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Chapter

Gaseous Biofuels to Sustainable Mobility

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Abstract

In an energy transition scenario, setting the target date for the year 2050, during which the master lines are established to achieve a 100% renewable energy generation system (both stationary, thermal and mobility and transportation), all studies indicate that this will be based on the so-called renewable energy mix. In relation to energy sources for transport, in this scenario, everything is foreseen the coexistence of fossil energies (natural gas and propane or autogas) to the detriment in favour of other fuels and energies from renewable sources, such as electricity (batteries) and gases of renewable origin (biomethane, hydrogen, and synthesis gas). That renewable gases have, beyond the significant reductions in pollutant emissions, is the complementarity they have with renewable energy sources such as solar and biogas, as will be seen later in the sections dedicated to the generation and production technologies of each of these fuels, where renewable energy sources play a fundamental role.

Keywords: biogas, biomethane, hydrogen

1. Introduction

In an energy transition scenario, setting the target date for the year 2050, for which the master lines are established to achieve a 100% renewable energy generation system (both stationary, thermal and mobility and transportation), all the revised studies indicate that energy sector will be based on the so-called renewable energy mix. In the meantime, biomethane and hydrogen (from renewable energy) could represent an effective strategy to move towards the targets set by the Renewable Energy Directive [1].

With regard to energy sources for transport, a coexistence of fossil energies is foreseen (natural gas and liquefied petroleum gases (LPG) or autogas), to the detriment in favour of other fuels and energies from renewable sources, such as electricity (batteries) and gases of renewable origin (biomethane, hydrogen and synthesis gas).

This chapter will focus on those energy sources based on gas in its different types and origins: natural gas, renewable natural gas or biomethane, hydrogen and synthesis gas. It has been decided not to include the autogas or LPG, because it is a fuel directly derived from petroleum, whose engine and distribution technology, unlike natural gas, is not compatible with gas fuels that could be renewable.

The main support levers that renewable gases have, beyond the significant reductions in pollutant emissions, is the complementarity they have with renewable energy sources such as solar and biogas, as will be seen later in the sections dedicated to the generation and production technologies of each of these fuels, where renewable energy sources play a fundamental role. In some scenarios, renewable resources for mobility could be considered a 'drop-in' fuel, which means they are interchangeable with a particular petroleum derived fuel. In this sense, the inclusion of these resources contributes to the gradual replacement of the fossil fuels without considerable investment in infrastructure.

2. Generation

2.1 Natural gas

Natural gas is a mixture of different hydrocarbons, usually gaseous, that occurs naturally in the subsurface [2]. It usually appears next to oil, at the top of the same deposits, and the composition, like that of crude oil, varies depending on where it comes from.

2.1.1 Origin and formation

The origin of the natural gas comes from the decomposition of organic matter, which took place between 240 and 70 million years ago, during the time when large reptiles and dinosaurs inhabited the planet (Mesozoic Era). This organic matter came from planktonic organisms that accumulated on the seabed of coastal platforms or in shallow basins of ponds and were buried under successive layers of land by the action of natural phenomena.

Most oil fields usually contain liquid and gaseous hydrocarbons [3]. Normally, gases, being less dense than liquid, tend to occupy the upper part of the porous rock, held by the impermeable rock that acts as a seal. Below is oil and below it, large saltwater deposits.

The discovery of natural gas dates back to ancient times in the Middle East. Thousands of years ago, it was found that there were natural gas leaks that set fire when they ignited, giving rise to the so-called 'burning sources'. In Persia, Greece or India, temples were erected for religious practices around these 'eternal flames' [4].

Natural gas was not known in Europe until it was discovered in Britain in 1659, although it was not commercialized until 1790. In 1821, the inhabitants of Fredonia (United States) observed gas bubbles that traced to the surface in a stream. William Hart, considered the 'father of natural gas', excavated the first American natural gas well.

During the nineteenth century, natural gas was almost exclusively used as a source of light. Its consumption remained very localized due to the lack of transport infrastructure that hindered the transfer of large quantities of natural gas over long distances. In 1890, there was an important change with the invention of leakproof joints in gas pipelines.

It was after the Second World War when the use of natural gas grew rapidly as a result of the development of gas pipeline networks and storage systems [5].

2.1.2 Composition

Although its composition varies depending on the reservoir, its main chemical species is 79–97% methane (in molar or volumetric composition), commonly

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	Component	Nomenclature	Natural state
Natural Gas	Methane	CH_4	Gas
	Ethane	C_2H_6	Gas
	Propane	C_3H_8	Liquefiable gas
	Butane	C_4H_{10}	Liquefiable gas
	Pentane	C_5H_{12}	Liquid
	Hexane	C_6H_{14}	Líquid
	Nitrogen	N_2	Gas
	Carbonic gas	$CO - CO_2$	Gas
	Hydrogen sulfide	H_2S	Gas
	Hydrogen	H_2S	Gas
	Water	H_2O	Gas

Table 1.
Natural gas composition. Source: Own elaboration from literature.

exceeding 90–95%. It also contains other gases such as ethane (0.1–11.4%), propane (0.1–3.7%), butane (<0.7%), nitrogen (0.5–6.5%), carbon dioxide (<1.5%), impurities (water vapour, sulphur derivatives) and traces of heavier hydrocarbons, mercaptans, noble gases and other gases (**Table 1**) [6].

During the extraction, some gases that are part of its natural composition are treated and separated for different reasons among others: by their low calorific value (such as nitrogen or carbon dioxide), by their dew point in the gas pipelines (by having a low saturation temperature) or by their resistance of liquefaction of gases (such as carbon dioxide, which solidifies when producing liquefied natural gas or LNG).

Propane, butane and other heavier hydrocarbons are separated in order to have an efficient and safe gas combustion. In the same sense, water (steam) is eliminated in order to avoid clogging gas pipelines because at high pressures methane hydrates could be formed. So, sulphur derivatives are purified to very low concentrations to prevent corrosion, odour formation and sulphur dioxide emissions (causing acid rain) after combustion.

Finally, and for security reasons, traces of mercaptans (including methyl mercaptan, CH_4S), which allow olfactory detection in case of leakage, are added for domestic use.

2.1.3 Natural gas reserves

Natural gas reservoirs are usually found at high depths, either on land ('onshore') or under the sea ('offshore'). Natural gas may be found in reservoirs in two states; 'free' or 'associated'. In the 'free' state, the gas is extracted independently, not together with other compounds, and when it is 'associated', it is mixed with hydrocarbons or other gases from the reservoir.

A natural gas reserve becomes a 'proven reserve' when determining the quantity and quality of the natural gas contained in said deposit, its duration being calculated based on the amount of gas it has and an estimate of the expected consumption. Since carrying out this research and resource calculation process in its entirety implies significant investments, it is common that certain reserves are

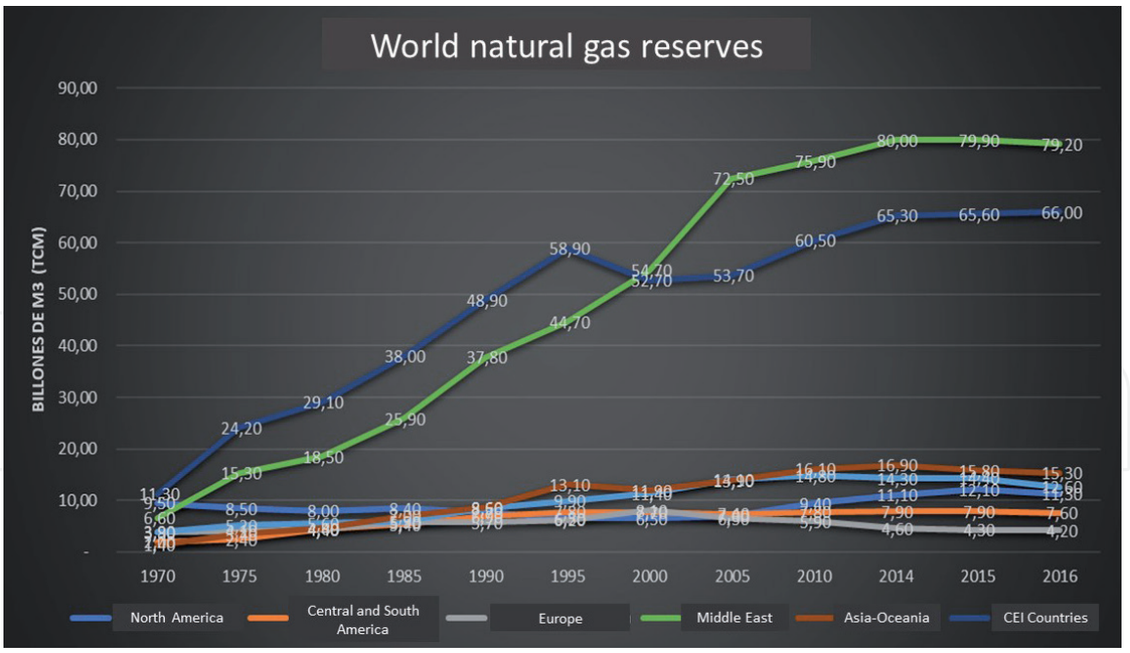


Figure 1.
Proven world reserves of natural gas (source: CEDIGAZ y Oil and Gas Journal. Own elaboration).

only geographically located and their potential is estimated, but they have not been subjected to such precise calculation studies until they are subjected to exploitation. However, gas-producing companies must have demonstrable reserves to guarantee the extraction and supply contracts they incur.

Figure 1 shows the distribution of proven natural gas reserves in the world by geographical area. The highest concentrations of gas are in the Middle East (41% of the world total), followed by the set of CIS countries (Commonwealth of Independent States) representing 31%. European reserves in a downtrend represent 2.7% of total reserves. In the industrial sector, the consumption of natural gas has increased at a faster rate than oil or coal in recent decades; it is estimated that natural gas and electricity will represent about two thirds of the energy used in the industry by 2040 [7].

Following recent research studies and obtaining new extraction technologies and despite the increase in global natural gas consumption, the amount of gas reserves has been increasing. However, new discoveries and the significance of new extraction technologies will have less and less weight, so it is essential to become aware of the efficient use of this resource as well as the research and development of alternative energy sources.

2.2 Biogas/biomethane

Biogas is a gas composed mainly of methane (CH_4) and carbon dioxide (CO_2), in varying proportions depending on the composition of the organic matter from which it was generated. The main sources of biogas are livestock and industrial agro waste, sludge from urban wastewater treatment plants (WWTPs) and the organic fraction of domestic waste. Biogas production through anaerobic digestion can utilise all kinds of organic material except lignin (**Table 2**) [8].

Purified biogas provides reductions in GHG emissions as well as several other environmental benefits when used as a vehicle fuel. Biogas emits less nitrogen oxide, hydrocarbon and carbon monoxide than gasoline or diesel, and engines fuelled by purified biogas are quieter than diesel engines [10].

Component	Livestock wastes	Agricultural wastes	Sewage sludge	Municipal waste	Landfill gas
CH_4	50-80%	50-80%	50-80%	50-70%	45-60%
CO_2	30-50%	30-50%	20-50%	30-50%	40-60%
H_2O	Saturated	Saturated	Saturated	Saturated	Saturated
H_2	0-2%	0-2%	0-5%	0-2%	0-0,02%
H_2S	0-1%	100-700 ppm	0-1%	0-8%	0-1%
NH_3	Traces	Traces	Traces	Traces	0,1-1%
CO	0-1%	0-1%	0-1%	0-1%	0-0,2%
N_2	0-1%	0-1%	0-3%	0-1%	2-5%
O_2	0-1%	0-1%	0-1%	0-1%	0,1-1%

Table 2.
Biogas composition. Source: Ref. [9].

2.2.1 Origin and formation

Biogas is generated from the processes of biological decomposition in the absence of oxygen (anaerobes), which allow biogas to be produced from organic matter, which occur in landfills or in closed reactors commonly known as anaerobic digesters [10]. The degassing of landfills through the capture of the generated biogas allows to improve the safety conditions of exploitation of said landfills, also taking place in many cases an energy use of the biogas collected. In the case of anaerobic digesters, organic matter (substrates) is fed, and certain operating conditions (residence time, temperature, etc.) are maintained. In order to maximize the production of biogas in digesters, it is usual to mix different types of substrates (co-digestion), allowing for the sufficient nutrient concentration required by anaerobic microorganisms. Using the co-digestion strategy, special care must be devoted to chosen mixtures that allow biological processes without inhibitions.

Anaerobic reactors. Anaerobic reactors consist of containers (usually cylindrical in shape), in which the organic matter called substrate is introduced, which will be digested by the action of anaerobic bacteria. Anaerobic digestion facilities also incorporate a gas container, which can be incorporated into the biodigester itself or independently of it as a gasometer.

Other additional elements that are part of the biodigestion facilities are:

- **Premix containers**: function is to homogenize and stabilize input mixtures, prior to entering the biodigester.

- **Sanitation systems**: certain 'inputs', such as animal by-products (not intended for human consumption category), must be sanitized through pasteurization processes, prior to entering biodigesters.

- **Biogas cleaning and upgrading treatments**: the cleaning process involves the passage of biogas through a series of filters, in which certain contaminant components are trapped (sulfur substances, siloxanes) that can damage the

mechanical elements used in their subsequent valorization (engines, boilers). The biogas upgrading is the treatment of capture of the CO_2 contained in the biogas, so that the concentration of CH_4 is increased, transforming the raw biogas into biomethane, reusable as renewable natural gas.

- **Energy recovery of biogas**: depending on the final use of the biogas produced, in those cases in which the biogas is not going to be treated for conversion into biomethane, the biogas can be used for energy recovery in cogeneration engines or turbines, to produce electrical and thermal energy, or directly in boiler for production of thermal energy.
- **Digestate treatment**: the input inputs to the biodigester, after passing through the biodigesters, can be processed for later use as a fertilizer. For this, the digestate is subjected to a series of processes (solid-liquid separation, extraction of mineral components, etc.), through which different fertilizer products are obtained such as solid biofertilizer, nitrogen and phosphorus.

Figure 2 shows the different components of an anaerobic biodigestion plant.

Stages of the anaerobic digestion process. During the anaerobic digestion processes, many types of bacteria are produced, which act during the different stages that make up the methanogenesis process, as described below (**Figure 3**).

Disintegration. Initially large particles of biomaterials are disaggregated, and polymers are dissolved as action of the continuous mixture and moderate temperature.

Hydrolysis. Hydrolysis consists in the process of breaking the longer chains of polymeric organic matter, through the action of enzymes secreted by hydrolytic bacteria. The complexity of this process will depend on the complexity of the organic matter entering the digester as well as the conditions in which the process occurs such as temperature, pH, retention time, the biochemical composition of the substrate, the size of particles, NH_4^+ concentration and the concentration of the hydrolysis products.

Fermentation or acidogenic stage. During this stage the fermentation of the soluble organic molecules takes place in compounds that can be used directly by the methanogenic bacteria (acetic, formic, H_2) and smaller organic compounds

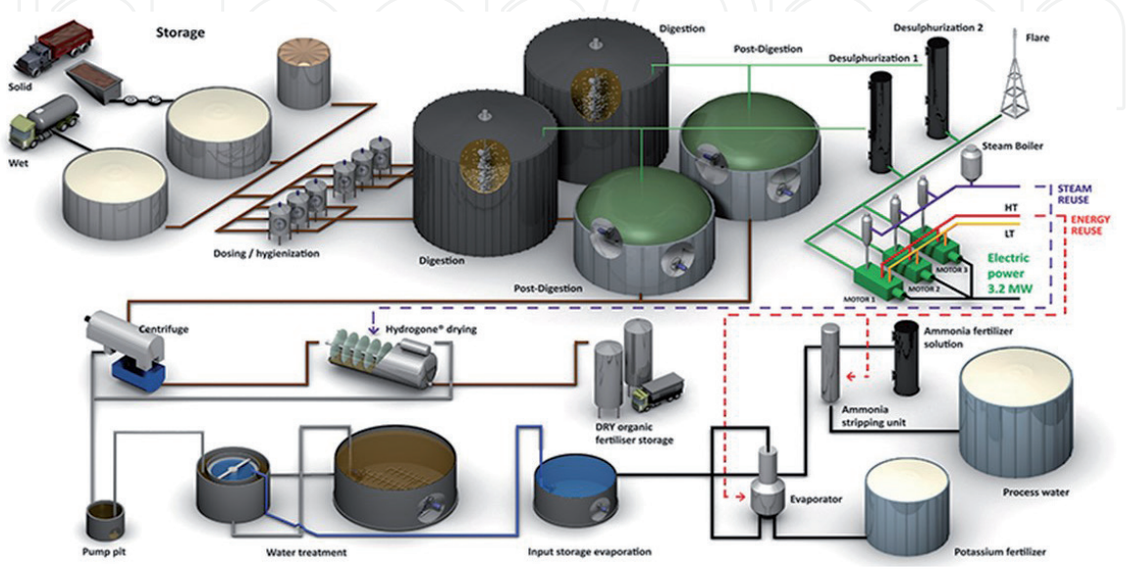


Figure 2.
Anaerobic biodigestion plant (source: BIOTIM®).

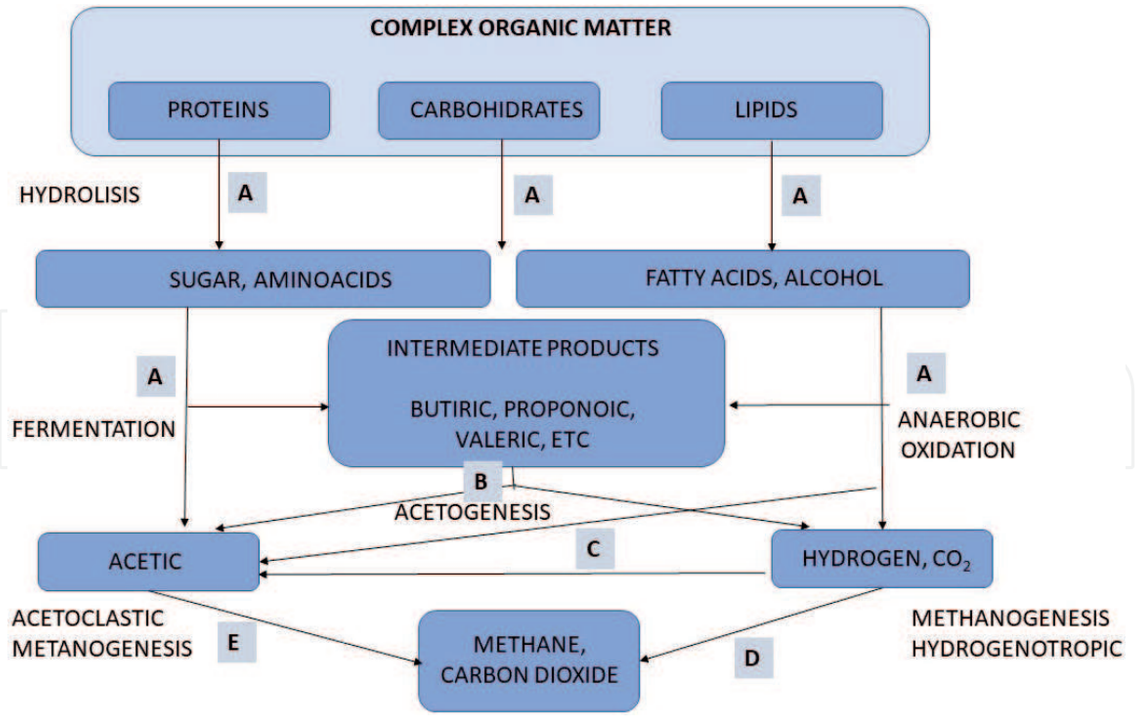


Figure 3.
Stages of the anaerobic biodigestion process [11].

(propionic, butyric, valeric, lactic and ethanol mainly) that have to be oxidized by acetogenic bacteria in the next stage of the process.

Acetogenic stage. While some fermentation products can be directly metabolized by methanogenic organisms (H_2 and acetic), others (ethanol, volatile fatty acids and some aromatic compounds) must be transformed into simpler products, such as acetate ($CH_3\ COO^-$) and hydrogen (H_2), through acetogenic bacteria.

At this stage of the process, most anaerobic bacteria have extracted all the food from the biomass and, as a result of their metabolism, eliminate their own waste products from their cells. These products, simple volatile acids, are the ones that will use as a substrate the methanogenic bacteria in the next stage.

Methanogenic stage. At this stage, a broad group of strict anaerobic bacteria acts on the products resulting from the previous stages. Methanogenic microorganisms can be considered as the most important within the consortium of anaerobic microorganisms, since they are responsible for the formation of methane and the elimination of the medium from the products of the previous groups, being, in addition, those that give name to the general biomethanization process.

Characterization of raw materials. To ensure a good yield in the production of biogas, it is necessary to make a correct selection of the raw materials that are going to be introduced into the biodigester.

For this, it is necessary to carry out previous tests (at laboratory scale), during which the suitability of each of the materials in terms of their methane production potential will be determined.

Biochemical oxygen demand. Biochemical oxygen demand (BOD) provides a measure of biodegradable organics present in a sludge and, in turn, can be used as a metric for the overall effectiveness of an anaerobic digester.

BOD is defined as the amount of oxygen, divided by the volume of the system, taken up through the respiratory activity of microorganisms growing on the organic compounds present in the sample (e.g. water or sludge) when incubated at a specified temperature (usually 20°C) for a fixed period (usually 5 days, BOD5) [12].

This parameter may be used to quantify the concentration of biodegradable organics present in sludge.

The measurement of this parameter provides information on the amount of biodegradable organic matter by the bacteria contained in the biodigester and therefore on the amount of methane that can be produced.

Chemical oxygen demand (COD). Chemical oxygen demand (COD) indicates the amount of oxygen needed to degrade a certain amount of organic matter. In COD tests, a sludge is refluxed in excess with a solution of potassium dichromate and sulphuric acid. As COD measures all organics in a sludge, its value is understandably higher than that of BOD. Thus, the ratio of BOD to COD can be used to represent the biodegradable fraction of a sludge.

Amount of dry matter and volatile solids. Dry matter or total solids are a parameter which indicates the concentration of organic matter that contributed in the feeding of the biodigester. On the other hand, volatile solids inform about the amount of organic matter that ours contains. Depending on the dry matter contained in the digester's input material, the type of digestion to be carried out will be determined, and therefore the type of digester that will be necessary to use for the process. Thus, in those cases where the dry matter concentration is less than 20% of the total, we will be talking about wet digestion and dry digestion when the amount of dry matter is greater than 20% of the total.

Carbon and nitrogen ratio. This is a determining parameter when evaluating the viability and potential performance of an anaerobic digestion process, so it must be considered during the selection process of the raw materials that will be used as inputs of the process. Thus C/N concentrations of 20/1 or 30/1 will give optimal results in digestion [13, 14]. However, low proportions of this ratio may be indicative of high concentrations of ammonium that are detrimental to the process, given the inhibitory nature of the nitrogen compounds process.

Process conditions. In addition to the type and characteristics of the raw material, the state of the same and its composition, the environmental conditions of the process inside the biodigester will largely determine the correct development of the process and the biogas production yield.

Temperature and pH, which are key parameters. Temperature (T) of the process will depend on the type of bacteria used in the process. Depending on the bacteria and the temperature conditions, we can distinguish between different types of processes:

- Mesophilic processes, which take place in a temperature range between 25 and 45°C, typically 35°C.
- Thermophilic processes are those that take place in temperature conditions above 45°C, typically 55°C.
- Psychrophilic processes are the least developed so far, in which the work of bacterias at temperatures around 20°C. Normally the psychrophilic conditions are referred for systems without any heat supply.

As for pH, in ideal conditions it must be in terms of neutrality, avoiding acidic and basic conditions. Excessive acidity (much less than 7) or a medium that is too caustic (much greater than 7) can reduce the metabolism of bacteria or even kill them.

Hydraulic retention time. The hydraulic retention time (HRT). It is the time that passes a flow in the digester from entering until leaving it. It can be referred to the liquid flow rate, the MS it contains or the time that the biomass (bacteria) resides inside the reactor before leaving with the sludge. HRT is an important

operational parameter for the anaerobic reactors which can affect the conversion of volatile solids (VS) into biogas. HRT is one of the main parameters to consider when designing the size of the digester [15], and in turn this will depend on the type and conditions of the raw materials used as inputs in the process.

Upgrading from biogas to biomethane or renewable natural gas. It is known as biogas upgrading, the treatment process through which the biogas obtained through anaerobic digestion is transformed into a renewable gas with a quality grade like fossil natural gas [16].

For the biogas to be transformed into renewable natural gas thus increasing its specific caloric value, it is necessary that a series of components such as CO_2, H_2O, sulphur compounds (H_2S), siloxanes, NH_4, O_2 and N_2 be removed from the initial gas stream [17]. For this there are currently different technologies, among which the following stand out. These technologies can be classified in two principal groups:

- Sorption technologies: adsorption and absorption
- Separation: membranes and cryogenic

Pressure swing adsorption (PSA). In this case, carbon dioxide is separated from the biogas by adsorption on a surface under elevated pressure. Molecular sieve materials such as zeolites and activated carbon are commonly used as adsorptive materials for biogas upgrading. The adsorbing material is regenerated by a sequential decrease in pressure before the column is reloaded again, hence the name of the technique.

Some of its advantages are the compactness of the equipment, low energy requirements, low capital investment and simplicity [18]. On the other hand, if hydrogen sulphide is present in the raw gas, it will be irreversibly adsorbed on the adsorbing material. In addition, water present in the raw gas can destroy the structure of the material. Therefore, hydrogen sulphide and water need to be removed before the PSA column.

Physical scrubbing (absorption). In an upgrading plant using the absorption technique, the raw biogas meets a counter flow of liquid in a column which is filled with plastic packing (in order to increase the contact area between the gas and the liquid phase). The principal behind the absorption technique is that carbon dioxide is more soluble than methane. The liquid leaving the column will thus contain increased concentration of carbon dioxide, while the gas leaving the column will have an increased concentration of methane.

Typically, either water or organic solvent (e.g. methanol, N-methyl pyrrolidone and polyethylene glycol ethers) are used to absorb CO_2 in physical absorption plants, whereas amine scrubbing is widely used for chemical absorption. Nowadays, water scrubbing accounts for ~41% of the biogas upgrading market [19].

Water scrubbing. The driving force of the process is the difference of solubility for CH_4 and CO_2 in water. CO_2 is more soluble in water than CH_4 [20]. With the increase in process pressure, this difference becomes higher, and the CO_2 is absorbed more quickly and to a larger quantity. In the scrubber column carbon dioxide is dissolved in the water, while the methane concentration in the gas phase increases. The gas leaving the scrubber has therefore an increased concentration of methane. The water leaving the absorption column is transferred to a flash tank where the dissolved gas, which contains some methane but mainly carbon dioxide, is released and transferred back to the raw gas inlet.

Membrane separation. It is based on the selective permeability property of membranes [21]. Dry membranes for biogas upgrading are made of materials that are permeable to carbon dioxide, water and ammonia. Hydrogen sulphide and oxygen permeate through the membrane to some extent, while nitrogen and methane

only pass to a very low extent. Usually membranes are in the form of hollow fibres bundled together. The process is often performed in two stages. Before the gas enters the hollow fibres, it passes through a filter that retains water and oil droplets and aerosols, which would otherwise negatively affect the membrane performance. Additionally, hydrogen sulphide is usually removed by cleaning with activated carbon before the membrane [22].

On the market, three types of membranes are typically used: polymeric, inorganic and mixed matrix membranes. Inorganic membranes have several advantages compared to polymeric, mainly due to their higher mechanical strength, chemical resistance and thermal stability. The current trend in industrial applications is to use mixed matrix membranes [17].

Cryogenic separation. This technique involves subjecting the biogas to high pressures and low temperatures, so that the CO_2 goes into its liquid state, while the methane remains in the gaseous state. Prior to subjecting the raw biogas to the cryogenization process, it must be pretreated to remove the sulphur compounds (H2S) contained "in the gas", since H_2S could damage heat exchangers [23]. On the other hand, volatile organic compounds (VOC) and siloxanes are efficiently removed during the cooling and condensation process, which is a natural part of the cryogenic improvement process.

2.3 Hydrogen

Hydrogen is currently one of the energy vectors that have the greatest potential for medium-term application, within the range of new alternative fuels to conventional petroleum products. The most important characteristic of hydrogen as an energy vector is that the energy yield of hydrogen is about 122 kJ/g, which is 2.75 times greater than hydrocarbon fuels [24].

Hydrogen is a clean fuel without toxic emissions and can easily be applied in fuel cells for electricity generation [25]. It may be stored as a gas under pressure or in a liquid state, or distributed through natural gas networks, thus representing an alternative with a high potential for long-term replacement of natural gas and as a gas compatible with natural gas in the short and medium terms [26].

Although hydrocarbons and coal are currently the main feedstock used for H_2 production [27], the need to increase the integration of renewable technologies will become unavoidable. Thus, this section will focus on the development of hydrogen production technologies compatible with renewable sources.

2.3.1 Hydrogen production

The hydrogen production will depend on two main variables: the feedstock (water or organic materials such as natural gas, biomass, coal or oil) and the origin of the energy to be used in the production process (conventional or renewable energy). If a water disponibility is possible, the main cost of hydrogen production by electrolysis is an electricity cost.

Thermolysis. It involves the application of heat (high temperatures) that causes the water molecule to rupture, resulting in hydrogen and oxygen. The direct decomposition of the water molecule, by thermal processes, requires temperatures around 2.500°K [28]. To reach these temperatures, it is necessary to use solar concentration technologies. However, the application of solar concentrators, to produce hydrogen by direct water thermolysis, leads to material problems and an increase in losses due to re-radiation, reducing absorption efficiency. An effective technique of separation of hydrogen and oxygen is necessary, to avoid an explosive mixture. These

handicaps are the reason why there is currently no pilot plant in which the direct decomposition of water takes place, which makes it unfeasible today [29].

As an alternative technique to direct thermolysis, solar thermochemical technology is proposed, based on the reduction of metal oxides [30]. These processes occur in two phases. The first phase consists in the reduction by means of the application of solar energy of the metallic oxide. The second phase, in which the application of heat is not necessary, consists in the exothermic hydrolysis of water, accompanied by the oxidation of the metal, to form hydrogen and the corresponding metal oxide [31].

Electrolysis. Electrolysis involves the breakdown of the water molecule through the application of electrical energy, resulting in hydrogen and oxygen. Traditionally, water electrolysis has been carried out in electrolytic cells formed by two electrodes immersed in an aqueous solution (electrolyte) [32]. Through the application of direct current, the dissociation of the water molecule occurred. The chemical reaction produced during the water electrolysis process is shown below:

$$H_2O \rightarrow 1/2\ O\ 2 + 2H^+ + 2e^-$$

$$2H^+ + 2e^- \rightarrow H_2$$

As already mentioned, the electrolysis process occurs in systems called electrolysers. Next, the main existing electrolyzer technologies are descriptively presented.

Polymeric membrane electrolyzers (PEM). In a polymer electrolyte membrane (PEM) electrolyzer, the electrolyte is a special solid plastic material. Water reacts at the anode to form oxygen and positively charged hydrogen ions (protons). Electrons flow through an external circuit, and hydrogen ions selectively move through the EMP to the cathode. In the cathode, hydrogen ions combine with the electrons in the external circuit to form gaseous hydrogen [33] (**Figure 4**).

Polymeric membrane electrifiers (PEM) are formed by a polymeric membrane, generally manufactured by a commercial polymer perfluorosulfonated acid (brand name of Nafion®) and by two carbon electrodes attached to both sides of the membrane (MEA) [33].

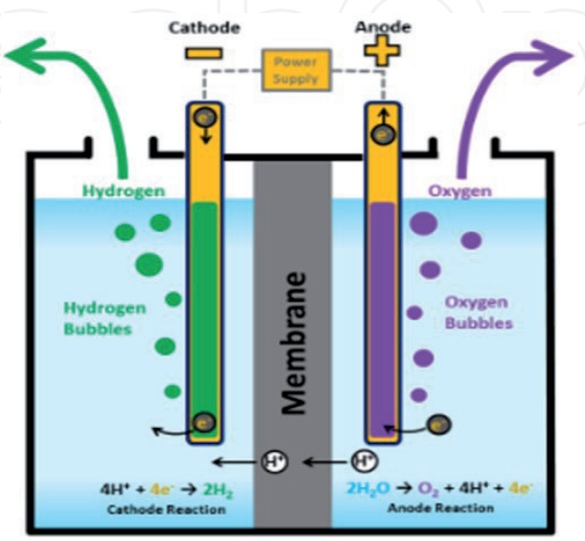


Figure 4.
Scheme of a polymeric membrane electrolyzer (PEM). Source: Green Power Co. Ltd.

Due to its acidic nature, expensive noble metal catalysts such as platinum at the hydrogen and iridium-oxide at the oxygen evolving electrode must be used. Catalyst substances are applied on the electrodes, which favours the processes of electron transfer and therefore increasing the yield of hydrogen production reactions [34].

The MEAs are installed between the so-called bipolar plates. These bipolar plates are responsible for the conduction of water inside the electrolyzer as well as the transport of the gases generated to the exit. In addition, they are responsible for providing mechanical stability to the system, ensuring electrical conductivity and evacuating the heat generated [33].

Alkaline electrolyzers. Alkaline electrolyzers are based on classical technology in which two electrodes are submerged in a solution or electrolyte. In the case of alkaline electrolyzers, the electrolyte consists of a solution of potassium hydroxide (KOH), in concentrations of 30–35%. In these electrolyzers, normally both the electrodes and the tank are made of nickel or a steel alloy with chrome and nickel, materials that can withstand the corrosive power of alkali solutions [35].

In these electrolyzers each of the cells is separated by a diaphragm that prevents the mixing of hydrogen and oxygen produced. These diaphragms are made of ceramic oxides coated with a metallic material. In addition to the membrane, the electrolyzers are formed by a current and voltage adjustment system, a supply water deionization unit and a gas separation device [36] (**Figure 5**).

Alkaline electrolyzers are more economical and durable, are recognized for their mature technology, are safe and can work with pressures up to 25 bars. It is the most mature technology, and due to its development, it is the most economical. Its effectiveness is around 62–82%, being it higher when more larger is the size of the electrolyzer [37].

Chemical conversion processes: reforming and gasification. Another of the technologies for the generation of hydrogen are those based on the processing of organic materials through two technologies called reforming and gasification.

Reforming. The reforming processes are the most common today for obtaining hydrogen. The reforming technology consists of the combination of a combination of hydrocarbons (natural gas, LPG, liquid hydrocarbons) and alcohols with water vapour, resulting in the generation of hydrogens from various chemical reactions [38].

Water steam reforming. Water reforming is based on the reaction of a fuel with water vapour on a catalyst [39]. The water vapour reforming process (known by the acronym SMR, steam methane reforming) may be applied to a wide variety of hydrocarbons (natural gas, LPG, liquid hydrocarbons, etc.) and alcohols. Of all of them, the most used for its availability and ease of handling is natural gas.

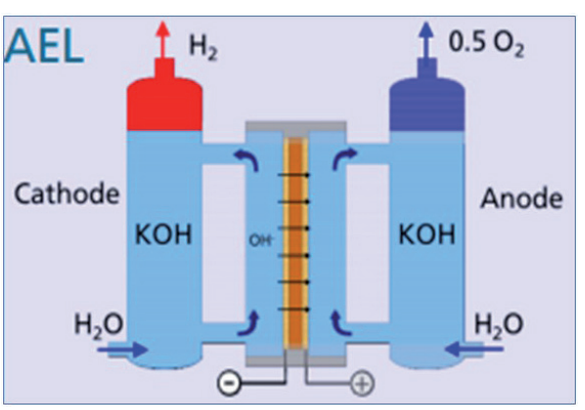


Figure 5.
Scheme of an alkaline electrolyzer. Source: Smolinka-Fraunhofer Institute für Solare Enegiesysteme ISE.

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

This reaction that is verified in the first phase is that of reforming itself, taking place at temperatures around 900°C in tubes through which methane and water vapour circulate through nickel-based catalyst beds. At the end of the process, the gas is directed towards a CO displacement unit in which the following reaction on copper catalysts is verified.

$$CO + H_2O \rightarrow CO_2 + H_2$$

The gas produced as a result of the two previous reactions passes through a condenser in which the water vapour is removed and finally reaches the third stage of the process, the purification process. The gas that reaches this unit is rich in hydrogen with carbon dioxide, water debris, carbon monoxide and methane. This gaseous stream is purified in a membrane separator or adsorption-desorption system (PSA: pressure swing adsorption.) From which, hydrogen is obtained with a purity of 99.999% [38].

Gasification. This technology produces synthesis gas ($CO + H_2$) by controlled heating of an organic waste at temperatures between 800 and 1000°C in an O_2 atmosphere or H_2O vapour. The synthesis gas obtained can be used as a direct fuel, as a source of H_2 or as a chemical raw material to prepare gasoline or diesel by means of the Fischer-Tropsch process. The use of water vapour in the feed allows to increase the production of hydrogen by reducing the production of tars and CO. Gasification, given the severity of the treatment, is particularly indicated for the treatment of plant residues that are difficult to use in other ways.

Among all the reactions involved, the steam reforming and the water-gas reaction should be noted for their importance in determining the degree of gasification and composition of the gaseous products obtained.

$$C_nH_mO_y + (2n - y)H_2O \rightarrow nC0_2 + (2n - y + m/2)H_2$$
(reforming or hydrolysis reaction)

$$CO + H_2O \leftrightarrow CO_2 + H_2 \text{ (water–gas equilibrium reaction)}$$

Fermentative hydrogen. Biological hydrogen production is possible under anaerobic conditions [40]. Some enzymes, called hydrogenases, are able to create H_2 molecules from H+, which is released as consequence of the anaerobic degradation of simple organic molecules, as sugars, into small fatty acids (mainly acetic acid). Digesters, with the same configuration as that of the ones used for biomethane production, can produce H_2 from different organic wastes. Shorter hydraulic retention times must be applied in order to avoid H_2 consumption by other groups of organism.

Photosynthetic hydrogen. Some species of microalgae contain hydrogenases that transform H^+ to H_2 under the absence of oxygen and solar illumination [41]. This process is a consequence of continuous electron motion in the light-related reactions. These electrons are used to reduce H^+ resulting in the creation of H_2 molecules.

2.4 Distribution and supply: biomethane, hydrogen, and natural gas

One of the main challenges that currently arise, to make viable the introduction of alternative fuels for vehicular use, is the logistics and supply of these fuels, from origin to the different points of supply.

Currently the only gas (not derived from petroleum), marketed for vehicular use, is natural gas. The supply of vehicular natural gas (NGV) is supplied through service stations or gas stations, to which natural gas arrives through road transport (in cryogenic or pressure tanks) and through the connection to networks of gas transportation.

The introduction of other alternative gases such as renewable natural gas (biomethane) and hydrogen is posing important challenges for gas companies, since the characteristics of these gases, although compatible with pre-existing natural gas networks, present a series of differences that will make the adaptation of the current infrastructure necessary and the need to create new distribution and distributed generation models.

Biomethane. Biogas generated in anaerobic digestion plants from agro-food waste, sewage treatment plants, landfills, etc. once purified and transformed into biomethane, with a quality equivalent to natural gas, might be injected into natural gas grids. For this, it will be necessary that the continuous measurement equipment is available at the injection point, which certifies the quality of the gas. There is a European regulation, UNE-EN 16726 Gas infrastructure, to standardize gas quality and the main parameters and their limits for the gases to be transported and/or injected into the natural gas network.

The control by the managers of the natural gas distribution networks and of the distribution of this new gas and the necessary quality and safety problems, to ensure that the distributed gas maintains the necessary conditions, implies an important technological update, which will require the implementation of new management and control tools, from the injection points to the supply.

To keep track of this valuable characteristic after having been mixed with fossil natural gas, a tracking mechanism is needed. Mass or energy balances serve reliable and complete retracing of biomethane from its production site to the final consumer.

Biomethane trade predominantly takes place in the country of its production. There are only a few examples of physical cross-border biomethane trade, e.g. from Germany to Sweden and to the Netherlands as well as from the UK to the Netherlands. If the market is not balanced, meaning demand exceeds supply or vice versa, cross-border trade is able to increase flexibility and transfer biomethane where it is needed. Barriers are often created by the different national regulatory frameworks, but they can be removed by harmonizing the national tracking systems which means that two different biogas registers are able to exchange biomethane amounts from the country of production to the country of final consumption.

Hydrogen. Being considered an energy vector this is a compatible gas with natural gas networks. However, this compatibility does not mean that H_2 can be transported as such in the same network; since it is a different molecule, it will be necessary to look for ways to be combined with natural gas or biomethane, obtaining a final gas with greater energy potential.

Thus, two main formulas are planned: injection of H_2 into the network (P2G), both in different % of H_2 injected into natural gas (power to gas—H_2), and the methane of H_2 for injection as synthetic natural gas.

The production of hydrogen, from the surplus of electricity, is an optimal way to absorb the excess (renewable) energy produced at times of demand, as an alternative form of storage [42]. Thus the energy 'stored' in the generated hydrogen (acting as an energy vector) can be combined with natural gas or biomethane transported in the gas network.

Alternatively, the H_2 produced can be recovered through CO_2 methane (discarded in the biogas to biomethane upgrade process), resulting in methane of renewable origin.

In economic terms, if connected to the grid, hydrogen can be produced subject to short-timescale variations in the power market or under flat rates through power purchase agreement (PPA) contracts. In the first case, production will happen especially at moments of low- and medium-power prices. There will be a certain number of operating hours at higher prices, causing hydrogen costs to increase. Electrolyzers may be operated as demand response assets to support energy balance over the grid [43], making profits from balancing or ancillary services (IRENA, 2018c). In the second case, hydrogen is produced at flat power rates under PPA contracts. In this case, operation can be continuous, which can improve the overall efficiency of the process—the higher the number of operating hours, the lower the hydrogen production costs. However, such baseload operation reduces the flexibility of the power system.

Other options to transport renewable fuels. For those cases where the transport of large volumes of gas, whether biomethane or hydrogen, is not required, they can be transported as compressed or liquefied gases in the cryogenic state. The choice of another method will depend on the amount of gas as well as the destination of the gas. Transport in the gaseous state does not allow the accumulation of large volumes of gas, unlike liquefaction (high pressure and low temperature) that will allow the storage of larger volumes.

Both liquefaction and gas compression will lead to important energy requirements, which will influence the final cost of gas distribution. The decision on the form of gas transportation will be linked to the other factors that affect the gas logistics chain, including the form of production (centralized or distributed), supply chain as well as access to the point of use.

As for transport methods, renewable gases, like other gases, can be distributed by ship, train and tank trucks. However, contrary to what happens with other gases of non-renewable origin such as natural gas, one of the main advantages of renewable gases is that these can be generated at points close to those of use, avoiding the need to carry out transportation on large routes, which involves the intensive use of energy.

2.4.1 Distributed production

As an alternative to the injection of biomethane and hydrogen in the natural gas distribution network, an alternative form of supply to end users is proposed, avoiding the use of the gas network. In those cases, in which the green gas generation location (biomethane or hydrogen) is far from the gas network, an isolated model or diffuse model is proposed.

Regarding biomethane as an alternative to the large biogas production facilities, linked to centralized biogas agro-livestock plants, or sewage treatment plants or urban waste plants, a model that has gained strength in recent years is the implantation of small-/medium-size biogas production plants with by-products of agricultural origin. These installations are mostly located in places far from large population centres and therefore without the possibility of connection to the gas network. To solve this handicap, these biogas production plants (and biomethane), if they can be close to communication roads (roads), with a large transit of livestock vehicles (tractors and other machinery) and trucks. Therefore, the production of biomethane in these plants, and the installation of dispensing stations for this renewable gas (gas stations), could be an important alternative to the transport of renewable gas through the gas network.

An alternative solution for isolated hydrogen generation and distributed supply would be through the development and implementation of so-called hydrogenators, or hydrogen production stations from renewable energy (photovoltaic and/or wind),

which is stored in batteries being used on demand for the production of hydrogen through the use of electrolyzers. In this way, this new fuel could be given access, in areas or road networks far from the main population centres.

3. Discussion and conclusion

3.1 Biogas and renewable natural gas (biomethane)

In recent years there has been a great controversy between detractors and defenders in relation to the environmental benefits of natural gas in general and renewable natural gas, against the use of conventional fossil fuels (diesel and gasoline) for vehicular use.

Among the detractors, various environmental groups and associations are used as main arguments against the benefits attributed to the use of gas as an alternative fuel, in that combustion of this in engines generates similar concentrations and even higher pollutant gases than fossil fuels. On the contrary, the studies that defend the environmental advantages of the use of gas as fuel defend the low emissions (mainly of particles) of the gas against other fossil fuels.

In this chapter, different alternative fuels to conventional fuels have been highlighted. In this sense, although it is true that CO_2 emissions from both natural gas and renewable natural gas will be very similar to those produced by conventional fuels, since both types of fuels have an organic (carbon) origin, it is important to highlight the other environmental advantages that alternative gas fuels have compared to conventional ones.

As already mentioned, the intention of presenting natural gas as a fuel has not been so much for its direct environmental benefits (which as it has already been described in a certain way if it has them) but for the importance that this can mean as a bridge to greater use of renewable natural gas.

Some of the environmental (and socio-economic) advantages that the deployment of renewable natural gas can present in a future scenario in which other energy sources such as electricity coexist could be the following.

3.1.1 Neutral CO_2 balance

However, as already said, the combustion of renewable natural gas (and biogas), if it would generate CO_2 emissions, given the renewable origin of the gas, these emissions would count as neutral in a global balance, given that the origin of the biogas is from organic materials, which in their origin have already absorbed atmospheric CO_2.

In addition to this advantage (neutrality), the management of organic waste for the production of biogas, if carried out in a controlled manner, avoids the bad or nonmanagement of organic waste (household waste, animal waste, other organic waste) that would entail the emission of CH_4 (uncontrolled natural digestion), with the important effect that this gas supposes in terms of atmospheric heating.

3.1.2 Atmospheric emissions

Although it is true that the use of biogas and biomethane as alternative fuels will not have a great impact on the global balance of CO_2 emissions if it will be a significant reduction in other emissions such as sulphur compounds and the suspended particles.

Specifically, it has been shown that in heavy vehicles, natural gas reduces NOx emissions up to 86% and particles 75%. In the case of buses, natural gas reduces NOx emissions up to 90% and particle emissions up to 69% compared to diesel. Additionally, natural gas does not have sulphur in its composition, so unlike diesel, it eliminates SOx emissions (Foundation for the Promotion of Industrial Innovation of the Higher Technical School of Industrial Engineers of the Polytechnic University of Madrid).

3.1.3 Circular economy and local development

In addition to the direct environmental advantages, it is necessary to highlight other advantages implicit in the use of biogas and biomethane, such as those linked to the new circular economy scenario and the much needed revitalization of rural areas.

The management of organic waste for the production of biogas for automotive and transportation allows to contribute to the so-called circular economy, whose purpose is the use of all waste generated, so that these are transformed into resources and thus close the productive circle, avoiding the demand for new resources and wasting on raw materials useful for other uses.

As for the different formats of production and management of renewable natural gas, as mentioned in the previous sections, a possible scenario for the development of an economy based on the use of waste and by-products for the generation of biogas could be based in a distributed generation model, in which the biogas generation points are directly linked to the production centres of the by-products. In this way, a broad framework of development possibilities could be opened at the local level, which would allow establishing a development path for those rural areas most in need of alternatives.

3.2 Hydrogen

It is presented in a very different scenario from that of biogas, since both its origin and its use as an alternative fuel are presented in a scenario with large differences compared to other alternative gases.

Hydrogen, as explained in the previous sections, originates from different processes that involve the use of external energy to cause the dissociation of the water molecule, releasing the hydrogen atoms. To carry out this process, depending on the origin of the energy source, it may be considered an environmentally sustainable process or not. In the case of hydrogen production, from renewable electricity (photovoltaic, wind or hydroelectric solar), the hydrogen thus produced if it can be considered a renewable fuel with zero emissions.

Hydrogen, in its use as a fuel in transport, is generally used to feed fuel cells, which generate electricity that is supplied to an electric motor, obtaining as its only residual gas water vapour, which is a completely free energy source of emissions. Also, hydrogen, in combination with residual CO_2 (e.g. from biogas upgrading processes), through a process known as power to gas, would lead to the production of methane that can be used, for example, in vehicles powered by renewable natural gas.

Additionally, neither atmospheric emissions nor CO_2 emissions are a problem for the use of hydrogen. In addition, the great advantage of using this technology, since as the only exhaust gas, water vapor is obtained, from the use of hydrogen as an energy source. With this, the cycle would be closed because hydrogen produced with water is returned to the environment.

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