# Membrane-Based Biogas and Biohydrogen Upgrading

Subjects: Materials Science, Coatings & Films
Contributor: Cenit Soto, Laura Palacio, Raúl Muñoz, Pedro Prádanos, Antonio Hernandez

Biogas and biohydrogen, due to their renewable nature and zero carbon footprint, are considered two of the gaseous biofuels that will replace conventional fossil fuels. Biogas from anaerobic digestion must be purified and converted into high-quality biomethane prior to use as a vehicle fuel or injection into natural gas networks.

Keywords: biogas ; biomethane ; biohydrogen ; membrane separation

## 1. Biogas and Biohydrogen as Green Energy Vectors

Biogas is produced via Anaerobic Digestion (AD) of residual biomass from diverse origins such as urban solid waste, livestock waste, agricultural waste, and wastewater. AD is a biological process (based on the action of micro-organisms) able to convert this residual biomass, by means of oxidations and reductions of organic carbon, to carbon dioxide and methane ($CO_2$ and $CH_4$, respectively) in the absence of oxygen [1][2]. This biological conversion is carried out through a sequence of hydrolysis, acidogenesis, acetogenesis and methanogenesis steps in an anaerobic digester [3]. Biogas is typically composed of $CH_4$ and $CO_2$ in a concentration range of 45–85% and 25–50%, respectively, and minor concentrations of other components such as $H_2O$ (5–10%), $N_2$ (~0–1%), $O_2$ (~0–0.5%), $H_2S$ (0–10,000 ppm), $NH_3$ (0–100 ppm) and hydrocarbons (0–200 mg $Nm^{-3}$) [4][5]. The biogas produced by AD represents an excellent alternative to fossil-based energy vectors [2], since biogas can be employed for the production of electricity, steam and heat, as a feedstock in fuel cells, as a green substitute of natural gas for domestic and industrial use or as a vehicle fuel [1]. The contribution of biogas in the European Union could account for 10% of the natural gas demand by 2030 and up to 30–40% by 2050.

Based on the latest report of the World Biogas Association [6], 50 million micro-scale digesters generating biogas for cooking or heating were in operation, mainly in China (42 million) and India (4.9 million). On the other hand, 18,774 large-scale plants devoted to generating 11 GW (a biomethane plant produces an average of 36 GWh per year) of electricity were in operation in 2021 in Europe, Germany being the leader in the European market with 11,279 in 2020 plants (140 plants/1 Mio capita), followed by Italy (1666 in 2020) and France (833 new plants in 2020) [4][7]. China with 6972 large scale digesters and the USA with 2200 AD plants in 2015 represented the second and third largest biogas producer in the world, respectively. The global electricity generation from biogas increased by 90% in six years (from 46,108 GWh in 2010 to 87,500 GWh in 2016) and by 11.5 % from 2016 to 2020 (from 87,500 GWh in 2016 to 96,565 GWh in 2020) [6][8].

Biogas can be purified and converted into a high-quality biomethane via three sequential processes: desulfurization (elimination of the $H_2S$), $CO_2$ removal and biomethane polishing (removal of the minor biogas contaminants) [9]. The European EN-16723 Standard for biomethane introduction into natural gas networks (UNE-EN 16723-1-2016) and automotive/vehicle fuel (UNE-EN 16723-2-2017) requires an effective cleaning of biogas. This UNE-EN 16723-1-2016 standard has resulted in a specific Spanish standard for biomethane injection into the natural gas grid, requiring a minimum methane content of 90% and a maximum $CO_2$ content of 2% (*v*/*v*) [10]. In 2017, the number of biogas upgrading plants in the world accounted for 700 plants, Europe being the leading region with 540 upgrading plants in operation.

At the end of 2020 (the most recent data available), 880 biogas upgrading plants with a production capacity of 2.43 billion $m^3$ were in operation in Europe (161 additional plants relative to 2019) [4][7]. By 2021 the increase in the number of biomethane plants is expected to be even faster since 115 plants have started operation by August 2021 [7].

On the other hand, biologically produced hydrogen (commonly referred to as biohydrogen) generated via Dark Fermentation (DF) represents another alternative bioenergy source [11]. Biohydrogen ($bioH_2$) has the potential to become a relevant $H_2$ generation platform for the creation of a green economy [12]. In this context, hydrogen has multiple advantages as a clean energy vector such as: (i) the combustion of $H_2$ gas can be pollution-free in fuel cells, (ii) its energy efficiency in $H_2$ fuel cells is approx. 50% higher than that of gasoline, (iii) it has a specific energy content of 122 kJ/g (~2.75-fold larger than conventional fossil fuels), (iv) its conversion efficiency to electricity could be doubled using fuel cells instead of gas turbines, and finally (v) it can be stored as a metal hydride.

Dark fermentation is based on hydrogen and carbon dioxide ($CO_2$) production via anaerobic bacteria [13] and/or algae growing in the absence of light and with high carbohydrate content as substrate [14][15]. The biohydrogen produced is mainly composed of hydrogen (40–60%) and carbon dioxide (47–60%) with traces of methane and $H_2S$ [16][17]. Currently, only 1% of hydrogen is produced from biomass [15]. This fact is probably due to the relatively late research on $bioH_2$ production by dark fermentation, where research is still conducted at a laboratory scale with a limited number of experiments at pilot scale [18]. Despite the fact that the $H_2$ yield from dark fermentation is higher than that of other processes, the main disadvantage of the gas generated during dark fermentation is its low hydrogen concentration (40–60%; *v*/*v*) [19], which hinders its direct use in fuel cells for electricity generation (where the purity of hydrogen is crucial to achieve high energy yields) [16]. Therefore, it is crucial to separate $H_2$ from the multiple gas by-products from DF, mainly $CO_2$, in order to obtain purified hydrogen. For instance, a hydrogen content of 73% can be obtained in a two-step gas membrane separation module [19].

The sustained use of non-polluting renewable energy vector such as biogas and $bioH_2$ is required to reduce the demand and dependence from fossil fuels [20]. Based on the International Energy Agency, the share of renewable and low-carbon transport fuels should increase up to 6.8% in 2030 in Europe, with advanced biofuels representing at least 3.6% of the total fuel consumption. The development of low footprint and cost technologies for the conversion of biogas to a purified biomethane and $bioH_2$ to pure $H_2$ is essential to guarantee the competitiveness of these green gas vectors as an energy source.

## 2. Biogas and Biohydrogen Purification with Membrane Technology

Nowadays, there are two main types of technologies for biogas purification, physicochemical and biological methods, while $bioH_2$ purification is only performed by physicochemical methods. Physicochemical technologies exhibit high energy and chemical demand, and therefore they present large operating costs and environmental impacts. As an example, this section will only focus on $CO_2$ removal technologies.

Pressure swing adsorption (PSA), cryogenic $CO_2$ separation, scrubbing with $H_2O$, chemical solutions or organic solvents, and membrane separation, dominate the biogas upgrading market nowadays [21], while cryogenic distillation, PSA and membrane separation are the most popular processes for $H_2$ purification at commercial scale [22][23][24].

Separation of gas mixtures through membranes has become a relevant unitary operation for the recovery of valuable gases and mitigation of atmospheric pollution, which offers several advantages over conventional gas separation methods [25]. Indeed, Membrane Separation (MS) is considered nowadays the most promising gas purification technology. Membrane separation relies on the interaction (physical or chemical) of certain gases with the membrane material [26]. The membranes used are selective physical barriers with certain components that permeate across them [27]. Gas separation by membrane technology is characterized by selectivity properties and flux, which supports a functional transport of the target gases across the barrier (permeability). This technology presents a low energy consumption, a simple operation, cost effectiveness, smaller footprint, a negligible chemical consumption and low environmental impacts [28][29]. The potential of MS to achieve high efficiencies of gas separation foster their use in different industrial applications including refineries and chemical industries, and recent advances in material science render MS a competitive technology [30]. The lifetime of commercial membranes account for 5–10 years [31]. Today, the use of membranes in industry includes the separation of $N_2$ or $O_2$ from air, separation of $H_2$ from gases such as $CH_4$, separation of $CH_4$ from biogas, separation of $H_2S$ and $CO_2$ from natural gas, etc. The use of membranes in separation processes is rapidly growing, especially in Europe.

A detailed economic study of the total costs of biogas purification is a difficult task nowadays due to the large number of parameters to be considered. However, Miltner and co-workers (2017) have published some general estimates and a comparison of the most common physicochemical technologies such as pressurized water scrubbing, amine scrubbing, pressure swing adsorption and gas permeation. This study included investment costs (15 years' depreciation), plant reliability of 98%, operational consumptions in terms of electricity and consumables (electricity price 15 €ct/kWh), as well as maintenance and overhaul (without engineering costs, taxes and revenues). Thus, the costs for an installation with a capacity of 250 $m^3$ $_{STP}$/h are in the range of 25 €ct/$m^3$ $_{STP}$, while these costs drop below 15 €ct/$m^3$ $_{STP}$ for capacities above 2000 $m^3$ $_{STP}$/h. This work concluded that gas permeation is slightly more advantageous for sizes below 1000 $m^3$ $_{STP}$/h. Overall, small-scale biogas upgrading entails higher capital and operational costs [32].

Ideally, membrane materials for gas separation should exhibit a high selectivity and big fluxes, excellent chemical, mechanical and thermal stability, a defect-free production and be cost effective. Membranes are classified according to the type of material, configuration, structure, composition, support material and industrial reactions, among others [33][34]

[35]. Four kinds of membranes are typically proposed for development and commercialization in hydrogen purification: (i) polymeric membranes (organic), (ii) porous membranes (ceramic, carbon, metal) (iii) dense metal membranes and (iv) ion conductive membranes, the last three also referred to as inorganic membranes [27]. In this context, dense-metal membranes and polymeric have experienced the largest advances in terms of scale-up [36]. The most commonly used polymeric membranes for gas separation are nonporous membranes, which are classified as glassy or rubbery. Of them, glassy polymers are most typically used for gas separation applications. These polymers include polysulfones (PSF), polycarbonates (PC) and polyimides (PI), which are often employed for the separation of $H_2/CH_4$, $H_2/N_2$ and $O_2/N_2$ [37]. On the other hand, membranes can be configured as hollow fibers, capillaries, flat sheets and tubular and can be installed in a suitable membrane module. The most commonly used modules are pleated cartridges, tubular and capillary, hollow-fiber and plate-and-frame and spiral-wound systems [38].

$H_2$ separation was one of the pioneered applications in gas separation membranes, DuPont (E. I. du Pont de Nemours and Co., Wilmington, DE, USA) being the pioneer in manufacturing small-diameter hollow-fiber membranes. Due to the limited productivity (or permeance) of these membranes and their high cost, Monsanto Co. (Monsanto Company, St. Louis, MO, USA) developed polysulfone hollow-fiber membranes, which considerably increased the transport through the fibers, and consequently were successfully implemented at industrial-scale for hydrogen recovery from ammonia purge gases [39]. Then, Separex Corp (Champigneulles, France) developed Separex® spiral-wound cellulose acetate membranes (including separations for natural gas and dehydration [39] providing better performance than hollow fiber membranes due to their high resistance of hydrogen impurities [40]. Polymeric membranes, especially polyimides, have been employed to separate hydrogen from gaseous mixtures ($N_2$, CO and hydrocarbons) based on their economic viability, easy processibility and satisfactory thermal stability (350–450 °C) [41]. Polyimide membranes with excellent heat resistances were introduced by Ube in Japan (Ube Industries, Ltd., Tokyo, Japan), and the refinery at Seibu Oils (Seibu Oil Company Limited, Onoba, Japan) was the first facility to apply them commercially [39]. Commercial membrane systems provide a $H_2$ purity of 90–95% during hydrogen purification with a moderate recovery of 85–90% [42].

At the beginning of the 1990s, gas mixture separation membranes with a poor recovery of methane and low selectivity were installed for the upgrading of landfill biogas [43]. In 2007, Air Liquide Medal™ further developed and tested new selective membranes combining high $CH_4$ recoveries with high $CH_4$ concentrations.

Today, membrane-based biogas upgrading can provide methane concentrations of 97–98% in the biomethane with a concomitant methane recovery above 98%, based on the high permeabilities of $CO_2$ in commercial membrane materials. The permeation rate mainly depends on the molecular size of the gas components and on the membrane construction material [44]. Membrane-based biogas upgrading at commercial scale is carried out at 6–20 bar, which entails energy consumption of 0.18–0.20 kWh/Nm$^3$ of raw biogas or 0.14–0.26 kWh/Nm$^3$ of biomethane [9].

In this regard, despite polymeric membranes having consistently demonstrated promising results and being commercially available at large-scale for hydrogen and biogas purification, their use is limited to 8–9 polymeric materials (e.g., cellulose acetate, polyimides, perfluoropolymer etc.) [45][46]. Therefore, further research in the field of material science needs to be conducted to achieve new membranes with superior gas separation properties: higher permeability, selectivity and stability (mainly restricted plasticization) [45].

## References

1. Andriani:, D.; Wresta, A.; Atmaja, T.D.; Saepudin, A. A review on optimization production and upgrading biogas through CO2 removal using various techniques. Appl. Biochem. Biotechnol. 2014, 172, 1909–1928.
2. Kougias, P.G.; Angelidaki, I. Biogas and its opportunities—A review. Front. Environ. Sci. Eng. 2018, 12, 14.
3. Zhang, Q.; Hu, J.; Lee, D.J. Biogas from anaerobic digestion processes: Research updates. Renew. Energy 2016, 98, 108–119.
4. EBA. 2020 Statical Report of the European Biogas Association 2020; EBA: Brussels, Belgium, 2021.
5. Toledo-Cervantes, A.; Estrada, J.M.; Lebrero, R.; Muñoz, R. A comparative analysis of biogas upgrading technologies: Photosynthetic vs. physical/chemical processes. Algal Res. 2017, 25, 237–243.
6. WBA Global Potential of Biogas. 2019. Available online: https://www.worldbiogasassociation.org/wp-content/uploads/2019/07/WBA-globalreport-56ppa4_digital.pdf (accessed on 28 August 2022).
7. EBA. 2021 Statistical Report of the European Biogas Association 2021; EBA: Brussels, Belgium, 2021.
8. IRENA. 2022. Available online: https://www.irena.org/bioenergy (accessed on 14 September 2022).

9. Angelidaki, I.; Treu, L.; Tsapekos, P.; Luo, G.; Campanaro, S.; Wenzel, H.; Kougias, P.G. Biogas upgrading and utilization: Current status and perspectives. Biotechnol. Adv. 2018, 36, 452–466.
10. BOE. Resolución de 8 de Octubre de 2018, de La Dirección General de Política Energética y Minas, Por La Que Se Modifican Las Normas de Gestión Técnica Del Sistema NGTS-06, NGTS-07 y Los Protocolos de Detalle PD-01 y PD-02; Boletín Oficial Del Estado: Madrid, Spain, 2018; pp. 102917–102948.
11. Bakonyi, P.; Nemestóthy, N.; Bélafi-Bakó, K. Biohydrogen purification by membranes: An overview on the operational conditions affecting the performance of non-porous, polymeric and ionic liquid based gas separation membranes. Int. J. Hydrog. Energy 2013, 38, 9673–9687.
12. Ramírez-Morales, J.E.; Tapia-Venegas, E.; Toledo-Alarcón, J.; Ruiz-Filippi, G. Simultaneous production and separation of biohydrogen in mixed culture systems by continuous dark fermentation. Water Sci. Technol. 2015, 71, 1271–1285.
13. Rittmann, S.; Herwig, C. A comprehensive and quantitative review of dark fermentative biohydrogen production. Microb. Cell Fact. 2012, 11, 20–25.
14. Das, D.; Veziroglu, T.N. Advances in biological hydrogen production processes. Int. J. Hydrogen Energy 2008, 33, 6046–6057.
15. Bharathiraja, B.; Sudharsanaa, T.; Bharghavi, A.; Jayamuthunagai, J.; Praveenkumar, R. Biohydrogen and biogas—An overview on feedstocks and enhancement process. Fuel 2016, 185, 810–828.
16. Ramírez-Morales, J.E.; Tapia-Venegas, E.; Nemestóthy, N.; Bakonyi, P.; Bélafi-Bakó, K.; Ruiz-Filippi, G. Evaluation of two gas membrane modules for fermentative hydrogen separation. Int. J. Hydrog. Energy 2013, 38, 14042–14052.
17. IEA. CO2 Emmisions from Fuel Combustion Highlights; International Energy Agency: Paris, France, 2019.
18. Tapia-Venegas, E.; Ramirez-Morales, J.E.; Silva-Illanes, F.; Toledo-Alarcón, J.; Paillet, F.; Escudie, R.; Lay, C.H.; Chu, C.Y.; Leu, H.J.; Marone, A.; et al. Biohydrogen production by dark fermentation: Scaling-up and technologies integration for a sustainable system. Rev. Environ. Sci. Biotechnol. 2015, 14, 761–785.
19. Mona, S.; Kumar, S.S.; Kumar, V.; Parveen, K.; Saini, N.; Deepak, B.; Pugazhendhi, A. Green technology for sustainable biohydrogen production (waste to energy): A review. Sci. Total Environ. 2020, 728, 138481.
20. Elbeshbishy, E.; Dhar, B.R.; Nakhla, G.; Lee, H.S. A critical review on inhibition of dark biohydrogen fermentation. Renew. Sustain. Energy Rev. 2017, 79, 656–668.
21. Muñoz, R.; Meier, L.; Diaz, I.; Jeison, D. A review on the state-of-the-art of physical/chemical and biological technologies for biogas upgrading. Rev. Environ. Sci. Biotechnol. 2015, 14, 727–759.
22. Liemberger, W.; Groß, M.; Miltner, M.; Harasek, M. Experimental analysis of membrane and Pressure Swing Adsorption (PSA) for the hydrogen separation from natural gas. J. Clean. Prod. 2017, 167, 896–907.
23. Hinchliffe, A.B.; Porter, K.E. A comparison of membrane separation and distillation. Chem. Eng. Res. Des. 2000, 78, 255–268.
24. Ockwig, N.W.; Nenoff, T.M. Membranes for hydrogen separation. Chem. Rev. 2007, 107, 4078–4110.
25. Sridhar, S.; Smitha, B.; Aminabhavi, T.M. Separation of carbon dioxide from natural gas mixtures through polymeric membranes—A review. Sep. Purif. Rev. 2007, 36, 113–174.
26. Ismail, A.F.; Khulbe, K.C.; Matsuura, T. Gas Separation Membranes: Polymeric and Inorganic; Springer: Ottawa, ON, Canada, 2015; ISBN 9783319010953.
27. Adhikari, S.; Fernando, S. Hydrogen membrane separation techniques. Ind. Eng. Chem. Res. 2006, 45, 875–881.
28. Chen, H.Z.; Chung, T.S. CO2-selective membranes for hydrogen purification and the effect of carbon monoxide (CO) on its gas separation performance. Int. J. Hydrog. Energy 2012, 37, 6001–6011.
29. Sridhar, S.; Bee, S.; Bhargava, S. Membrane-based gas separation: Principle, applications and future potential. Chem. Eng. Dig. 2014, 1, 1–25.
30. Bernardo, P.; Drioli, E.; Golemme, G. Membrane gas separation: A review/state of the art. Ind. Eng. Chem. Res. 2009, 48, 4638–4663.
31. Bauer, F.; Hulteberg, C.; Persson, T.; Tamm, D. Biogas Upgrading—Review of Commercial Technologies; SGC Rapport; Svenskt Gastekniskt Center AB: Malmö, Sweden, 2013; Volume 270.
32. Miltner, M.; Makaruk, A.; Harasek, M. Review on available biogas upgrading technologies and innovations towards advanced solutions. J. Clean. Prod. 2017, 161, 1329–1337.
33. Vinoba, M.; Bhagiyalakshmi, M.; Alqaheem, Y.; Alomair, A.A.; Pérez, A.; Rana, M.S. Recent progress of fillers in mixed matrix membranes for CO2 separation: A review. Sep. Purif. Technol. 2017, 188, 431–450.

34. Al-Mufachi, N.A.; Rees, N.V.; Steinberger-Wilkens, R. Hydrogen selective membranes: A review of palladium-based dense metal membranes. Renew. Sustain. Energy Rev. 2015, 47, 540–551.
35. Sazali, N.; Salleh, W.N.W.; Ismail, A.F. Synthetic polymer-based membranes for hydrogen separation. In Synthetic Polymeric Membranes for Advanced Water Treatment, Gas Separation, and Energy Sustainability; Elsevier: Amsterdam, The Netherlands, 2020; pp. 273–292.
36. Edlund, D. Hydrogen membrane technologies and application in fuel processing. In Hydrogen and Syngas Production and Purification Technologies; Liu, K., Song, C., Subramani, V., Eds.; Wiley-Blackwell: Hoboken, NJ, USA, 2009; pp. 357–384. ISBN 978-0-471-71975-5.
37. Jeon, Y.W.; Lee, D.H. Gas membranes for CO2/CH4 (Biogas) separation: A review. Environ. Eng. Sci. 2015, 32, 71–85.
38. Strathmann, H. Membrane separation processes: Current relevance and future opportunities. AIChE J. 2001, 47, 1077–1087.
39. Perry, J.D.; Nagai, K.; Koros, W.J. Polymer membranes for hydrogen separations. MRS Bull. 2006, 31, 745–749.
40. Kaboorani, A.; Riedl, B.; Blanchet, P.; Fellin, M.; Hosseinaei, O.; Wang, S. Nanocrystalline Cellulose (NCC): A renewable nano-material for Polyvinyl Acetate (PVA) adhesive. Eur. Polym. J. 2012, 48, 1829–1837.
41. Freeman, B.D.; Pinnau, I. Gas and Liquid Separations Using Membranes: An Overview. In Advanced Materials for Membrane Separations; ACS Symp., Ser.; Freeman, B.D., Pinnau, I., Eds.; American Chemical Society: Washington, DC, USA, 2004; Volume 876, pp. 1–23.
42. Peramanu, S.; Cox, B.G.; Pruden, B.B. Economics of hydrogen recovery processes for the purification of hydroprocessor purge and off-gases. Int. J. Hydrog. Energy 1999, 24, 405–424.
43. Petersson, A.; Wellinger, A. Biogas upgrading technologies—Developments and innovations task 37—Energy from biogas and landfill gas IeA bioenergy aims to accelerate the use of environmental sound and cost-competitive bioenergy on a sustainable basis, and thereby achieve a substant. IEA Bioenergy 2009, 13, 1–19.
44. Baker, R.W.; Low, B.T. Gas separation membrane materials: A perspective. Macromolecules 2014, 47, 6999–7013.
45. Basu, S.; Khan, A.L.; Cano-Odena, A.; Liu, C.; Vankelecom, I.F.J. Membrane-based technologies for biogas separations. Chem. Soc. Rev. 2010, 39, 750–768.
46. Ozturk, B.; Demirciyeva, F. Comparison of biogas upgrading performances of different mixed matrix membranes. Chem. Eng. J. 2013, 222, 209–217.