Review

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

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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 CO₂ 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

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$_2$S, 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).
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 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].

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.

<table>
<thead>
<tr>
<th>Biomethane Production Pathway</th>
<th>Production in 2020 (TWh/y)</th>
<th>Production in 2030 (TWh/y)</th>
<th>Production in 2050 (TWh/y)</th>
<th>Total Existing Potential (TWh/y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biogas upgrading</td>
<td>24.7–79.4</td>
<td>334.94–467.6</td>
<td>1088.9</td>
<td>865.6–13.9</td>
</tr>
<tr>
<td></td>
<td>510.67</td>
<td>885</td>
<td></td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>221.11–278.89</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gasification with methanation</td>
<td>-</td>
<td>885</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PtM</td>
<td>-</td>
<td>5.9–13.9</td>
<td>266.7</td>
<td>-</td>
</tr>
<tr>
<td>Biogas upgrading and gasification with methanation</td>
<td>88.61</td>
<td>200–222.2</td>
<td>-</td>
<td>1521.4–2467.8</td>
</tr>
</tbody>
</table>

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.

Figure 3. European biomethane production in EU-27 and Europe. Adapted from EBA [39].
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$_2$S is formed during the microbiological reduction of compounds that contain sulfur, and it can lead to corrosion problems [49]. The existing methods for H$_2$S 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$_2$S removal are FlashH$_2$S [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].

Adsorption technologies employ an adsorbent that selectively captures CO₂ 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 CO₂ 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 CO₂ and H₂S 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 CO₂ 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 CO₂ 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 CO₂ 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% CO₂, 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 (PSA) | Absorption (WS) | | | MS | CS |
|----------------|------------------|-----------------|------------------|------------------|
| Compounds that must be pre-removed | H₂S and H₂O [51,61,63,69] | H₂S (if the concentration is high) [61,63,65] | H₂S (recommended) [61,63] | H₂S (if the concentration is high) [61,63] | H₂S and H₂O [61,63] | H₂S and H₂O [52,61] |
| Technology separates N₂ and O₂ | Yes [51,54,66,69] | No [65,66] | Yes [61] | No [65,66] | No [65,66] | Partly separates O₂ but not N₂ [65] | Possible if LBM is obtained [51,55] |
| Water demand (dm³/Nm³ biogas) [65] | 0 | 0.4–4 | 0 | 0.03 | 0 | 0 |
| Heat demand (kWh/Nm³ biogas) | 0 [65,69,78] | 0 [65,69,78] | <0.2 [78] | 0.10–0.15 [69] | 0.50–0.75 [78] | 0.4–0.8 [69] | 0 [65,69,78] | 0 [69,78] |
| Electricity consumption (kWh/Nm³ biogas) | 0.15–0.30 [65] | 0.20–0.30 [65] | 0.20–0.29 [65] | 0.12–0.14 [65] | 0.20–0.30 [65] | 0.20–0.28 [78] | 0.20–0.30 [65] | 0.18–0.21 [78] | 0.72 [78] |
| 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 [52,54,61,77] | 1–4 [65] | <0.1 [52,65,69] | <0.5 [54,65] | <1 [51,61] | <1 |
| | 10–12 [66] | 0.5–2 [69] | <1 [52] | <0.5 [77] | <1 [52] | 0.5–20 [63] | <2 |
| | 1.5–10.0 [69] | 2 [63] | <4 | 4 [51] | 0.1–2.0 [69] | 0.1–2.0 [69] | <1 [77] | <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 €.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>PSA</th>
<th>WS</th>
<th>OPS</th>
<th>AS</th>
<th>MS</th>
<th>CS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific CAPEX for different flows (€/(Nm³/h))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000 Nm³/h biogas</td>
<td>1750 [77]</td>
<td>1000 [77]</td>
<td>1000 [77]</td>
<td>2000 [77]</td>
<td>1782 [61]</td>
<td>-</td>
</tr>
<tr>
<td>1000 Nm³/h biogas</td>
<td>2592 [61]</td>
<td>2187 [61]</td>
<td>3078 [61]</td>
<td>2916 [61]</td>
<td>2750 [65]</td>
<td>600 Nm³/h:</td>
</tr>
<tr>
<td>250 Nm³/h biogas</td>
<td>4455 [61]</td>
<td>4000 [65]</td>
<td>4455 [61]</td>
<td>5000 [62]</td>
<td>6000 [52,66]</td>
<td>-</td>
</tr>
<tr>
<td>100 Nm³/h biogas</td>
<td>3000 [79]</td>
<td>5000 [66,79]</td>
<td>3890 [61]</td>
<td>5000 [62]</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Maintenance costs (% of CAPEX) [65]</td>
<td>-</td>
<td>2–3</td>
<td>2–3</td>
<td>3</td>
<td>3–4</td>
<td>-</td>
</tr>
<tr>
<td>Maintenance costs for 1000 m³/h biogas (m€/y) [61]</td>
<td>56</td>
<td>15</td>
<td>39</td>
<td>59</td>
<td>25</td>
<td>-</td>
</tr>
<tr>
<td>Availability (%)</td>
<td>94 [61,78]</td>
<td>96 [61,78]</td>
<td>96 [61,78]</td>
<td>91 [61,78]</td>
<td>98 [61,78]</td>
<td>-</td>
</tr>
<tr>
<td>Number of plants in Europe (2019) [80]</td>
<td>79</td>
<td>175</td>
<td>17</td>
<td>103</td>
<td>173</td>
<td>10</td>
</tr>
<tr>
<td>(WS + PSA)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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 CO₂ 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 CO₂ 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 NH₄OH [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 NH₄OH have a higher theoretical CO₂ capture capacity compared...
Separation via Phase Addition
- Inorganic Solvent Scrubbing
  - NaOH regeneration, the reaction that takes place is the inverse of Equation (1).
- Calcium Hydroxide
- Lime treatment
- Regeneration or carbon storage with waste material [68].

**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.

\[
\begin{align*}
2\text{NaOH} + \text{CO}_2 & \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \\
2\text{KOH} + \text{CO}_2 & \rightarrow \text{K}_2\text{CO}_3 + \text{H}_2\text{O} \\
\text{Ca(OH)}_2 + \text{CO}_2 & \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \\
\text{NH}_4\text{OH} + \text{CO}_2 & \rightarrow (\text{NH}_4)^+ \text{HCO}_3^- 
\end{align*}
\]

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\(_4\)OH 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>
<thead>
<tr>
<th>Solvent and Concentration</th>
<th>Apparatus</th>
<th>Operating Conditions</th>
<th>Biogas Composition (% Vol)</th>
<th>Product Purity (Highest CH₄, Lowest CO₂)</th>
<th>Loading Capacity (kg CO₂/kg Solvent Solution)</th>
<th>Comments</th>
<th>Case/Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5 M NaOH</td>
<td>Glass cylinder (H = 54 cm; D = 5 cm)</td>
<td>Ambient T</td>
<td>65.79% CH₄, 34.2% CO₂</td>
<td>96.23% CH₄, 3.76% CO₂</td>
<td>0.29</td>
<td></td>
<td>1/[86] (lab-scale tests)</td>
</tr>
<tr>
<td>1.5 M KOH</td>
<td>Glass cylinder (H = 54 cm; D = 5 cm)</td>
<td>Ambient T</td>
<td>65.79% CH₄, 34.2% CO₂</td>
<td>92.1% CH₄, 7.89% CO₂</td>
<td>0.18</td>
<td>Saturation after 12 min</td>
<td></td>
</tr>
<tr>
<td>0.5 M Ca(OH)₂</td>
<td>Glass cylinder (H = 54 cm; D = 5 cm)</td>
<td>Ambient T</td>
<td>65.79% CH₄, 34.2% CO₂</td>
<td>85.99% CH₄, 14% CO₂</td>
<td>0.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₄OH (10% aqueous sol.)</td>
<td>Glass cylinder (H = 54 cm; D = 5 cm)</td>
<td>Ambient T</td>
<td>65.79% CH₄, 34.2% CO₂</td>
<td>59.8% CH₄, 40.1% CO₂</td>
<td>0.63</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12% vol NaOH</td>
<td>Packed column (H = 2 m; D = 0.1 m)</td>
<td>Liquid flow: 72 kg/h, Gas flow: 6 kg/h</td>
<td>59.8% CH₄, 40.1% CO₂</td>
<td>85.9% CH₄, 10.8% CO₂, 3.3% H₂O</td>
<td>-</td>
<td>NH₄ scrubbing can be improved by adding a WS process afterwards to reduce NH₃ concentration</td>
<td>2/[85] (lab-scale tests)</td>
</tr>
<tr>
<td>5% vol NH₃</td>
<td>Packed column (H = 2 m; D = 0.1 m)</td>
<td>Liquid flow: 72 kg/h, Gas flow: 6 kg/h</td>
<td>59.8% CH₄, 40.1% CO₂</td>
<td>85.9% CH₄, 10.8% CO₂, 3.3% H₂O</td>
<td>-</td>
<td>NH₄ scrubbing can be improved by adding a WS process afterwards to reduce NH₃ concentration</td>
<td>2/[85] (lab-scale tests)</td>
</tr>
<tr>
<td>10% NaOH</td>
<td>Packed column (H = 1.8 m; D = 0.3 m)</td>
<td>Liquid flow: 72 kg/h, Gas flow: 6 kg/h</td>
<td>59.8% CH₄, 40.1% CO₂</td>
<td>85.9% CH₄, 10.8% CO₂, 3.3% H₂O</td>
<td>-</td>
<td>Saturation after 6 h and cleaning of the system for corrosion after 3 h</td>
<td>3/[72] (pilot-scale tests)</td>
</tr>
<tr>
<td>0.1 M NaOH</td>
<td>Glass cylinder (H = 1 m; D = 0.07 m)</td>
<td>Liquid flow: 72 kg/h, Gas flow: 6 kg/h</td>
<td>59.8% CH₄, 40.1% CO₂</td>
<td>85.9% CH₄, 10.8% CO₂, 3.3% H₂O</td>
<td>-</td>
<td>Saturation after 6 h and cleaning of the system for corrosion after 3 h</td>
<td>4/[89] (lab-scale tests)</td>
</tr>
<tr>
<td>0.1 M Ca(OH)₂</td>
<td>Glass cylinder (H = 1 m; D = 0.07 m)</td>
<td>Liquid flow: 72 kg/h, Gas flow: 6 kg/h</td>
<td>59.8% CH₄, 40.1% CO₂</td>
<td>85.9% CH₄, 10.8% CO₂, 3.3% H₂O</td>
<td>-</td>
<td>Saturation after 6 h and cleaning of the system for corrosion after 3 h</td>
<td>4/[89] (lab-scale tests)</td>
</tr>
</tbody>
</table>
### Table 4. Cont.

<table>
<thead>
<tr>
<th>Solvent and Concentration</th>
<th>Apparatus</th>
<th>Operating Conditions</th>
<th>Biogas Composition (% Vol)</th>
<th>Product Purity (Highest CH(_4), Lowest CO(_2))</th>
<th>Loading Capacity (kg CO(_2)/kg Solvent Solution)</th>
<th>Comments</th>
<th>Case/Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pig manure: 1 g NH(_4^+)/L</td>
<td>Lab-scale stirrer bath</td>
<td>(p = 0.1) Mpa (T = 313) K</td>
<td>70% CH(_4), 30% CO(_2)</td>
<td>87.5% CH(_4), 12.5% CO(_2) (theoretical)</td>
<td>0.0031</td>
<td>Saturation after 15 min; fertilizer rich in N and C</td>
<td>5/[90] (lab-scale tests)</td>
</tr>
<tr>
<td>Effluent from a digester treating pig manure: 1.1 g NH(_4^+)/L</td>
<td>Column filled with laboratory packing ((H = 0.99) m; (D = 0.08) m)</td>
<td>(p = 0.1) Mpa (T = 313)–318 K (T) (gas) = 288–293 K</td>
<td>60% CH(_4), 40% CO(_2) (landfill gas)</td>
<td>97% CH(_4), 2% CO(_2)</td>
<td>-</td>
<td>-</td>
<td>6/[83] (pilot-scale tests)</td>
</tr>
<tr>
<td>53% mass concentration KOH</td>
<td>Column filled with laboratory packing</td>
<td>(p = 0.1) Mpa (T = 313)–318 K (T) (gas) = 288–293 K</td>
<td>51% CH(_4), 39.36% CO(_2), 0.21% O(_2) (2940.61) ppm H(_2)S</td>
<td>89.3% CH(_4)</td>
<td>-</td>
<td>-</td>
<td>7/[91] (lab-scale tests)</td>
</tr>
<tr>
<td>0.2 M Ca(OH)(_2)</td>
<td>-</td>
<td>Biogas flow: 5 L/min Solution flow: 30 L/min</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
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$_2$CO$_3$ (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$_4$OH 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].

$$\text{Na}_2\text{CO}_3 + \text{Ca(OH)}_2 \rightleftharpoons 2\text{NaOH} + \text{CaCO}_3$$  \hspace{1cm} (5)

$$\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$$  \hspace{1cm} (6)

$$\text{CaO} + \text{H}_2\text{O} \rightleftharpoons \text{Ca(OH)}_2$$  \hspace{1cm} (7)

The regeneration of alkali compounds using waste material has been studied by Bacicocchi 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$_2$CO$_3$ and K$_2$CO$_3$, 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 $\text{Ra}$ is the ion-exchange resin.

$$\text{(NH}_4\text{)}_2\text{HCO}_3 + \text{Ra} \rightleftharpoons \text{Ra}·\text{H}_2\text{CO}_3 + \text{NH}_3$$  \hspace{1cm} (8)

$$\text{Ra}·\text{H}_2\text{CO}_3 \rightleftharpoons \text{Ra} + \text{CO}_2 + \text{H}_2\text{O}$$  \hspace{1cm} (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 CO₂ removal [100]. In addition to CO₂, H₂S and NH₃ 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 H₂S 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 N₂ 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.

<table>
<thead>
<tr>
<th>Substrate Type</th>
<th>Desorption Compound</th>
<th>Biogas Composition (%vol CH₄)</th>
<th>CH₄ in Upgraded Gas (%vol)</th>
<th>CH₄ Losses (%)</th>
<th>Comments</th>
<th>Case/Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sludges</td>
<td>Air</td>
<td>-</td>
<td>87</td>
<td>8</td>
<td>-</td>
<td>1/[49] (best performance from different experiments)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>Air</td>
<td>58</td>
<td>69</td>
<td>1.3</td>
<td>Low sludge flow rate and high gas flow rate lead to higher CH₄ concentration and lower CH₄ losses</td>
<td>2/[100] (computer simulations)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrogen-rich</td>
<td>Air</td>
<td>69</td>
<td>66</td>
<td>-</td>
<td>Bad performance due to ammonia inhibition and pH increase</td>
<td>3/[100] (lab-based platform)</td>
</tr>
<tr>
<td>substrate</td>
<td>Vacuum (40 kPa)</td>
<td>69</td>
<td>63</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>55</td>
<td>64</td>
<td>-</td>
<td>Addition of organic acids to air stripping may achieve better results</td>
<td>4/[100] (lab-based platform)</td>
</tr>
<tr>
<td>Substrate</td>
<td>Vacuum (40 kPa)</td>
<td>60</td>
<td>62</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>mixture with</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>less N than 3/</td>
<td>Vacuum (40 kPa) with</td>
<td>49</td>
<td>61</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>organic acids</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manure</td>
<td>-</td>
<td>60</td>
<td>81</td>
<td>1.8</td>
<td>H₂S reduction from 1100–1500 ppm to 150–300 ppm and reduction of nitrogen by 11–21%</td>
<td>5/[101] (pilot plant)</td>
</tr>
<tr>
<td>Chicken</td>
<td>Air</td>
<td>55</td>
<td>60–70</td>
<td>3.7–10.3</td>
<td>Up to 60% H₂S removal</td>
<td>6/[99] (lab-based platform)</td>
</tr>
<tr>
<td>manure</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.1.3. Catalytic Methanation

Methanation consists of converting the CO\textsubscript{2} present in the biogas into methane by continuously adding H\textsubscript{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\textsubscript{2} reacts with H\textsubscript{2} to produce CH\textsubscript{4} [102] through a very exothermic reaction:

\[
\text{CO}_2 + 4 \text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O} \tag{10}
\]

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\textsubscript{2} methanation, given its relatively high activity, outstanding CH\textsubscript{4} selectivity, and lower cost compared to noble metals [105] (catalyst at 250–350 °C and 10–20 bar) [79]. CO\textsubscript{2} can be separated from the CH\textsubscript{4} in raw biogas, but the latest research shows that feeding the reactor with pre-treated biogas (CH\textsubscript{4} and CO\textsubscript{2} after the removal of H\textsubscript{2}S 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\textsubscript{2} catalyst. This was tested in a simulated biogas methanation reaction, achieving CO\textsubscript{2} conversion values as high as 70%. The effect of the H\textsubscript{2}/CO\textsubscript{2} molar ratio on the simulated biogas feed was evaluated, demonstrating that substoichiometric H\textsubscript{2}/CO\textsubscript{2} molar ratios are suitable for obtaining high-quality upgraded biogas. CO\textsubscript{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\textsubscript{4} content (up to 99%) with nearly 100% conversion of CO\textsubscript{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\textsubscript{2} sequestration that happens spontaneously in nature [90]. In this process, CO\textsubscript{2} reacts with CaO and forms CaCO\textsubscript{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:

\[
\text{CaO} + \text{CO}_2 \rightleftharpoons \text{CaCO}_3 \tag{11}
\]
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$_2$S [90]. Andersson [112] used a wood ash filter and obtained a concentration of 0% for both CO$_2$ and H$_2$S in the outlet gas. 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$_2$S 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>
<thead>
<tr>
<th>Ash Filter Type</th>
<th>Biogas Composition (% Vol)</th>
<th>Upgraded Gas Composition (% vol)</th>
<th>Loading Capacity (kg CO$_2$/t Ash)</th>
<th>Comments</th>
<th>Case/Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA from MSWI</td>
<td>58% CH$_4$, 95 ppm H$_2$S</td>
<td>99% CH$_4$, 1.4 ppm H$_2$S</td>
<td>13.9</td>
<td>This process is called BABIU (Bottom Ash for Biogas Upgrading)</td>
<td>1/[113] (pilot plant)</td>
</tr>
<tr>
<td>Ash from biomass incineration plant</td>
<td>Gas rich in CO$_2$</td>
<td>-</td>
<td>15.4</td>
<td>Saturation time * of 300 min</td>
<td>2/[90] (lab-scale tests)</td>
</tr>
<tr>
<td>Mussel shell ash</td>
<td>-</td>
<td>95% CH$_4$</td>
<td>1.4</td>
<td>Saturation time * of 30 min</td>
<td>3/[90] (lab-scale tests)</td>
</tr>
<tr>
<td>Wood chip ash</td>
<td>65% CH$_4$, 35% CO$_2$</td>
<td>98% CH$_4$</td>
<td>0.14 (dry ash)</td>
<td>Two serial reactors utilize the ash’s total CO$_2$ capacity; the pH of the ash (approx. 13) was reduced by 2–3 units</td>
<td>4/[116] (lab-scale tests)</td>
</tr>
<tr>
<td>Wood pellet ash</td>
<td>65% CH$_4$, 35% CO$_2$, 100–600 ppm H$_2$S</td>
<td>Almost 100% CH$_4$ and 0 ppm H$_2$S</td>
<td>35–135 (wet ash)</td>
<td>0.56–1.25 kg H$_2$S/t wet ash</td>
<td>Pure CH$_4$ was achieved for a few hours, while H$_2$S removal was longer-lasting</td>
</tr>
<tr>
<td>Mixture of fly ash (10%) and BA (90%) from a biomass incineration plant</td>
<td>68.4% CH$_4$, 31.2% CO$_2$, 250 ppm H$_2$S</td>
<td>95% CH$_4$, 5% CO$_2$, &lt;2 ppm H$_2$S</td>
<td>48</td>
<td>Saturation time * of 42 min and 300–350 kg of BOF to produce bio-compressed NG to fill up one vehicle</td>
<td>6/[118] (lab-scale tests)</td>
</tr>
</tbody>
</table>

* 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$_2$S 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$_2$S, 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$_2$S, 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$_2$S. 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$_2$S removal; Sahota and co-authors used leaf waste biochar and obtained a reduction in H$_2$S 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.

<table>
<thead>
<tr>
<th>Biochar Type</th>
<th>Biogas Composition (% Vol CH$_4$)</th>
<th>Case/Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn stover</td>
<td>90</td>
<td>1/[123]</td>
</tr>
<tr>
<td></td>
<td>&lt;5 ppb H$_2$S</td>
<td></td>
</tr>
<tr>
<td>Pine</td>
<td>92.3 (mesophilic T) 79 (thermophilic T)</td>
<td>2/[119]</td>
</tr>
<tr>
<td>White oak</td>
<td>89.8 (mesophilic T) 78.5 (thermophilic T)</td>
<td>3/[119]</td>
</tr>
<tr>
<td>Walnut shell</td>
<td>77.5–98.1</td>
<td>4/[125]</td>
</tr>
</tbody>
</table>

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 CO₂ and impurities can then be stored in geological deposits of NG hydrates (NGH), leading to an exchange of in situ CH₄ hydrate for a CO₂-dominated hydrate and a simultaneous release of CH₄ 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 SO₂ (from landfill gas), H₂S, N₂, and H₂, 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 CO₂·5.75H₂O or 4CH₄·23H₂O [133]) have been described: carbon dioxide hydrates and biogas hydrates [129]. The first consists of forming CO₂ hydrates selectively from biogas. This is possible since CO₂ forms hydrates at lighter conditions than methane [129]. Also, H₂S is removed simultaneously with CO₂. This way, the upgraded biogas is obtained, and then the hydrate phase is dissociated to recover CO₂ [130]. The second method, biogas hydrates, forms hydrates of CO₂ and methane, and then it releases the components selectively: first the CO₂ and then methane [129]. This process requires more energy than forming only CO₂ hydrates, but the external energy required can be minimized using proper process integration [129]. H₂S 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.

<table>
<thead>
<tr>
<th>Method</th>
<th>Operating Conditions</th>
<th>Promoter</th>
<th>Biogas Composition (%vol)</th>
<th>CH₄ in Upgraded Gas (%Vol)</th>
<th>CO₂ in Upgraded Gas (%Vol)</th>
<th>Case/ (Reference)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ hydrates</td>
<td>T (K) 278.15, p (MPa) 6</td>
<td>SDS 300 ppm</td>
<td>60% CH₄, 40% CO₂</td>
<td>70</td>
<td>30</td>
<td>1/[130] (up-scaled apparatus)</td>
</tr>
<tr>
<td>CO₂ hydrates</td>
<td>T (K) 275.1, p (MPa) 4.5</td>
<td></td>
<td>55% CH₄, 37.5% CO₂, 5% N₂, 2% O₂, 0.5% H₂</td>
<td>70.1</td>
<td>22.4</td>
<td>2/[135] (up-scaled apparatus)</td>
</tr>
</tbody>
</table>

4.4. Biological Technologies

Biological technologies’ purpose is to convert the CO₂ in biogas into methane through methods that employ microorganisms or algae biomass. The biological removal of CO₂ from biogas is still in an early stage of research, with hydrogenotrophic CO₂ reduction to CH₄ and photosynthetic CO₂ assimilation being the two most promising technologies under scale-up [136]. Hydrogen generation involves using energy for electrolysis, and most biochemical systems for CO₂ 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 CO₂, 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].

\[
\text{CO}_2 + \text{H}_2\text{O} + \text{photons} + \text{nutrients} \rightarrow \text{O}_2 + \text{CH}_{1.63}\text{N}_{0.14}\text{O}_{0.43}\text{P}_{0.006}\text{S}_{0.005} + \text{waste heat} \quad (12)
\]

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 CO₂ 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 H₂S [70]. Eukaryotic microalgae and prokaryotic cyanobacteria remove CO₂ 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 H₂S is attracting significant attention due to its simultaneous occurrence during CO₂ capture in algal–bacterial photobioreactors, which will drastically reduce the operational cost of biogas enhancement. Other biotechnology for removing H₂S includes biotrickling filtration [136]. Moreover, the biological disposal of H₂S 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, Arthospira, 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$_2$S can inhibit microalgal growth. However, the presence of H$_2$S-oxidizing bacteria and the chemical oxidation of H$_2$S that takes place in the photobioreactor (operating at high dissolved oxygen concentrations under non-sterile conditions) result in the oxidation of H$_2$S 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 microalgal culture media are a limitation [141]. So is the high methane loss due to its solubility in a large volume of microalgal 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$_2$S 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 CO₂ 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 CO₂ 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 CO₂ 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 H₂-assisted ex situ biogas upgrading is hindered by a large solubility discrepancy between H₂ and CO₂. dMBfR enables a precise supply of CO₂ and H₂, 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 H₂, allowing its absorption via archaea. An appropriate method for H₂ 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 H₂ 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% CH₄ [80]. Pilot-scale experiments show that methane content of 95% in biogas has been achieved with a continuous injection of H₂ 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 H₂S 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].

\[
\text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-. \quad (13)
\]

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 com-
bined 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 “Biominalization”, “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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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.

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