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Review

Biogas Steam Reforming in Wastewater Treatment Plants: Opportunities and Challenges

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Abstract: Hydrogen as an energy vector is going to play an important role in the global energy mix. On the other hand, wastewater management has become a worldwide concern, as urban settlements have been considerably increasing for decades. Consequently, biodigestion to produce biogas (rich in methane) in water treatment plants could be an interesting starting point to obtain a valuable gas that can be converted into hydrogen through steam reforming. The aim of this work was to review the main aspects concerning steam reforming of biogas from wastewater treatment plants. For this purpose, the whole chain, from water treatment to hydrogen production and purification, was considered, paying attention to the main challenges and new technologies for its optimization. Thus, a wide range of possibilities is offered, from direct energy use of syngas to high purification of hydrogen (mainly through pressure swing adsorption or membrane reactors), presenting advantages and disadvantages. In any case, the role of catalysts seems to be essential, and aspects such as hydrogen sulfide and coke deposition control should be addressed. In conclusion, biogas steam reforming applied to wastewater treatment plants is a reality, with serious possibilities for its global implementation at the industrial level, according to techno-economic assessment.

Keywords: methane; anaerobic biodigestion; catalysis; coke deposition; sewage sludge; hydrothermal carbonization; membrane reactor; pressure swing adsorption; sulfhydric acid; hydrogen production

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1. Introduction

There is an increasing concern (from local to international, from individual to global society) about environmental problems such as waste management and the sustainable use of resources like water. In that sense, the United Nations has established the so-called Sustainable Development Goals (SDG), where many of these issues have been covered, as in the case of Goal 6, "Clean Water and Sanitation". Indeed, one of the main goal targets included in this point is the need to improve water quality by reducing pollution, eliminating dumping, minimizing the release of hazardous chemicals and materials, halving the proportion of untreated wastewater, and substantially increasing recycling and safe reuse globally by 2030, expanding international cooperation and support to developing countries in water and sanitation-related activities and programs, like wastewater treatment [1]. On the other hand, there are other interesting goals like Goal 7 (Affordable and Clean Energy), 11 (Sustainable Cities and Communities) and 12 (Responsible Consumption and Production), whose specific goal targets are improving energy efficiency, reducing the adverse per capita environmental impact of cities and waste generation reduction through prevention, recycling, and reuse [1].

With this regard, the role of wastewater, especially in urban areas, seems to be a serious concern from an environmental point of view, as not only is it necessary to purify water before discharging it in rivers, but also the management of wastes, such as sewage sludge, is required.

In order to face this challenge, more and more wastewater treatment plants (WWTP) are implemented every year, as can be seen in Figure 1 in the case of France (selected as an example in Europe). Considering this country, wastewater treatment plants increased by around 15% from 2014 to 2021, which is a significant growth, especially considering that France, Germany, Netherlands, Switzerland, Sweden, Finland or Denmark, among others, exceed 99% of people connected to wastewater treatment plants, pointing out the great effort made by these countries to contribute to the correct management of wastewater. Indeed, according to databases such as the Global HydroWASTE database, there are more than 18,000 wastewater treatment plants in Europe, with 3 million kilometers of sewer network across the European Union [2,3].

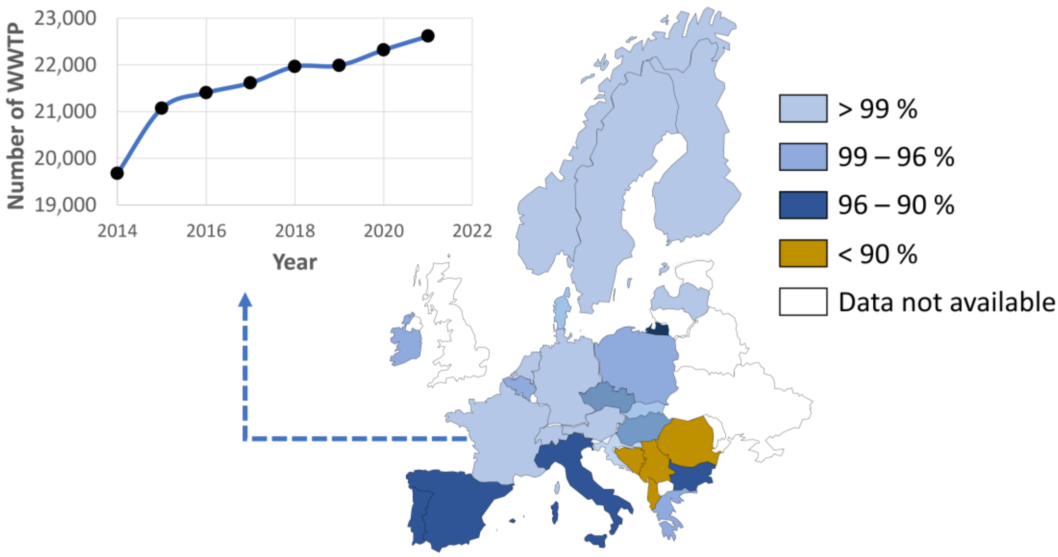

Figure 1. Percentage of people connected to wastewater treatment plants (WWTP) in Europe. WWTP evolution in France from 2014 to 2021. Source: [4,5].

On the other hand, if this increase was observed in such a connected country, it is expected that other countries with a lower percentage of people connected to WWTP (for instance, in Mediterranean countries like Spain and Italy or, especially, in Balkan countries such as Albania, Bosnia and Herzegovina, or Serbia) will increase the implementation of WWTP in the near future, as there is room for improvement to increase connectivity to WWTP by implementing more facilities devoted to this purpose.

Consequently, this increasing trend in the number of wastewater treatment plants in Europe could be equally applied to other developing countries worldwide in the long run [6]. This way, it is estimated that around 110,000 municipal wastewater treatment plants are located in a total of 129 countries, serving up to 2.7 billion people worldwide (approximately 35% of the global population) [7].

This fact points out that there is a global concern about this subject (countries like China or India recently produced up to 40 Mts of sewage per year), with the subsequent increasing interest in using environmental wastes as feedstocks for energy or chemical production [8]. In any case, operating these plants implies the generation of sewage sludge, which is expected to be constantly increased worldwide.

Nevertheless, a wide range of technologies are applied in WWTP, where water treatment is the main objective, but also there are other parallel technologies, such as biodigestion, where biogas (rich in methane) is produced from sewage, which can be used for energy purposes (for instance, electricity conversion) through different devices or technologies (like fuel cells, gas/petrol or diesel engines, gas or steam turbines, etc.) or by different chemical routes, such as methane partial oxidation reforming (POR), dry reforming (DR), autothermal reforming (ATR) or steam reforming (SR) to produce synthesis gas, including hydrogen [9–12].

Specifically, there are more and more WWTPs coupled to biogas production. For instance, in the case of the US, there were 14,780 municipal WWTPs, and 1484 of them digest sludge to produce biogas, according to the US Environmental Protection Agency (USEPA) [13,14]. This fact points out the room for improvement regarding the implementation of biodigestion in WWTPs around the world, with the foreseeable increase in biogas production in the medium and long term. Consequently, the possibilities for steam reforming of biogas from wastewater are countless, with increasing trends in the use of its raw material.

Hydrogen presents a key role in multisectorial defossilization and decarbonization, which is expected to reach zero net emissions by 2050, with the subsequent increase in hydrogen demand (expected up to USD 12 trillion by 2050) [15–17]. This is due to the fact that it implies an excellent environmentally friendly energy carrier, which can be obtained through steam reforming from different natural sources such as biomass [18,19]. Currently, 48% of total hydrogen production is obtained via natural gas steam reforming, 30% via petroleum fraction, 18% via coal gasification and 4% via electrolysis [20].

This fact proves that the use of biogas could be an interesting alternative for hydrogen production, as it presents some similarities to natural gas (both have methane as their majority compound). In addition, synthesis gas could be suitable for Fischer–Tropsch or methanol synthesis, which are also very interesting chemical routes that could equally enhance the valorization of biogas.

1.1. Wastewater Treatment Plants

Taking into account the context of this review article, which is focused on biogas steam reforming, it is vital to understand how a wastewater treatment plant usually works, where there are some stages that are important to understand the relevance of biogas during catalytic steam reforming, as key factors such as quality of biogas (including methane and hydrogen sulfide content) or sewage sludge production will depend on the performance in these facilities. These stages can be categorized into pre-treatment, primary, secondary, and tertiary treatments, which are included in Figure 2.

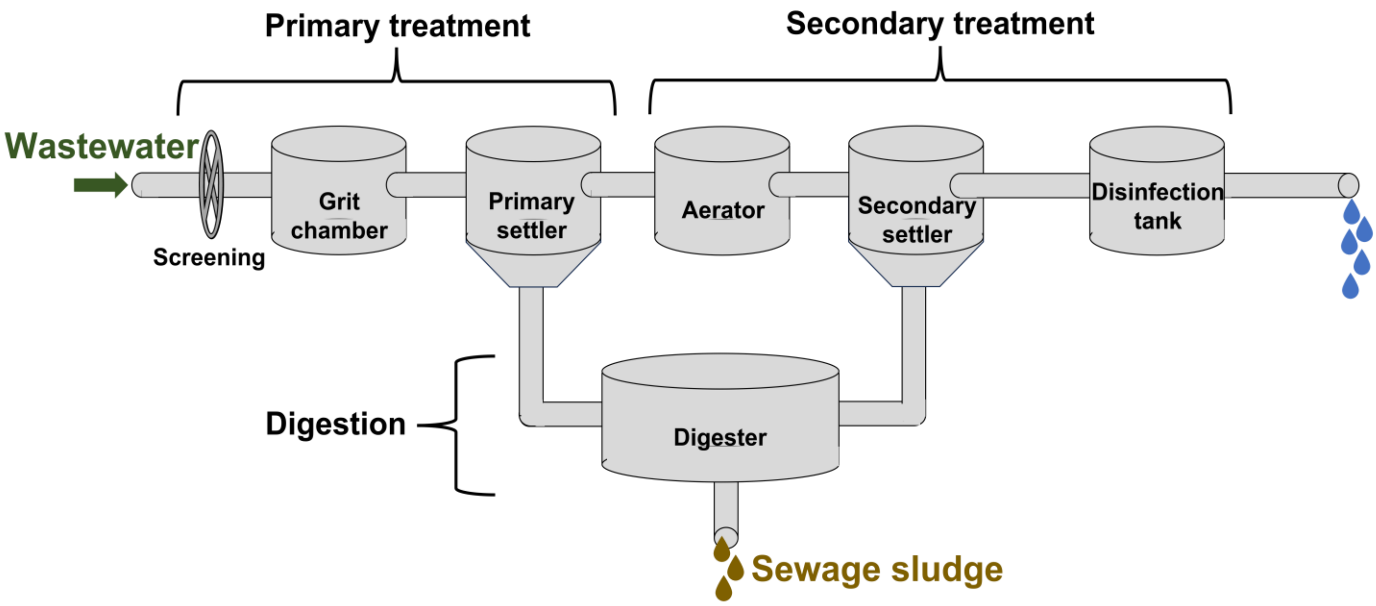

Figure 2. Main treatments take place in a wastewater treatment plant, including anaerobic digestion, where biogas is produced.

- Pretreatment: Suspended solids (floating charge, sand, gravel, etc.) that can cause problems in subsequent treatments due to their nature or size are removed during this stage. It includes the separation of large solids, roughing, screening, dilaceration, dewatering, de-oiling, degreasing and pre-aeration, among others.
- Primary treatment: It implies the separation by physical means of suspended particles not retained in pre-treatment. This treatment can be considered mechanical,

mainly based on gravity or mechanical devices to remove pollutants. Consequently, the removal of organic matter can be considered negligible. The main processes corresponding to this stage are sedimentation (primary settling, including coagulation, flocculation, and flotation), gravity separation, and sludge evacuation.

- Secondary treatment: During this stage, organic matter is removed or at least reduced by using aerobic and anaerobic microorganisms, transforming it into settleable solids that can be easily separated, making it a resourceful technology for sewage sludge management [21]. Specifically, a secondary treatment tank receives the wastewater from the primary treatment after the initial removal of sludge and surface impurities. Before the introduction of wastewater in this secondary treatment tank, 40–60% of solids had already been removed from water, with further removal in this secondary treatment (up to 90%). Thus, there are key steps during secondary treatment, like aeration and sludge sedimentation, included in Table 1.

Table 1. Main steps in secondary treatments.

Step	Description
Aeration	It supplies large amounts of oxygen to wastewater for aerobic bacteria and other micro-organisms, helping to break down many dangerous organic materials in sewage. The resulting clumps, called activated sludge, settle to the bottom of the wastewater. The aerated wastewater is deposited in a secondary sedimentation tank.
Secondary sedimentation or clarification	It is usually combined with aeration in a tank: aeration takes place at the top surface, and sludge sedimentation takes place at the bottom. This material is rich in bacteria and other microbes responsible for organic material breakdown and solid, oil or waste removal.

Tertiary treatment: Finally, this treatment (which is costly) is the most complete procedure for treating wastewater, aiming to remove residual organic load and other pollutants (like P and N) not removed in secondary treatment.

1.2. Biogas Production in Wastewater Treatment Plants

Biogas is a gaseous fuel with a high percentage of methane (normally above 50%, along with other compounds such as carbon dioxide, nitrogen, or oxygen, among others), which is normally produced through the fermentation of organic matter. In the case of wastewater treatment plants, sewage sludge can be used as an interesting source for biogas production through anaerobic digestion.

Anaerobic digestion is a process used to stabilize sludge and is the natural process of breaking down organic matter by microorganisms in the absence of air [22,23]. As a consequence, sludge is stabilized, and biogas is generated. Figure 3 shows the main steps that take place during anaerobic digestion [24,25]:

- Hydrolysis: In this stage, large chains of organic polymers contained in biomass are broken down into smaller constituent parts (monomers such as sugars, amino acids, or fatty acids) and dissolved so that microorganisms in digesters can process them.
- Acidogenesis: It implies further breakdown of the remaining components by acidogenic bacteria, generating volatile fatty acids, ammonia, carbon dioxide, and hydrogen sulfide (which will play an important role in many aspects of biogas steam reforming), among others.
- Acetogenesis: The byproducts generated during acidogenesis are further processed by acetogens, mainly producing acetic acid, carbon dioxide and hydrogen (at a lower extent).
- Methanogenesis: Finally, methanogens convert the previous intermediate products to obtain methane, carbon dioxide and water, which are the majority components of

biogas (apart from other traces obtained in previous stages such as H_2S, which will play an important and negative role as explained in further sections).

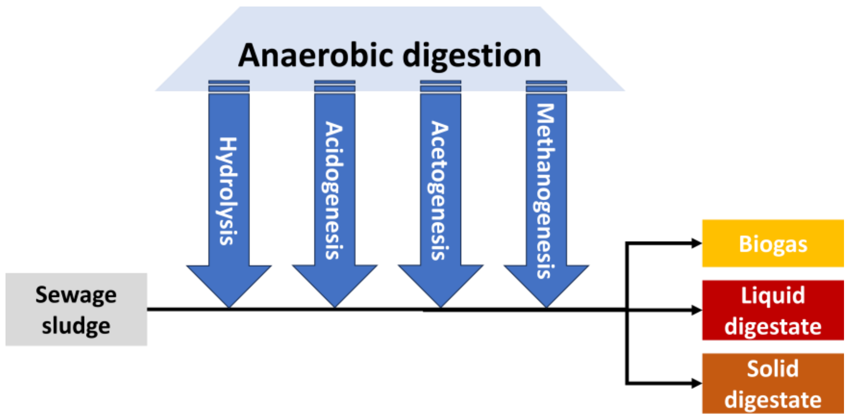

Figure 3. Main stages during anaerobic digestion of sewage wastewater.

It should be noted that this process is highly dependent on pH, which should be between 6.5 and 8. The remaining material is called digestate, including indigestible material or dead microorganisms, and it can be obtained in liquid and solid states.

In order to select the right design for a digester, frequent organic loading rates and short retention times are essential. Nevertheless, there are plenty of configurations for a digester depending on the requirements of the anaerobic digestion process, the use of additives, the nature of the sewage, etc., obtaining single-phase and multiphase digesters that can use different technologies such as fixed dome method, floating drum method, polythene tube digester plants or earth pit plants.

During anaerobic production to produce biogas, many factors should be considered to obtain high yields with high methane percentages. For instance, temperature could affect microbial communities in biodigesters, clearly affecting biogas production performance [26]. Another aspect to be considered at this point (affecting final quality parameters of biogas such as methane composition) is the possibility of enhancing biogas production through multiple techniques, including organic, inorganic, and biological additives that can enhance microbial activity inside the digester [23,27–30].

Depending on the kind of raw material or operational parameters, among other factors such as the kind of digester selected, biogas composition can vary (especially concerning methane percentage, which is indispensable in biogas steam reforming and its yield or industrial design), with the subsequent change in its main properties, as observed in Table 2 [22]. Thus, the nature of the substrate during anaerobic digestion and the design of the biogas production process determines the composition of raw biogas [31]. According to this table, even if a specific biogas source is considered, a wide range of methane composition was found depending on many factors like process conditions or seasonality.

Table 2. Main characteristics of biogas from different sources.

	Sewage	Biomass	Organic Waste	Landfill Gas
Reference	[22,32–34]	[35]	[36,37]	[32,38,39]
CH_4, %	17.9–70	55–70	40–70	25–75
CO_2, %	30–50	27–44	30–60	7–60
N_2, %	2–6	--	--	0–25
O_2, %	0–5	--	--	0.01–3
H_2S, ppm	0–2000	0–3	--	Trace

It should be noted the high and variable concentration of H_2S that can be found in anaerobic digestion of SS, up to 2000 ppm, which can play an important role in the final configuration of a biogas steam reforming system, as it will be seen in further sections.

Typical natural gas contains (compared to biogas) a higher percentage of methane (89–96%), ethane (1.8–5.1%), lower amounts of carbon dioxide (up to 1%) and oxygen (0.1%), a similar proportion of nitrogen (1.3–5.6%) and a variable composition of hydrogen sulfide (from 0.001 to 0.1%) [10,40].

1.3. Biogas Steam Reforming

Hydrogen production is a perfect example of green chemistry, contributing to the sustainable growth of population areas [41] with many advantages such as the fact that it is clean energy, it presents a high energy density, its combustion does not generate evolved pollutants, and it is considered one of the most interesting energy types [42]. Pure hydrogen, as well as syngas (a mixture of hydrogen with CO), are gaining importance, as they can be used as an energy carrier or in interesting industrial processes, like methanol synthesis (or more complex compounds) through Fischer–Tropsch reactions.

Apart from primary hydrogen production depending on fossil fuel energy, electrolysis and pyrolysis or more innovative techniques such as bio-hydrogen production [42], one of the possible chemical routes to obtain hydrogen or syngas is steam reforming of methane, present in several industrial gases like natural gas or biogas. Thus, depending on the chemical conditions or the use of additional steps like a membrane reactor, hydrogen at different purity levels can be obtained [10,43].

Steam reforming of methane or simply steam methane reforming (see Equation (1)) is an endothermic reaction that usually takes place at high temperatures, between 750 and 950 °C and a wide range of pressure values (between 5 and 20 bar).

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H^0_{298} = +206\ \mathrm{kJ/mol} \tag{1}$$

The presence of CO_2 plays an important role in biogas steam reforming, as a second reaction takes place, included in Equation (2).

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \qquad \Delta H^0_{298} = +247\ \mathrm{kJ/mol} \tag{2}$$

This way, the simultaneous methane conversion through these chemical routes can lead to biogas bi-reforming or simply biogas steam reforming [44]. It should be noted that another reaction can take place during this process, that is, the water–gas shift reaction (WGS), as observed in Equation (3). Thus, both chemical reactions contribute to a higher yield in hydrogen production and, therefore, higher hydrogen concentrations are found at the reactor outlet.

$$H_2O + CO \leftrightarrow CO_2 + H_2 \qquad \Delta H^0_{298} = -41\ \mathrm{kJ/mol} \tag{3}$$

If Equations (1) and (3) are combined, Equation (4) is obtained:

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \qquad \Delta H^0_{298} = +165\ \mathrm{kJ/mol} \tag{4}$$

Consequently, regarding the above, many factors should be considered to optimize biogas steam reforming, such as methane purity, temperature, pressure, the use of catalysts and other purification techniques, such as pressure swing adsorption or membrane reactors. These factors will be explained in detail in the following sections.

1.4. Scientific Interest in Biogas Steam Reforming: Trends in Research

Considering the energy possibilities of biogas (and, by extension, methane) through the abovementioned power technologies, it is no wonder that this subject has attracted the attention of the scientific community, as observed in Figure 4. This way, similar trends and shares were observed for search criteria like "steam methane reforming" (whose publication evolution in the last two decades is included in Figure 4a and article distribution is included in Figure 4b) and "biogas steam reforming" (Figure 4c for published article evolution and Figure 4d for field distribution of these articles). This fact points out the similarities between methane and biogas (whose majority component is the former) and the equivalent use in energy industries.

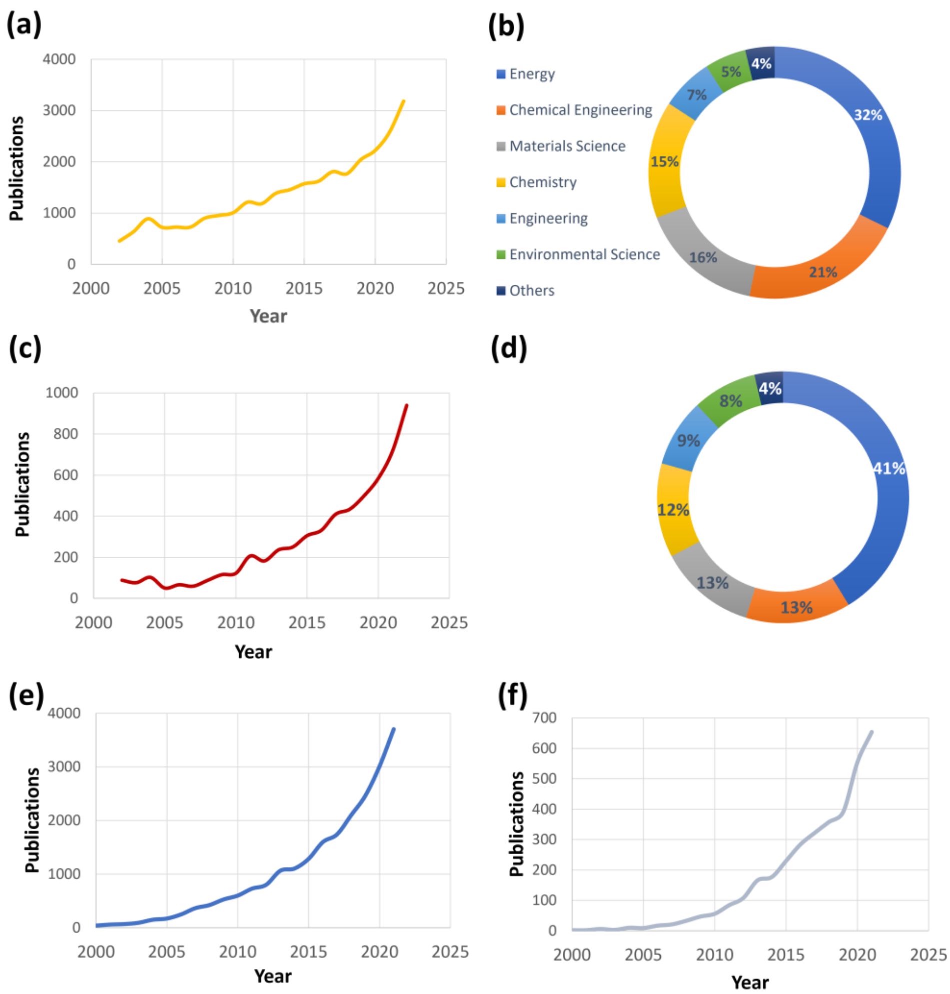

Figure 4. Scientific interest in methane (**a**,**b**), biogas (**c**,**d**) steam reforming and WWTP (**e**,**f**) over time and according to different scientific fields. Source: [45].

Specifically, publications about steam methane reforming have considerably increased in the last two decades, increasing the number of published articles sixfold. As a consequence, this technology seems to be a promising subject in the short and medium term. The different disciplines interested in methane steam reforming are Energy (with nearly a third of total publications), which points out the importance of this process for hydrogen production and its energy use; Chemical Engineering, where the implementation of this process is vital, was the second most important discipline, with 21% of total articles, whereas Materials Science (16%), possibly focused on many materials taking part in steam reforming like catalyst or adsorbent characterization, ranked third. Other fields like Chemistry (in order to understand reaction mechanisms that might take place), Engineering (similar to Chemical Engineering) or Environmental Science (which points out the importance of this process to produce hydrogen from such pollutant compounds like methane) are also interested in steam methane reforming.

Concerning biogas steam reforming, some slight differences were found compared to steam methane reforming. Thus, the increase in published articles was considerable from 2010, showing exponential growth in the last decade. On the other hand, even though the discipline profile was similar to methane steam reforming, a higher percentage of journals devoted to Energy (at the expense of the rest of the disciplines) was found, with 41% of total articles. This could be due to the fact that biogas could be considered a renewable energy and a possible alternative or replacement for natural gas, whose energy purposes and similarities have been widely explained in the literature [10,21,46].

According to Figure 4e (search corresponding to the term "WWTP"), it can be observed an exponential increase in published articles in the last two decades, whereas this increase seemed to start later in the case of WWTP applied to biogas production (Figure 4f, corresponding to the search term "WWTP + biogas"), proving again the increasing interest of the subject dealt in this review article.

1.5. Scope of This Review: Bibliometric Analysis

The core collection of Clarivate's Web of Science (WoS) was investigated for all entries in the literature on the topics of (Methane and/or steam and reforming) for the last 20 years, paying special attention to the last 5-year period (2018–2023). The search, which was made from January to July 2023, returned 51,822 results. In total, after a thorough selection, up to 280 articles were considered for inclusion in this review work, finally including 152 published articles (mainly research works and, to a lesser extent, proceeding papers or patents).

1.6. Objective of This Work

Regarding the above, the aim of this work was to review research works dealing with steam reforming of biogas from biodigestion in wastewater treatment plants to obtain hydrogen, putting in context every aspect of this process (from wastewater treatment to hydrogen purification) and paying attention to the most innovative techniques used for this purpose, as well as the main challenges related to them. In addition, the wide range of possibilities for biogas steam reforming is covered, including some interesting configurations found in the literature. Finally, techno-economic assessments of some aspects related to biogas steam reforming are included to emphasize the implementation of this technology at an industrial scale.

2. Technology and Chemical Conditions

In this section, general comments about the technology used during biogas steam reforming, as well as the specific circumstances applied to this process compared to other steam reforming processes, are included.

This way, there are many studies in the literature with the possible application of mature or emerging technologies to improve biogas steam reforming, mainly focused on biogas quality (for instance, to improve methane percentage through pressure swing adsorption, PSA) or the final product (to improve hydrogen proportion, as in the case of PSA or the use of membrane reactors).

Also, other processes such as methanol production or Fischer–Tropsch applied to syngas obtained from biogas steam reforming might be an interesting alternative, especially if H_2/CO ratios are suitable for this purpose. In that sense, these processes could avoid costly purification stages as they can use hydrogen and carbon dioxide mixtures directly.

The main technologies related to biogas steam reforming are observed in Figure 5. In that sense, there are many treatments that can be carried out to improve the quality of biogas and its products or the performance during steam reforming. For instance, biogas upgrading through different techniques, such as CO_2 removal, could be an interesting way to improve biogas steam reforming by increasing CH_4 percentage in final biogas [47]. In addition, biogas upgrading by biogas recirculation during anaerobic digestion seems to be an effective way to increase methane percentage (up to 90%) and reduce hydrogen sulfide content in final biogas [48], which could imply a better performance of this biogas during steam reforming. In any case, upgraded biogas could be equally used as biomethane or an alternative for natural gas if carbon dioxide removal is effective.

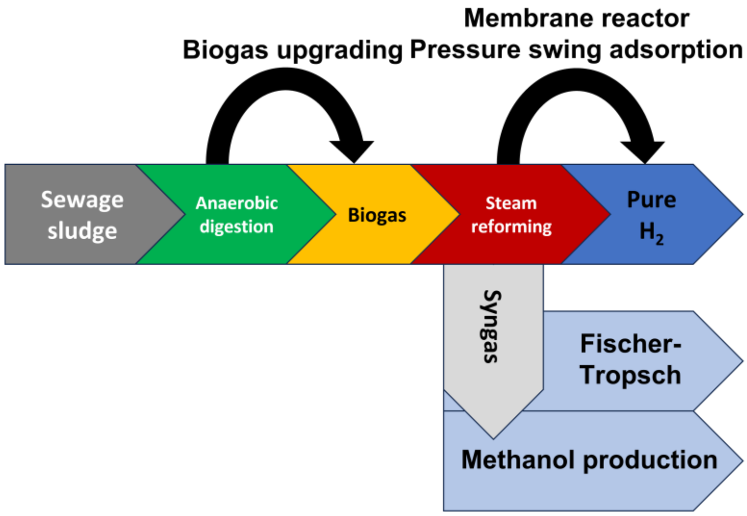

Figure 5. Main possibilities applied to biogas steam reforming.

Regarding the higher quality of biogas steam reforming products, carbon dioxide removal might be an attractive point to increase hydrogen percentage. Thus, CO_2 removal through molten carbonate fuel cells could be an interesting way to improve hydrogen purity, achieving up to 95% CO_2 capture [49]. Obviously, as explained in the following sections, the use of a membrane reactor or pressure swing adsorption could considerably increase hydrogen purity (up to 99% in some cases). This review work will be focused on these techniques.

Nevertheless, the direct use of syngas produced during steam reforming (that is, the mixture of H_2 and CO at different ratios) could be an interesting alternative if purification techniques are not available in order to produce interesting products through Fischer–Tropsch (such as hydrocarbons or paraffin) or methanol.

2.1. Influence of Chemical Conditions on Biogas Steam Reforming

Regarding the main chemical conditions observed in biogas steam reforming (or biogas bi-reforming), there are some factors that should be considered, such as the effect of temperature, pressure or steam-to-carbon ratio [50]. These are the main chemical conditions affecting steam reforming, but there are also other circumstances (as explained throughout this review) that could equally affect SR performance, such as the presence of hydrogen sulfide even at low concentrations.

Thus, temperature plays an important role, as methane conversion in biogas increases with temperature (from a temperature range of 500–1000 °C), mainly due to the endothermic nature of the main chemical reactions that take place (included in Equations (1) and (2)). In that sense, some studies have proved that biogas steam reforming cannot take place below 350 °C. In addition, in order to avoid coke deposition, which is an undesirable effect that can deactivate catalysts used in this process, high temperatures are recommended. For that purpose, the thermal stability of catalysts should be high, and that is the reason why ceramic-based nickel catalysts are extensively used in this context [12,51].

Pressure is another interesting aspect, as there seem to be two opposite effects regarding this parameter. In that sense, minimum pressure values (at least 3–5 bar) seem to be required to make the interaction among molecules included in biogas more frequent and effective, whereas excessive pressure (exceeding 20 bar, normally) seems to promote the equilibrium shift towards reagent generation, as SR and WGS reactions show an increase in molecules when products are obtained. Consequently, a pressure range of 3–20 bar is recommended, and a specific choice within this range will depend on other factors such as pressure or S/C ratio.

Concerning the steam ratio (another important parameter), it should be noted that the stoichiometric ratio observed in Equations (1) and (3) should be achieved, with higher S/C ratios, ranging from 3 to 6 in most cases observed in the literature, due to the two following reasons:

- The excess of one of the reagents will promote the equilibrium shift towards product generation, increasing methane and carbon monoxide conversion and, therefore, improving hydrogen yield and concentration in the final gas. The higher the purity, the better for further purification steps or treatments.
- It has been proven that high S/C ratios avoid coke generation (and deposition in some important parts of the reactor, such as catalyst surface or membrane, if they are used for hydrogen purification) during methane (and subsequently biogas) steam reforming. As explained in further sections, coke deposition is one of the most limiting factors in a steam reforming system, as it can contribute to a drastic decrease in the useful life of some components, such as membrane reactors or catalysts.

In that sense, the use of steam requires additional energy costs, which require the adjustment and optimization of the water supply to make the process more efficient. Indeed, this is one of the most interesting subjects in the implementation of biogas steam reforming, as explained in further sections. Additionally, excess steam can be easily removed through heat-exchange systems, collecting water, and obtaining a dry gas for further treatments or analyses. However, this step is also costly and should be efficiently designed to avoid energy loss. For this reason, it is not suitable to select S/C ratios excessively higher compared to the theoretical values (S/C = 2), as the energy consumption to provide more steam at high temperatures is large [51–53].

2.2. Pressure Swing Adsorption

Pressure swing adsorption (PSA) is a technique used to increase the purity of a certain compound included in a mixture of gases. In the case of this review work, two main purification processes could take place: first, methane upgrade in biogas production in order to improve the performance during biogas steam reforming, and second, hydrogen purification in the mixture of gases obtained after biogas steam reforming.

This is a separation process where, at room or ambient temperature, the pressure of different beds (with selective adsorbents, normally microporous or mesoporous solids such as silica gel, zeolite or activated carbon) is increased to trap gas. Thus, gas molecules are linked to the selective adsorbent at high pressure depending on many factors, such as adsorption forces.

In the case of hydrogen (see a configuration devoted to hydrogen purification in Figure 6), these forces are weak due to the fact that it is a highly volatile gas with low polarity, whereas other components such as nitrogen, carbon monoxide or carbon dioxide are highly adsorbable in the different beds. Once these gases are adsorbed, pressure in different beds decreases and increases alternatively in order to carry out the desorption of waste gases (by reducing their gas-phase partial pressures within the column so that the adsorbent can be reused) and the subsequent release of high purity hydrogen [47,54]. In the case of H_2 PSA units designed to treat steam reformer synthesis gases (a similar product as expected in biogas steam reforming), each adsorption bed is, in general, configured as a layered bed with the bottom layer near the feed end filled with activated carbon and the top layer near the product end filled with zeolite. The activated carbon layer acts as a protective bed, adsorbing and desorbing mainly CO_2 and CH_4, whereas the zeolite layer mainly removes CO and N_2.

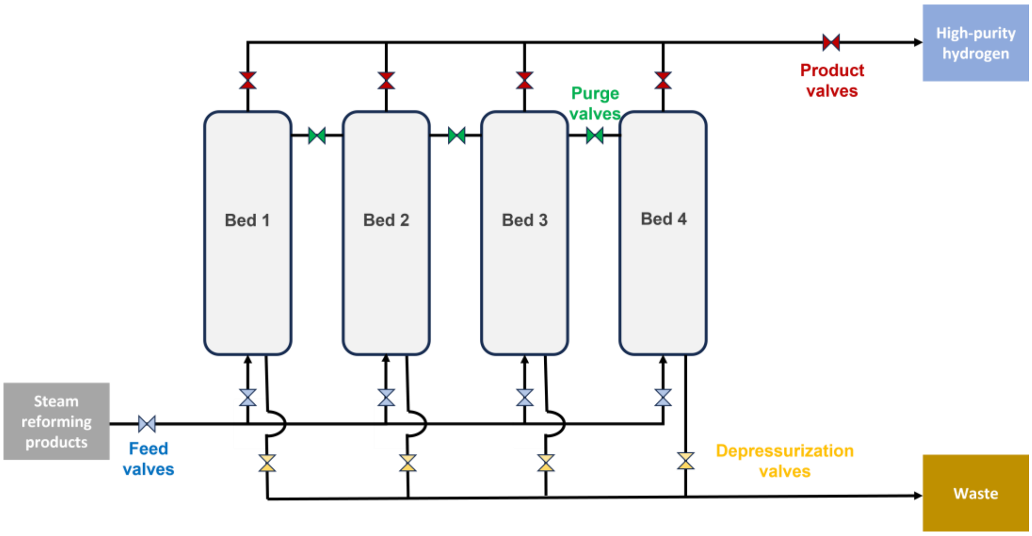

Figure 6. PSA facilities for biogas steam reforming products.

Even though there are many PSA units (from small to very large sized facilities) operating worldwide devoted to hydrogen purification from various feed sources (such as coke oven gas, refinery, methanol and ethylene exhaust gas, syngas coal gasifier and steam reformer synthesis gas), not many studies are specifically devoted to the specific case of biogas steam reforming, although the abovementioned sources could give us an idea about the conditions used for this purpose, working at different pressures (from 8 to 65 bar), hydrogen content (from 55 to 90%) and with different impurities such as CO_2, CH_4, CO, C_3H_8 or C_4H_{10}, being a versatile technique to obtain high purity hydrogen (up to 99.9%) [55,56]. The feed steam could also contain vapor, which is a possibility after biogas steam reforming, and PSA conditions can admit operating temperatures close to ambient temperature, at around 20–40 °C.

2.3. Membrane Reactors

The use of membrane reactors (MR) in gas-phase reactions has gained relevance in the last decade. Thus, its application in hydrogen purification processes has equally been interesting, with a tremendous track record found in the literature. Specifically, Pd-based membranes are very interesting in that sense, as they present high selectivity to separate hydrogen from gas streams [57,58].

Thanks to the higher permeability of hydrogen compared to other compounds included in biogas, such as unreacted methane, carbon dioxide or carbon monoxide, among others, hydrogen generated during steam reforming easily permeates through the membrane, with the subsequent increase in purity, reported to be up to 99% in many cases. This way, due to the removal of one of the products of steam reaction production, the balance of the reactions taking place to produce hydrogen (see Equations (1)–(3)) will be shifted towards product generation, with the subsequent enhancement of the reaction conversion, implying the following advantages:

- Hydrogen is obtained in high purity.
- The rest of the reagents (in unreacted form), apart from the products, can be easily managed to carry out other chemical routes.
- The reaction takes place at milder reaction conditions, as lower temperatures or pressure are required, among others.
- Equally, the amount of active phase in catalysts could be reduced.
- As a consequence, the energy/economic cost of steam reforming would be drastically reduced, implying a higher competitiveness at the industrial level.

For that purpose, there are plenty of materials to be used in membrane reactors, such as inorganic MR, polymeric MR, electrochemical MR, etc. In this review, we will focus on inorganic membrane reactors, which usually are the most popular kind used in the literature. In addition, there is a wide range of configurations, such as tubular (tube in tube), multichannel, etc., most of them differing in shape, size, thickness, reactor configuration (packed-bed or fluidized-bed, staged membrane reactors where the catalytic reaction and separation takes place at different areas or catalytic membrane reactors where the catalytic reaction and separation takes place simultaneously at the same place), or permeation area, among others [59]. As previously explained, inorganic membrane reactors, with Pd-based MR being the most used ones, are highly appreciated in the literature due to their adaptability to different operating conditions such as working pressure, temperature, purity requirement for hydrogen (which is usually removed from the reaction medium to obtain high-purity hydrogen at the outlet), etc. Thus, membranes based on metallic, ceramic, zeolite, carbon, or composite are especially useful to carry out steam reforming processes due to their resistance to high temperatures.

As explained, the use of membrane reactors could affect the typical chemical conditions in biogas steam reforming. The chemical conditions could be milder as the process takes place with a balanced shift towards product generation, but there are also other factors that should be taken into account when membrane reactors are used in steam reforming processes, which are also connected to correct catalyst performance, as explained in further sections [57–59]:

- Pressure: In this case, there are two opposite effects. On the one hand, according to stoichiometric equations observed in Equations (1) and (2), an increase in mole number towards product generation takes place, making the conversion of reactants unfavorable with pressure. On the other hand, pressure plays a positive effect on the performance of MR, as it favors hydrogen permeation through the membrane. In this case, this latter effect overrides the former effect, obtaining higher conversions with pressure in global terms. However, there is one interesting point to consider, like the pressure resistance of the membrane, which is usually given by the nature of the MR and thickness. Thus, high pressures could promote membrane cracking, generating areas where most gases in the reaction medium, apart from hydrogen, could pass through the MR, which is an undesirable effect as it would imply a considerable decrease in hydrogen purity. To sum up, there are offsetting effects when it comes to pressure, advising high pressures to a certain extent, depending on the kind of membrane.
- Temperature and space velocity: In this case, higher temperatures favor steam reforming of biogas, as well as a decrease in space velocity increases the residence time of biogas in the reactor, fostering H_2 generation and, therefore, increasing its partial pressure, which is suitable for a correct permeation through the membrane. Considering that most membrane reactors are prepared to work at high temperatures and considering that with this configuration, energy savings are assured thanks to lower temperature reactions (between 400–600 °C according to studies included in Table 3), there is no concern about the effect of high temperatures on MR integrity. Nevertheless, it would be advisable not to exceed 600 °C to ensure a long membrane lifetime.
- Coke deposition: This is one of the most worrying factors affecting MR performance. Due to the chemical reactions during steam reforming, especially when low S/C ratios are selected, coke deposition on the catalyst or the membrane can take place, hindering a suitable H_2 transition through MR.
- H_2S from biogas: Another problem related to the nature of biogas is the presence, even at low concentrations (up to 100–200 ppm), of hydrogen sulfide. Thus, it is necessary to remove this compound from the original biogas, preferably before steam reforming (see Figures 5 and 7), to avoid problems in biogas steam reforming systems. Obviously, membrane reactors, as a possible component in these kinds of facilities, are no exception, as H_2S could provoke poisoning on the surface of the membrane (generating palladium sulfide), possibly leading to the rupture of the membrane

layer, especially when they are thin. To avoid this undesirable effect, apart from the obvious removal once biogas is generated, alloys such as Pd-Cu or Pd-Au could be an alternative.

Table 3. Membrane reactors are used in biogas and SMR according to recent studies.

Membrane	Chemical Conditions	Comments	Reference
Pd-Au	420 °C, 300 kPa, 4100 h^{-1}, Ni/Al_2O_3 catalyst	30% H_2 recovery, 40% CH_4 conversion	[60]
Pd-Ag	550 °C, 1 bar, water feed of 20%	Up to 73.1 mol of H_2 per 100 mol of biogas	[61]
Pd/Al_2O_3	450 °C, 3.5 bar, S/C = 4, 11,000 h^{-1}, Ni/Al_2O_3 catalyst	70% H_2 recovery with high purity (>96%)	[62]
$Pd\text{-}Au/Al_2O_3$	500 °C, 30 atm, 1134 h^{-1}, Ru and Ni/Al_2O_3 catalyst	282 mL/min of permeated hydrogen	[63]
$Pd\text{-}Au/Al_2O_3$	600 °C, 150 kPa, 0.2–1.3 h^{-1}, $Rh(1\%)/MgAl_2O_4/Al_2O_3$ catalyst	80% H_2 recovery	[64]
Pd-Ag	450 °C, 0.4 MPa, S/C = 3, Ru/Al_2O_3 catalyst	80% H_2 recovery	[65]
Pd-Ru	400–600 °C, 350 kPa, S/C = 3, Ni/Al_2O_3 catalyst	CH_4 conversion and H_2 recovery close to 100%	[66]

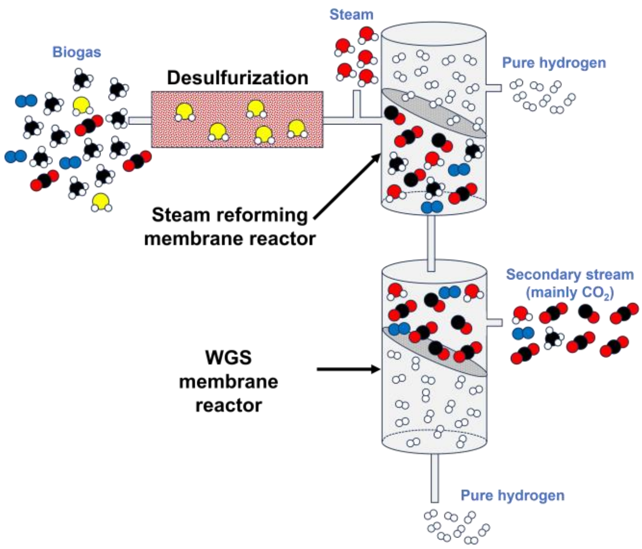

Figure 7. Typical setting for biogas steam reforming through membrane reactors.

Considering the above, a possible assembly for hydrogen production based on membrane reactors is included in Figure 7.

Even though there have been few studies about the specific use of membrane reactors in biogas steam reforming, some works with the use of methane for this purpose were equally interesting to point out the abovementioned reasoning. In addition, other studies used synthetic biogas to carry out their experiments or covered biogas steam reforming simulations based on thermodynamic methods. Thus, as observed in Table 3, the chemical conditions were considerably lower compared to typical steam reforming processes (where up to 1000 °C or 20 bar are commonly used), obtaining considerable methane conversions and hydrogen recoveries.

These milder reaction conditions are interesting when it comes to the service life of these facilities, and maintenance tasks could be less frequent (for instance, catalyst replacement would take place in longer periods). Another important aspect would be the ease of replacement of membranes, especially when they are deteriorated (which would imply hydrogen drain to waste gas).

3. Use of Catalysts

As briefly explained in previous sections, the role of catalysts in steam reforming in general and in methane or biogas (whose majority compound is methane) in particular is essential for the implementation of a competitive technology at the industrial level. In that sense, the role of heterogeneous catalysts is important, with a wide range of catalysts used in the literature possibly due to the fact that there is a wide variety of catalyst support (considering materials, sizes and shape, among other factors) and active phase, mainly Ni and Pd, among others. In this section, the most popular catalysts used and their main deactivation processes are covered, which are determining factors in the possible implementation of this technology at an industrial scale.

3.1. Catalysts Used in Biogas Steam Reforming

Considering the fact that biogas is mainly composed of methane, it is no wonder that many catalysts used in steam methane reforming can be equally used in biogas steam reforming. This way, typical configurations such as heterogeneous catalysts, mainly Ni-based ones, have been widely studied in the literature. For that purpose, the selection of the right catalyst support is essential, as it should present a series of interesting characteristics for this purpose, such as high thermal and mechanical stability, high surface area and porosity or coke resistance, among others. Specifically, many studies (as observed in Table 4) have pointed out the great performance offered by alumina supports, which is usually a recurring alternative in many industries for heterogeneous catalysis. Thus, its high mechanical and thermal stability, along with the high specific volume, allows the preparation of a wide range of catalysts at different concentrations, with the subsequent versatility for research in this field. Regarding catalyst shape, there are plenty of possibilities, as observed in Figure 8, where some of the main catalyst configurations are shown. Thus, even though some of them seem to be similar (for instance, pellets and tablets or hollow extrudates and rings), they present subtle differences, such as differences in length or diameter, which are essential to ensure the right contact between biogas and the active phase during steam reforming processes and to allow the mass transfer phenomena. In addition, depending on pressure or flow, some of these catalyst supports can be suitable or not, as some undesirable events, such as pressure drop, could take place, needing to redesign the biogas steam reforming process. That is the reason why size, configuration or porosity are vital parameters that should be considered in engineering design for the implementation of biogas steam reforming plants.

Table 4. Catalysts used in biogas steam reforming, according to recent studies.

Catalyst	Chemical Conditions	Methane Conversion, %	Reference
Ni/Al_2O_3	850 °C; S/C: 1.2; 7 bar; fixed-bed reactor	99	[67]
Ni-La/Si	800 °C; S/C: 0.8; 1 bar; fixed-bed reactor	90	[68]
$Ni/NiAl_2O_4/Al_2O_3$ (7.4%)	850 °C; S/C: 1.5; 1 bar, fixed-bed reactor	99	[69]
Mo_2C-Ni/ZrO_2	700 °C; S/C: 0.8; 1 bar; fixed-bed reactor	74	[70]
Ni-hydrotalcite promoted by Rh (0.5%)	Combined steam/dry reforming, 900 °C; S/C: 2; 0.5 MPa; fixed-bed reactor	98	[71]
Ni-Al_2O_3 (10%)	600–800 °C; S/C: 0.88–1.77; 1 atm; fixed-bed reactor	>80	[72]
Ni/CaO-Al_2O_3	750 °C; S/C: 2.2; fixed-bed reactor	>90	[73]
$Pt/Ce_{0.8}Nb_{0.2}O_{2-\gamma}/Al_2O_3$	800 °C; S/C: 3; 1 atm; parallel fixed-bed reactor system	>90	[74]

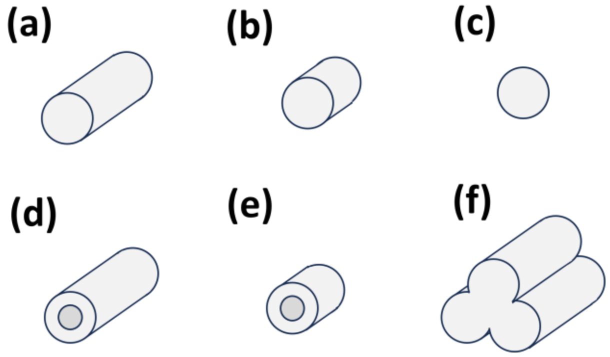

Figure 8. Examples of typical shapes used for catalyst supports: (**a**) pellet; (**b**) tablet; (**c**) sphere; (**d**) hollow extrudates; (**e**) ring; (**f**) trilobe.

Table 4 shows recent studies about catalytic biogas steam reforming. In all cases, high methanol conversion values were obtained, although this conversion could be considerably reduced due to the deactivation process of catalysts, mainly on account of coke deposition, reducing its activity up to 80% in different time ranges, mainly depending on the reaction conditions carried out for each experiment. In any case, the use of a catalyst allowed for the selection of mild reaction conditions (by reducing reaction temperature or pressure) compared to the typical chemical reaction conditions selected for this process (that is, up to 1000 °C and 15–20 bar) [10].

3.2. Catalyst Deactivation

Apart from the obvious effectiveness and selectivity desired for catalysts in every chemical reaction, durability (or lifetime) during biogas steam reforming is especially important to be considered when it comes to heterogeneous catalysts, especially in cases such as Ni-based catalysts. Thus, the maintenance tasks, including catalyst replacement, should be as frequent as possible to make the process as efficient and competitive as possible. In addition, there are many deactivation mechanisms caused by a wide range of factors derived from mechanical, thermal, or chemical processes [75] that will be explained in the following subsections. Nevertheless, the lifetime of a catalyst can be equally affected by other factors, such as the kind and form of the catalyst or operating conditions like pressure, temperature, and reactants [76]. Thus, the main deactivation processes are the following:

- Sintering: It is caused by the agglomeration and growth of catalyst metal crystallites, mainly due to high temperatures. Considering that steam reforming processes usually take place at high temperatures (above 500–600 °C, generally), this phenomenon should be considered. According to Hüttig and Tammann temperatures, which determine a certain metal's atom migration or crystallite migration (usually considered as one-third and one-half of the melting point of the corresponding metal, respectively), reaction temperatures for biogas steam reforming are high enough to allow surface and bulk atom migration in Ni, Pt or Mo based catalysts. There are three stages in the metal particle size increase on the support's surface. Firstly, atomic migration takes place, with the subsequent detachment from crystallites and migration through the support surface, joining to bigger metal particles. Second, these crystallites can migrate and collide with each other, generating larger particles. Finally, these particles can spread on the catalyst surface. Sintering is usually related to a decrease in catalyst activity due to two main factors. First, agglomeration implies a decrease in the surface area of active sites, reducing efficiency. Second, the increase in size of these crystallites can block pores on catalyst support, which can contain further active sites that otherwise would be available to convert methane molecules into hydrogen and synthesis gas [43,75]. Apart from temperature, sintering can be influenced by other factors, such as catalyst structure and, porosity and metal-support interactions. Thus, regarding the latter, strong metal-support interactions could reduce or inhibit sintering effects [76].

- Poisoning: It usually implies strong chemisorption of species on catalytic sites, blocking these sites and subsequently avoiding the steam reforming of methane in biogas. There are plenty of chemical products that can poison catalysts in biogas steam reforming, but the most important one is hydrogen sulfide (H_2S), which is usually present in biogas after anaerobic biodigestion (due to methane bacteria and reduction bacteria activity during this process, and on account of the high organic content in sewage sludge, with 50%), ranging from 5 to up to 200 ppm. These quantities, apart from the poisoning effect, are harmful or even deadly, promote corrosion processes in steam reforming facilities, and decrease the heating value of fuel gases, which make H_2S removal an important issue in these kinds of facilities [77,78]. This way, a recent study about a heterogeneous reactor model was proposed to simulate deactivation results found in the literature, finding a good agreement between the literature values and this model, which was equally validated by an industrial parametric case study [79]. To avoid the negative effect of poisoning caused by hydrogen sulfide, the use of adsorbents or absorbents seems to be a suitable alternative to remove hydrogen sulfide before biogas steam reforming, reducing its concentration up to negligible concentrations (below 5 ppm) before the introduction of biogas in steam reforming facilities. Thus, the use of alkanol amines (such as methyl ethanolamine or methyl diethanolamine), alkaline salts, organic solvents, deep eutectic solvents or ionic liquids, as well as adsorbents like zeolites, metal oxides or carbon-based sorbents could be interesting treatments to solve this problem at ambient pressure and low operating temperatures, as explained in further sections [78,80].
- Coke deposition: This is another important and negative factor having to do with the physical formation of carbon deposits because of gas-phase chemical reactions, in this case implying methane cracking, Boudouard reactions or CO disproportionation [76,81]. In general, the degree of carbon deposition in reforming reactions depends on the temperature and the oxidant-to-carbon ratio. Equations (5)–(7) shows the main reactions taking place:

$$CH_4 \rightarrow 2C + 2H_2 \qquad \Delta H^0_{298} = +75\ \mathrm{kJ/mol} \tag{5}$$

$$2CO \rightarrow C + CO_2 \qquad \Delta H^0_{298} = -173\ \mathrm{kJ/mol} \tag{6}$$

$$CO + H_2 \rightarrow C + H_2O \qquad \Delta H^0_{298} = -131\ \mathrm{kJ/mol} \tag{7}$$

  Thus, carbon deposition can present negative side effects, like deactivation or blockage of active sites, which would dramatically decrease the effectiveness of the catalyst over reaction time. Different stages take place during coke deposition, with different effects depending on the severity of this process with time. This way, coke chemisorption or adsorption takes place on active sites, reducing their access to reactants. In further stages, coke diffusion or dispersion to generate active site encapsulation occurs, completely blocking active sites to reactants, and pore blockage takes place, preventing methane molecules from reacting in available active sites. In order to avoid this process, strong metal-support interactions can be an interesting effect to avoid dislodgement of metal particles, whereas metal particle size can play an important role in controlling coke deposition [73].

As it can be inferred, there are some products or residues that are not convenient for suitable performance during biogas steam reforming, affecting different aspects of this process. In the following section, these by-products and their action are explained in detail, proposing a series of alternatives to neutralize their negative effect.

4. Residues during Biogas Production and Their Influence on Its Steam Reforming

During biogas production through the biodigestion of wastewater, different kinds of residues are obtained, having a strong influence on biogas steam reforming. Nevertheless, some of them, such as sewage sludge, present a great opportunity for the implementation of circular economy or green chemistry policies, as will be discussed. Thus, the main residues are the following:

4.1. Hydrogen Sulfide

H_2S is generated during biodigestion, mainly due to the presence in wastewater of amino acids containing sulfur, such as methionine or cysteine. Even though H_2S can present a positive effect in some industries, for instance, when it comes to Hg^0 removal from coal syngas by using biochar (where 400 ppm of hydrogen sulfide could imply 99% Hg^0 decrease due to elemental sulfur conversion into active sulfur species that capture Hg^0) [82,83], in biogas steam reforming it presents many disadvantages. The presence of this compound is extremely detrimental in many ways, as it is harmful at low concentrations (even ppm), being deadly if high peak concentrations (about 200 ppm) over time are achieved. Moreover, the presence of negligible concentrations of this pollutant could contribute to corrosion in wastewater treatment plants or steam reforming facilities (if biogas is used).

Furthermore, hydrogen sulfide could influence the suitable performance of membrane reactors, if used, for hydrogen purification during biogas steam reforming. As previously explained, the poisoning effect, even at low concentrations (ppm), could take place in palladium membranes, where palladium sulfide could be generated, with subsequent poisoning and membrane damage if the H_2S concentration is severe.

Finally, H_2S has adverse effects on catalysts used in steam reforming, especially when it comes to Ni-based catalysts, where poisoning could take place even at 5 ppm. Consequently, it is vital to remove hydrogen sulfide content in biogas before steam reforming takes place, requiring the use of techniques such as absorption or adsorption for this purpose [84–88].

Based on these reasons, the removal of hydrogen sulfide from biogas once it is generated after anaerobic digestion is essential, recommending trace concentrations at most if a long lifetime of many components included in a biogas steam reforming system is desired, apart from an optimal hydrogen generation and/or generation during this process.

For this purpose, there are many ways to remove or retain H_2S from biogas, as explained in Table 5. It should be noted the use of different and varied techniques such as adsorption, absorption, or biological methods [87,89–91], which assures a wide range of alternatives that can be easily adapted to the specific circumstances of anaerobic biodigesters coupled to wastewater treatment plants, facilitating the feasibility of implementation and customization of wastewater treatment plants.

In any case, some aspects, such as the capacity of adsorption/absorption (which will allow it to require replacement less frequently, implying savings), the service life or the reusability of the product, the management of the adsorbent when it is exhausted, or the ease of recognition when the adsorbent or absorbent requires a replacement are essential to select the right desulphurization method for each circumstance.

Specifically, there are some research studies focused on H_2S removal applied to biogas production (see Table 6), which can give an approximate idea about the possible specific implementation of these techniques to our subject. This way, a wide range of techniques, that is, physical, chemical and biological, were used to remove hydrogen sulfide from biogas at very mild conditions (most of these works were carried out at room or ambient temperature and low pressure), thus obtaining a wide range of hydrogen sulfide removal (from 26 to practically 100%), which can be used for different purposes depending on the nature and poisoning resistance of catalyst or membrane reactor, among other factors.

Table 5. Main techniques used for desulphurization.

Technique	Characteristics	Advantages	Disadvantages
In situ biological oxidation with air	Air supply to the gas phase Thiobacillus consume oxygen during oxidation of H_2S to S, which precipitates on the surface or is absorbed by the slurry	Simplicity and low cost	Possible explosive gas generation is not efficient in reducing H_2S completely
In situ biological oxidation with iron compounds	Iron chloride or hydroxide supply to the liquid phase, generating precipitation of FeS	Simplicity and low cost	Not efficient to reduce H_2S content completely
Ex situ biological oxidation	Use of immobilized microorganisms in biofilters, trickling beds or packed bed scrubbers. H_2S is oxidized to sulfur or sulfate	Separation performance up to 98%	Not efficient to reduce H_2S content completely and continuously
Chemical absorption	NaOH, $Ca(OH)_2$, $FeCl_2$, $Fe(OH)_3$, ethanolamines, etc.	High removal efficiencies, even for fluctuating H_2S content	High specific cost and use of chemicals
Absorption in polar solvents	Absorption in water and organic components. H_2S can be easily absorbed by increasing pressure or reducing process temperature	Efficient removal at high temperatures	Expensive method if cooling is required
Adsorption on metal oxides or hydroxides	Fe, Zn and Cu salts	High H_2S removal (<1 ppm)	Saturated material is needed to be regenerated or replaced
Adsorption on activated carbon	Impregnated on KI or H_2SO_4 with oxygen dose to oxidize H_2S to sulfur	Possibility of waste valorization to obtain activated carbons	High costs and difficult regeneration of activated carbon applied to industry. Poor selectivity.

Table 6. Specific studies devoted to H_2S removal in biogas.

Desulphurization Technique	Conditions	H_2S Removal	Reference
Mesoporous silica supported ZnO (15%) adsorbent	Ambient temperature (25 °C), 1 atm, 13,648 h^{-1}	<1 ppm for 200 min	[92]
Hematite-based sorbents	Room temperature, atmospheric pressure	<1 ppm for 150 min	[93]
Adsorption-absorption technique with activated carbon and iron compounds	22–27 °C, 6–19 mBar	100% desulphurization	[94]
Bioscrubber with activated sludge and NO_3^-/NO_2^- mixture	Industrial relevant conditions. Biogas flow rate of 5 m^3/h and 0.3 bar	>95% removal	[95]
Anoxic biotrickling system using nitrite as an electron acceptor	Mimic biogas was used	26% removal	[96]
ZnO-based adsorbent	28 °C, 1 atm	>99%	[97]

4.2. Carbon Dioxide

CO_2, another by-product obtained during biogas production, presents some disadvantages, such as its contribution to the greenhouse gas effect. In some cases, carbon dioxide capture has been widely used to obtain biomethane to be injected into the natural gas grid (whose composition, depending on the country, should not exceed around 2–6% of carbon dioxide for that purpose) or to be used as a local vehicle fuel. For that purpose, the use of membrane gas permeation allowed the purification of methane in biogas up to 80–99.5% [89].

Additionally, for better performance during steam reforming, high percentages of methane (at the expense of carbon dioxide or nitrogen) are desirable. Thus, several studies have focused on the improvement of biogas processing in order to obtain high yields of methane, including techniques such as:

- Water scrubbing: Due to the high water solubility of carbon dioxide and the cheapness of this technique, it has been widely used for years.
- Chemical scrubbing: By using alkali or alkanol amines, CO_2 is separated from biogas through chemical absorption.
- Pressure swing adsorption: Based on the selective adsorption over methane on several materials such as alumina, zeolite or activated carbons through some stages such as pressurization, feed, blowdown and purge.
- Membrane separation: By using different semi-permeable polymeric membranes, carbon dioxide permeates through these membranes, whereas most methane is retained. It should be noted that, in order to avoid deterioration in membranes, biogas should be previously treated to remove steam, hydrogen sulfide or ammonia, among other compounds.
- Cryogenic separation: Carbon dioxide, among other pollutants, is liquefied and removed in three consecutive stages, reaching temperature ranges from −45 to −120 °C.
- etc.

All these techniques constitute the general biogas upgrading, with endless possibilities, which can be perfectly adapted to the normal development in a wastewater treatment plant [24,31,98–101].

4.3. Sewage Sludge

One of the main wastes obtained during wastewater anaerobic biodigestion is activated sewage sludge (SS), which can be a waste with difficult management if it is not properly treated. Nevertheless, as previously explained, it can be an interesting starting point for the implementation of some techniques that could fit the biorefinery concept. Its main characteristics are included in Table 7.

Table 7. The main characteristics of sewage sludge on a dry basis (except for moisture) [102–105].

Proximate Analysis	%
Moisture	65–84.2
Ash content	20–61
Volatile matter	30–71.5
Fixed carbon	1–20
Ultimate analysis	%
C	18.30–53.24
H	2.90–8.38
N	2.5–9.59
S	0.30–5.62
O	14.60–48.50

Apart from the fact that different kinds of sewage sludge can be obtained in water treatment plants (primary or secondary sewage sludge), the characteristics of sewage sludge can vary depending on factors like season or day, plant location, the kind of treatment processes, etc. That is the reason why a wide range is observed in each parameter in the previous table. Thus, a wide variety of compounds, such as nontoxic products, toxic pollutants, phosphorous and nitrogenous compounds, pathogens and microorganisms and a considerable amount of water. One interesting issue regarding sewage sludge is the high amount of moisture, including free, interstitial, vicinal and bound water, which could imply a cost increase if some steps like drying are required for further treatments for its valorization.

Sewage sludge is a waste with many traditional uses, like landfilling, that could compromise the environment. Recently, some interesting uses of biogas slurries have been considered, combining them with deer manure during anaerobic fermentation in order to improve biogas production and its methane percentage [106]. Specifically, and regarding biogas steam reforming, the use of some techniques such as pyrolysis, hydrothermal carbonization (HTC) or activation could produce a valuable product like active carbons or biofuels [107–112], with a wide range of uses as observed in Figure 9. Apart from that, this figure could be integrated into a biorefinery context, where liquids and gas obtained from multiple technologies could be an interesting energy and product source [113].

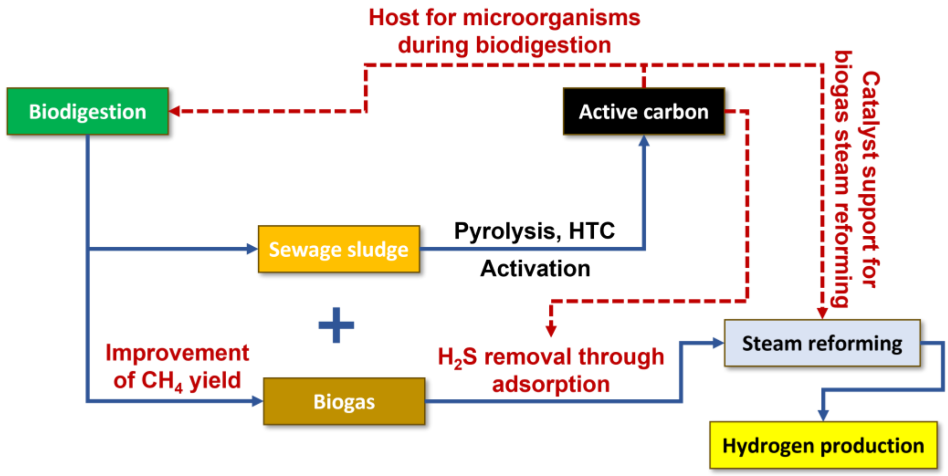

Figure 9. The role of sewage sludge in biogas steam reforming (in red dashed lines).

According to this figure, there are three ways in which sewage sludge can contribute to better performance during biogas steam reforming for more effective hydrogen production. In any case, active carbon production from sewage sludge is necessary, where thermal processes such as pyrolysis, HTC or activation through gasification could play an important role. It should be noted that sewage sludge presents high moisture levels, which requires an additional energy cost in order to dry this waste for pyrolysis and gasification processes (where high temperatures, up to 800–900 °C, take place). Indeed, in microwave pyrolysis of sludge for hydrogen production, the control of moisture content could promote H_2 generation by enhancing the steam reforming reaction [103]. In the case of HTC (mainly used in waste treatments such as lignocellulosic or agricultural wastes or wastewater, among others), it does not need this previous step and milder temperatures were observed (between 200 and 250 °C), transforming wet wastes into solid biofuel (hydrochar), gas (mainly carbon dioxide) and liquid phase rich in organic and inorganic compounds. As a consequence, hydrothermal carbonization presents a series of advantages compared to pyrolysis, such as simplicity and low cost (due to the low-temperature values required); it does not require organic solvents (contributing to green chemistry processes); higher solid yields with chemical structures similar to natural coals; HTC is exothermic and autocatalyzed due to hydronium ion generation, which promotes carbonization processes; no gas is released during HTC, minimizing gas emission to the environment; tar generation is avoided; biomass does not need a previous drying pre-treatment, as in the case of pyrolysis; HTC offers a wide range of chemical conditions, which assures a wide variety of characteristics (from size, surface and functionality) in biochar. These are the reasons why this technique has gained interest in recent years to convert wastewater into interesting products through HTC. In that sense, some studies have covered this possibility for digestate management in wastewater facilities [114]. In the same way, interesting results were found for hydrochars produced from sewage, with high HHV and fixed carbon, which could be used as solid biofuel [115,116].

Regardless of the method selected, once active carbons are obtained, three main uses have been observed in water treatment plants and steam reforming processes (apart from other uses like soil amendment through adsorption of pollutants in air and water, as studied in other research and review works [117,118]).

Firstly, active carbon can be used during biodigestion, acting as a host for microorganisms. Anaerobic digestion implies stages like hydrolysis, acidogenesis or methanogenesis, obtaining methane and other compounds like H_2S. Thus, biochar or active carbon is a porous material to which microorganisms can adhere, improving anaerobic digestion performance, encouraging biofilm formation and improving methanogen colonization [8]. In addition, it contributes to the removal of chemical oxygen demand, reducing the lag phase during methanogenesis and, increasing methane production (and improving the elemental composition of solid digestate, which is important for its use as fertilizer. Moreover, some contaminants or by-products that could inhibit biodigestion can be adsorbed by surface functional groups in biochar. On the other hand, biochar addition can increase alkalinity in an anaerobic digestion medium, reducing ammonia inhibition and acid stress to microorganisms implied in the process, and the porous nature of biochar promotes microorganism colonization (such as bacteria and archaea). Finally, functional groups in biochar can enhance methane yield through direct or indirect electron transfer among anaerobic microbes. Therefore, the process rate can be accelerated, reducing up to 24 h the lag phase of methanogenic microbes [8].

Secondly, the possible use of activated carbons for H_2S removal could be feasible, taking into account the possibility of sewage sludge reuse in water treatment plants. The use of biochar from sewage sludge pyrolysis could be an interesting starting point for activated carbon generation through further thermal treatment with carbon dioxide, steam, or oxygen to increase its specific surface area or pore volume at ambient temperature [119]. In addition, and considering the combined use of activated carbons obtained from this waste with other agricultural or food wastes like bark, husks or spent coffee grains, this kind of adsorbent is quite cheap as the raw material from which it is obtained is easily available carbon sources. Additionally, the combined use of activated carbons with other materials like zeolites, metal oxides (which can be obtained from alternative treatment of sewage sludge like calcinations) or porous organic polymers could be an interesting way to obtain synergistic effects on pollutant adsorption, as they can provide additional active sites for H_2S capture. On the other hand, the use of active carbons as hosts of some microorganisms could be suitable for hydrogen sulfide conversion to S [21]. In addition, biochar could be used for carbon dioxide sequestration, with different efficiencies (from 20 to 31.59%) depending on the raw material used for biochar production [120].

Thirdly, the use of active carbons or biochar as catalyst support for heterogeneous catalysis could be useful due to its high surface area and adjustable pore size and volume (depending on heating rate, among other factors). Additionally, its low-cost production and environmental friendliness could attract the attention of the scientific community.

5. Industrial Scale and Main Configurations

Even though there is plenty of research about methane and biogas steam reforming at a laboratory scale, the same cannot be said for the implementation of this technology at a semi-industrial or industrial level. Nevertheless, as it was inferred from previous sections, the subject of this review attracted the interest of multidisciplinary fields, especially Engineering and Chemical Engineering, whose main purpose is the applicability of scientific and technical findings on an industrial scale. Thus, some works are emerging dealing with possible configurations for biogas (or methane) steam reforming, with a wide range of possibilities depending on many factors such as easy replacement of components, cost reduction, inlet flow rate, higher hydrogen generation/separation, the degree of purity required according to the use of the gas obtained during steam reforming, the possible combination of biogas from different sources, the possibility of coupling biogas steam reforming to other technologies, etc.

Thus, according to the literature, many questions can emerge, like the following, which can determine the configuration of semi-industrial or industrial facilities:

- What is the initial inlet flow gas or the required outlet flow gas? In other words, what is the capacity of the wastewater treatment plant, and what percentage of biogas is going to be devoted to hydrogen production through steam reforming?
- Does the system require a highly efficient desulfurization process? Is hydrogen sulfide content in crude biogas stable enough, or does it depend on seasonality? What kind of system do we need, and what design is required to ensure a nearly complete H_2S removal?
- Will the steam reforming process be carried out in one single reactor or various reactors to adapt to the different reactions that take place (for instance, WGS)?
- If membrane reactors are used, how are they going to be implemented? In the same reactor or after the reaction takes place (as a separation unit)? Are other alternatives, such as PSA, going to be used? If not, is the synthesis gas generated going to be directly used to simplify the process or reduce costs?
- Is biogas steam reforming going to be used with parallel technologies, taking part in biorefineries with high atom efficiency or economy?
- How is the final outlet gas flow going to be used? Is it going to be immediately processed, stored, or transported by pipelines?
- etc.

In other words, we need to be absolutely sure of the level of purity required in biogas and the level of purity required in outlet gas (especially concerning H_2 levels), as well as the relative costs of this technology.

In general, there are some interesting works where the possibility of a typical steam reforming system applied to biogas was assessed, as in the case of Chouhan et al. [121], whose simulation in an industrial reformer for hydrogen production offered a model for this process, finding optimum feed conditions (molar feed rate = 21 kmol/h, P = 25 bar, T = 650 °C, S/C = 4 and heat flux = kW/m^2) and suggesting the possibility of using existing industrial reformers for this purpose, which could be a very interesting point that proves the feasibility of implementation of biogas steam reforming. In addition, other studies pointed out the possibility of the implementation of steam reforming (and its similarities with dry reforming) of CO_2-rich gas to obtain hydrogen, especially in the case of Ni-based catalysts, where high amounts of steam are required in order to avoid carbon formation [122].

On the other hand, other works are focused on applying a mathematical model for a suitable reactor design for biogas steam reforming (which is the essential part of reforming systems) with the corresponding experimental approach [123]. Thus, the model was validated by comparing a reactor with a Ni/CeO_2 catalyst, showing a good agreement between the experimental and theoretical results, being a good tool to advance reactor design for fuel reforming technology. A similar study was carried out by Amini et al., where numerical simulations have been carried out to design the reactor. Thus, this model pointed out that, following the optimal values for the correct design of the steam reformer, up to 20% increase in hydrogen production could be obtained compared to petrochemical industrial data [124]. Equally, another study pointed out the good adjustment of a theoretical model to an experimental facility for a steam reforming system based on 5% Ru/Al_2O_3 catalyst [125], reinforcing the idea that mathematical models could be an interesting way to assess the possibility of steam reforming design at industrial level. With this regard, these simulation studies point out the possibility of a real and successful implementation of biogas steam reforming systems, which could be equally applied in wastewater treatment plants.

According to recent studies, there are interesting assemblies having to do with biogas steam reforming, as in the case of Negri et al., whose modular plant (which is a patented technology) to convert biogas into advanced biofuels such as bio-methanol or bio-dimethyl ether contains a steam reforming section to obtain biogas, which is further processed to obtain the abovementioned compounds [126]. This way, biogas steam reforming taking part in further processes can be an important way to implement this technology at the industrial level.

If biogas upgrading is considered, some studies have pointed out the possibility of using composite alumina carbon molecular sieve membranes to be easily installed in existing reforming gas for hydrogen production. Thus, carbon emissions can be reduced by 95%, with an increase in hydrogen cost of 15% [127].

Regarding hydrogen purification techniques, the implementation of PSA in biogas steam reforming obtained from palm oil mill effluent has been recently simulated at the industrial level, including a desulfurization system and three reactors, the first one for steam reforming at 850 °C, the second one for high-temperature WGS at 380 °C, and the third one for low-temperature WGS at 200 °C, with minimal pressures of 800 kPa. Thus, hydrogen with 99.9% purity was obtained [128].

As it can be inferred from these previous studies, it is clear that steam reforming of biogas share, in all cases, some points or stages in common, like the following:

- There is an upgrade of biogas, with a necessary step to remove hydrogen sulfide from crude biogas, but some biogas upgrade steps regarding carbon dioxide capture could be included before or after steam reforming [17].
- Normally, a couple of reactors are required to carry out biogas steam reforming with different configurations (fixed bed or fluidized bed). This way, the reformer reactor (in general, at 750–850 °C) coupled to a WGS reactor (it could be a couple of reactors for high-temperature WGS and low-temperature WGS [12]) is a typical configuration for this technology.
- Afterward, a purification system can be included within the reactors or coupled to them, as in the case of membrane reactors or pressure swing adsorption systems. In any case, the products obtained during steam reforming could be directly used for other processes such as Fischer–Tropsch or methanol synthesis. Everything will depend on the purpose of biogas steam reforming, which proves the high versatility of this technique to be adapted to every requirement in wastewater treatment plants.

Specifically, to illustrate the abovementioned possibilities, Figures 10–12 show some examples or proposals for biogas steam reforming to obtain high-purity hydrogen. For instance, as observed in Figure 10, a reformer reactor coupled to a WGS reactor was selected, with a desulfurization and a pressure swing adsorption system.

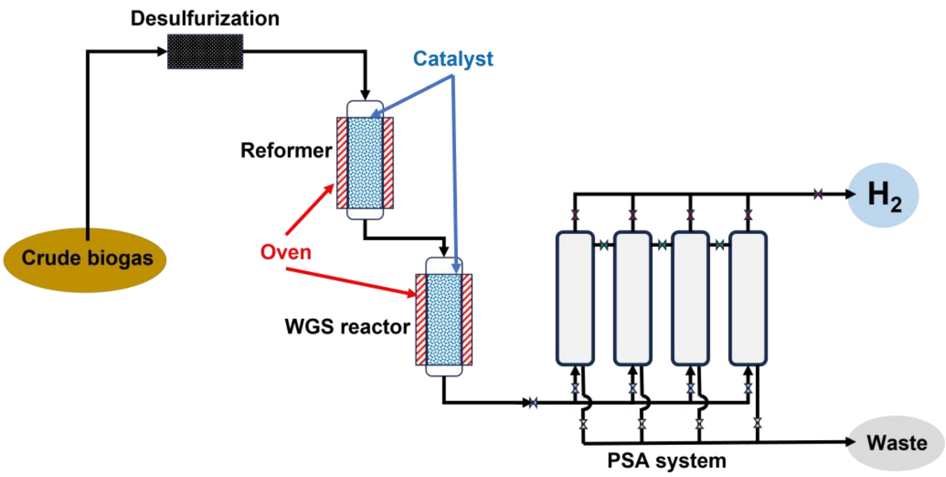

Figure 10. First configuration for biogas steam reforming, including pressure swing adsorption (PSA).

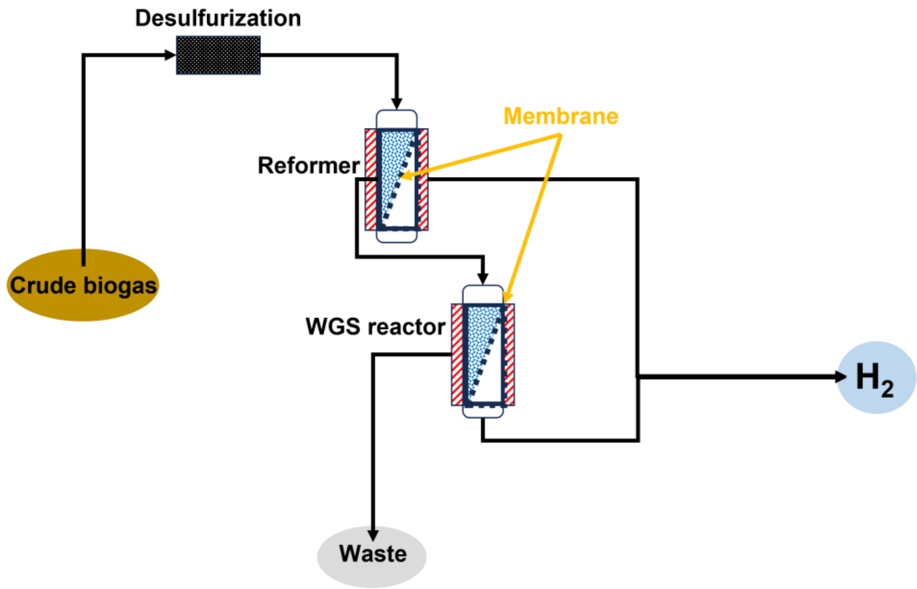

Figure 11. A second configuration for biogas steam reforming includes membrane reactors (that is, including membranes in reactors).

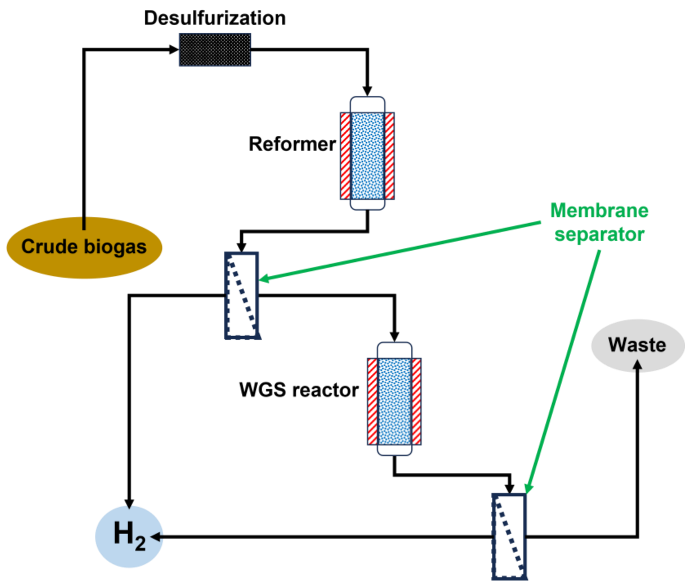

Figure 12. Third configuration for biogas steam reforming, including membrane purification outside the reactors.

This way, the waste and hydrogen stream are generated during the final phase, whereas in the case of the second configuration included in Figure 11, there are two hydrogen streams directly obtained from the reformer membrane reactor and the WGS membrane reactor.

Furthermore, a more complex configuration can be found in Figure 12, where the membrane reactors are only used to separate the evolved gas generated in the reformer and WGS reactor. These configurations can be used to adapt old steam reforming systems (where hydrogen was not obtained with high purity) to membrane purification systems. Equally, two high-purity streams are obtained.

It should be noted that these systems require further units, such as water traps, after steam reforming to remove moisture in the resulting gas. In addition, as mentioned, these units can count on three reactors to carry out high-temperature WGS and low-temperature WGS.

6. Techno-Economic Studies

One of the main issues concerning the possible implementation of a technology at the industrial scale is the study of energy/generation costs and the life cycle assessment of the process. This fact has attracted the interest of researchers whose techno-economic studies applied to biogas steam reforming are becoming more and more abundant, as observed in Table 8.

In that sense, as there are several configurations to carry out a steam reforming process, these studies are varied and focused on specific and limiting components that can determine or, at least, highly influence the final economic or life cycle result. Regarding biogas steam reforming, this discipline is no exception, and some studies have focused on specific technologies applied to hydrogen production from this source. Even though there are not many specific studies about steam reforming of biogas from anaerobic digestion in wastewater plants, other sources offering similar biogas composition have been included in this review, as it points out the fact that these studies would be perfectly applicable to our case.

In any case, these apparently disjoint scientific articles seem to share some points in common, like the following:

- They are focused on proving the economic feasibility of every aspect related to biogas steam reforming, covering specific subjects such as desulphurization technology, catalyst efficiency and service life, or hydrogen purification techniques such as the use of membrane reactors (where the nature of the membrane and its service life can vary the economic cost of this technology) or pressure swing adsorption technology. In addition, heating systems (to keep reactors at high temperatures, especially during steam reforming reaction) and cooling systems (to remove steam from outlet gas once the reaction takes place) play an important role in the economic feasibility of biogas steam reforming systems.
- Consequently, the initial quality of the biogas obtained during anaerobic digestion of sewage sludge could be a decisive factor, as explained in previous sections in the case of methane (higher purity in CH_4 would imply a better efficiency during the process, although coke deposition could be accelerated) and hydrogen sulfide (its presence, even at ppm concentrations, could drastically reduce the useful life of steam reforming facilities, especially in the case of catalyst and membrane reactor deactivation).
- In some studies, the role of green chemistry or circular economy is important to make the process more efficient compared to other industries. In that sense, the combination of biogas steam reforming with other technologies in order to make the process feasible (for instance, the use of solar or wind energy to cut energy costs, especially in processes such as heating the reformer or heat exchange [129,130]) has gained interest in recent years. In addition, as explained in the case of sewage sludge, some wastes obtained in wastewater plants could be interesting to promote or improve many aspects concerning biogas steam reforming, especially in H_2S purification or catalyst support production.
- There seem to be opposite trends depending on the desired hydrogen purity obtained in this process: on the one hand, high-purity hydrogen implies the use of expensive technologies that could compromise the economic feasibility of a biogas steam reforming system, whereas the use of mixture gases such as synthesis gas could be easier to treat (although other technologies such as the implementation of Fischer–Tropsch could imply higher costs). On the other hand, high-purity hydrogen is valuable, which could offset the initial extra costs when it comes to the implementation of steam reforming at the industrial level.
- Thus, in some cases where the economic costs are not suitable for the implementation of this technology at the industrial level (for instance, compared to natural gas steam reforming, according to some studies that consider that the implementation of this technology is more suitable [131]), there is a need for institutional support (especially fostered by international agencies or governments) in order to make these kinds of

processes more economically efficient compared to mature industries. Nevertheless, these efforts could be worth it in the long term, as the ecological analysis of these systems usually implies high-efficiency values, which can offset the initial costs of implementation of this technology, being preferable to other equivalent technologies such as natural gas steam reforming [131]. In addition, biogas steam reforming has been considered a promising technique due to its high ecological efficiency, concluding that this is a technically and economically feasible technology [132]. In that sense, the role of tax considerations (highly influenced by green policies) when it comes to techno-economic assessment is vital, as it can determine the economic feasibility of this kind of industry.

Table 8. Studies about techno-economic or life cycle assessment applied to biogas steam reforming.

Study	Main Characteristics	Comments	Ref.
Simulation of biogas steam reforming from palm oil mill effluent (POME)	Desulfurization, three reactors for reforming, high-temperature WGS and low-temperature WGS	20,000 kg of POME per hour, 963.31 tonnes of hydrogen (99.9%) can be obtained per year, making this process technically and economically feasible	[128]
Technical, economic, and ecological aspects of hydrogen production by biogas steam reforming	Discontinuous biogas steam reforming, with reforming and WGS reactor, using biogas for the steam boiler	Efficiency of steam reforming was 80%. Payback period of 8 years, with a high ecological efficiency of 95%	[69]
Techno-economic assessment of biogas catalytic steam reforming	Desulfurization, syngas decarbonization through iron-calcium looping systems and pressure swing adsorption to obtain pure hydrogen	Lower hydrogen costs (5%) and CO2 capture costs (25%) thanks to iron/calcium looping. The plant size was 50,000 Nm^3/h H_2 (99.95%) and 40 MW net power output	[133]
Study of energy efficiency in biogas steam reforming	Steam reforming optimization focused on temperature, S/C ratio and catalyst (Ni-MgO-$CeZrO_2$)	Optimum conditions: S/C = 1.5 and T = 700 °C. The authors found that these conditions were energy-effective and applicable to actual reforming processes	[81]
Tri-generation system for power, cooling and hydrogen production based on biogas steam reforming	A multi-generation integrated energy system powered by biogas energy is proposed, integrating steam reforming and purification methods	Net power output = 108.7 KW; cooling load = 888.7 K; hydrogen production = 703.3 kg/h Initial capital return = 5.73 years	[134]
On-site hydrogen supply through SMR	A case study in Foshan (China)	Potential use of skid-mounted hydrogen production systems based on SMR, requiring technological innovation in reforming technology, reformer, catalyst, system integration and intelligent control	[135]
Economic analysis of SMR from swine manure	The system included the reformer, shift reactor and pressure swing adsorption	The ecological efficiency was high (97.73%), with a plant exergy efficiency of 76% and 8-year payback, allowing additional value to pig farms	[136]
Techno-economic assessment of biogas steam reforming	Included a steam reformer, WGS reactor and PSA	Lower investment costs compared to biomass steam gasification, pointing out the importance of tax considerations in techno-economic assessments	[137]
Study of the possible implementation of a membrane reformer for biogas steam reforming	Including sulfur removal, reformer, high-temperature WGS reactor, low-temperature WGS reactor and PSA	Compared to a reference case, this system presented lower hydrogen cost production, increasing the system efficiency by 20%	[138]
Energy and exergy analysis of biogas steam and autothermal reforming	Use of Pd-membrane steam reactor for hydrogen purification and a WGS reactor	High energy production efficiency (59.8%)	[139]

As observed in this table, every detail counts when it comes to improving the efficiency and economic feasibility of any component of a biogas (or equivalent) steam reforming system, apart from other important sections included in a typical wastewater treatment plant that could have to do with the suitable performance of the subject under consideration in this review. Moreover, these studies point out one interesting fact, like the possibility of implementation in other steam reforming plants regardless of the source selected for biogas generation (not only devoted to biogas obtained through wastewater anaerobic digestion to hydrogen conversion).

Another interesting aspect that would indicate the interest in these technologies applied to real industries is the considerable number of registered patents about biogas (or methane) steam reforming. Thus, in recent years, researchers and inventors have taken a great interest in this subject, as can be observed in Table 9. Basically, a patent is focused on trying to exploit an innovative idea mainly for commercial or industrial purposes, so they needs to be practical and to solve a real problem found, for instance, at the industrial level. That is the reason why, in the case of this review work, the main concerns covered by these patents are the following:

- Some patents try to directly make the most of the products obtained during methane steam reforming. As explained in this review, an interesting and economical alternative for pure hydrogen generation is the direct use of syngas obtained during steam methanol-reforming, pointing out a practical and simple way to exploit biogas generated in WWTPs.
- Also, some works are focused on hydrogen purification after steam reforming. This would imply an increase in the quality and price of the final product, which is an interesting aspect to consider, especially if maintenance and costs to carry out this purification are moderate.
- In many cases, a proposal of a specific facility is also included, pointing out some innovative parts of the steam reforming process. As observed in this work, the configuration of steam methane reforming is essential and should be specifically adapted to each case.
- In these facilities, the combination with other sustainable systems (such as solar systems) is used for a less costly process, as explained in previous sections.
- Finally, patents are not unfamiliar with the role of catalysts during this process, proposing interesting ideas to make them more effective, selective and, especially, durable.

Table 9. Selection of most current patents focused on methane steam reforming (2018–2023).

Description	Details	Reference
Hydrogen production by methane steam reforming	A process to obtain hydrogen from a feed gas with hydrocarbons. The system includes a SR reactor and a WGS reactor	[140]
Methane steam reforming unit for hydrogen production combined with other technologies	The system consists of a methane steam reforming unit coupled to a photovoltaic power generation energy storage module, including a membrane reactor for hydrogen purification	[141]
Syngas production from steam methane reforming	A synthesis gas plant is proposed, including a gas separation unit and burners	[142]
Methane steam reforming reaction device	A global methane steam reforming module is presented, using a ceramic composite membrane and with the aim of obtaining high-purity products during the process	[143]
Device for producing hydrogen by steam reforming	Recommended for gas with high methane and high carbon hydrocarbon content, as in the case of natural gas (and possibly biogas). It includes a feed gas pre-treatment, a reaction and a separation assembly	[144]
Nickel-based catalyst	A catalyst composed of a porous carrier and nickel species is proposed for methane steam reforming, including a preparation method	[145]
Red mud oxygen carrier	It showed a good methane conversion rate and high H_2 purity, CO selectivity, H_2/CO ratio, cycling stability and carbon deposition resistance; the reduced oxygen carrier can be regenerated through steam	[146]
Foam monolithic catalysts	Preparation method of foam catalysts, offering better performance compared to traditional fixed-bed catalysts (smaller reactor sizes and stable methane conversion)	[147]
Optimization of Ni catalyst on inorganic oxide pellet support	The catalyst presented high durability against carbon deposition	[148]
Anti-sintering methane steam reforming catalyst	The preparation of catalysts with high resistance to sintering is included, showing a high activity	[149]

In conclusion, these patents (which are recent and will presumably increase in the near future) point out the promising future (and present reality) of steam methane reforming, which could be perfectly applied to biogas obtained in WWTPs.

7. Conclusions and Future Research

Regarding the above, the main findings inferred from this review work are the following:

- Biogas steam reforming could be a suitable method for hydrogen or syngas production, involving another method for wastewater management. Depending on many factors such as methane purity in biogas, H_2S content or the required purity of H_2, the implementation of this technology could be easily adapted thanks to the use of techniques such as desulphurization, pressure swing adsorption to increase methane or hydrogen concentration or membrane reactors to enhance hydrogen production.
- In that sense, some factors, such as coke deposition or high H_2S content, could hinder a suitable performance in biogas steam reforming at different levels. For instance, catalysts and membrane reactors could reduce their effectiveness due to these circumstances.
- Also, biogas steam reforming could be an interesting starting point to produce syngas, which might be used in Fischer–Tropsch and methanol synthesis. Consequently, and depending on the degree of purity of the product obtained during biogas steam reforming, the possibilities of this technique within the context of a biorefinery could be very interesting and easily adaptable.
- Sewage sludge, obtained after biogas production, could play an important role in wastewater treatment plants. Thus, its reusability as active carbon obtained through pyrolysis/gasification could enhance the valorization of this byproduct, even increasing the sustainability of biogas steam reforming in several ways, such as H_2S adsorption, catalytic support or biodigestion enhancer.
- Regarding economic assessment, there are some limiting or decisive components that will determine the economic feasibility or life cycle of a certain facility devoted to biogas steam reforming, depending on the techniques coupled to the typical steam reforming. Thus, the role of catalysts, as well as membrane reactors, among others, seems to be an interesting point to enhance the efficiency of a steam reforming system applied to biogas obtained in wastewater treatment plants.
- Finally, there is an increasing interest in this subject, including studies covering specific case studies of the application of biogas for its use in steam reforming technologies. Even though there are some areas of knowledge where there is a lack of specific works dealing with the application of this technology to WWTP, the coverage carried out by research works about equivalent products (such as biogas from other sources or methane) points out the real feasibility of the implementation of these innovative technologies in steam reforming systems applied to WWTP. However, more economical and scale-up studies are required to prove the efficiency of steam reforming applied to biogas.
- Regarding future research, it is clear that there are some aspects in this field that should be addressed, such as global techno-economic assessment (including operating and capital expenses, as well as energy consumption or the impact of maintenance operations, among others) of specific WWTP coupled to biogas steam reforming facilities. Thus, the use of catalysts and purification techniques specifically applied to this discipline are welcome, paying special attention to the increase in the useful life of these technologies, which will improve techno-economic analyses.
- To sum up, even though biogas has been extensively studied in the literature concerning different aspects such as its production or energy use, there are several opportunities to go beyond and make WWTP more efficient and sustainable by coupling innovative techniques such as membrane reactors or pressure swing adsorption, where there are endless opportunities to make biogas upgrades or steam reforming more competitive. Accordingly, innovations in these technologies are expected in the short term.

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Abbreviation

Abbreviation	Term
ATR	Autothermal reforming
DR	Dry reforming
HTC	Hydrothermal carbonization
MR	Membrane reactor
POR	Partial oxidation reforming
PSA	Pressure swing adsorption
S/C	Steam to carbon ratio
SDG	Sustainable Development Goals
SMR	Steam methane reforming
SR	Steam reforming
SS	Sewage sludge
WGS	Water–gas shift reaction
WWTP	Wastewater treatment plant

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