in Upgraded Gas (%Vol)	Case/ (Reference)
	T (K)	*p* (MPa)					
CO_2 hydrates	278.15	6	SDS 300 ppm	60% CH_4 40% CO_2	70	30	1/[130] (up-scaled apparatus)
CO_2 hydrates	275.1	4.5		55% CH_4, 37.5% CO_2, 5% N_2, 2% O_2, 0.5% H_2	70.1	22.4	2/[135] (up-scaled apparatus)

4.4. Biological Technologies

Biological technologies' purpose is to convert the CO_2 in biogas into methane through methods that employ microorganisms or algae biomass. The biological removal of CO_2 from biogas is still in an early stage of research, with hydrogenotrophic CO_2 reduction to CH_4 and photosynthetic CO_2 assimilation being the two most promising technologies under scale-up [136]. Hydrogen generation involves using energy for electrolysis, and most biochemical systems for CO_2 removal rely on adding hydrogen to the biogas in order to enhance methane production.

4.4.1. Photosynthetic Biogas Upgrading: Microalgae

Photosynthetic biogas upgrading takes advantage of the ability of microalgae to bioconvert CO_2, in the presence of water, light, and nutrients, into algae biomass, oxygen, and heat [75]. The process is called oxygenic photosynthesis, and it is described in Equation (12) [52].

$$CO_2 + H_2O + \text{photons} + \text{nutrients} \rightarrow O_2 + CH_{1.63}N_{0.14}O_{0.43}P_{0.006}S_{0.005} + \text{waste heat} \quad (12)$$

The main advantages of this process are that wastewater or residual nutrients from an anaerobic digester can be used as the source of nutrients for microalgae, enabling the integration of biogas upgrading with wastewater treatment and reducing the eutrophication potential of AD. The process is held at ambient temperature and has a low demand for reagents, which means a reduction in operational costs compared to other technologies. The CO_2 from the biogas is not released into the atmosphere. Additionally, in the process, apart from upgraded biogas, microalgae biomass is obtained, which can be used as feedstock for the production of biofuels [52,90]. The potential methane recovery through the photoautotrophic biogas upgrading process is 97%, with the simultaneous removal of H_2S [70]. Eukaryotic microalgae and prokaryotic cyanobacteria remove CO_2 from the raw biogas using water, nutrients, and solar radiation. The removal of VMSs, VFAs, and siloxanes from biogas could eventually be carried out through biotechnologies since they are biodegradable molecules, which would support a priori a better environmental and economic performance [137]. Among biological methods, the photosynthetic removal of H_2S is attracting significant attention due to its simultaneous occurrence during CO_2 capture in algal–bacterial photobioreactors, which will drastically reduce the operational cost of biogas enhancement. Other biotechnology for removing H_2S includes biotrickling filtration [136]. Moreover, the biological disposal of H_2S does not require the use of chemicals and has a lower cost. Wastewater or digestate from an anaerobic digester can be used as a source of nutrients for microalgae.

The most-used microalgae species are *Chlorella*, *Arthrospira*, and *Spirulina* [52]. They can be used in closed or open photobioreactors [75]. Closed systems achieve higher photosynthetic performance and lower land and water needs, but their investment costs and energy demand are higher. On the other hand, open photobioreactors have lower

investment and operational costs, but their photosynthetic performance is poorer, and they need more water and land.

A process of biological biogas upgrading, like any other biological process, requires that the biogas components are not inhibitors or toxic to the biological microorganisms (in this case, microalgae) [138]. Methane is the main component of biogas, and according to Meier et al. [138], the same species can reduce their growth rates when exposed to biogas containing 80% methane. CO_2 is the other major component of biogas, and it has been found that high concentrations of this gas may have inhibitory consequences. Traditionally, concentrations of 5% of CO_2 were considered inhibitory for microalgae growth, but the research carried out for the treatment of flue gases has led to the discovery of species that can tolerate CO_2 concentrations of up to 60% [52]. The presence of H_2S can inhibit microalgae growth. However, the presence of H_2S-oxidizing bacteria and the chemical oxidation of H_2S that takes place in the photobioreactor (operating at high dissolved oxygen concentrations under non-sterile conditions) result in the oxidation of H_2S into sulfate, which presents no inhibitory effects on microalgae [52].

The fixation of CO_2 results in the release of oxygen, impacting the ultimate gas quality [75]. In the process, 1 mol of oxygen is produced for each mol of captured CO_2 [139]. If the biogas is directly injected into a closed photobioreactor, oxygen will be released into the biogas, achieving high concentrations (5–25%) [52]. Mixtures of oxygen and methane may be explosive; for this reason, its concentration must be diminished. Furthermore, most standards for biomethane quality require a concentration of oxygen lower than 1% [139]. In Spain, the oxygen content in biomethane for grid injection must be lower than 0.3 mol% (if it complies with certain specifications; if not, the maximum oxygen content is 0.01 mol%) [140]. Thus, efforts have been made to decouple oxygen desorption from CO_2 capture. An alternative is to separate the process into two stages, consisting of biogas scrubbing in an external column that is interconnected with the photobioreactor via variable microalgae broth recycling. Using the two-stage method, concentrations of oxygen below 1% have been achieved, and methane losses have been estimated to be <1% because of the low aqueous solubility of methane [52]. Mass transfer and the solubility of CO_2 in microalgae culture media are a limitation [141]. So is the high methane loss due to its solubility in a large volume of microalgae culture media and the difficulty of collecting the final biogas. The lack of microalgal species tolerant to elevated CO_2 and the introduction of oxygen from microalgal photosynthesis into the final biogas are also challenges [20].

Different species and configurations obtain different compositions of the upgraded gas. For example, *Chlorella* sp. *MB-9*, *Arthrospira platensis*, and *Spirulina platensis* obtained methane concentrations of up to 90%, 82%, and 74% with CO_2 assimilation of 85%, 100%, and 86%, respectively [75]. H_2S can be removed via this upgrading method.

Through the symbiosis of microalgae and fungi, an improvement in biogas was also demonstrated, with a CO_2 removal rate of 61.08% using *G. lucidum*/*C. vulgaris* pellets. Additionally, the use of vitamin B12 significantly enhanced the photosynthetic performance of the pellets [142]. These findings contribute to advancing the development and application of symbiotic systems, particularly in wastewater treatment and biogas enhancement [143].

4.4.2. Biological Methanation

In biological hydrogen methanation (BHM), the catalysts are autotrophic hydrogenotrophic methanogens, and the process takes place with no additional energy requirement [61]. These bacteria already exist in every AD plant, so it is only necessary to provide them with the needed H_2 [102]. The BHM process uses the Sabatier reaction, catalyzed via specific archaea of the Methanothermobacter genus, which is capable of converting H_2 and CO_2 into CH_4 with water as a by-product [144].

Methanogens can operate under either mesophilic or thermophilic conditions within the pH range of 6.5–8. To render the process renewable, the hydrogen required for the enhancement of raw biogas must also be derived from renewable energy sources through water electrolysis to produce hydrogen [75].

BHM can be achieved in three different ways: in situ, ex situ, and hybrid upgrade technology [102]. In situ technology consists of feeding hydrogen directly into a digester (Figure 6a), while ex situ upgrade technology involves CO_2 from external sources that is introduced together with hydrogen into a reactor containing hydrogenotrophic methanogens (Figure 6b). Finally, hybrid upgrade technology consists of a combination of both in situ and ex situ biogas upgrading in order to optimize the process [61]. It allows part of the CO_2 conversion to take place during the initial AD process, with the final step being a purification process [106]. Under optimal pH and temperature conditions, approximately 99% of potential methane can be recovered through an in situ process. Ex situ methanation is more similar to the biological PtM production pathway, but it can be used together with other technologies to convert the separated CO_2 from the biogas into more methane, thus increasing the carbon utilization of the facility. An example of a technology combination is the use of a dual-membrane aerated biofilm reactor (dMBfR), as H_2-assisted ex situ biogas upgrading is hindered by a large solubility discrepancy between H_2 and CO_2. dMBfR enables a precise supply of CO_2 and H_2, making it an ideal combination for efficient biological biogas upgrading [145]. In situ biogas upgrading showed superior performance compared to ex situ biogas upgrading. BHM may require a significant amount of energy due to the processes necessary for the effective solubilization of H_2, allowing its absorption via archaea. An appropriate method for H_2 solubilization in liquid is agitation, but this option entails a high energy demand [144]. Opting for a low-energy-demand alternative would offer greater benefits. However, at a larger scale, employing intense agitation for enhanced H_2 solubilization could be reasonable. There are different reactor systems, such as continuously stirred tank reactors, diffusion-based reactors, fixed-film bioreactors, minimal-liquid bioreactors, soil-based fixed-film reactors, and hollow-fiber reactors [144].

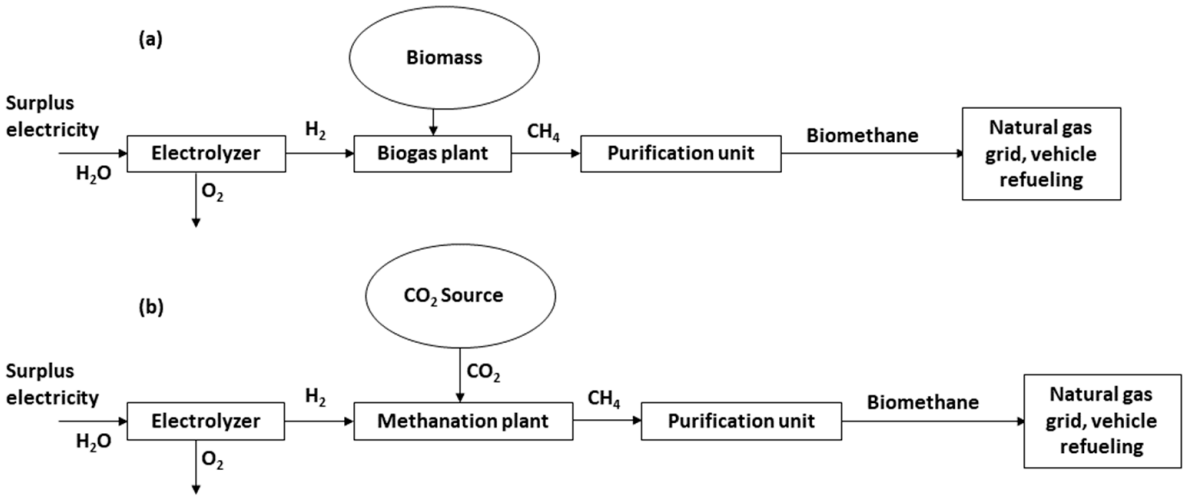

Figure 6. (**a**) In situ and (**b**) ex situ biological hydrogen methanation. Adapted from [102].

BHM is still at a pilot stage [102], but there is already one upgrading plant that injects biomethane into the gas grid that uses this method; it is located in Switzerland and has been in operation since 2019, providing biomethane with 96% CH_4 [80]. Pilot-scale experiments show that methane content of 95% in biogas has been achieved with a continuous injection of H_2 into the biogas reactor [66]. At a laboratory scale, in situ methanation under thermophilic operation (65 °C) not only obtained a methane concentration of 90%, but a content of 98% under mesophilic conditions (37 °C) has also been achieved [54]. Concentrations of 99% methane have also been reported [75]. For ex situ methanation, the final methane content can be between 79 and 98%, depending on the type of reactor used [75]. Furthermore, methanogens can even remove part of the H_2S present in raw biogas [52].

4.4.3. Ecological Lung

The enzyme carbonic anhydrase (CA) is present in human blood, and it catalyzes the dissolution of CO_2 formed during metabolism in the cells [49,78]. Once the dissolved CO_2 reaches the lungs in the form of carbonate, the same enzyme catalyzes the reverse reaction (Equation (13)) [49].

$$H_2O + CO_2 \rightleftharpoons H+ + HCO_3. \quad (13)$$

Thus, the potential of the enzyme to dissolve CO_2 from biogas and obtain higher concentrations of methane through a process named ecological lung or industrial lung has been identified. This technology aims to mineralize carbon dioxide using CA, an enzyme present in nearly all vertebrate organisms. In 2005, a research group achieved purity of 99% methane using an immobilized CA enzyme for biogas upgrading [146]. The production cost of the enzyme remains high, and the viability of the process is affected by factors such as the lifetime of the immobilized enzyme [147].

The reaction rate of CA catalysis is much faster than the rate at which CO_2 is combined with chemically absorbing molecules such as amines [148]. Enzyme immobilization can broaden the applications of natural catalysts by enhancing the catalytic stability of enzymes [149].

Fosbøl et al. [150] conducted a study of rate-based modeling for biogas upgrading by applying reactivated slow tertiary amines to reduce energy consumption. This was achieved using CA enzymes as additives in the slow-reacting solvent.

In 2014, a Canadian company announced the development of a high-performance CA enzyme [151]. The enzyme can be used to catalyze scrubbing processes of carbon capture using salt solutions as solvents, with the potential to reuse the sequestrated CO_2. The obtained CO_2 absorption kinetics are similar to those of amine solutions, with the advantage that regeneration is achieved at temperatures below 80 °C. The advantages are lower capital and operational costs compared to AS and the generation of high-purity CO_2 suitable for reuse applications [151].

5. Discussion and Future Perspectives

Biogas and biomethane are promising forms of renewable energy derived from readily available raw materials. They generate clean and sustainable energy within the context of a circular economy [152]. Over the last two decades, research has focused on new and more efficient technologies to enhance sustainability and decrease operating costs, which are crucial for small-scale AD units. Current commercial technologies for biogas upgrading are proven to be effective in providing high-quality biomethane, but they are energy- and resource-intensive, and in some cases, captured CO_2 is released back into the environment.

Currently, technological advancements have led to the development of more cost-effective and efficient plants due to the increasing interest in biogas upgrading. The demand for additional plants has also spurred the development of standardized upgrading units, further reducing costs [147]. New approaches developed within the framework of the European Green Deal, such as the EU Methane Strategy [17], the Energy System Integration Strategy [153], and the "From Farm to Fork Strategy" [154], emphasize the importance of biogas [33]. In this context, biogas is a promising source of sustainable energy, and it demonstrates the potential to replace fossil fuel-based energy sources.

5.1. Process Complexity

Some biogas upgrading technologies still require significant improvements before they can be commercialized. Technological limitations vary among methodologies. For example, regarding WS technology, a challenge to address is determining the biogas production yield under thermophilic conditions, as studies have predominantly been conducted under psychrophilic and mesophilic conditions until now [155].

"In-situ enrichment" is a suitable technology for biogas produced in AD plants but not for landfill biogas. The principle is based on aqueous CO_2 equilibrium [156]. Indeed, dissolved CO_2 in the sludge is desorbed in a bubbled column. Methane enrichment is obtained because CO_2–free sludge can re-adsorb CO_2 from biogas in digester headspace. But some difficulties have been found in laboratory tests, mainly due to pH variations that may disrupt the anaerobic process (e.g., ammonia inhibition), and such performance has not been significant. Furthermore, other studies have demonstrated a positive effect of CO_2 on AD. Bajón Fernández et al. [157] have shown the capacity of AD to transform the additional CO_2 injected into a laboratory-scale digester into methane. They concluded that their findings could result in the on-site valorization of concentrated CO_2 streams to potentially increase methane production.

As an "in-situ enrichment", the utilization of "biochar" is only suitable for AD plants. In recent years, biochar has been attracting increasing interest as an additive in AD, and many studies have shown that biochar improves methanogenesis in the AD process. As a result, the methane production rate is significantly enhanced [158,159]. Biochar can act as a support for cell immobilization and microbial growth (promoting the formation of a biofilm on biochar) [160]. It is also an electron conductor that can stimulate direct interspecies electron transfer (DIET) [159], and it improves the buffering capacity [161], etc. Research is still currently very active. The main drawback is that biochar is not a commercial product (the biochar market does not exist) [162], and consequently, industrialization would be not possible. Also, other additives for AD are being studied, such as nutrient complementation [163], ash [164], nanoparticles [165], iron salts [166], magnetite-doped activated carbon [167], etc.

Polymer resins have not been investigated enough. Studies such as those by Ding and Jiang [168] demonstrate that research efforts continue towards the synthesis of highly porous polymers for the capture and conversion of CO_2 on a laboratory scale.

In recent years, research has also been interested in CO_2 capture via clathrate hydrate formation [169]. Gas hydrate technology is a very attractive technology, but up to now, its separation efficiency has remained limited, and further research is needed.

Ecological or industrial lung (also called "Biomineralization", "Enzymatic Carbon Dioxide Capture", or merely "Carbonic Anhydrase") is an example of biomimicry. Current research efforts are directed at Carbon Capture and Storage (CCS), but findings can be applied to biogas upgrading. Indeed, this enzyme could be used to improve gas separation efficiency in membranes [170] or amine scrubbers [149]. Nevertheless, more research needs to be conducted to overcome several technical barriers (the identification and characterization of supports for CA immobilization, the characterization of new and different CAs, the design of continuously operating reactors, media regeneration, et cetera) and achieve a cost-effective biomimetic technology [171–173].

Ash filter technology is suitable for small-scale AD plants and landfill biogas. Therefore, this technology is probably the easiest to industrialize of all emerging technologies presented herein. However, a significant disadvantage is that ash from the same source but different origins can have different chemical compositions, affecting its melting point and making the results of the produced filter material inconsistent [111].

Methanation (catalytic or biological) is the most interesting and promising technology because it is the only one whose main objective is the valorization of CO_2. Biogas upgrading through the utilization of carbon dioxide, rather than its removal, is a suitable strategy in this direction. Trace pollutants from the biogas are potential catalyst poisons, resulting in a need for more periodical replacement compared to biological methanation, which exhibits a good tolerance of impurities. This approach faces technical problems because of the limited solubility of H_2 in water. It is expected that, with the development of hydrogen, methanation will undergo an important improvement [174]. Therefore, improving and developing catalysts with high activity, CH_4 selectivity, and stability, as well as a long lifespan, is one of the key areas of intense research [104].

5.2. Environmental Challenges

For biogas upgrading technologies, ensuring environmental sustainability often relies on various factors, such as resource efficiency, emission types, associated risks, and more. For example, thermal decomposition is well on track to recover the used solvent. The utilization of waste streams is presented as an environmentally friendly alternative to recovering a solvent via a chemical reaction. The development of new solvents is mainly focused on improving energy efficiency [175]. The innovative separation of CO_2 from biogas through adsorption and desorption using polymeric resins has the potential to reduce the energy demand; however, it needs to be tested over the long term in a biogas plant before implementation. It has been proven that many of the less-expensive technologies for biogas upgrading are quite inefficient [176].

Sustainable waste management, including waste prevention and reduction, has become a priority to reduce pollution and greenhouse gas emissions [177]. The application of biochar presents certain advantages, such as not requiring recovery after its usage; furthermore, biochar production helps enhance waste management [178]. It improves the quality of digestate and contributes to soil fertility improvement [179]. However, there are still no studies that comprehensively explain the role of biochar in biogas generation. Most studies describe the production of biochar from different sources. Ash utilization is an example of waste valorization, resource efficiency, and circular economy.

The utilization of bacterial and algal fermentation to remove CO_2 is the most environmentally friendly process, but biological processes are complex. The technique using microalgae can be employed simultaneously for wastewater treatment, as well as biogas upgrading, as an environmentally friendly process [106].

Other studies emphasize the environmental benefits of methanation in freight transport, highlighting the direct methanation of biogas as a more sustainable way to utilize biogenic CO_2 as a carbon source for biomethane synthesis. However, other environmental impact categories should also be considered [180].

5.3. Economic Challenges

Due to the high operating costs associated with biogas upgrading, improvement technologies face significant economic challenges. Most studies indicate that upgrading technologies are expensive when it comes to commercialization. Therefore, they focus on reducing operational costs. WS is currently the most-applied technology due to its low capital and operation costs. However, MS has undergone the highest growth in recent years [20].

Absorption is a common process for capturing CO_2 in industry, and several solvents are available (amines, sodium hydroxide, aqueous ammonia, ionic liquids, hot potassium carbonate, etc.). The solvent regeneration step is a classic example of a costly process that consumes high amounts of energy and may jeopardize the economic viability of biomethane facilities [175]. Therefore, most research in this area has focused on alkali solvents' regeneration. Indeed, alkali solvents are usually cheaper than other solvents such as amines, but their poor regeneration limits their deployment. Hence, the challenge lies in being able to regenerate and recycle the reactive solvent.

Other studies have focused on waste as a raw material to produce low-cost solvents, which allows higher carbon utilization. For instance, Kim et al. [181] investigated human urine to produce an "original" solvent for biogas upgrading. In any case, economic evaluations are required to identify the comparative cost-effectiveness of these alternatives versus the existing ones (namely pressurized WS and amine-based absorption amine scrubbing, which are the most widespread technologies for biogas upgrading).

Several effects of biochar additions and other additives on the AD process have been reported in the literature; the material addition to AD might complement conventional upgrading technologies to reduce operational costs. Another technology that might complement conventional technologies and significantly reduce operational costs is the utilization of ash as a CO_2 sorbent in a fixed-bed adsorption column.

Currently, methanation is not economically viable; however, the prospect of feasibility is anticipated in the future when a system with a significant proportion of intermittent renewables becomes available. The direct methanation of biogas poses both a challenge and an opportunity by avoiding the CO_2 separation step, which is crucial for economic sustainability. While CO_2 methanation has advanced in catalyst development, the process design still needs adjustments for economic viability and adaptations to smaller decentralized plants [110]. Although the direct methanation of biogas with adiabatic and cooled reactors can produce SNG, the technical design and applications are highly relevant in terms of their costs compared to methanation. The total cost of SNG remains high, but it is very sensitive to the prices of biogas and electricity [182]. The cost and wear of the catalyst, reactor cooling, and post-treatment costs are still being analyzed in theoretical studies and early demonstration plants [107].

Biological technologies rely on the availability of hydrogen, which can be obtained through electrolysis. Although they are in a developmental stage, a substantial cost reduction is expected with the availability of standardized electrolyzers [106].

5.4. Future Research Prospects

Biogas upgrading technologies require numerous improvements, as they still constitute an emerging field that needs further investigation. Future research should focus on reducing costs and enhancing the efficiency of these technologies to address economic and environmental challenges. PtM offers a valuable opportunity to store surplus renewable energy in the NG grid, thereby enhancing energy security. While industrial-scale tests and ongoing process optimization are currently underway, further investigations are necessary to substantiate and refine the viability of this innovative technology.

The primary determinant of the implementation of a given technology will be the capital expenditure cost. These technologies have the potential to enhance the economic performance of biogas plants and, more broadly, the renewable energy sector, thereby bolstering energy security. Predicting the dominant technology in biogas upgrading is challenging, as it heavily relies on capital and operational expenditure costs, as well as incentives mandated by energy grid providers and governmental decisions. At present, these technologies are not sufficiently mature to replace traditional ones. Nevertheless, considering them as "complementary technologies" for use in pretreatment steps to support conventional technologies holds the potential for reducing operational costs. Future research and innovations must also guarantee the enduring viability of the processes.

6. Conclusions

This review has provided an update on the latest research, summarizing recent progress in biogas upgrading technologies to help achieve sustainable development, increase energy security, and achieve the GHG reduction goals aligned with EU targets.

Biomethane, generated through the cleaning and upgrading of biogas, has the potential to serve as a renewable alternative to NG without requiring modifications to existing infrastructure. This untapped energy resource could play a significant role in the EU's energy transition.

Emerging biogas upgrading technologies that are currently being researched and are in pilot phases show promise for future sustainable energy production. Though some proven and widely used technologies exist, the ongoing efforts aim to address technical and economic challenges, highlighting the need for innovative solutions in this field. Biological biogas upgrading, with its potential for an increased methane yield, lower energy requirements, and the avoidance of costly chemicals, is a key player. PtM technology emerges as a particularly promising avenue.

Author Contributions: Conceptualization, T.L.R. and P.M.B.B.; methodology, T.L.R., M.G.M. and P.M.B.B.; software, A.F.L.; validation, A.F.L., S.F.A. and P.M.B.B.; formal analysis, A.F.L., T.L.R., M.G.M., S.F.A. and P.M.B.B.; investigation, T.L.R., M.G.M., A.F.L., S.F.A. and P.M.B.B.; resources, A.F.L., T.L.R., M.G.M. and P.M.B.B.; data curation, T.L.R., M.G.M. and P.M.B.B.; writing—original draft preparation, T.L.R., M.G.M., A.F.L. and P.M.B.B.; writing—review and editing, A.F.L., S.F.A. and P.M.B.B.; visualization, A.F.L. and T.L.R.; supervision, M.G.M., S.F.A. and P.M.B.B.; project administration, P.M.B.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

AD: anaerobic digestion: APC: Air Pollution Control; AS: amine scrubbing; AwR: Alkali Absorption with Regeneration; BA: bottom ash; BABIU: Bottom Ash for Biogas Upgrading; BHM: biological hydrogen methanation; BOF: Basic Oxygen Furnace; CA: carbonic anhydrase; CAPEX: capital expenditure; CS: cryogenic separation; dMBfR: dual-membrane aerated biofilm reactor; EBA: European Biogas Association; EU: European Union; GHG: greenhouse gas; ISS: inorganic solvent scrubbing; LBM: liquefied biomethane; MEA: monoethanolamide; MS: membrane separation; MSWI: municipal solid waste incineration; NG: natural gas; OFMW: Organic Fraction of Municipal Waste; OPEX: operational expenditure; OPS: Organic Physical Scrubbing; PSA: Pressure Swing Adsorption; PtM: Power-to-Methane; SDS: sodium dodecyl sulfate; SNG: synthetic natural gas; TSA: Temperature Swing Adsorption; VMSs: Volatile Methylsiloxanes; VOCs: Volatile Organic Compounds; VSA: Vacuum Swing Adsorption; WS: Water Scrubbing; WWTP: Wastewater Treatment Plant.

References

1. Communication from the Commission to the European Parliament, the European Council, the Council, the European Economic and Social Committee, and the Committee of the Regions. A Green Deal Industrial Plan for the Net-Zero Age. Available online: https://commission.europa.eu/strategy-and-policy/priorities-2019-2024/european-green-deal/green-deal-industrial-plan_en (accessed on 20 December 2023).
2. Communication from the Commission to the European Parliament, the European Council, the Council, the European Economic and Social Committee, and the Committee of the Regions. The European Green Deal. Available online: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=COM:2019:640:FIN (accessed on 18 November 2023).
3. European Commission. *EU Energy in Figures—Statistical Pocketbook 2023*; Publications Office of the European Union: Luxembourg, 2023.
4. Communication from the Commission to the European Parliament and the Council. European Energy Security Strategy. Available online: https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:52014DC0330 (accessed on 20 September 2023).
5. European Environment Agency. A Framework Strategy for a Resilient Energy Union with a Forward-Looking Climate Change Policy. Available online: https://www.eea.europa.eu/policy-documents/com-2015-80-final (accessed on 20 September 2023).
6. European Commission. Green Paper on the Security of Energy Supply. Available online: https://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=LEGISSUM:l27037 (accessed on 20 September 2023).
7. IEA (International Energy Agency). Russia's War on Ukraine. Available online: https://www.iea.org/topics/russias-war-on-ukraine (accessed on 14 February 2024).
8. European Biogas Association. EBA Statistical Report 2022. Available online: https://www.europeanbiogas.eu/SR-2022/EBA (accessed on 12 December 2023).
9. Communication from the Commission to the European Parliament, the European Council, the Council, the European Economic and Social Committee, and the Committee of the Regions. REPowerEU Plan. Available online: https://commission.europa.eu/strategy-and-policy/priorities-2019-2024/european-green-deal/repowereu-affordable-secure-and-sustainable-energy-europe_es (accessed on 20 December 2023).
10. European Commission. Climate Strategies and Targets 2018. Available online: https://ec.europa.eu/clima/policies/strategies_en (accessed on 26 September 2023).

11. Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions: Energy 2020—A Strategy for Competitive, Sustainable and Secure Energy. Available online: https://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=LEGISSUM:en0024 (accessed on 20 December 2023).
12. El País Economía. Available online: https://elpais.com/economia/2018/05/04/actualidad/1525444638_932682.html (accessed on 26 May 2023).
13. Perez, A. *La Trampa Global Del Gas. Un Puente al Desastre*, 1st ed.; Rosa Luxemburg Stiftung; ODG: Brussels, Belgium, 2017.
14. Kollamthodi, S.; Norris, J.; Dun, C.; Brannigan, C.; Twisse, F.; Biedka, M.; Bates, J. *The Role of Natural Gas and Biomethane in the Transport Sector*; Ricardo Energy & Environment: Harwell Oxford, UK, 2016.
15. European Commission. Methane Emissions. Available online: https://energy.ec.europa.eu/topics/oil-gas-and-coal/methane-emissions_en (accessed on 13 February 2024).
16. Financial Times. Available online: https://www.ft.com/content/2cce7954-7587-11e8-b326-75a27d27ea5f (accessed on 15 June 2023).
17. Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions on an EU Strategy to Reduce Methane Emissions. Available online: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:52020DC0663 (accessed on 26 November 2023).
18. Appels, L.; Baeyens, J.; Degrève, J.; Dewil, R. Principles and Potential of the Anaerobic Digestion of Waste-Activated Sludge. *Prog. Energy Combust. Sci.* **2008**, *34*, 755–781. [CrossRef]
19. Martín-Hernández, E.; Guerras, L.S.; Martín, M. Optimal Technology Selection for the Biogas Upgrading to Biomethane. *J. Clean. Prod.* **2020**, *267*, 122032. [CrossRef]
20. Nguyen, L.N.; Kumar, J.; Vu, M.T.; Mohammed, J.A.H.; Pathak, N.; Commault, A.S.; Sutherland, D.; Zdarta, J.; Tyagi, V.K.; Nghiem, L.D. Biomethane Production from Anaerobic Co-Digestion at Wastewater Treatment Plants: A Critical Review on Development and Innovations in Biogas Upgrading Techniques. *Sci. Total Environ.* **2021**, *765*, 142753. [CrossRef] [PubMed]
21. Duic, N.; Cajner, F.; Puksec, T. *Factsheets on Current Biogas/Biomethane Handling Practices*; University of Zagreb: Zagreb, Croatia, 2016.
22. IRENA (International Renewable Energy Agency). Biogas for Road Vehicles: Technology Brief. Available online: https://www.irena.org/publications/2017/Mar/Biogas-for-road-vehicles-Technology-brief (accessed on 15 November 2023).
23. European Commission. Mandate to CEN for Standards for Biomethane for Use in Transport and Injection in Natural Gas Pipelines 2010. Available online: https://law.resource.org/pub/eu/mandates/m475.pdf (accessed on 20 September 2023).
24. European Commission. Assistance to Assessing Options Improving Market Conditions for Bio-Methane and Gas Market Rules. Available online: https://op.europa.eu/en/publication-detail/-/publication/d24343db-5ee8-11ec-9c6c-01aa75ed71a1/language-en (accessed on 28 December 2023).
25. European Biogas Association (EBA). Six National Biomethane Registries Are Developing the Foundation for Cross-Border Biomethane Trade in Europe. Available online: https://www.europeanbiogas.eu/six-national-biomethane-registries-developing-foundation-cross-border-biomethane-trade-europe/ (accessed on 26 October 2023).
26. Álvarez Rodríguez, J. La Co-Digestión Anaerobia Como Un Sistema de Producción Energética. In *Biocombustibles Retos y Oportunidades*; Lema Rodicio, J.M., Bello Bugallo, P.M., Eds.; USC: Santiago de Compostela, Spain, 2009; ISBN 978-84-613-46-721.
27. Achinas, S.; Achinas, V.; Euverink, G.J.W. A Technological Overview of Biogas Production from Biowaste. *Engineering* **2017**, *3*, 299–307. [CrossRef]
28. Ariunbaatar, J.; Panico, A.; Esposito, G.; Pirozzi, F.; Lens, P.N.L. Pretreatment Methods to Enhance Anaerobic Digestion of Organic Solid Waste. *Appl. Energy* **2014**, *123*, 143–156. [CrossRef]
29. van Lier, J.B.; Mahmoud, N.; Zeeman, G. *Anaerobic Wastewater Treatment*; IWA Publishing: London, UK, 2008.
30. Angelidaki, I.; Xie, L.; Luo, G.; Zhang, Y.; Oechsner, H.; Lemmer, A.; Munoz, R.; Kougias, P.G. Biogas Upgrading: Current and Emerging Technologies. In *Biofuels: Alternative Feedstocks and Conversion Processes for the Production of Liquid and Gaseous Biofuels*; Elsevier: Amsterdam, The Netherlands, 2019; pp. 817–843.
31. Sikarwar, V.S.; Zhao, M.; Fennell, P.S.; Shah, N.; Anthony, E.J. Progress in Biofuel Production from Gasification. *Prog. Energy Combust. Sci.* **2017**, *61*, 189–248. [CrossRef]
32. Rajendran, K.; Drielak, E.; Sudarshan Varma, V.; Muthusamy, S.; Kumar, G. Updates on the Pretreatment of Lignocellulosic Feedstocks for Bioenergy Production—A Review. *Biomass Convers. Biorefin* **2018**, *8*, 471–483. [CrossRef]
33. Molino, A.; Chianese, S.; Musmarra, D. Biomass Gasification Technology: The State of the Art Overview. *J. Energy Chem.* **2016**, *25*, 10–25. [CrossRef]
34. Woolcock, P.J.; Brown, R.C. A Review of Cleaning Technologies for Biomass-Derived Syngas. *Biomass Bioenergy* **2013**, *52*, 54–84. [CrossRef]
35. Le, T.A.; Kim, M.S.; Lee, S.H.; Kim, T.W.; Park, E.D. CO and CO_2 Methanation over Supported Ni Catalysts. *Catal. Today* **2017**, *293–294*, 89–96. [CrossRef]
36. Götz, M.; Lefebvre, J.; Mörs, F.; McDaniel Koch, A.; Graf, F.; Bajohr, S.; Reimert, R.; Kolb, T. Renewable Power-to-Gas: A Technological and Economic Review. *Renew. Energy* **2016**, *85*, 1371–1390. [CrossRef]
37. Mazza, A.; Bompard, E.; Chicco, G. Applications of Power to Gas Technologies in Emerging Electrical Systems. *Renew. Sustain. Energy Rev.* **2018**, *92*, 794–806. [CrossRef]
38. Ghaib, K.; Ben-Fares, F.-Z. Power-to-Methane: A State-of-the-Art Review. *Renew. Sustain. Energy Rev.* **2018**, *81*, 433–446. [CrossRef]

39. EBA. Statistical Report of the European Biogas Association 2023. Available online: https://www.europeanbiogas.eu/eba-statistical-report-2023/ (accessed on 12 February 2024).
40. Redexis Foundation. Available online: https://fundacion.redexis.es/assets/docs/Redexis-BIOMETANO_23062022.pdf (accessed on 16 February 2024).
41. The European Network of Transmission System Operators for Gas (ENTSOG). Ten Years Network Development Plan. Scenario Report. Annex II: Methodology. Available online: https://www.entsog.eu/tyndp#entsog-ten-year-network-development-plan-2018 (accessed on 20 December 2023).
42. AEBIOM. A Biogas Road Map for Europe. Brussels: 2009. Available online: https://www.big-east.eu/downloads/Brochure_BiogasRoadmap_WEB[1].pdf (accessed on 3 September 2023).
43. Kampman, B.; Leguijt, C.; Scholten, T.; Tallat-Kelpsaite, J.; Brückmann, R.; Maroulis, G.; Lesschen, J.P.; Meesters, K.; Sikirica, N.; Elbersen, B. *Optimal Use of Biogas from Waste Streams: An Assessment of the Potential of Biogas from Digestion in the EU Beyond 2020*; European Commission: Brussels, Belgium, 2017.
44. EBA. How Gas Can Help to Achievethe Paris Agreement Target in an Affordable Way. Available online: https://www.europeanbiogas.eu/how-gas-can-help-to-achievethe-paris-agreement-target-in-an-affordable-way/ (accessed on 20 September 2023).
45. Svensson, M. Biomethane for Transport Applications. In *The Biogas Handbook*; Elsevier: Amsterdam, The Netherlands, 2013; pp. 428–443.
46. Statistical Report of the European Biogas Association 2018. Available online: https://www.europeanbiogas.eu/eba-statistical-report-2018/ (accessed on 3 September 2023).
47. Green Gas Grids. Proposal for a European Biomethane Roadmap. Available online: https://www.europeanbiogas.eu/green-gas-grids-project-proposal-european-biomethane-roadmap/ (accessed on 22 October 2023).
48. International Energy Agency. *Natural Gas Information*; International Energy Agency: Paris, France, 2018.
49. Petersson, A.; Wellinger, A. *Biogas Upgrading Technologies—Developments and Innovations*; IEA Bioenergy: Paris, France, 2010.
50. Ryckebosch, E.; Drouillon, M.; Vervaeren, H. Techniques for Transformation of Biogas to Biomethane. *Biomass Bioenergy* **2011**, *35*, 1633–1645. [CrossRef]
51. Awe, O.W.; Zhao, Y.; Nzihou, A.; Minh, D.P.; Lyczko, N. A Review of Biogas Utilisation, Purification and Upgrading Technologies. *Waste Biomass Valoriz.* **2017**, *8*, 267–283. [CrossRef]
52. Muñoz, R.; Meier, L.; Diaz, I.; Jeison, D. A Review on the State-of-the-Art of Physical/Chemical and Biological Technologies for Biogas Upgrading. *Rev. Environ. Sci. Biotechnol.* **2015**, *14*, 727–759. [CrossRef]
53. Gaj, K.; Cichuta, K. Combined Biological Method for Simultaneous Removal of Hydrogen Sulphide and Volatile Methylsiloxanes from Biogas. *Energies* **2022**, *16*, 100. [CrossRef]
54. Miltner, M.; Makaruk, A.; Harasek, M. Review on Available Biogas Upgrading Technologies and Innovations towards Advanced Solutions. *J. Clean. Prod.* **2017**, *161*, 1329–1337. [CrossRef]
55. Linders, M.; Latsuzbaia, R.; Van Heck, R.; Goetheer, E. A Novel Electrochemical Process for H_2S Removal from Biogas. In Proceedings of the 5th International Conference on Renewable Energy Gas Technology, Tolouse, France, 3–4 May 2018.
56. Atelge, M.R.; Senol, H.; Djaafri, M.; Hansu, T.A.; Krisa, D.; Atabani, A.; Eskicioglu, C.; Muratçobanoğlu, H.; Unalan, S.; Kalloum, S.; et al. A Critical Overview of the State-of-the-Art Methods for Biogas Purification and Utilization Processes. *Sustainability* **2021**, *13*, 11515. [CrossRef]
57. Gaj, K. Adsorptive Biogas Purification from Siloxanes—A Critical Review. *Energies* **2020**, *13*, 2605. [CrossRef]
58. Singh, R.; Shukla, A. A Review on Methods of Flue Gas Cleaning from Combustion of Biomass. *Renew. Sustain. Energy Rev.* **2014**, *29*, 854–864. [CrossRef]
59. Petersson, A. Biogas Cleaning. In *The Biogas Handbook*; Elsevier: Amsterdam, The Netherlands, 2013; pp. 329–341.
60. Seader, J.D.; Henley, E.J. *Separation Process Principles*, 2nd ed.; Wiley: Hoboken, NJ, USA, 2006; ISBN 978-0471464808.
61. Ullah Khan, I.; Hafiz Dzarfan Othman, M.; Hashim, H.; Matsuura, T.; Ismail, A.F.; Rezaei-DashtArzhandi, M.; Wan Azelee, I. Biogas as a Renewable Energy Fuel—A Review of Biogas Upgrading, Utilisation and Storage. *Energy Convers. Manag.* **2017**, *150*, 277–294. [CrossRef]
62. Chen, X.Y.; Vinh-Thang, H.; Ramirez, A.A.; Rodrigue, D.; Kaliaguine, S. Membrane Gas Separation Technologies for Biogas Upgrading. *RSC Adv.* **2015**, *5*, 24399–24448. [CrossRef]
63. Aile, N. *Biogas to Biomethane Technology Review*; Vienna University of Technology: Vienna, Austria, 2012.
64. Kadam, R.; Panwar, N.L. Recent Advancement in Biogas Enrichment and Its Applications. *Renew. Sustain. Energy Rev.* **2017**, *73*, 892–903. [CrossRef]
65. Bauer, F.; Hulteberg, C.P.; Persson, T.; Tamm, D. *Biogas Upgrading—Review of Commercial Technologies*; Lund University: Lund, Sweden, 2013.
66. Sun, Q.; Li, H.; Yan, J.; Liu, L.; Yu, Z.; Yu, X. Selection of Appropriate Biogas Upgrading Technology—A Review of Biogas Cleaning, Upgrading and Utilisation. *Renew. Sustain. Energy Rev.* **2015**, *51*, 521–532. [CrossRef]
67. Zhou, K.; Chaemchuen, S.; Verpoort, F. Alternative Materials in Technologies for Biogas Upgrading via CO_2 Capture. *Renew. Sustain. Energy Rev.* **2017**, *79*, 1414–1441. [CrossRef]
68. Abdeen, F.R.H.; Mel, M.; Jami, M.S.; Ihsan, S.I.; Ismail, A.F. A Review of Chemical Absorption of Carbon Dioxide for Biogas Upgrading. *Chin. J. Chem. Eng.* **2016**, *24*, 693–702. [CrossRef]

69. Beil, M.; Beyrich, W. Biogas Upgrading to Biomethane. In *The Biogas Handbook*; Elsevier: Amsterdam, The Netherlands, 2013; pp. 342–377.
70. Scholz, M.; Frank, B.; Stockmeier, F.; Falß, S.; Wessling, M. Techno-Economic Analysis of Hybrid Processes for Biogas Upgrading. *Ind. Eng. Chem. Res.* **2013**, *52*, 16929–16938. [CrossRef]
71. Yang, L.; Ge, X. Biogas and Syngas Upgrading. *Adv. Bioenergy* **2016**, *1*, 125–188.
72. Zhao, Q.; Leonhardt, E.; MacConnell, C.; Frear, C.; Chen, S. Purification Technologies for Biogas Generated by Anaerobic Digestion. CSANR Research Report 2010-001. In *Climate Friendly Farming*; Compressed Biomethane; Washington State University: Wenatchee, WA, USA, 2010; Chapter 9; pp. 1–24.
73. Esposito, E.; Dellamuzia, L.; Moretti, U.; Fuoco, A.; Giorno, L.; Jansen, J.C. Simultaneous Production of Biomethane and Food Grade CO_2 from Biogas: An Industrial Case Study. *Energy Environ. Sci.* **2019**, *12*, 281–289. [CrossRef]
74. Baena-Moreno, F.M.; Rodríguez-Galán, M.; Vega, F.; Vilches, L.F.; Navarrete, B.; Zhang, Z. Biogas Upgrading by Cryogenic Techniques. *Environ. Chem. Lett.* **2019**, *17*, 1251–1261. [CrossRef]
75. Angelidaki, I.; Treu, L.; Tsapekos, P.; Luo, G.; Campanaro, S.; Wenzel, H.; Kougias, P.G. Biogas Upgrading and Utilization: Current Status and Perspectives. *Biotechnol. Adv.* **2018**, *36*, 452–466. [CrossRef] [PubMed]
76. Niesner, J.; Jecha, D.; Stehlik, P. Biogas Upgrading Technologies: State of Art Review in European Region. *Chem. Eng. Trans.* **2013**, *35*, 517–522. [CrossRef]
77. Sahota, S.; Shah, G.; Ghosh, P.; Kapoor, R.; Sengupta, S.; Singh, P.; Vijay, V.; Sahay, A.; Vijay, V.K.; Thakur, I.S. Review of Trends in Biogas Upgradation Technologies and Future Perspectives. *Bioresour. Technol. Rep.* **2018**, *1*, 79–88. [CrossRef]
78. Bailón Allegue, L.; Hinge, J. *Biogas and Bio-Syngas Upgrading*; Danish Technological Institute: Aarhus, Denmark, 2012.
79. Blom, H.; Mccann, M.; Westman, J. *Small-Scale Upgrading and Refinement of Biogas*; Poeyry SwedPower AB: Stockholm, Sweden, 2012.
80. International Energy Agency. Biogas Upgrading Plants List. Available online: https://www.iea.org/reports/outlook-for-biogas-and-biomethane-prospects-for-organic-growth/an-introduction-to-biogas-and-biomethane (accessed on 22 September 2023).
81. Yang, L.; Ge, X.; Wan, C.; Yu, F.; Li, Y. Progress and Perspectives in Converting Biogas to Transportation Fuels. *Renew. Sustain. Energy Rev.* **2014**, *40*, 1133–1152. [CrossRef]
82. Huang, H.; Chang, S.-G.; Dorchak, T. Method to Regenerate Ammonia for the Capture of Carbon Dioxide. *Energy Fuels* **2002**, *16*, 904–910. [CrossRef]
83. Lombardia, L.; Corti, A.; Carnevale, E.; Baciocchi, R.; Zingaretti, D. Carbon Dioxide Removal and Capture for Landfill Gas Up-Grading. *Energy Procedia* **2011**, *4*, 465–472. [CrossRef]
84. McLeod, A.; Jefferson, B.; McAdam, E.J. Biogas Upgrading by Chemical Absorption Using Ammonia Rich Absorbents Derived from Wastewater. *Water Res.* **2014**, *67*, 175–186. [CrossRef]
85. Abdeen, F.R.H.; Mel, M.; Jami, M.S.; Ihsan, S.I.; Ismail, A.F. Improvement of Biogas Upgrading Process using Chemical Absorption at Ambient Conditions. *J. Teknol.* **2017**, *80*, 1. [CrossRef]
86. Ahmad, F.; Khan, S.; Gupta, N. Application of Alkaline Chemicals for Biogas Methane Enrichment. *Ecol. Environ. Conserv.* **2016**, *22*, 983–992.
87. Siriwardane, R.V.; Robinson, C.; Shen, M.; Simonyi, T. Novel Regenerable Sodium-Based Sorbents for CO_2 Capture at Warm Gas Temperatures. *Energy Fuels* **2007**, *21*, 2088–2097. [CrossRef]
88. Yeh, J.T.; Resnik, K.P.; Rygle, K.; Pennline, H.W. Semi-Batch Absorption and Regeneration Studies for CO_2 Capture by Aqueous Ammonia. *Fuel Process. Technol.* **2005**, *86*, 1533–1546. [CrossRef]
89. Tippayawong, N.; Thanompongchart, P. Biogas Quality Upgrade by Simultaneous Removal of CO_2 and H_2S in a Packed Column Reactor. *Energy* **2010**, *35*, 4531–4535. [CrossRef]
90. Unidad Mixta de Movilidad Sostenible. El Gas Natural y El Biometano Como Combustible Para Movilidad Marítima y Agraria. Available online: https://energylab.es/listado/unidad-mixta-movilidad-sostenible/ (accessed on 20 May 2023).
91. Srichat, A.; Suntivarakorn, R.; Kamwilaisak, K. A Development of Biogas Purification System Using Calcium Hydroxide and Amine Solution. *Energy Procedia* **2017**, *138*, 441–445. [CrossRef]
92. Hsueh, H.T.; Chien, T.W.; Ko, T.H.; Huang, T.T.; Chu, H. The Regeneration of Ammonia Solution by Calcium Hydroxide for Carbon Dioxide Absorption from the Flue Gas. *Glob. Environ. Eng.* **2015**, *2*, 23–28. [CrossRef]
93. Baciocchi, R.; Carnevale, E.; Costa, G.; Lombardi, L.; Olivieri, T.; Paradisi, A.; Zanchi, L.; Zingaretti, D. Pilot-Scale Investigation of an Innovative Process for Biogas Upgrading with CO_2 Capture and Storage. *Energy Procedia* **2013**, *37*, 6026–6034. [CrossRef]
94. Baciocchi, R.; Carnevale, E.; Corti, A.; Costa, G.; Lombardi, L.; Olivieri, T.; Zanchi, L.; Zingaretti, D. Innovative Process for Biogas Upgrading with CO_2 Storage: Results from Pilot Plant Operation. *Biomass Bioenergy* **2013**, *53*, 128–137. [CrossRef]
95. Baciocchi, R.; Carnevale, E.; Costa, G.; Gavasci, R.; Lombardi, L.; Olivieri, T.; Zanchi, L.; Zingaretti, D. Performance of a Biogas Upgrading Process Based on Alkali Absorption with Regeneration Using Air Pollution Control Residues. *Waste Manag.* **2013**, *33*, 2694–2705. [CrossRef] [PubMed]
96. Astrup, T.F. *Management of APC Residues from W-t-E Plants. An Overview of Management Options and Treatment Methods*; ISWA General Secretariat: Rotterdam, The Netherlands, 2008.
97. UK Essays. Air Pollution Control Residues. Available online: https://www.ukessays.com/essays/engineering/air-pollution-control-residues.php?cref=1 (accessed on 26 May 2023).

98. Yellezuome, D.; Zhu, X.; Liu, X.; Liu, X.; Liu, R.; Wang, Z.; Li, Y.; Sun, C.; Hemida Abd-Alla, M.; Rasmey, A.-H.M. Integration of Two-Stage Anaerobic Digestion Process with in Situ Biogas Upgrading. *Bioresour. Technol.* **2023**, *369*, 128475. [CrossRef]
99. Boontawee, S.; Koonaphapdeelert, S. In-Situ Biomethane Enrichment by Recirculation of Biogas Channel Digester Effluent Using Gas Stripping Column. *Energy Procedia* **2016**, *89*, 78–84. [CrossRef]
100. Hansson, M.; Laurell, J.; Nordberg, Å.; Rasmuson, Å.C.; Liu, J.; Nistor, M.F.; Strömberg, S.; Costa, J. *In-Situ Methane Enrichment of Raw Biogas in the Anaerobic Digestion Process*; Svenskt Gastekniskt Center AB: Malmö, Sweden, 2013.
101. Andersson, J.; Olsson, H.; Ascue, J.; Rogstrand, G.; Edström, M.; Nordberg, Å. *In-Situ Methane Enrichment during Anaerobic Digestion of Manure—Pilot Scale Tests*; Report 50; Swedish Institute of Agricultural and Environmental Engineering: Uppsala, Sweden, 2014.
102. Lecker, B.; Illi, L.; Lemmer, A.; Oechsner, H. Biological Hydrogen Methanation—A Review. *Bioresour. Technol.* **2017**, *245*, 1220–1228. [CrossRef]
103. Memon, M.; Jiang, Y.; Hassan, M.; Ajmal, M.; Wang, H.; Liu, Y. Heterogeneous Catalysts for Carbon Dioxide Methanation: A View on Catalytic Performance. *Catalysts* **2023**, *13*, 1514. [CrossRef]
104. Tan, C.H.; Nomanbhay, S.; Shamsuddin, A.H.; Park, Y.-K.; Hernández-Cocoletzi, H.; Show, P.L. Current Developments in Catalytic Methanation of Carbon Dioxide—A Review. *Front. Energy Res.* **2022**, *9*, 795423. [CrossRef]
105. Rönsch, S.; Schneider, J.; Matthischke, S.; Schlüter, M.; Götz, M.; Lefebvre, J.; Prabhakaran, P.; Bajohr, S. Review on Methanation—From Fundamentals to Current Projects. *Fuel* **2016**, *166*, 276–296. [CrossRef]
106. Khan, M.U.; Lee, J.T.E.; Bashir, M.A.; Dissanayake, P.D.; Ok, Y.S.; Tong, Y.W.; Shariati, M.A.; Wu, S.; Ahring, B.K. Current Status of Biogas Upgrading for Direct Biomethane Use: A Review. *Renew. Sustain. Energy Rev.* **2021**, *149*, 111343. [CrossRef]
107. Dannesboe, C.; Hansen, J.B.; Johannsen, I. Catalytic Methanation of CO_2 in Biogas: Experimental Results from a Reactor at Full Scale. *React. Chem. Eng.* **2020**, *5*, 183–189. [CrossRef]
108. Balzarotti, R.; Drago Ferrante, G.; Italiano, C.; Laganà, M.; Francis, L.F.; Vita, A.; Cristiani, C.; Pino, L. RhNi/CeO_2 Catalytic Activation of Alumina Open Cell Foams by Dip-Spin Coating for the CO_2 Methanation of Biogas. *Surf. Coat. Technol.* **2022**, *441*, 128563. [CrossRef]
109. Guilera, J.; Filipe, M.; Montesó, A.; Mallol, I.; Andreu, T. Carbon Footprint of Synthetic Natural Gas through Biogas Catalytic Methanation. *J. Clean. Prod.* **2021**, *287*, 125020. [CrossRef]
110. Tommasi, M.; Degerli, S.N.; Ramis, G.; Rossetti, I. Advancements in CO_2 Methanation: A Comprehensive Review of Catalysis, Reactor Design and Process Optimization. *Chem. Eng. Res. Des.* **2024**, *201*, 457–482. [CrossRef]
111. Kusnere, Z.; Spalvins, K.; Bataitis, M. Wood Ash Filter Material Characterization as a Carrier Material for Ex-Situ Biomethanation of Biogas in Biotrickling Filter Reactors. *Environ. Clim. Technol.* **2023**, *27*, 92–102. [CrossRef]
112. Andersson, J. *Uppgradering Av Biogas Med Aska Från Trädbränslen*; Swedish University of Agricultural Sciences: Uppsala, Sweden, 2013; p. 48.
113. Mostbauer, P.; Lombardi, L.; Olivieri, T.; Lenz, S. Pilot Scale Evaluation of the BABIU Process—Upgrading of Landfill Gas or Biogas with the Use of MSWI Bottom Ash. *Waste Manag.* **2014**, *34*, 125–133. [CrossRef]
114. Han, B.; Yu, X.; Ou, J. *Self-Sensing Concrete in Smart Structures*, 1st ed.; Butterworth-Heinemann: Oxford, UK, 2014; ISBN 9780128005170.
115. Gopinath, S.; Mehra, A. Carbon Dioxide Sequestration Using Steel Slag—Modeling and Experimental Investigation. In *Carbon Dioxide Sequestration in Cementitious Construction Materials*; Pacheco-Torgal, F., Shi, C., Palomo Sanchez, A., Eds.; Woodhead Publishing: Sawston, UK, 2018; pp. 65–80.
116. Andersson, J.; Nordberg, Å. Biogas Upgrading Using Ash from Combustion of Wood Fuels: Laboratory Experiments. *Energy Environ. Res.* **2017**, *7*, 38. [CrossRef]
117. Fernández-Delgado Juárez, M.; Mostbauer, P.; Knapp, A.; Müller, W.; Tertsch, S.; Bockreis, A.; Insam, H. Biogas Purification with Biomass Ash. *Waste Manag.* **2018**, *71*, 224–232. [CrossRef]
118. Sarperi, L.; Surbrenat, A.; Kerihuel, A.; Chazarenc, F. The Use of an Industrial By-Product as a Sorbent to Remove CO_2 and H_2S from Biogas. *J. Environ. Chem. Eng.* **2014**, *2*, 1207–1213. [CrossRef]
119. Shen, Y.; Linville, J.L.; Ignacio-de Leon, P.A.A.; Schoene, R.P.; Urgun-Demirtas, M. Towards a Sustainable Paradigm of Waste-to-Energy Process: Enhanced Anaerobic Digestion of Sludge with Woody Biochar. *J. Clean. Prod.* **2016**, *135*, 1054–1064. [CrossRef]
120. Zhao, W.; Yang, H.; He, S.; Zhao, Q.; Wei, L. A Review of Biochar in Anaerobic Digestion to Improve Biogas Production: Performances, Mechanisms and Economic Assessments. *Bioresour. Technol.* **2021**, *341*, 125797. [CrossRef] [PubMed]
121. Younas, M.; Sohail, M.; Leong, L.K.; Bashir, M.J.; Sumathi, S. Feasibility of CO_2 Adsorption by Solid Adsorbents: A Review on Low-Temperature Systems. *Int. J. Environ. Sci. Technol.* **2016**, *13*, 1839–1860. [CrossRef]
122. Lee, J.; Kim, K.-H.; Kwon, E.E. Biochar as a Catalyst. *Renew. Sustain. Energy Rev.* **2017**, *77*, 70–79. [CrossRef]
123. Shen, Y.; Linville, J.L.; Urgun-Demirtas, M.; Schoene, R.P.; Snyder, S.W. Producing Pipeline-Quality Biomethane via Anaerobic Digestion of Sludge Amended with Corn Stover Biochar with In-Situ CO_2 Removal. *Appl. Energy* **2015**, *158*, 300–309. [CrossRef]
124. Sahota, S.; Vijay, V.K.; Subbarao, P.M.V.; Chandra, R.; Ghosh, P.; Shah, G.; Kapoor, R.; Vijay, V.; Koutu, V.; Thakur, I.S. Characterization of Leaf Waste Based Biochar for Cost Effective Hydrogen Sulphide Removal from Biogas. *Bioresour. Technol.* **2018**, *250*, 635–641. [CrossRef] [PubMed]

125. Linville, J.L.; Shen, Y.; Ignacio-de Leon, P.A.; Schoene, R.P.; Urgun-Demirtas, M. In-Situ Biogas Upgrading during Anaerobic Digestion of Food Waste Amended with Walnut Shell Biochar at Bench Scale. *Waste Manag. Res. J. A Sustain. Circ. Econ.* **2017**, *35*, 669–679. [CrossRef] [PubMed]
126. Raab, K.; Lamprecht, M.; Brechtel, K.; Scheffknecht, G. Innovative CO_2 Separation of Biogas by Polymer Resins: Operation of a Continuous Lab-scale Plant. *Eng. Life Sci.* **2012**, *12*, 327–335. [CrossRef]
127. Safai, D.; Schmid, M.-O.; Scheffknecht, G. Biogas Upgrading with Polymer Resins in a Technical Scale Plant—Scale-up and First Operating Points. In Proceedings of the 5th International Conference on Renewable Energy Gas Technology, Tolouse, France, 3–4 May 2018.
128. Meng, Y.; Jiang, J.; Gao, Y.; Aihemaiti, A.; Ju, T.; Xu, Y.; Liu, N. Biogas Upgrading to Methane: Application of a Regenerable Polyethyleneimine-Impregnated Polymeric Resin (NKA-9) via CO_2 Sorption. *Chem. Eng. J.* **2019**, *361*, 294–303. [CrossRef]
129. Arca, S.; Poletti, L.; Poletti, R.; D'Alessandro, E. Upgrading of Biogas Technology through the Application of Gas Hydrates. In Proceedings of the 7th International Conference on Gas Hydrates (ICGH 2011), Edinburgh, UK, 17–21 July 2011; Curran Associates: New York, NY, USA, 2011.
130. Castellani, B.; Rossi, F.; Filipponi, M.; Nicolini, A. Hydrate-Based Removal of Carbon Dioxide and Hydrogen Sulphide from Biogas Mixtures: Experimental Investigation and Energy Evaluations. *Biomass Bioenergy* **2014**, *70*, 330–338. [CrossRef]
131. Di Profio, P.; Canale, V.; D'Alessandro, N.; Germani, R.; Di Crescenzo, A.; Fontana, A. Separation of CO_2 and CH_4 from Biogas by Formation of Clathrate Hydrates: Importance of the Driving Force and Kinetic Promoters. *ACS Sustain. Chem. Eng.* **2017**, *5*, 1990–1997. [CrossRef]
132. Sinehbaghizadeh, S.; Saptoro, A.; Amjad-Iranagh, S.; Mohammadi, A.H. Understanding the Influences of Different Associated Gas Impurities and the Kinetic Modelling of Biogas Hydrate Formation at the Molecular Scale. *Energy* **2023**, *282*, 128893. [CrossRef]
133. EBI ChEBI Database. Available online: https://www.ebi.ac.uk/chebi/searchId.do?chebiId=CHEBI:132140 (accessed on 30 December 2023).
134. Moghaddam, E.A.; Larsolle, A.; Tidåker, P.; Nordberg, Å. Gas Hydrates as a Means for Biogas and Biomethane Distribution. *Front. Energy Res.* **2021**, *9*, 568879. [CrossRef]
135. Castellani, B.; Morini, E.; Bonamente, E.; Rossi, F. Experimental Investigation and Energy Considerations on Hydrate-Based Biogas Upgrading with CO_2 Valorization. *Biomass Bioenergy* **2017**, *105*, 364–372. [CrossRef]
136. Passos, F.; Mota, C.; Donoso-Bravo, A.; Astals, S.; Jeison, D.; Muñoz, R. Biofuels from Microalgae: Biomethane. In *Energy from Microalgae*; Springer: Cham, Switzerland, 2018; pp. 247–270.
137. Accettola, F.; Guebitz, G.M.; Schoeftner, R. Siloxane Removal from Biogas by Biofiltration: Biodegradation Studies. *Clean. Technol. Environ. Policy* **2008**, *10*, 211–218. [CrossRef]
138. Meier, L.; Pérez, R.; Azócar, L.; Rivas, M.; Jeison, D. Photosynthetic CO_2 Uptake by Microalgae: An Attractive Tool for Biogas Upgrading. *Biomass Bioenergy* **2015**, *73*, 102–109. [CrossRef]
139. Meier, L.; Barros, P.; Torres, A.; Vilchez, C.; Jeison, D. Photosynthetic Biogas Upgrading Using Microalgae: Effect of Light/Dark Photoperiod. *Renew. Energy* **2017**, *106*, 17–23. [CrossRef]
140. Noticias Jurídicas. Available online: https://noticias.juridicas.com/base_datos/Admin/res211212-iet.html (accessed on 24 June 2023).
141. Bose, A.; O'Shea, R.; Lin, R.; Murphy, J.D. A Perspective on Novel Cascading Algal Biomethane Biorefinery Systems. *Bioresour. Technol.* **2020**, *304*, 123027. [CrossRef]
142. Xu, B.; Liu, J.; Zhao, C.; Sun, S.; Xu, J.; Zhao, Y. Induction of Vitamin B12 to Purify Biogas Slurry and Upgrade Biogas Using Co-culture of Microalgae and Fungi. *Water Environ. Res.* **2021**, *93*, 1254–1262. [CrossRef]
143. Zhang, H.; Xu, B.; Zhao, C.; Liu, J.; Zhao, Y.; Sun, S.; Wei, J. Simultaneous Biogas Upgrading and Biogas Slurry Treatment by Different Microalgae-Based Technologies under Various Strigolactone Analog (GR24) Concentrations. *Bioresour. Technol.* **2022**, *351*, 127033. [CrossRef]
144. Rusmanis, D.; O'Shea, R.; Wall, D.M.; Murphy, J.D. Biological Hydrogen Methanation Systems—An Overview of Design and Efficiency. *Bioengineered* **2019**, *10*, 604–634. [CrossRef] [PubMed]
145. Wu, K.-K.; Zhao, L.; Zheng, X.-C.; Sun, Z.-F.; Wang, Z.-H.; Chen, C.; Xing, D.-F.; Yang, S.-S.; Ren, N.-Q. Recovery of Methane and Acetate during Ex-Situ Biogas Upgrading via Novel Dual-Membrane Aerated Biofilm Reactor. *Bioresour. Technol.* **2023**, *382*, 129181. [CrossRef] [PubMed]
146. Mattiasson, B. *Ekologisk Lunga för Biogasuppgradering*; Svenska Biogasföreningen: Lund, Sweden, 2005.
147. Persson, M.; Jonsson, O.; Wellinger, A. Task 37—Biogas Upgrading to Vehicle Fuel Standards and Grid Injection. *IEA Bioenergy* **2006**, *37*, 20–21.
148. Alper, E.; Lohse, M.; Deckwer, W.-D. On the Mechanism of Enzyme-Catalysed Gas—Liquid Reactions: Absorption of CO_2, into Buffer Solutions Containing Carbonic Anhydrase. *Chem. Eng. Sci.* **1980**, *35*, 2147–2156. [CrossRef]
149. Zhang, Y.-T.; Zhang, L.; Chen, H.-L.; Zhang, H.-M. Selective Separation of Low Concentration CO_2 Using Hydrogel Immobilized CA Enzyme Based Hollow Fiber Membrane Reactors. *Chem. Eng. Sci.* **2010**, *65*, 3199–3207. [CrossRef]
150. Fosbøl, P.L.; Gaspar, J.; Jacobsen, B.; Glibstrup, J.; Gladis, A.; Diaz, K.M.; Thomsen, K.; Woodley, J.M.; von Solms, N. Design and Simulation of Rate-Based CO_2 Capture Processes Using Carbonic Anhydrase (CA) Applied to Biogas. *Energy Procedia* **2017**, *114*, 1434–1443. [CrossRef]

151. Fradette, L.; Lefebvre, S.; Carley, J. Demonstration Results of Enzyme-Accelerated CO_2 Capture. *Energy Procedia* **2017**, *114*, 1100–1109. [CrossRef]
152. Mignogna, D.; Ceci, P.; Cafaro, C.; Corazzi, G.; Avino, P. Production of Biogas and Biomethane as Renewable Energy Sources: A Review. *Appl. Sci.* **2023**, *13*, 10219. [CrossRef]
153. Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and Committee of the Regions Powering a Climate-Neutral Economy: An EU Strategy for Energy System Integration. Available online: https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=CELEX:52020DC0299 (accessed on 28 December 2023).
154. Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and Committee of the Regions A Farm to Fork Strategy for a Fair, Healthy and Environmentally Friendly Food System. Available online: https://food.ec.europa.eu/horizontal-topics/farm-fork-strategy_en (accessed on 28 December 2023).
155. Tomczak, W.; Gryta, M.; Grubecki, I.; Miłek, J. Biogas Production in AnMBRs via Treatment of Municipal and Domestic Wastewater: Opportunities and Fouling Mitigation Strategies. *Appl. Sci.* **2023**, *13*, 6466. [CrossRef]
156. Wang, X.-H.; Xu, X.-J.; Cai, J.; Zheng, H.-X.; Chen, Y.-X.; Pang, W.-X.; Yu, Y.; Sun, C.-Y.; Chen, G.-J. CO_2 Concentration in Aqueous Solution from Gas–Liquid Equilibrium System to Gas–Liquid–Hydrate Coexistence System. *Gas. Sci. Eng.* **2023**, *115*, 205024. [CrossRef]
157. Bajón Fernández, Y.; Soares, A.; Villa, R.; Vale, P.; Cartmell, E. Carbon Capture and Biogas Enhancement by Carbon Dioxide Enrichment of Anaerobic Digesters Treating Sewage Sludge or Food Waste. *Bioresour. Technol.* **2014**, *159*, 1–7. [CrossRef]
158. Wang, P.; Peng, H.; Adhikari, S.; Higgins, B.; Roy, P.; Dai, W.; Shi, X. Enhancement of Biogas Production from Wastewater Sludge via Anaerobic Digestion Assisted with Biochar Amendment. *Bioresour. Technol.* **2020**, *309*, 123368. [CrossRef] [PubMed]
159. Qiu, L.; Deng, Y.F.; Wang, F.; Davaritouchaee, M.; Yao, Y.Q. A Review on Biochar-Mediated Anaerobic Digestion with Enhanced Methane Recovery. *Renew. Sustain. Energy Rev.* **2019**, *115*, 109373. [CrossRef]
160. He, P.; Zhang, H.; Duan, H.; Shao, L.; Lü, F. Continuity of Biochar-Associated Biofilm in Anaerobic Digestion. *Chem. Eng. J.* **2020**, *390*, 124605. [CrossRef]
161. Pan, J.; Ma, J.; Liu, X.; Zhai, L.; Ouyang, X.; Liu, H. Effects of Different Types of Biochar on the Anaerobic Digestion of Chicken Manure. *Bioresour. Technol.* **2019**, *275*, 258–265. [CrossRef]
162. Maroušek, J.; Strunecký, O.; Stehel, V. Biochar Farming: Defining Economically Perspective Applications. *Clean. Technol. Environ. Policy* **2019**, *21*, 1389–1395. [CrossRef]
163. Romero-Güiza, M.S.; Vila, J.; Mata-Alvarez, J.; Chimenos, J.M.; Astals, S. The Role of Additives on Anaerobic Digestion: A Review. *Renew. Sustain. Energy Rev.* **2016**, *58*, 1486–1499. [CrossRef]
164. Sailer, G.; Eichermüller, J.; Poetsch, J.; Paczkowski, S.; Pelz, S.; Oechsner, H.; Müller, J. Optimizing Anaerobic Digestion of Organic Fraction of Municipal Solid Waste (OFMSW) by Using Biomass Ashes as Additives. *Waste Manag.* **2020**, *109*, 136–148. [CrossRef] [PubMed]
165. Ajay, C.M.; Mohan, S.; Dinesha, P.; Rosen, M.A. Review of Impact of Nanoparticle Additives on Anaerobic Digestion and Methane Generation. *Fuel* **2020**, *277*, 118234. [CrossRef]
166. Yun, S.; Zhang, C.; Wang, Y.; Zhu, J.; Huang, X.; Du, T.; Li, X.; Wei, Y. Synergistic Effects of Fe Salts and Composite Additives on Anaerobic Digestion of Dairy Manure. *Int. Biodeterior. Biodegrad.* **2019**, *136*, 82–90. [CrossRef]
167. Barua, S.; Zakaria, B.S.; Lin, L.; Dhar, B.R. Magnetite Doped Granular Activated Carbon as an Additive for High-Performance Anaerobic Digestion. *Mater. Sci. Energy Technol.* **2019**, *2*, 377–384. [CrossRef]
168. Ding, M.; Jiang, H.-L. One-Step Assembly of a Hierarchically Porous Phenolic Resin-Type Polymer with High Stability for CO_2 Capture and Conversion. *Chem. Commun.* **2016**, *52*, 12294–12297. [CrossRef] [PubMed]
169. Kida, M.; Goda, H.; Sakagami, H.; Minami, H. CO_2 Capture from CH_4–CO_2 Mixture by Gas–Solid Contact with Tetrahydrofuran Clathrate Hydrate. *Chem. Phys.* **2020**, *538*, 110863. [CrossRef]
170. Fu, Y.; Jiang, Y.-B.; Dunphy, D.; Xiong, H.; Coker, E.; Chou, S.S.; Zhang, H.; Vanegas, J.M.; Croissant, J.G.; Cecchi, J.L.; et al. Ultra-Thin Enzymatic Liquid Membrane for CO_2 Separation and Capture. *Nat. Commun.* **2018**, *9*, 990. [CrossRef]
171. Karlsson, M.; Nygren, P. *Enzymatic Upgrading of Biogas*; Energiforsk: Stockholm, Sweden, 2015.
172. Fougerit, V. *Development of an Innovative Process for Biogas Purification through the Implementation of Membrane Contactors*; Université Paris Saclay: Paris, France, 2017.
173. González, J.M.; Fisher, S.Z. Carbonic Anhydrases in Industrial Applications. *Subcell Biochem.* **2014**, *75*, 405–426.
174. Thema, M.; Bauer, F.; Sterner, M. Power-to-Gas: Electrolysis and Methanation Status Review. *Renew. Sustain. Energy Rev.* **2019**, *112*, 775–787. [CrossRef]
175. de Meyer, F.; Jouenne, S. Industrial Carbon Capture by Absorption: Recent Advances and Path Forward. *Curr. Opin. Chem. Eng.* **2022**, *38*, 100868. [CrossRef]
176. Ahmed, S.F.; Mofijur, M.; Tarannum, K.; Chowdhury, A.T.; Rafa, N.; Nuzhat, S.; Kumar, P.S.; Vo, D.-V.N.; Lichtfouse, E.; Mahlia, T.M.I. Biogas Upgrading, Economy and Utilization: A Review. *Environ. Chem. Lett.* **2021**, *19*, 4137–4164. [CrossRef]
177. Andlar, M.; Belskaya, H.; Morzak, G.; Ivančić Šantek, M.; Rezić, T.; Petravić Tominac, V.; Šantek, B. Biogas Production Systems and Upgrading Technologies: A Review. *Food Technol. Biotechnol.* **2021**, *59*, 387–412. [CrossRef] [PubMed]
178. Lee, M.E.; Steiman, M.W.; St. Angelo, S.K. Biogas Digestate as a Renewable Fertilizer: Effects of Digestate Application on Crop Growth and Nutrient Composition. *Renew. Agric. Food Syst.* **2021**, *36*, 173–181. [CrossRef]

179. Samoraj, M.; Mironiuk, M.; Izydorczyk, G.; Witek-Krowiak, A.; Szopa, D.; Moustakas, K.; Chojnacka, K. The Challenges and Perspectives for Anaerobic Digestion of Animal Waste and Fertilizer Application of the Digestate. *Chemosphere* **2022**, *295*, 133799. [CrossRef]
180. Bidart, C.; Wichert, M.; Kolb, G.; Held, M. Biogas Catalytic Methanation for Biomethane Production as Fuel in Freight Transport—A Carbon Footprint Assessment. *Renew. Sustain. Energy Rev.* **2022**, *168*, 112802. [CrossRef]
181. Kim, H.; Choi, H.; Lee, C. The Potential Use of Human Urine as a Solvent for Biogas Upgrading. *J. Water Process Eng.* **2020**, *36*, 101343. [CrossRef]
182. Gutiérrez-Martín, F.; Rodríguez-Antón, L.M.; Legrand, M. Renewable Power-to-Gas by Direct Catalytic Methanation of Biogas. *Renew. Energy* **2020**, *162*, 948–959. [CrossRef]