

Review

# Technologies for Biogas Upgrading to Biomethane: A Review

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**Abstract:** The environmental impacts and high long-term costs of poor waste disposal have pushed the industry to realize the potential of turning this problem into an economic and sustainable initiative. Anaerobic digestion and the production of biogas can provide an efficient means of meeting several objectives concerning energy, environmental, and waste management policy. Biogas contains methane (60%) and carbon dioxide (40%) as its principal constituent. Excluding methane, other gasses contained in biogas are considered as contaminants. Removal of these impurities, especially carbon dioxide, will increase the biogas quality for further use. Integrating biological processes into the bio-refinery that effectively consume carbon dioxide will become increasingly important. Such process integration could significantly improve the sustainability of the overall bio-refinery process. The biogas upgrading by utilization of carbon dioxide rather than removal of it is a suitable strategy in this direction. The present work is a critical review that summarizes state-of-the-art technologies for biogas upgrading with particular attention to the emerging biological methanation processes. It also discusses the future perspectives for overcoming the challenges associated with upgradation. While biogas offers a good substitution for fossil fuels, it still not a perfect solution for global greenhouse gas emissions and further research still needs to be conducted.

**Keywords:** anaerobic digestion; biogas upgrading; biomethane; bio-succinic acid; CO<sub>2</sub> utilization; feasibility assessment

## 1. Introduction

In the last decades, fossil fuels have been utilized at a high rate as the main energy source for the industrial process as well as daily usage. The result is the increasing crisis of global energy and environmental problems. It has been predicted that the global consumption of energy will increase nearly threefold in the next thirty years [1]. Massive carbon dioxide (CO<sub>2</sub>) emission during fossil fuel combustion has raised the concern on energy sustainability and environmental protection issues. The rate of CO<sub>2</sub> that is presently being released at a global scale is more than 1000 kg/s, although it is the imbalance between emissions and sinks that is responsible for the increasing CO<sub>2</sub> concentration in the atmosphere [2]. The reductions of CO<sub>2</sub> emission into the atmosphere can only be achieved by either reducing the CO<sub>2</sub> emissions from the sources or increasing the usage of CO<sub>2</sub>. A wide-ranging research plan is needed to develop a variety of carbon utilization technologies suitable for utilizing the abundance of carbon waste in the atmosphere, integrating enabling technologies and resources, and producing a wide range of carbon-based products. Therefore, extensive research needs to be

conducted to address the knowledge gaps throughout the carbon utilization landscape in order to reduce greenhouse gas emissions (GHG) while generating economic value. The conversion of CO<sub>2</sub> into added-value chemicals and fuels is considered as one of the great challenges of the 21st century.

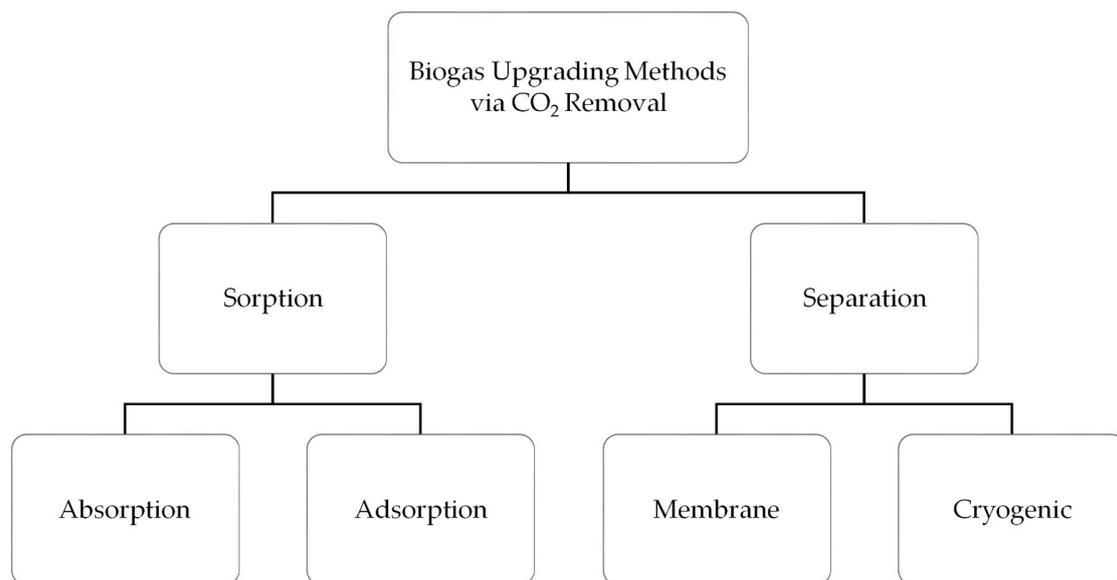
To achieve sustainable development, energy resources with low environmental impact should be utilized. Besides petroleum, biomass is the largest source of carbon-rich material available on Earth [3]. Biorefineries represent tremendous potential for the efficient utilization of renewable resources. A biorefinery can be described as a facility that integrates biomass conversion processes and technologies in a sustainable and efficient way to produce a variety of marketable products (food, feed, chemicals, and materials) and energy (biofuels, power, and/or heat) from biomass. Biogas is a well-established renewable energy source for combined heat and power (CHP) generation. Biogas production is a treatment technology that generates renewable energy and recycles organic waste into a digested biomass, which can be used as fertilizer and soil amendment. Biogas is considered a renewable energy source due to the fact that the organic waste has consumed carbon dioxide in the photosynthesis process, and as such can be described as carbon-neutral [4]. The amount of wastes and residues generated has led to the demand for technologies and processes that can help to reduce these residues, which can help achieve the ambitious objective of “zero-waste” targets (or, at least, waste minimization) while obtaining valuable commodities, including renewable-based methane-rich product gas streams. In these regards, waste management technologies based on the anaerobic digestion of different residual streams, such as municipal solid wastes in landfills, agriculture crops, and urban wastewaters that allow the production of biogas, have played a significant role in the last decades. To date, efforts have been made to improve the methane (CH<sub>4</sub>) yield during anaerobic digestion. Feedstock selection, process design and operation, digestion enhancement, and co-digestion with multiple substrates have been extensively studied, and several reviews are available [5–9].

Commercial biogas production has increased since it can be used as fuel or energy production while contributes to a lower GHG concentration when it is collected in a closed process and not emitted to the atmosphere. Depending on the nature of the substrate and pH of the reactor, biogas produced consists of CH<sub>4</sub> in a range of 50–70% and CO<sub>2</sub> at a concentration of 30–50%, with the addition of minor components such as hydrogen sulfide (H<sub>2</sub>S), nitrogen (N<sub>2</sub>), oxygen (O<sub>2</sub>), siloxanes, volatile organic compounds (VOCs), carbon monoxide (CO), and ammonia (NH<sub>3</sub>). It is estimated that biogas usage in the world will be doubled in the coming years, increasing from 14.5 GW in 2012 to 29.5 GW in 2022 [10,11]. Apart from CH<sub>4</sub>, the remaining components in biogas are undesirable and considered as impurities. Basically, there are two steps involved in biogas treatment, cleaning (removal of minor unwanted components of biogas), and upgrading (removal of CO<sub>2</sub> content) [10,11]. After the processes, the final product is called biomethane which composed of CH<sub>4</sub> (95–99%) and CO<sub>2</sub> (1–5%), with no trace of H<sub>2</sub>S. Biogas cleaning is usually considered the first step for biogas applications and is an energy-demanding process. The second treatment is called “biogas upgrading” and aims to increase the low calorific value of the biogas, and thus, to convert it to a higher fuel standard [12]. Nowadays, there are different treatments targeted at removing the undesired compounds from the biogas, thus expanding its range of applications. High CH<sub>4</sub> purity biogas has the same properties as natural gas, especially in terms of heating value, therefore, this clean biogas is qualified to be injected into a natural gas grid [13]. An early notable review report on biogas upgrading was published in 2009, providing a complete view on the situation of biogas upgrading at that time, however, the topic on CO<sub>2</sub> removal was only briefly discussed [14]. More review reports on biogas purification and upgrading had appeared recently. The first of them was by Ryckebosch and others (2011) [15] discussing the state of affairs of different techniques for biogas transformation and their functions, efficiency, and barriers. Next, Bauer et al. (2013) [16] reviewed and compared the commercial technologies on biogas upgrading. In later years, Sun et al. (2015) [12] had come out with a more detailed review on biogas upgrading technology, focusing on biogas purity and impurities, CH<sub>4</sub> recovery and loss, upgrading efficiency, investment, and operating cost. These were among the many reviews that were conducted on the topic of biogas upgrading involving CO<sub>2</sub> removal. Therefore, in this review, an attempt is made to

present new technologies for biogas upgrading via the utilization and conversion of CO<sub>2</sub> rather than the removal of CO<sub>2</sub>. The already matured technologies will only be briefly summarized.

## 2. Biogas Upgrading via Carbon Dioxide Removal Technologies

As a means to upgrade biogas to a higher fuel standard, that is, to remove unwanted components such as CO<sub>2</sub> and H<sub>2</sub>S thus increasing its specific caloric value, several different approaches have been proposed [17,18]. The mature technologies that are today currently applied for biogas upgrading are illustrated in Figure 1. The focus of this section is to summarize the important details regarding current CO<sub>2</sub> removal technologies rather than going into details on it.



**Figure 1.** Technologies for biogas upgrading via CO<sub>2</sub> removal route.

The gas sorption is divided into two categories: physical and chemical scrubbing. Physical scrubbing and chemical scrubbing processes were summarized in Figures 2 and 3 respectively. Next, the adsorption method was usually done in a process called pressure swing adsorption and can be seen as a summarized point in Figure 4. Then, the term separation is applied in membrane technology and cryogenic separation and depicted as in Figures 5 and 6, respectively.

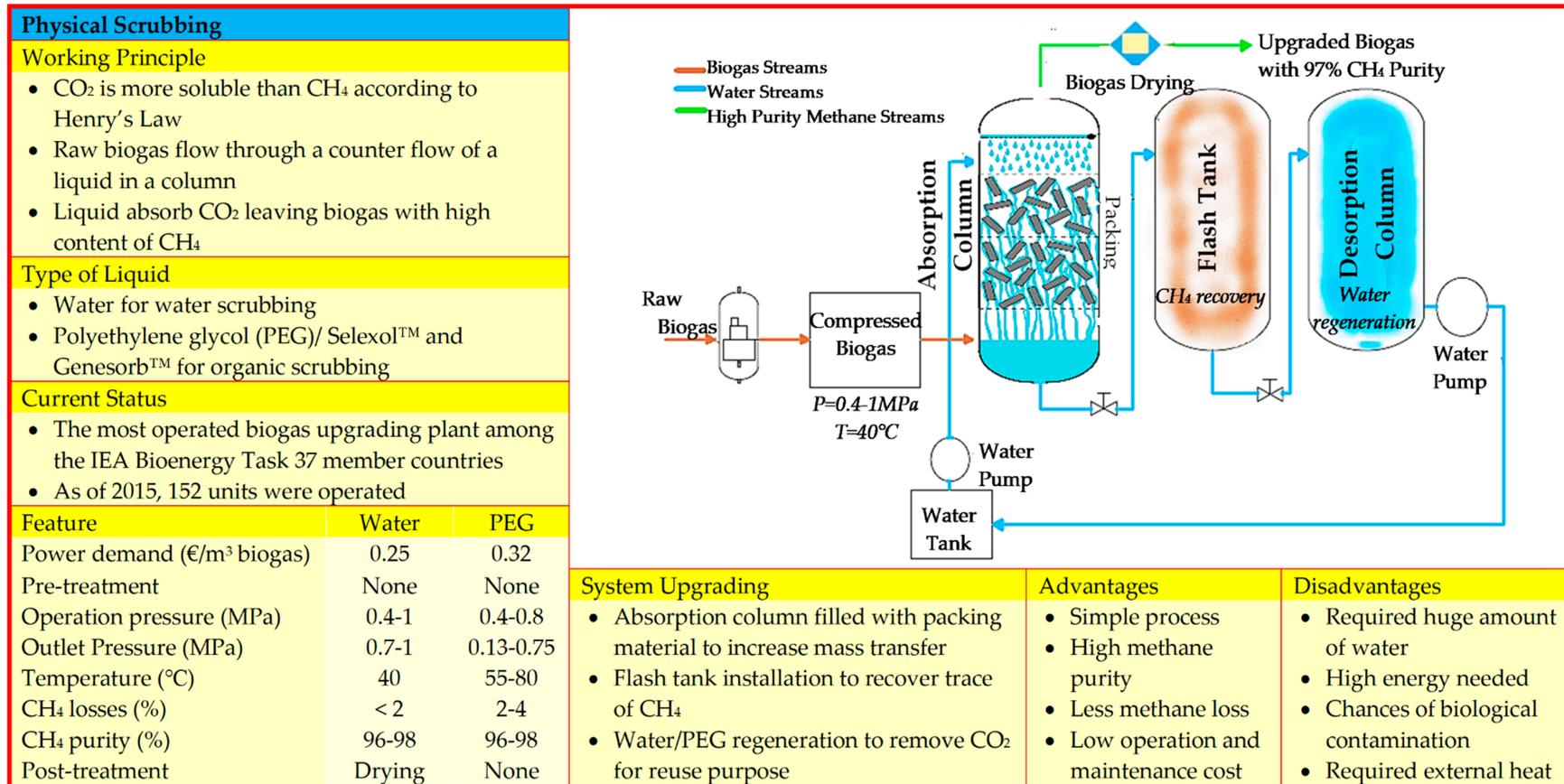


Figure 2. Summary of fundamental knowledge on physical scrubbing technology [15,19–28].

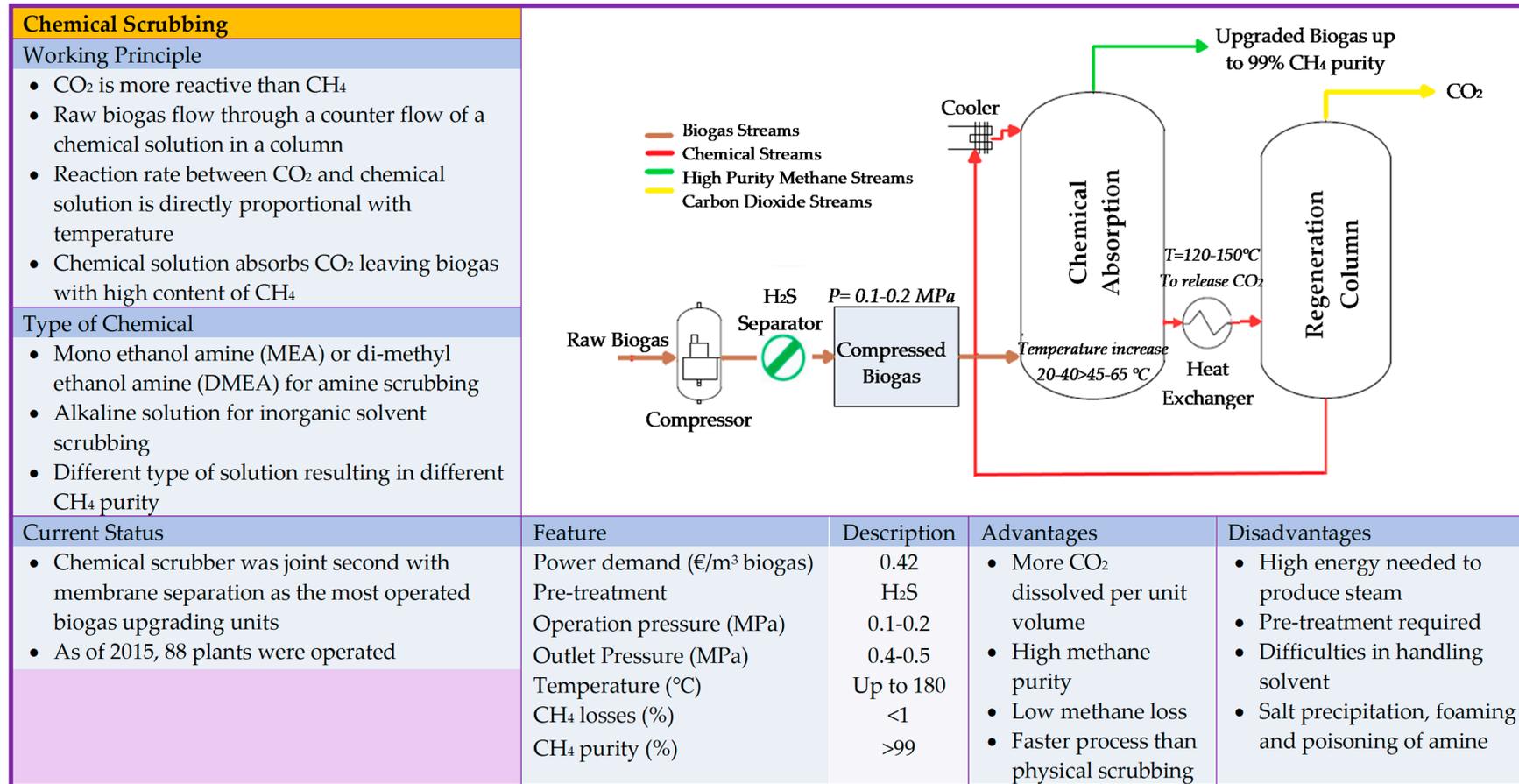


Figure 3. Summary of basic information on chemical scrubbing technology [15,19,20,25,27–32].

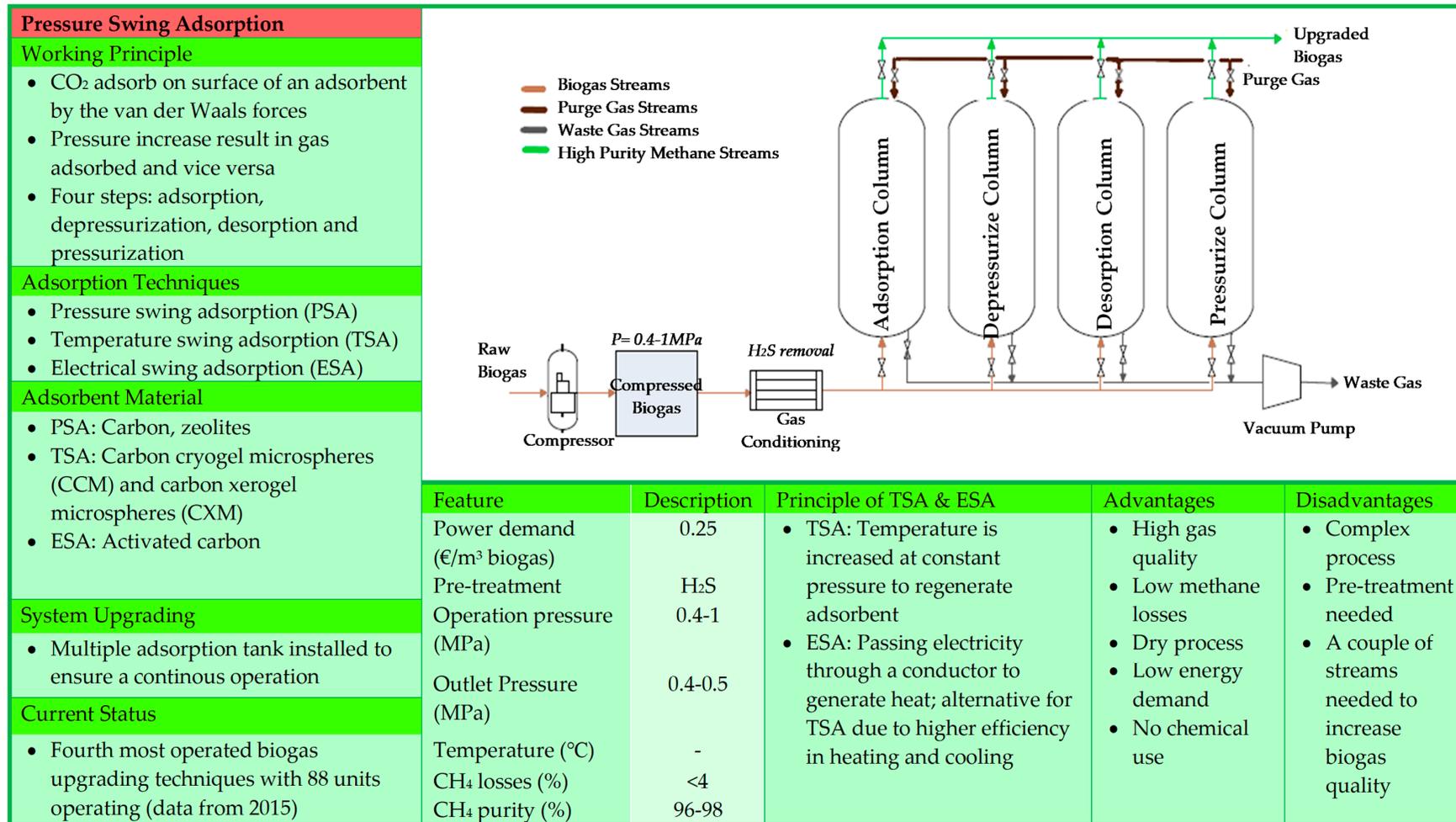


Figure 4. Depicts information on pressure swing adsorption technology [19,20,25,28,33–37].

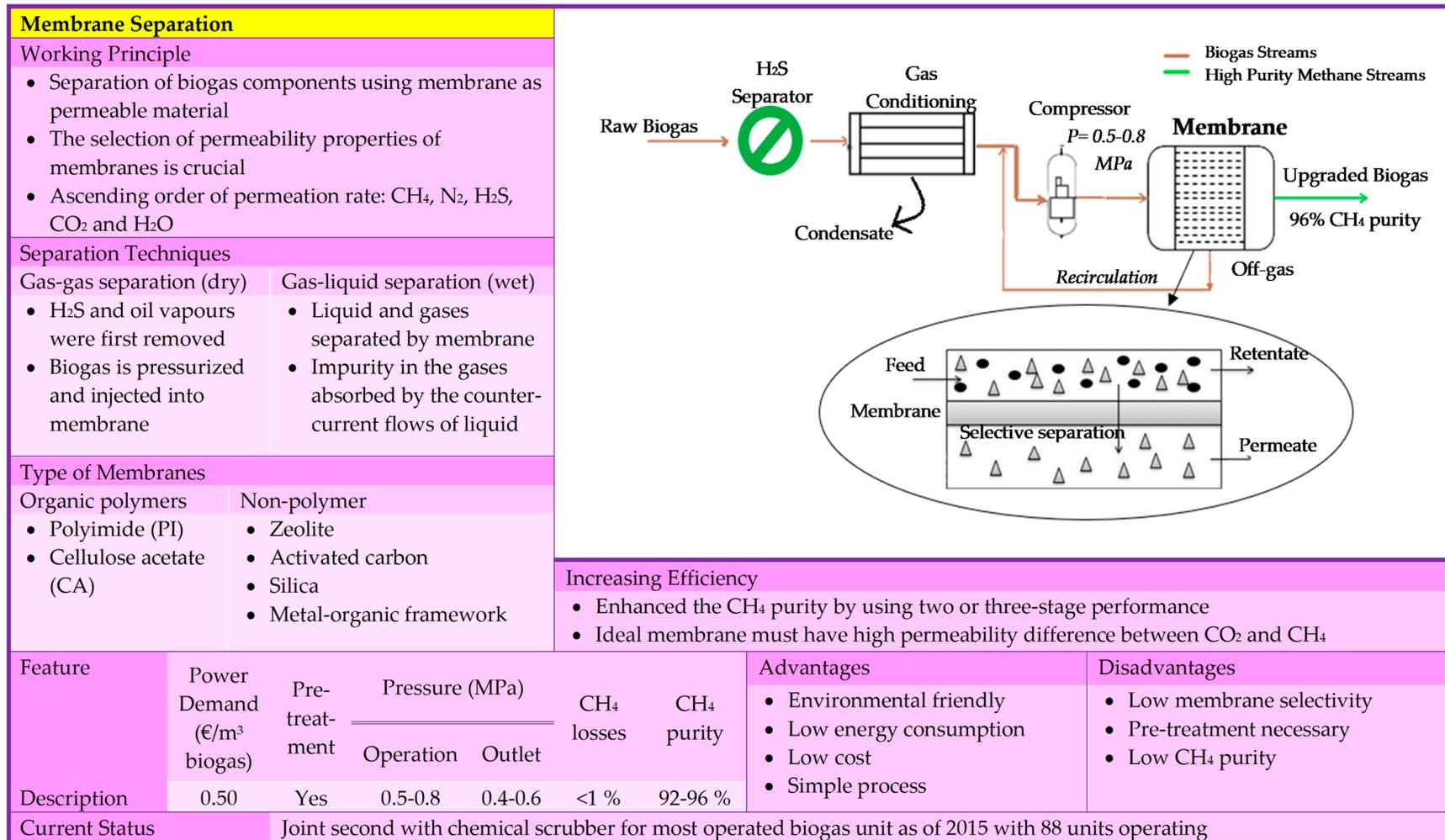


Figure 5. Summary of base knowledge of membrane separation technology [20,21,25,27–29,38,39].

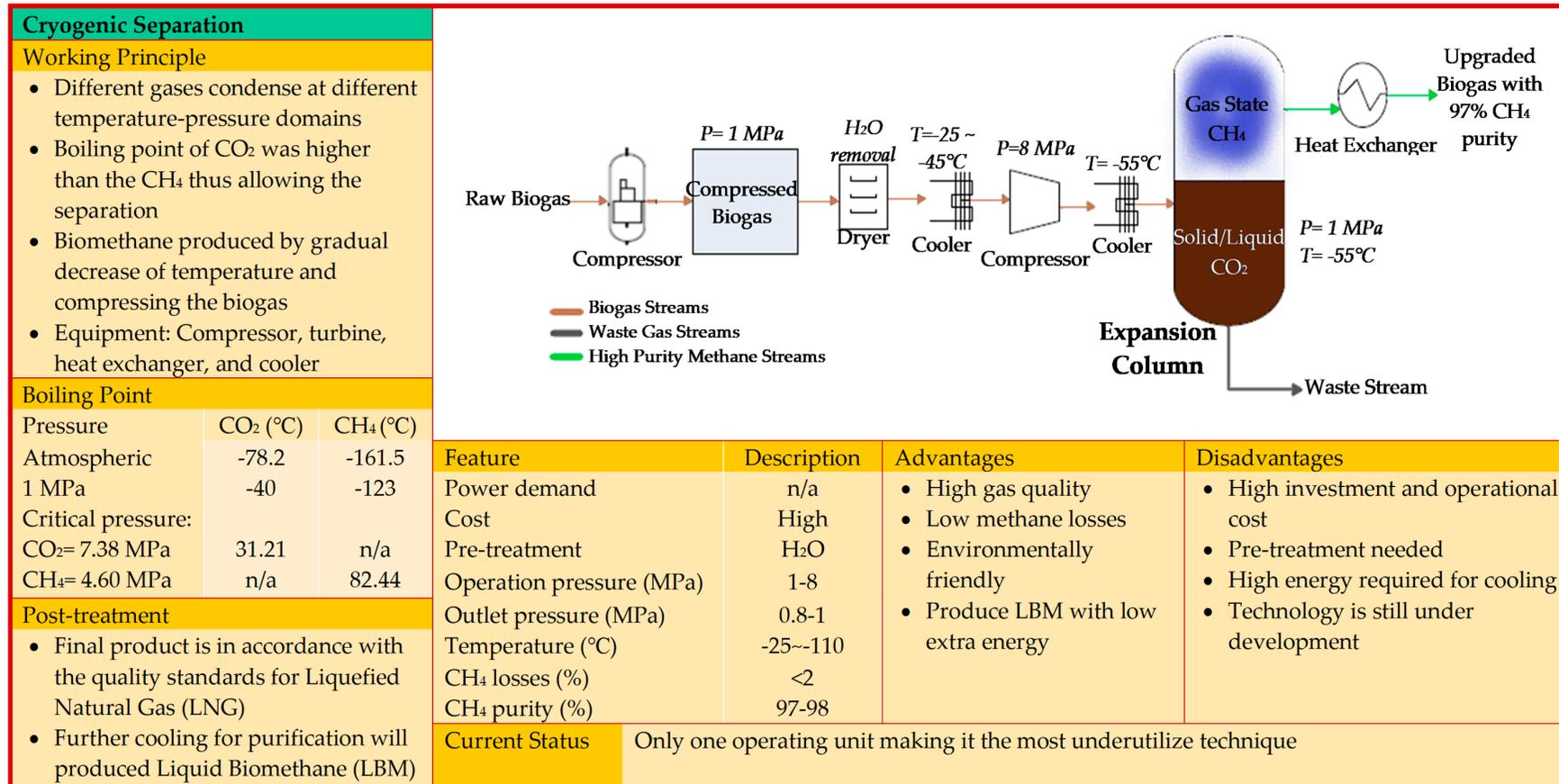


Figure 6. Depicts fundamental knowledge on cryogenic separation [15,19,20,25,28,29,40–43].

The benefits of biogas to the environment are often discussed as a sustainable source of fuels [44]. However, some biogas components released from biogas upgrading are associated with GHG, especially CO<sub>2</sub>. The direct impacts of excessive CO<sub>2</sub> emission are global warming, ocean acidification, and carbon fertilization. The released CO<sub>2</sub> needs to be disposed of. It includes the processes of CO<sub>2</sub> liquifying and injection into underground aquifers. The drawback of this process is the possibility of CO<sub>2</sub> leaking and returning to the surface. Furthermore, the cost of CO<sub>2</sub> disposal is very high and uncertain (among the factors that contribute to cost are the size of the plant and the distance). Thus, a possible solution for this problem is through CO<sub>2</sub> utilization technology. This technology holds big potential for a new way of upgrading biogas, since the benefits of utilizing CO<sub>2</sub> could potentially overcome the cost of CO<sub>2</sub> disposal and reduce the cost of biogas upgrading. The next section of this review will focus on the discussion of various techniques for the utilization of CO<sub>2</sub> as reported in the literature.

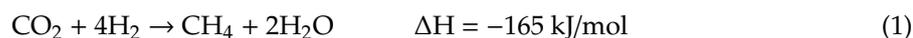
### 3. Biogas Upgrading via Carbon Dioxide Utilization Technologies

In the previous section, biogas was upgraded to enrich the methane content and treated directly as fuel without essential chemical changes. The technologies are always changing, and researchers have developed methods to further explore the value of raw biogas. In recent years, biogas has been used as feedstock in producing chemical material by utilizing the CO<sub>2</sub> content in the biogas [45]. In addition, this low-grade biogas will benefit society by the production of high-quality products instead of inefficient heat supply that results in higher pollution. This section will discuss the state-of-art of emerging technologies for biogas upgrading through CO<sub>2</sub> utilization.

#### 3.1. Chemical Processes

It is well known that using CO<sub>2</sub> as a feedstock for the synthesis of commodity chemicals and fuels has the potential to be beneficial for the economy and environment [46]. CO<sub>2</sub> with the molecular weight of 44.01 and critical density of 468 kg/m<sup>3</sup> can be in a liquid state at a pressure below 415.8 kPa and in the form of solid under −78 °C. It is a massively produced waste and the main contributor to global warming. Despite the potential, the challenges that arise from the utilization of CO<sub>2</sub> are the need for large inputs of energy and the strong bonds that are not particularly reactive due to its kinetic and thermodynamic stability. For instance, it is not affected by heat under normal conditions until the temperature reaches about 2000 °C [47]. Consequently, the process of converting CO<sub>2</sub> requires stoichiometric amounts of energy-intensive reagents that lead to the generation of other waste and increasing GHG footprints. Thus, the main challenge is to develop a new technology that can reduce the use of non-renewable energy and reduce GHG emissions.

Methanation reaction, also called a Sabatier reaction is a reaction between CO<sub>2</sub> and H<sub>2</sub> to produce CH<sub>4</sub> and water (H<sub>2</sub>O). Although the reaction is between CO<sub>2</sub> and H<sub>2</sub>, there is the potential of using biogas directly as feedstock for CO<sub>2</sub> methanation as CH<sub>4</sub> content in the biogas has only a little influence on the reaction at high pressure [48]. The research has found that the methanation of CO<sub>2</sub> above 0.8 MPa will be ideal to decrease the effect of CH<sub>4</sub> on the conversion process [49]. CH<sub>4</sub> is consumed by the consumer widely as a fuel in 2014 (3500 billion cubic meters) [50]. The main source of CH<sub>4</sub> is natural gas, and occasionally as a result of synthetization. The process of hydrogenation of CO<sub>2</sub> to CH<sub>4</sub> using Ni catalyst is explained by Sabatier reaction in Equation (1) [51].

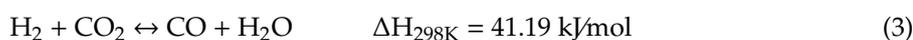


The research in the improvement of catalysts is still developing. Challenges that need to be confronted include the catalysts that can operate at lower temperatures where the reaction more promising and preventing the deactivation of nickel-based catalysts due to sintering and oxidation. Sintering occurs due to the high temperature and water while oxidation is due to the presence of H<sub>2</sub> [52,53]. The improvement of catalysts and processes that have been recently discovered are simplified in Table 1.

**Table 1.** Improvement of catalysts in methane production.

Modification	Description/Results	Reference
Ruthenium <i>Electrochemical</i>	More advanced than nickel but costly	[54]
N-doped carbon Copper-on-carbon	Using the standard three-electrode or H cells Faradaic efficiencies 80% to 94%	[55–57]
Copper	Electrodeposited on a carbon gas diffusion electrode 38 mA/cm <sup>2</sup> densities of methane formation	[56]

On the other hand, by changing the nature of catalysts to less reactive catalysts result in the production of methanol. In 2015, approximately 70 billion kg of methanol (CH<sub>3</sub>OH) was produced worldwide from the synthetization of syngas (H<sub>2</sub> + CO<sub>2</sub>) obtained directly from fossil fuels [58–61]. The mechanism of methanol production, seen in Equation (2), involves a side reaction between CO<sub>2</sub> and H<sub>2</sub> to produce CO and H<sub>2</sub>O based on water gas-shift reaction as shown by Equation (3).



The methanol formation here is an exothermic reaction and the molecular weight of molecules with carbon decrease. Thus, there will be an increase in pressure and a decrease in temperature for selectivity. But, as mentioned earlier, CO<sub>2</sub> is not very reactive and needs a high reaction temperature (>513 K) for CO<sub>2</sub> conversion to occur. In recent years, a lot of research has been done on the catalysts used for direct hydrogenation of CO<sub>2</sub> to methanol, and the results have shown that high pressure is needed to achieve high methanol selectivity [58,62,63]. The most suitable catalyst is not yet available in the current industry. Two challenges for catalyst development are the huge amount of water produced by both reactions that inhibit the product and the undesirable reverse water gas–shift reaction that consumes hydrogen, thus results in a decrease in the yield for methanol. Copper-zinc-aluminum oxide catalyst is often used in CO<sub>2</sub> hydrogenation. The process is run at 5.0–10.0 MPa and 473–523 K. But, the catalyst is not effective again for hydrogenating pure CO<sub>2</sub> [64]. Significant amounts of research into the direct hydrogenation of CO<sub>2</sub> to methanol is continuing. Some of the researches are simplified in Table 2.

**Table 2.** Modification of direct hydrogenation of CO<sub>2</sub> to methanol.

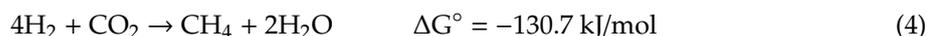
Modification	Description/Result	Reference
Transition metal carbides:		
1. Molybdenum carbide (Mo <sub>2</sub> C) and cementite (Fe <sub>3</sub> C)	High CO <sub>2</sub> conversion and good methanol selectivity	[65]
2. Tantalum carbide (TaC) and Silicon carbide (SiC)	Almost inactive	
Two-stage bed system	Higher performance	[66]
Heterogeneous copper-based catalysts	Based on CO hydrogenation	[59]
Molybdenum-bismuth bimetallic chalcogenide electrocatalyst	Produce methanol with 70% of Faradaic efficiency with requirement of acetonitrile/ionic liquid electrolyte solution	[67]

Another product that can be obtained from the methanation of CO<sub>2</sub> is carbon monoxide. CO is usually obtained through partial oxidation of hydrocarbons or coal at high temperatures around 800 °C. CO is a valuable feedstock in the synthesis of different commodities such as methanol and other higher-order hydrocarbons. The method of obtaining CO from CO<sub>2</sub> from the methanation process is the reverse water–gas shift reaction (shown in Equation (3)) as the major by-product [68]. The

reaction is endothermic and requires a high temperature (~500 °C). A wide range of heterogeneous catalysts often used are copper-, iron-, or ceria-based systems for the reverse water–gas shift reaction. The problems of these catalysts are poor thermal stability and undesired side product often formed. Due to this thermodynamic constraint, it is unlikely for the research on converting CO<sub>2</sub> to CO using reverse water–gas shift reaction to advance beyond this stage. Furthermore, there are other potential routes to generate CO from CO<sub>2</sub> at a significantly more advanced state. To directly reduce CO<sub>2</sub> to CO and O<sub>2</sub>, the use of electrochemical splitting provides an alternative way. Unfortunately, the subject will not be discussed further in this paper, but information on the process can be obtained here [69,70].

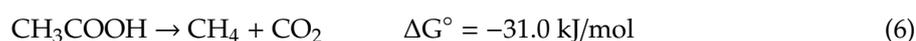
### 3.2. Biological Processes

Biological processes complement chemical options due to its uniqueness of carbon utilization resource requirements and product opportunities. It focuses on the aptitude of microorganisms to convert CO<sub>2</sub> into useful products. Biological fixation of CO<sub>2</sub> is a sustainable solution to reduce CO<sub>2</sub> content in biogas due to its nature which is environmentally-friendly and eliminates the step of captured CO<sub>2</sub> disposal [71]. One of the biological methods to utilize CO<sub>2</sub> in biogas relies on the utilization of H<sub>2</sub> for the conversion of CO<sub>2</sub> to CH<sub>4</sub> based on the action of hydrogenotrophic methanogens. The reaction is shown in Equation (4).



The source of H<sub>2</sub> is the hydrolysis of water. To ensure the method is sustainable, electricity needed in the hydrolysis process came from renewable sources, such as solar and wind. One of the disadvantages of H<sub>2</sub> was its low volumetric energy density, resulting in storage difficulties [72]. This H<sub>2</sub> assisted biogas upgrading can occur in a so-called in-situ and ex-situ biological biogas upgrading. Ex-situ upgrading had been discussed in previous sections and includes absorption, adsorption, membrane separation, and cryogenic methods. It requires the CO<sub>2</sub> to be removed first, thus defeating the purpose of utilizing the CO<sub>2</sub> in biogas, which is the focus of this topic. Ex-situ upgrading will not be discussed further but the review can be found here [73]. Meanwhile, the process of in-situ upgrading does not require the CO<sub>2</sub> to be removed first, rather it will be converted into CH<sub>4</sub> leading to a significant increment in biogas purity [13].

In-situ biological biogas upgrading uses the injection of H<sub>2</sub> inside a biogas reactor during anaerobic digestion to react with CO<sub>2</sub>, resulting in CH<sub>4</sub> production by the action of autochthonous methanogenic archaea [13]. This can be operated through two different pathways: hydrogenotrophic methanogenesis and Wood–Ljungdahl [74]. Hydrogenotrophic methanogenesis performs direct conversion of CO<sub>2</sub> to CH<sub>4</sub> with the addition of H<sub>2</sub> as a source of electrons, according to Equation (4). Meanwhile the Wood–Ljungdahl pathway indirectly converts CO<sub>2</sub> to CH<sub>4</sub> via two reactions according to Equations (5) and (6).



The CO<sub>2</sub> is converted to acetate acid with the help of homoacetogenic bacteria. Then the acetate acid is converted into CH<sub>4</sub> with the present of acetoclastic methanogenic archaea. H<sub>2</sub> plays a crucial role in the whole process of anaerobic digestion. Exogenous addition of H<sub>2</sub> results in the increase of both hydrogenotrophic methanogens and homoacetogenic species, producing acetate from H<sub>2</sub> and CO<sub>2</sub> [75]. The downside of adding H<sub>2</sub> to the process is the inhibition of syntrophic acetogens which are involved in propionate and butyrate degradation and syntrophic acetate oxidizers (SAO) [76]. It is important to control the concentration of H<sub>2</sub> to ensure the equilibrium of biochemical reactions. The process is illustrated in Figure 7.

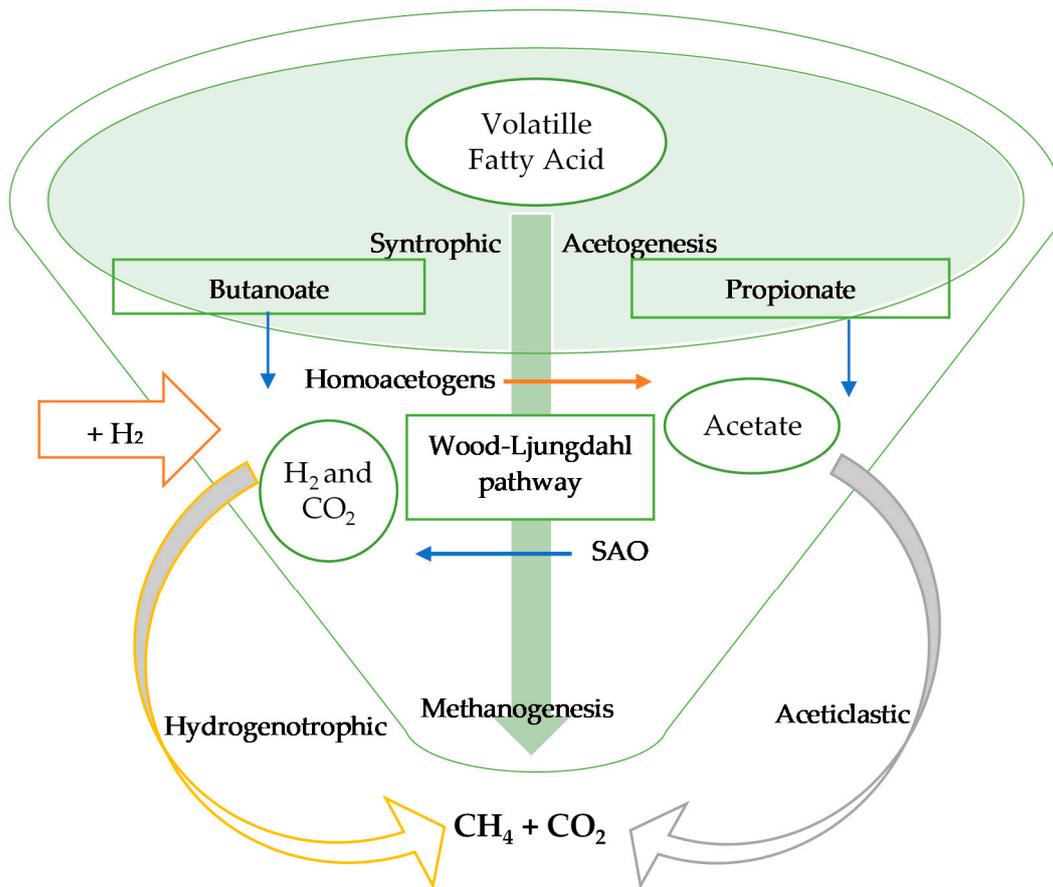


Figure 7. Metabolic pathways for hydrogen assisted methanogenesis [25].

One type of biogas reactor often used in this process is called “continuous stirred tank reactor” (CSTR). The process is heavily connected to the pH level in the reactor. The main challenge is to prevent a pH value above 8.5 because it will lead to methanogenesis inhibition [77,78]. Another challenge arises from the oxidation of the volatile fatty acid (VFA) and alcohols associated with the concentration of the injected hydrogen. To prevent the increasing of the pH level and VFA oxidation, co-digestion with acidic waste [79] and injection of high H<sub>2</sub> concentrations in reactor [80] were proposed to solve the problems, respectively. Additionally, a ton of research had been done on how to increase the efficiency of the process. A select few of these are listed in Table 3.

Table 3. In-situ enriched H<sub>2</sub> upgrading technologies.

Reactor Type	Upgrading Technology	Substrate	Temperature (°C)	HRT (days)	H <sub>2</sub> Flow (L/L-days)	pH	CH <sub>4</sub> (%)	CO <sub>2</sub> (%)	Reference
1.5 (R1) and 2L (R2) CSTR	a) Mesophilic digester with external H <sub>2</sub> addition b) Thermophilic digester with external H <sub>2</sub> addition	Cattle ma-nure	35–55	R1 = 25 R2 = 20	R1 = 0.192 R2 = 0.510	R1 = 7.78 R2 = 7.95	89 85	7 9	[78]
120 mL Batch bottle	Exogenous H <sub>2</sub> addition	Maize Leaf	52	24	0.04–0.10	7–8	88–89	10–12	[81]
Two 600 mL CSTR	Co-digested substrates with exogenous H <sub>2</sub> addition	Cattle ma-nure and whey	55	15	1.5–1.7	7.7–7.9	53–75	6.6–13	[79]
Two 3.5 L CSTR	H <sub>2</sub> addition	Cattle ma-nure	55	14	28.6 mL/L/h	8.3	68	12	[82]

### 3.3. Assessment on Feasibility of Biogas Upgrading

In methanation and biological reaction, costs that need to be considered are investment and operational costs, on top of costs associated with H<sub>2</sub> electrolysis and methanation. Assumptions made were that a large-scale plant for conversion was constructed and that the declining future cost for H<sub>2</sub> electrolysis was achieved due to the higher market penetration rate.

#### 3.3.1. Cost Estimation

H<sub>2</sub> electrolysis involves the production of H<sub>2</sub> and O<sub>2</sub> from electricity (renewable) and water. There are two techniques that can carry out hydrolysis, the low-temperature process, and the high-temperature process. However, the lack of flexibility of high-temperature electrolysis had impaired the use of it [83]. Thus, a further assumption was made based on the low-temperature process. Based on these assumptions, investment costs obtained were in the range of 656–768 €/kW; the operating costs were about four percent of it; efficiency was 67%; and electricity consumption was 4.1 kWh/m<sup>3</sup> [84,85]. The cost of water supply is negligible because it was considered less relevant and can be obtained from the methanation reaction.

For the methanation reaction, besides investment and operating cost, there were costs for capturing CO<sub>2</sub> from biogas and H<sub>2</sub> storage. Assuming the implementation of the system was at well-established biogas upgrading units, the cost can be neglected. During methanation, heat was released and will be used to capture the CO<sub>2</sub> from the biogas, resulting in zero cost on heat generation. The water obtained can be used for H<sub>2</sub> hydrolysis. The storage of H<sub>2</sub> in steel tanks is a well-established technology and can be put at 27 €/kWh as investment costs [86]. The investment cost for the methanation plant can be assumed in the range of 652–785 €/kW; and the operating costs were about four percent of it [85]. However, for biological process, the technique is still under development and the cost cannot be estimated.

In addition, estimation of producing methanol from biogas was done by Zhang et al. (2017) [87]. In the literature, different analyses are taken to calculate the cost. For a plant scale of 5 × 10<sup>6</sup> kg/day methanol, the total cost will be in range of USD 827 million to USD 1036 million. For comparison, capital cost for fossil fuel-based methanol was around USD 480 million [88]. From an economical point of view, it can be concluded that industrial exploitation of biogas has a long path ahead of them to be on the same level with current fossil fuel-based processes. For sure, by upgrading biogas by converting CO<sub>2</sub> to methane and methanol is relevant but is now not a viable short-term benefit when compared to already established technologies.

#### 3.3.2. Advantages and Disadvantages

The created mixture in the form of biomethane has a strong resemblance to natural gas. Thus, the distribution of biomethane can be done from existing gas pipelines. This displays a major advantage, as the infrastructure for transporting the biomethane already exists. In contrast to H<sub>2</sub>, new distribution network is needed if it became the main energy carrier. Second, production of biomethane can help balance the electric grid. For example, renewables energy such as solar and wind are intermittent and not flexible enough. By producing biomethane, it helps to make use of excess electricity produced whenever the demand is low. On the other hand, biomethane can be used as fuel in a power plant when the demand is high and exceeding the limit of produced electricity. Finally, unlike electricity, biomethane is carbon neutral and can be stored efficiently for future use.

One of the drawbacks of the technique is low efficiency. When converting biogas into biomethane using H<sub>2</sub>, the efficiency is only 60%. In addition, if the biomethane produced was to be used to produce electricity, the efficiency drops to 36%. After analyzing the cost, a question is raised: is this technique economically viable? At the moment, the technique is not viable. However, it is likely to be possible in the future when a system with a large share of intermittent renewables are available.

#### 4. Novel Technologies in Carbon Dioxide Conversion

In recent years, the development of new technologies has resulted in the production of a useful commodity by the discovery of new converting processes of CO<sub>2</sub> from waste and atmosphere. These efforts led to the limiting of GHG emissions to the atmosphere of climate-altering pollutants. While CO<sub>2</sub> has been safely used for enhanced oil and carbon feedstock, there is an increased focus on identifying options for re-use of CO<sub>2</sub> for other purposes. There were three stages of development in CO<sub>2</sub> conversion technologies, which can be classified as past, present, and future [65]. In the past, CO<sub>2</sub> conversion technologies focused on producing urea, methanol, cyclic carbonate, and salicylic acid. Then its focus shifted to the making of CO<sub>2</sub> based polymers, fuels, and reactions such as methanation and dry reforming. Meanwhile, CO<sub>2</sub> conversion technologies in the future are predicted to be focusing on production of carboxylic and succinic acid (SA). Thus, this section will be focusing on the possibility of producing SA from CO<sub>2</sub> components in biogas.

SA (C<sub>4</sub>H<sub>6</sub>O<sub>4</sub>), also known as butanedioic acid is a four-carbon diacid used as a platform for synthesis of various commodities as shown in Figure 8. It is mostly produced from LPG or petroleum oil through specific chemical process. Although, recent analysis revealed that production of bio-SA from bacterial fermentation, which is a renewable source, can be more cost-effective than the traditional processes [89]. In recent years, the advancement of bio-based production of SA was very significant, and as a consequence, a variety of microorganisms has been engineered for the synthesis of SA from sugars, glycerol, or acetate [90]. Furthermore, the CO<sub>2</sub> is fixed into the bacteria reducing the greenhouse gas emission that lead to pollution. In fact, carbon footprint of bio-SA production is 0.85 kg CO<sub>2</sub> eq/kg compared to 1.8 kg CO<sub>2</sub> eq/kg of carbon footprint by petroleum-based SA [91]. One way to operate a CO<sub>2</sub> fixation process is through reductive tricarboxylic acid (TCA) cycle. In this anaerobic SA production which fully operated under pure CO<sub>2</sub> condition, 1 mol CO<sub>2</sub> can produce 1 mol of SA [92]. However, to establish a truly circular bio-economy and utilizing the abundant industrial by-product of CO<sub>2</sub>, valorization of CO<sub>2</sub> as a substitute to the sugar-based substrates is today of particular relevance [93]. Moreover, if the off-gas from biogas industries could be effectively utilized as a CO<sub>2</sub> source for SA fermentation, it will simultaneously decrease the cost of the whole process while meeting the commercial-scale requirements for natural gas grid [94].

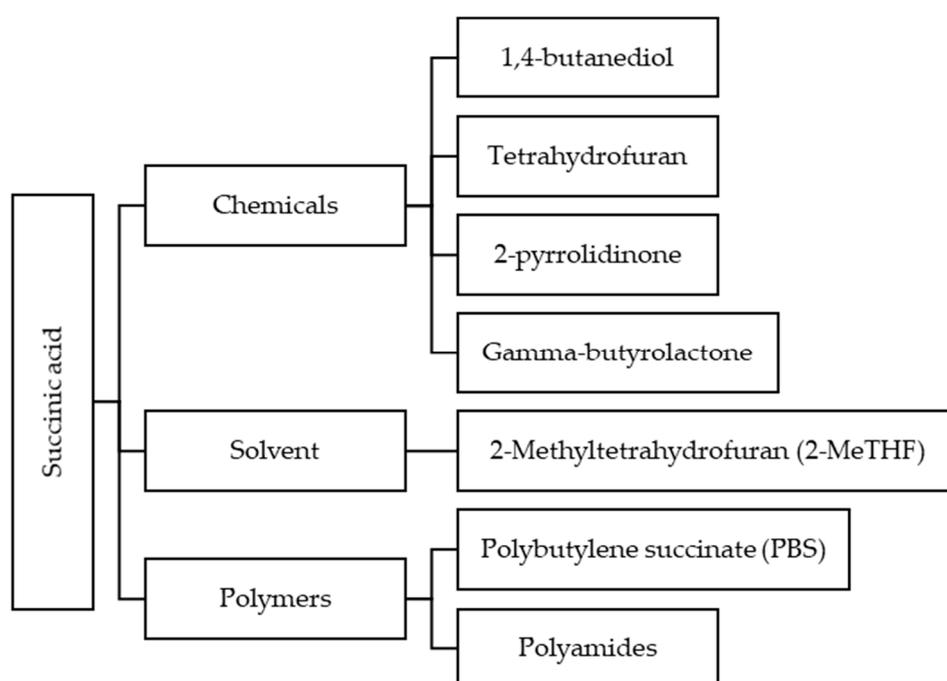
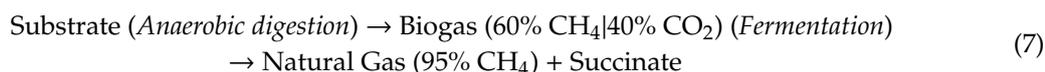


Figure 8. Potential products by using succinic acid (SA) as feedstock [95].

#### 4.1. Simultaneous Biogas Upgrading and Bio-Succinic Acid Production

As mentioned earlier, biogas consists of 60% CH<sub>4</sub> and 40% CO<sub>2</sub>. The presence of CO<sub>2</sub> limits the use of biogas. In 2014, Gunnarsson et al. (2014) [96] had come out with a novel approach for converting the CO<sub>2</sub> component in biogas into SA through a biological process. The study demonstrates a new biogas upgrading technology, which makes use of bacterial fermentation to simultaneously produce high-purity CH<sub>4</sub> and bio-SA. The microorganism used was a strain of *Actinobacillus succinogenes* 130Z (DSM 22257). Application properties are as follows: Substrate: Glucose 30–32 g/L; reactors: 3-L; T: 37 °C; pH: 6.75; ω: 200 rpm; t: 24 h; P: 101.325 and 140 kPa; gas–liquid ratio: 8.3:1 and 5:1. The results of the study are tabulated in Table 4. Stages of the processes are simplified in Equation (7).



Based on Table 4, slight over-pressure during fermentation was ideal for the solubility of CO<sub>2</sub>, thus increasing the CH<sub>4</sub> content in biogas. Increasing the pressure while reducing the ratio also affects other parameters, as CO<sub>2</sub> consumption rate increased by 16.4%, SA concentration increased by 6.2%, and SA yield increased by 13.8%. The final 95% CH<sub>4</sub> purity produced was similar to that of commercial biogas upgrading technologies (95–98%) [21]. This study sparks vast potentials for future investigation on the large-scale implementation for practical application in industries. Then in 2018, a group of inspired researchers from Germany, led by Patrick Ballmann, provided a plan to further study this new concept of simultaneous upgrading by replacing the glucose with lignocelluloses from straw [97]. A further modification was done on the straw to provide a suitable strain for SA production while reducing the by-products. To this state, only *A. succinogenes* has been used for SA production coupled with biogas upgrading [25]. That remained the case for a few years until Babaei et al. (2019) [98] conducted an experiment using *Basfia succiniciproducens* (DSM 22022) as a bacterial strain for the fermentation of SA.

**Table 4.** Performance of the system at different pressure and gas–liquid ratio.

Gas-liquid ratio	Pressure (kPa)			
	101.325		140	
	8.3:1	5:1	8.3:1	5:1
CO <sub>2</sub> solubility (mM)	9.15	9.15	16.7	16.7
CO <sub>2</sub> fixation rate (L CO <sub>2</sub> /L-d)	1.35	1.52	2.59	1.77
CH <sub>4</sub> purity (%)	76.4	85.2	91.1	95.4
SA yield (g/g)	0.60	0.56	0.62	0.63
SA productivity (g/L-h)	0.53	0.53	0.60	0.56
SA concentration (g/L)	12.85	12.74	14.39	13.53
By-products concentration (g/L)	9.5	11.63	8.65	9.96

The experiment conducted by Babaei et al. (2019) [98] was to determine the possibilities of expanding the simultaneous SA production with a biogas upgrading process by using organic fraction of household kitchen waste (OFHKW) as substrate, replacing the common use of glucose while comparing the performance of *A. succinogenes* and *B. succiniciproducens* in producing SA. OFHKW was broken down by enzymatic hydrolysis to produce monomeric fermentable sugars prior to the fermentation process. The experiment was divided by two major parts: The first was to determine the condition for *B. succiniciproducens* to produce SA, the second was to prove the ability of *B. succiniciproducens* to conduct a simultaneous biogas upgrading with SA production. Application properties, results, and discussion of the study are simplified in Table 5.

**Table 5.** Summary of the fermentation process using either *B. succiniciproducens* or *A. succinogenes* as bacterial strain.

Task	Application Properties	Results	Discussion
SA Production	Carbon source: MgCO <sub>3</sub> 5–100 g/L; Substrate: OFHKW 17, 25, 35 & 60 g/L; Serum bottles: 250-mL; T: 37 °C; pH: 6.7 ± 0.1; ω: 150 rpm	<i>B. succiniciproducens</i> SA concentration: Maximum titer of 17.9 ± 0.43 g/L; Overall reaction: Substrate + 2 CO <sub>2</sub> → 2 lactate + 2 acetate + 2 formate	Higher substrate concentration results in higher SA production; <i>B. succiniciproducens</i> is preferred for SA fermentation due to better performances at lower concentration, whereas the by-products were lower
		<i>A. succinogenes</i> SA concentration: Maximum titer of 21.1 ± 3.5 g/L	
Simultaneous Upgrading	Carbon source: Biogas; Substrate: OFHKW 17 g/L; Reactors: 3-L; T: 37 °C; pH: 6.7; ω: 200rpm; t: 8 h; P: 130 & 140 kPa	<i>B. succiniciproducens</i> SA concentration: 3.8 ± 0.8 g/L (0.25 g <sub>SA</sub> /g <sub>glucose</sub> ); CO <sub>2</sub> content: 8.0% (v/v) reduction; CH <sub>4</sub> content: 4.7% (v/v) increase	In term of duration and sugar consumption rate, <i>B. succiniciproducens</i> (8 h) is still superior than <i>A. succinogenes</i> (24 h); The best way to conduct fermentation process was by gradual additional of substrate instead of starting with high substrate concentration
		<i>A. succinogenes</i> SA concentration: 14.39 g/L; CH <sub>4</sub> content: 31% (v/v) increase	

This novel approach of using household waste as a substrate to produce SA provides the information on how to accomplish a fermentation process using either *A. succinogenes* or *B. succiniciproducens*. The research will be a benchmark for fellow researchers to utilize other home-grown or local products in the production of SA. Additionally, this study proves the ability of *B. succiniciproducens* to be an alternative as a bacterium capable of converting CO<sub>2</sub> content in biogas into SA. Nevertheless, further studies still need to be done on other bacteria to identify the possibilities of upgrading biogas while producing SA.

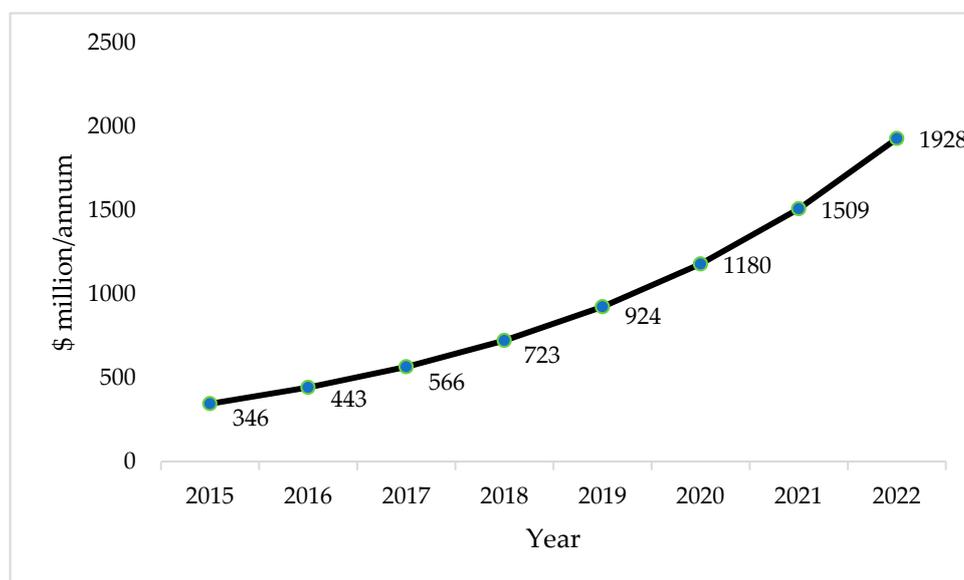
#### 4.2. Future Perspective of Succinic Acid Production

These studies proved that both biomethane and biochemical (SA) can be produced by utilizing unconventional biomasses. To further improve the utilization of CO<sub>2</sub> in biogas, research can be done on metabolic engineering of some other bacteria to produce higher SA titer with no by-products. On top of using *A. succinogenes* 130Z (DSM 22257) and *B. succiniciproducens* (DSM 22022), other bacterial strains had been identified that hold a potential to convert CO<sub>2</sub> in biogas into SA. Fermentation techniques are also a factor in increasing the SA titer. Some of the bacterial strain and fermentation techniques that can possibly be integrated into SA fermentation technique are listed in Table 6. Although these studies were aimed at the direct conversion of CO<sub>2</sub> into SA, it will set a base for further research on integrating it in simultaneous biogas upgrading.

Additionally, to implement this technology on a larger scale, further improvement of the simultaneous biogas upgrading, and succinic acid production technology is required. Because there is still no available matured technology in the market, cost breakdown cannot be conducted. Nevertheless, the demand for bio-SA has been increasing over the years. By selling the produced SA, it will reduce the cost of whole operation. Market forecast of bio-SA was conducted by different researchers and can be seen in a simplified form in Figure 9. This reflects the relevance of producing bio-SA in the future.

**Table 6.** Summary of performances of succinic acid fermentation studies by various microorganisms.

Microorganism	Reactor Type/ Fermentation Technique	Substrate	Titer (g/L)	Yield (g/g)	Reference
<i>A. succinogenes</i>	Repeat-batch	Glucose	33.9	0.86	[99]
<i>A. succinogenes</i> 130Z	Suspended cell	Glucose	10.4	0.27–0.73	[99]
<i>A. succinogenes</i> 130Z	Recycled cell	Glucose	18.6	0.50–0.59	[100]
<i>A. succinogenes</i> 130Z	Batch	Whey	21.5	0.57	[101]
<i>A. succinogenes</i> 130Z	Continuous	Corn	39.6	0.78	[102]
<i>A. succinogenes</i> FZ53	Batch	Glucose	105.8	0.8	[103]
<i>M. succiniciproducens</i>	Batch	Glucose	14	0.7	[104]
<i>M. succiniciproducens</i>	Batch	Whey	13.5	0.72	[105]
<i>M. succiniciproducens</i> MBEL55E	Suspended cell	Lactose	10.3	0.63–0.69	[105]
<i>M. succiniciproducens</i> MBEL55E	Suspended cell	Glucose Xylose	14.1	0.34–0.61	[100]
<i>M. succiniciproducens</i> MBEL55E	Recycled cell	Glucose	12.8	0.48–0.64	[100]
<i>M. succiniciproducens</i> LPK7	Recycled cell	Glucose	12.9	0.10–0.71	[106]
<i>A. succiniciproducens</i>	Continuous	Whey	24	0.72	[103]
<i>A. succiniciproducens</i> ATCC No. 29305	Suspended cell	Lactose	24.0	0.62–0.72	[107]
<i>A. succiniciproducens</i> ATCC No. 29305	Suspended cell	Lactose	14.0	0.81–0.94	[108]
<i>A. succiniciproducens</i> ATCC No. 29305	Suspended cell	Glucose	29.6	0.73–0.82	[109]
<i>A. succiniciproducens</i> ATCC No. 29305	Suspended cell	Glycerol	16.1	1.23–1.50	[110]
<i>A. succiniciproducens</i> ATCC No. 53488	Recycled cell	Glucose	16.5	0.74–0.83	[111]



**Figure 9.** Market forecast of bio-SA volume from the year 2015 to 2022 [112].

The evaluation of the performance of microbial conversion of CO<sub>2</sub> into SA is an important step in providing practical solutions, knowledge, and addressing the gaps in the current understanding [113]. While SA is still widely produced from petrochemical and glucose because of ubiquitous substrate availability, simple process design and high productivities, effort toward producing SA from CO<sub>2</sub>

as sustainable source is still growing and will be applicable if technical barriers that needed to be identified such as limiting gas transfer rates can be overcome [114].

## 5. Conclusions

Global industrial emission of carbon dioxide had risen to an all-time high in 2018 and it is unlikely to reduce soon [115,116]. Growing demand for oil and natural gas globally overshadowed the effort in the development of renewable energy. Furthermore, fossil-fuel infrastructure is still expanding, particularly in developing countries. If current trends continue, the fear of the worst effects of global warming—extreme weather, rising sea levels, plant and animal extinctions, ocean acidification, major shifts in climate, and unprecedented social upheaval—will be inevitable. One of the solutions for these problems is the utilization of bio-natural gas as the substitutes for fossil fuels. In fact, biogas reduces the emission of carbon dioxide while capturing methane, ensuring a cleaner environment. While these are major leaps toward cleaner fuels, still there is room for improvement. Major research had been made from time to time on the techniques to upgrade the biogas to a higher degree. Throughout the years, various technologies and techniques had been developed on how to fully utilize biogas and its by-product so there is no waste release into the environment. One major hurdle for biogas implementation is the cost which hurts its potential employment. While biogas is not the perfect solution for global greenhouse gas emissions, its place in the world of waste management has been very much solidified and will continue to evolve in the coming years.

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