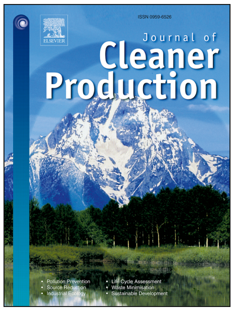


Renewable based biogas upgrading

Diego Curto, Mariano Martín

PII: S0959-6526(19)30867-4

DOI: https://doi.org/10.1016/j.jclepro.2019.03.176

Reference: JCLP 16180

To appear in: *Journal of Cleaner Production*

Received Date: 30 October 2018

Revised Date: 14 February 2019

Accepted Date: 15 March 2019

Please cite this article as: Curto D, Martín M, Renewable based biogas upgrading, *Journal of Cleaner Production* (2019), doi: https://doi.org/10.1016/j.jclepro.2019.03.176.

7030

Renewable based biogas upgrading

Diego Curto, Mariano Martín[1]

Department of Chemical Engineering. University of Salamanca. Plz. Caídos 1-5. 37008. Salamanca (Spain)

Abstract

A facility for the upgrading of biogas from the organic matter within municipal waste into biomethane using renewable hydrogen has been analyzed. For it to be fed to the grid, CO_2 is to be transformed. Methanation of the CO_2 with renewable hydrogen is carried out. Solar and/or wind energy are the power sources for the facility. The design problem is formulated as a multiperiod optimization one for the selection of the renewable technology or combination of technologies for the production of hydrogen. Two cases of study are evaluated, regions where either wind or solar availability are high, UK and Spain respectively, and two modes of operation, continuum upgrading of the biogas or variable. Continuum upgrading is more expensive due to the large contribution of the renewable hydrogen production into the cost. Variable upgrading rate benefits from biogas storage and makes the most of the available wind and solar energy. While in the UK wind is enough to upgrade the biogas, in Spain Solar is preferred, but the large area required results in the need to use wind turbines in case continuum upgrading is required. The framework is general to analyze the type of facility that operates best in any country.

Keywords: Renewable Energy, Biogas, Biomethane, upgrading, Multiperiod optimization

---

[1] Corresponding author. Tel.: +34 923294479
Email address: mariano.m3@usal.es

1.-Introduction

Waste is one of society's more important concerns because of the large volume of residues generated and the challenge that its composition represents to the communities (WEC, 2016). Circular economy has become a rising trend towards valorisation, providing a second life to the residues (Korhonen et al. 2018). Its application to different waste sources leads to its recycle and reuse in various forms, among them the development of the waste-to-energy initiative. The type of residue determines its exploitation opportunities. Anaerobic digestion has been presented as one of the more promising ones because of the products, a digestate with a high content of nutrients, and biogas. The potential to biogas from waste can substitute current use of natural gas in many regions. In spite of the large investment required to build the processing facilities (Taifouris and Martín, 2018), as long as biogas is upgraded to natural gas composition, the shipping infrastructure is already available. Furthermore, biogas is not only a source of methane, but CO_2 is an additional carbon source for the production of chemicals (Hernández et al., 2017), and allows the renewable production of biodiesel where the digestate provide the nutrients for algae growing and the biogas is used is used to produce renewable methanol (Hernández and Martín, 2017). As a result, the target of net zero emissions in power production is getting closer (Davis et al., 2018).

However, for biogas to be injected into the current natural gas pipelines, it must be upgraded. Two alternative paths can be followed. On the one hand, CO_2 capture technologies can be used. Among them the main technologies that can be identified are amine absorption (GPSA 2004), where different solvents have been evaluated specifically for biogas upgrading (Moreno et al., 2017), the use of pressure swing adsorption (PSA) systems, where different adsorbents such as activated carbon, silica gel and zeolite 13X are among the common choices for biogas processing (Ferella, et al 2017), and membranes (He et al, 2018). Optimization studies have been reported for post combustion removal of CO_2 using membranes, chemical absorption (Hasan, et al., 2012a) or PSA (Hasan, et al 2012b), as well as within process design for the production of ethanol (Martín & Grossmann 2011). These technologies are highly energy intensive. Moreover, their principle of operation consists of removing a chemical, CO_2 that can be a source of carbon. By separating it, another problem arises, since a use for it must be found. Alternatively, methanation can be used. Methanation is a common treatment technology to remove traces of CO and CO_2 from syngas in the production of ammonia. The process consists of the production of methane from CO_2 and hydrogen. The advantage is the use of CO_2 to increase the methane production capacity (Tynjala, 2015).

The drawback is the need for renewable hydrogen. Davis and Martín (2014a) used hydrolytic hydrogen to store wind energy by CO_2 methanation. Later, the use of solar and wind as energy sources was evaluated for the same case (Davis and Martín, 2014b). The high cost of PV panels and wind turbines resulted in the need to carefully select the allocation of the solar fields and wind farms for its cost to be competitive with current fossil-based methane (de la Cruz and Martín, 2016). However, biogas methanation poses a number of additional challenges due to the amount of methane already in the gas stream that reduces the methanation yield. Recently, some experimental studies have presented this technology as an upgrading alternative instead of removing the CO_2 (Stangeland et al 2017). According to this last work, further catalyst development is required but the evaluation of various reactors is already in progress (Schidhauer and Biollaz, 2015). Even CO_2 methanation within the digester is being studied (Tynjala, 2015). The technology has already been tested at the level of proof of concept (Kirchbacher, 2016). However, the need for renewable energy for the production of sustainable hydrogen as well as the actual design of the plant determines the sustainability of this technology. Hydrogen production is highly energy intensive. Solar photovoltaics and wind turbines represent a high cost for the facility jeopardizing the possibility of using biogas as a substitute for fossil-based natural gas as well as compromising the sustainability of the biogas upgrading step.

In this work an integrated facility for the production of biomethane via biogas upgrading using renewable hydrogen is designed at conceptual level. Mathematical optimization techniques have been used for the optimal process design, selecting the power technologies, wind turbines and/or PV panels, for the production of renewable hydrogen. Two modes of operation corresponding to two different plant designs are evaluated, continuum or variable upgrading, that depend on the availability and cost of the renewable hydrogen production technology. The aim is to evaluate the competitiveness of this technology to substitute natural gas with a sustainable counterpart. The rest of the paper is structured as follows. Section 2 shows a description of the integrated production of biomethane from waste and water. Section 3 presents the modelling approach, the main features and assumptions. In section 4 the results are discussed and finally some remarks are presented in section 5.

2. Overall Process Description

The process can be divided into three subsections: biogas production, hydrogen production and biogas purification/upgrading (biomethane generation).

Organic waste and water are fed to a reactor where the residue is anaerobically digested to produce biogas and digestate. The composition of the biogas is what makes it interesting for further use. Apart from methane, the most desirable species for its use as a power source, carbon dioxide contributes with 35 – 50% by volume to the mixture (Gunaseelan, 1997). CO_2 is a valuable species because it represents another carbon source as it has been presented in previous works (Hernández and Martín, 2016). The challenge is that it is highly stable for further transformation. Other species in small amounts such as hydrogen sulphide, nitrogen, ammonia and moisture are present in the mixture and define the actual process. The digestate can be further used as fertilizer. However, it is out of the scope of this paper to pursue its analysis because it has been already evaluated in previous works of the group (Martín–Hernández et al., 2018).

The final use of biogas requires a composition absent of species that can lead to the production of air pollution such as nitrogen oxides and sulphur dioxide. Furthermore, the methanation of the CO_2 is a catalysed reaction. The catalyst is poisoned by the presence of H_2S. Thus, the biogas is processed though a system of fixed beds to remove the traces of ammonia, employing a zeolite bed, and a bed of oxides for the removal of the H_2S (Rykenbosh et al., 2011). After these processing stages, the biogas is mainly methane and CO_2 that can be mixed with hydrogen to transform the CO_2 into methane.

The hydrogen used in the methanation stage needs to be obtained from renewable resources. Among them, based on previous studies, the production of hydrogen via biomass gasification is discarded. Together with hydrogen, CO_2 is also produced reverting nature's CO_2 capture process via photosynthesis (Martín and Grossmann, 2011). Furthermore, in a previous work that compares various technologies to produce renewable hydrogen, biomass was not selected (Martín and Davis, 2015). Thus, water electrolysis is the technology of choice. The power required in the electrolysis as well as for gas compression must come from renewable resources. In this work wind and/or solar energy, photovoltaics (PV), are considered. From the electrolyzer two streams are obtained, one from the anode, the oxygen, and another one from the cathode, the hydrogen. Even though solid polymer electrolytes are gaining attention nowadays, a more mature technology, an alkaline type of electrolyzer, is used. As a result, both gas streams are saturated with water. The removal of water is carried out by simple condensation. The condensed water is recycled back to the electrolyzer to limit the water footprint of the facility. For hydrogen to be further used in synthesis and for the oxygen to be sold, further processing is required. The oxygen must be dehydrated, using a zeolite bed, and compressed. The hydrogen contains traces of oxygen that is a challenge for the use of hydrogen. It is removed by catalytic synthesis of water in a deoxo reactor, and it is dehydrated before being mixed with the biogas.

The third stage of the process consists of the methanation of the CO_2 within the biogas. It is a difficult stage since the presence of methane in the mixture reduces the yield of the reaction and an excess of hydrogen is needed. The gas phase is fed to the reactor at the appropriate temperature and pressure. A system consisting of a compressor followed by a heat exchanger is used. The order is such that the system benefits from the temperature of the gas after compression. In the reaction water is produced. To reduce the consumption of water, it is recycled to the electrolyzer. The excess of hydrogen required to drive the equilibrium to methane is recovered using membrane made of palladium and it is recycled back to the mixing point between biogas and hydrogen. In Figure 1 a scheme of the process described above is shown.

Figure 1.- Integrated biogas upgrading facility

3. Process model.

The process described in section 2 is modelled unit by unit using a first-principle based approach, including mass and energy balances, thermodynamic principles for gas processing, phase equilibrium for gas – liquid contact, chemical equilibrium for reactor yield estimation, as well as rules of thumb and experimental data for the yield of particular equipment such as wind turbines, solar panels and electrolyzers, see Grossmann and Martín (2012) for a summary of the alternative modelling approaches and Martín (2016) for the basic principles. The main variables of the model are the mass flows as well as the operating temperatures and pressures of each of the units. The solution to the design will lead to the optimal values for each one of them, as well as the selection of the use of the power source, the PV panels and/r the wind turbines. For this process, the species involved are within the set *J* = { Wa, CO_2, CO, O_2, N_2, H_2S, NH_3, CH_4, SO_2, C, H, O, N, Norg, P, K, S, Rest, Cattle_slurry, Pig_slurry, P_2O_5, K_2O}. The following subsections summarize the assumptions employed to model each of the units.

3.1.-Biogas production section.

The model for the digester can be found in detail in León and Martín (2016). In short, the composition of the biogas is computed by formulating a mass balance. Experimental data are used to determine the yield to biogas from the waste. The remaining comprises the digestate. The digestate can only be used as a fertilizer if an appropriate NPK index is achieved, the ratio of nitrogen, phosphorous and potassium in the residue.

The biogas processing through packed beds requires its compression to favour the removal of the impurities, ammonia and sulphur dioxide, and to overcome the pressure drop. Each compression stage in the entire process is modelled as polytropic. Eqs. (1)-(2) are used to compute the exiting temperature and the power consumed, with temperatures in K and pressures in kPa. The efficiency of the compression stages is assumed to be 0.85 (Walas, 1990) and the polytropic coefficient is assumed to be 1.4.

$$T_{out/compresor} = T_{in/compressor} + T_{in/compressor}\left(\left(\frac{P_{out/compressor}}{P_{in/compressor}}\right)^{\frac{z-1}{z}} - 1\right)\frac{1}{\eta_c} \quad (1)$$

$$\mathrm{W}_{(Compressor)} = (F)\cdot\frac{R\cdot z\left(\mathrm{T}_{in/compressor}\right)}{\left((\mathrm{M}_w)\cdot(z-1)\right)}\frac{1}{\eta_c}\left(\left(\frac{P_{out/compressor}}{P_{in/compressor}}\right)^{\frac{z-1}{z}} - 1\right) \quad (2)$$

The first processing stage is the removal of ammonia and sulphur hydride. In principle two different beds can be used. However, the small amount present in the biogas and to simplify the process, a single unit is modelled consisting of two types of beds, one appropriate for the removal of ammonia, zeolites, and another for the removal of H_2S. The removal yield of both is assumed to be 100%. Ammonia is eliminated from the main stream by adsorption, that it is favoured at low temperatures, 25ºC, and moderated pressures, 400-500 kPa. For the H_2S removal to be efficient under similar operating conditions a bed of Fe_2O_3 is installed (Rykenbosh et al., 2011). The mechanism that governs H_2S removal consists of the following chemical reaction:

$$Fe_2O_3 + 3H_2S \rightarrow Fe_2S_3 + 3\ H_2O$$

The ammount of sulphur hydride in the stream does not suggest the need for further dehydration to remove the water produced. The bed can be regenerated using oxygen as follows:

$$2Fe_2S_3 + 3O_2 \rightarrow 2FeO_3 + 6S$$

3.2.- Hydrogen production section

3.2.1. Energy production

The power for water splitting as well as for the numerous compression stages involved is to be provided by renewable resources. Solar PV panels and wind turbines are considered.

Wind Turbine farm. The selection of the wind turbine is a problem on its own as it was presented in the literature (de la Cruz and Martín, 2016). However, for this case the Nordex N100-2500 turbine is selected. The power produced is modelled as a function of the wind speed as given in eq. (3) where the parameters of the power curve are P_{rated} equal to 2,500 kW, *a* , 8.226 m/s, and m, 0.806 s/m (de la Cruz and Martín, 2016). The cost for the installed turbine is assumed to be 1600 €/kW (Davis and Martín, 2014b).

$$P = \frac{P_{rated}}{1+e^{(-(v-a)m)}} \tag{3}$$

Solar field. According to the literature, a solar PV panel of 8 m^2 provides 1 kW_p (Maaβse et al., 2011). The installation costs are of the order of 1,080 $/$kW_p$ (Goodrich et al., 2012). The power generated per panel is estimated using eq. (4) as a function of the local solar incidence, I. The efficiency of the panel, ω, is assumed to be 75%.

$$P_{panel} = \frac{0.75}{24} A_{panel} I \left(\frac{kWh}{m^2 d}\right)\omega \tag{4}$$

3.2.2 Water splitting section.

Hydrogen is obtained in an alkaline electrolyzer operating at 80 ºC and 101 kPa. A solution of 25% KOH is used as electrolyte. Water splitting takes place following the reaction below.

$$2\ H_2O \rightarrow 2\ H_2 + O_2$$

The model of the electrolyzer consists of a mass balance given by the stoichiometry of the reaction. The flowrate of the hydrogen and oxygen produced depends on the energy provided. The energy required to split water is beyond that given by the water enthalpy of formation due to losses. A value of 175,000 kJ/kgH_2 from the literature is used to perform the energy balance to the electrolyzer (NEL Hydrogen, 2012). Water splitting from a solution results in two gases phases, that of the oxygen and that of the hydrogen, saturated with water, φ=1. The water flow accompanying the gases is computed using the vapor pressure of water (Sinnot, 1999) at the operating conditions of the electrolyzer as per eqs. (5)-(8).

$$p_{sat\_atm} = e^{\left(A-\frac{B}{(C+T)}\right)}; \tag{5}$$

$$p_{v\_atm} = \varphi \cdot p_{sat\_atm}; \tag{6}$$

$$y = \frac{M_{w,water}}{M_{w,drygas}} \cdot \frac{p_{v\_atm}}{\left(p_{air} - p_{v\_atm}\right)}; \tag{7}$$

$$\mathrm{fc}(\mathrm{Wa}) = (\mathrm{fc}(drygas))\cdot y \tag{8}$$

For the purpose of the economic evaluation, a single electrolyser is assumed to produce 0.0124 kg H_2/s (NEL Hydrogen, 2012).

Both gas streams are treated before storage or further use. Following the path of the oxygen, the water is condensed at 25ºC and recycled to the electrolyzer. The gas is still saturated with water at this pressure and temperature and the flow of water in the gas phase is computed using eqs. (5)-(8). The heat capacities of the species in the gas phase are symbolically integrated as a function of the temperature that is left as a variable. Next, it is compressed to 450 kPa in a polytropic compressor modelled using eqs. (1)-(2), cooled down again to 25ºC and dehydrated in a zeolite bed, assuming a water removal ratio of 99.97, before its final compression for storage at 9 MPa. The hydrogen stream is processed differently. After water condensation and compression to 450 kPa, the traces of oxygen are removed in a deoxo reactor. The reactor operates at 90ºC. Thus, the hydrogen flow is heated up in a heat exchanger, HX5. This heat exchanger is modeled based on energy and mass balances. In the reactor water is formed from its constituents, see eq. (9). The reactor is modelled using the mass balance given by the stoichiometry of the reaction, neglecting the heat of reaction. The conversion is assumed to be 99.7%.

$$2\,\mathrm{H_2} + \mathrm{O_2} \rightarrow 2\,\mathrm{H_2O} \tag{9}$$

Because of the formation of water, the stream is dehydrated right after the reaction using a zeolite bed before the hydrogen is mixed with recycled hydrogen and biogas. Note that all streams are at 450 kPa at the mixing point.

3.3.- Methanation stage

The methanation stage is a mature technology that has been studied over the years (Davies and Lihou, 1971). The main challenge of the methanation of biogas is the already large amount of methane in the purified biogas stream which determines the need for an excess of hydrogen. The high cost of renewable hydrogen defines the flowsheet of this section. Two main reactions govern the methanation of CO_2, the methanation, eq. (10), and the water gas shift reaction, eq. (11).

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \tag{10}$$

$$CO_{2(g)} + H_{2(g)} \leftrightarrow CO_{(g)} + H_2O_{(g)} \tag{11}$$

The operating conditions of the reactor require adjustment of the feed temperature and pressure using compressor 6 and HX9, modelled as a polytropic compressor using eqs. (1)-(2) and a mass balance and using mass and energy balances respectively. The yield of the methanation is computed by the equilibrium constants of eqs. (10)-(11) given by eq. (12), (Davies and Lihou, 1971). T is given in ºC and P in kPa

$$\begin{gathered} kp_1 = 10266.76 \cdot Exp^{[-\frac{26830}{T+273.15}+30.11]} = \frac{P_{CO} \cdot P_{H_2}^3}{P_{CH_4} \cdot P_{H_2O}} \\ kp_2 = \exp\left(\frac{4400}{T+273.15} - 4.063\right) = \frac{P_{CO_2} \cdot P_{H_2}}{P_{CO} \cdot P_{H_2O}} \end{gathered} \tag{12}$$

Thus, the model for the reactor consists of the elementary mass balances to carbon, hydrogen and oxygen atoms, eq. (13), together with the equilibrium constants in eq. (12)

$$\begin{gathered} n_{CO_2}\Big|_{in} = n_{CH_4} + n_{CO} + n_{CO_2}\Big|_{out} \\ 2 \cdot n_{H_2}\Big|_{in} = 4 \cdot n_{CH_4} + 2n_{H_2} + 2n_{H_2O}\Big|_{out} \\ 2 \cdot n_{CO_2}\Big|_{in} = n_{H_2O} + n_{CO} + 2 \cdot n_{CO_2}\Big|_{out} \end{gathered} \tag{13}$$

Furthermore, an energy balance is formulated assuming global isothermal operation, eq. (14)-(16). However, the reactor is a multibed one with intercooling steps after each one of the beds.

$$Q_{products} = \sum_i fc_{(i,Reactor,Turbine)} \cdot (\Delta H_f + \int_{T_{ref}}^{T_{out}} CpdT) \tag{14}$$

$$Q_{\mathrm{reactants}} = \sum_{j=\mathrm{inlets}} \sum_i fc_{(i,HX7,Reactor)} \cdot (\Delta H_f + \int_{T_{ref}}^{T_{in}} CpdT) \tag{15}$$

$$Q_{(Reactor)} = (Q_{products} - Q_{\mathrm{reactants}}) \tag{16}$$

Additional operating constraints are added to ensure its operation. First, the typical range of operating pressure is imposed from 101 kPa to 3 MPa (Gassner and Marechal, 2009). Second, the feed temperature must be from 140 to 350 ºC (Gorke et a, 2005). Finally, to the composition of the feed must meet the constraint given by eq. (17) to avoid carbon deposition on the catalyst, (Bader et al., 2011),

$$\frac{n_{H_2} - n_{CO_2}}{n_{CO} + n_{CO_2}} \geq 3 \tag{17}$$

After the reactor, the gas product is cooled down and water condenses. The amount of condensed water is computed using eqs. (5)-(8) and it is recycled back to the electrolyzer reducing water consumption. The excess of hydrogen required to achieve methanation is recovered using a palladium membrane that operates at the reactor pressure. The membrane is modelled using a simple mass balance. Hydrogen is assumed to be obtained pure at 450 kPa for its recycle. A recovery of 97% is considered. Downstream of the membrane, a PSA system is added to process the gas before feeding it to the natural gas grid. No further expansion of the biomethane is assumed.

4.-Solution procedure.

A multiperiod optimization formulation is developed to evaluate the possibility of processing and upgrading the biogas from the organic matter within the urban waste over time considering the seasonal variability in wind and solar energy. In the case of the use of wind energy, a two-stage procedure can be used. First, the optimal turbine for the allocation can be selected based on de la Cruz and Martín's (2016) work. The second stage of the study is the one presented in this work, having preselected a turbine.

Two operation modes are evaluated: a) Constant methane production based on the continuous processing of waste or, due to the large investment required in hydrogen production, b) the biogas produced can be stored and processed over time depending on the availability of wind/solar energy.

A) In the first operation mode, it is assumed that the chemical units from the facility will operate on a continuous basis due to the need for processing a certain flowrate of waste. Therefore, the need for wind turbines and /or solar panels will be based on the availability of energy sources and the fixed biogas production rate. Along the operation, there could be an excess of power that can be directly sold to the grid, no storage is considered in this study. The objective function for continuum upgrading is given by eq. (18) and the system is modelled as described in section 3. The model consists of 1,300 equations and 2,000 variables.

$$\begin{gathered}
\mathrm{Z} \;=\; \mathrm{fc}_{\mathrm{CH4}}\text{-Wind} - \mathrm{Solar\_t} + \mathrm{C}_{Electricity} \sum_{j \in \{months\}} ExcessPower_{generated,j} \\
\mathrm{Wind} = \frac{1}{3} n_{turbines} \cdot C_{turbine} \cdot P_{nom}\, t_{yr} \\
\mathrm{Solar} = \frac{1}{3} n_{panel} \cdot (P_{panel} + C_{Area} \cdot A_{Panel})\, t_{yr} \\
ExcessPower = (n_{turbines} - n_{turbused}) \cdot P_{nom}\, t_{month} + (n_{panel} - n_{panelused}) \cdot t_{month} \\
n_{panel} \cdot A_{Panel} \le A_{Max}
\end{gathered} \tag{18}$$

The formulation is general to analyze facilities in any location and can be extended to hourly variations in solar or wind availability. However, for the sake of the example monthly variability is considered.

B) The second operation mode considers that the upgrading capacity varies monthly so that the chemical units will not operate at full capacity, to make the most of the availability of solar and wind resources and the investment. The mathematical complexity of the multiperiod model suggests a different solution approach compared to the one presented in case A. Assuming that the intensive variables remain constant and that only the extensive ones, such as mass and energy flowrates, change, following the work by Martín (2016), a second problem is formulated. Surrogate input–output models are developed from the optimal operating conditions of the plant as a function of the power input to compute the need for raw materials and the yield to the various products per kW of power used. This power must be produced either by wind turbines or solar PV panels. The investment involves accounting for the largest number of turbines or panels needed at any month. The problem is formulated in eq. (19) assuming 12 monthly periods, per. The model consists of around 100 equations and variables.

$$
\begin{gathered}
\mathrm{Z} = \text{Biomethane-Wind} - \text{Solar} \\
\text{Wind} = \frac{1}{3} n_{turbines} \cdot C_{turbine} \cdot P_{nom}\, t_{yr} \\
\text{Solar} = \frac{1}{3} n_{panel} \cdot (P_{panel} + C_{Area} \cdot A_{Panel})\, t_{yr} \\
\text{Biomethane} = \mathrm{CH_4\_prod} \cdot t_{yr} \\
\sum_{per} \mathrm{BioCH}_{4(\mathrm{per})} \cdot t_{month} = \text{Biomethane} \\
\mathrm{BioCH}_{4(\mathrm{per})} \cdot \mathrm{K}_{\mathrm{H2/BG}} = \mathrm{ElectroH}_{2(\mathrm{per})} \\
\mathrm{PowerUsed}_{(\mathrm{per})} = \mathrm{ElectroH}_{2(\mathrm{per})} \cdot \mathrm{P}_{\mathrm{H2}} \\
\left(n_{turbused,per}\right) \cdot P_{nom} + (n_{panelused,per}) \cdot P_{panel} \geq \mathrm{PowerProd}_{(\mathrm{per})} \\
\mathrm{PowerProd}_{(\mathrm{per})} \geq \mathrm{PowerUsed}_{(\mathrm{per})} \\
n_{turbines} \geq n_{turbused,per} \\
n_{panel} \geq n_{panelused,per} \\
n_{panel} \cdot A_{Panel} \leq A_{Max}
\end{gathered} \tag{19}
$$

A_{panel} is equal to 8 m^2 and A_{max} es $2.5 \cdot 10^5$ m^2. In the appendix the parameters of the surrogate model given in eq. (19) are shown.

Finally, the investment and production costs of the two alternatives are estimated. Two cases of study are considered, the same ones presented in Martín (2016). One in a region with high solar incidence and moderate wind speed, the South of Spain, and another one with high wind speed and low solar intensity, the North of the UK, in this way we cover the variability of renewable resources. Biogas is assumed to be stored within the digester for the period of time required, since their design typically allows it. Biomethane is directly fed to the already existing infrastructure and therefore, no storage cost is assumed. However, the formulation is general and can be used to evaluate the most appropriate design for biogas upgrading as a function of the availability of solar and wind as well as for the type of organic waste.

5.-Results

This section summarizes the results corresponding with the two cases of study, Spain and the UK, and the two modes of operation, either continuum methanation of the biogas produced from the organic matter within municipal waste, where the use of renewable sources will be variable following the availability of solar and wind, or variable upgrading rate, taking advantage of the possibility of storing biogas for a certain time and minimizing the cost of solar panels or wind turbines. A monthly average of 10 kg/s of waste is to be processed (León and Martín, 2016). This amount corresponds to around one sixth of the production of waste of Madrid, Spain (INE, 2018).

5.1.-Plant operation

Table 1 shows the main operating conditions of the major units involved in the process of biogas upgrading using electrolytic hydrogen for the two cases of study and the two operating modes, either the continuous operation of the biogas facility and therefore, the continuum production of hydrogen considering the variation in the resource availability, solar and wind, or the optimal multiperiod operation of such a plant for the same total flowrate of waste to process. In both cases of study, Spain and UK, variable operation is more efficient to make the most of the use of wind and solar energy. Due to the high contribution of the turbines and panels to the cost, and the possibility of storing biogas for a certain period of time, this alternative is the most promising.

Table 1.- Main operating and design parameters

To estimate the environmental advantage of the integrated facility developed in this paper, the CO_2 emissions mitigated are estimated. By transforming the CO_2 within the biogas into biomethane using solar or wind power, instead of removing it, the production capacity of the facility increases by 44%, resulting in a larger substitution of fossil-based natural gas. As a result, the CO_2 mitigated by using this additional methane instead of fossil CH_4 is 10 times larger than the emissions due to the use of the wind turbines needed to provide the power required (at 0.011 kg CO_2/kWh) and 2.3 times the emissions generated when using PV panels (at 0.048

$kgCO_2/kWh$). Based on Table 1, any of the modes of operation yields a facility with additional 2- and 10-times reduction in CO_2 emissions compared to the base case of the production of biogas. The integrated facility is cleaner than the simple production of biogas as power source. The values for the CO_2 emitted by the technologies are taken from Schlömer et al. (2014). Note that the emissions due to CO_2 capture from methane would provide an even larger advantage in favor of this design.

Figures 2 and 3 show the operating profiles for the continuum and variable biogas upgrading in Spain. Figure 2 presents the relative usage of turbines and panels on a monthly basis, so as to be able to provide the hydrogen required for methanation. Winter period, December and January, are the ones that require the largest usage due the fact that solar is the main energy resource and its availability is limited. Figure 3 shows the monthly production capacity of methane if the use of solar and wind energy is optimized. The profile is somehow the opposite. In this case there is no need for wind turbines and the system makes the most of the summer period to produce methane. Again, the possibility of storing methane provides an interesting alternative for this mode to be attractive.

Figures 4 and 5 show the results for the second case of study, the UK. The high wind speeds and the wind profile over time results in a more stable usage of turbines and solar panels in the case continuum biogas methanation is considered. During fall both, panels and turbines, reach full or close to full usage. Opposite to the case of Spain, turbines are used up to a higher lever due to the larger availability of wind energy. Figure 5 shows the monthly production capacity to make the most of air velocity and solar energy. In this case, the number of wind turbines to purchase is less than half the previous mode of operation, see Figure 4. The production capacity of methane is higher in spring and fall, but more regular over time than in the case of Spain.

Figure 2.- Usage of turines and panels over time: Spain

Figure 3.- Monthly production capacity for fixed used of energy collecting units: Spain

Figure 4.- Usage of turines and panels over time: UK

Figure 5.- Monthly production capacity for fixed used of energy collecting units: UK

5.2.-Economic evaluation.

In spite of the wide use of cost estimations, it is still an art. Different methods can be found in the literature but most of them rely on the estimation of the equipment cost. In particular the factorial method in Sinnot (1999) is used to evaluate the processing and investment cost. The typical estimation error using this procedure is around 20-30% (Sinnot, 1999).

The investment cost of the integrated facility that upgrades biogas into biomethane uses the factors of a plant that processes fluids and solids, to estimate the fixed and total investment costs from the cost of the units. Note that the cost of the wind turbines (Davis and Martín, 2016) and that of the solar panels (IREA, 2012) already includes their installation. To estimate the cost of compressors, vessels, heat exchangers they are sized as presented in the supplementary material of Martín and Grossmann (2011). Their size is a function of the power, the weight of steel and the heat exchanger area respectively. Their cost is estimated updating the correlations obtained in Almena and Martín (2015) from Matche (MATCHE, 2004). Saur (2008) is the source for the cost of the electrolyzers. The installed cost of these units is assumed to the 1.5 times their cost. Other items such as piping, isolation, instrumentation and the utility system are computed as a fraction of the equipment cost (UC), excluding the turbines or PV panels, as follows. Piping represents 20% of the UC, isolation adds up to 15% of UC, instrumentation cost is estimated as 20% of UC and the utility system cost corresponds to 10% UC. The cost of the land used to install the units is assumed to be 8.5 M€. The solar field preparation cost is estimated in 5.5 €/m^2 (Maaßen et al. 2011). Over these costs, the fixed cost (FC), fees add up to 0.75% of FC. Administrative expenses and overheads represent 7.5% of the direct costs (fees plus FC) and 5% of the FC respectively. The plant start-up cost is considered to be 3.5% of the investment. The sum of FC plus the fees and the start-up represent the investment cost (IC).

Apart from the investment cost, the biomethane production costs are estimated. The competitiveness of this facility relies on biomethane cost to be comparable with natural gas, the fossil counterpart that aims to substitute. The average annual cost is estimated considering items such as labor costs, assumed to be 0.4% of IC, unit maintenance, 1.1% of FC, amortization, assumed to be linear with time over 20 years, the taxes, 0.5% of IC, overheads, 1% IC, and administration, estimated as 5% of the labor, maintenance, amortization, taxes and overheads.

Table 2 summarizes the investment and production costs. Figure 6 shows the breakdown of the production costs for continuum a) and variable operation, c) and the share of the three major sections of the process for continuum b) and variable operation d) in Spain and Figure 7 presents the results for UK under the same scenarios of operation. The most competitive costs are obtained when solar and/or wind energy are used in a more efficient way due to the current large costs of the collecting devices such as wind turbines and solar panels. Thus, if possible, it is more interesting to store the biogas for a longer period of time so as to upgrade it when the energy is available. Note that storage and distribution are assumed at no cost as if already belonging to the natural gas existing infrastructure and using the multiple digesters as biogas storage tanks. By upgrading the biogas following the availability of solar or wind energy, competitive costs for methane can be obtained. However, the continuum production of methane results in the need for a larger number of pieces of equipment to collect solar or wind energy due to their time variability. Current prices of the PV panels result in high costs for upgrading biogas using solar energy. However, while the use of turbines is more economic nowadays, in the next 30 years their price is expected to decrease only by 25%, while the price of PV panels is expected to decrease by 90% (Sanchez and Martín, 2018). Another interesting result is the fact that under the expected prices for collecting devices by 2050, the continuum operation in the UK is better than that following the availability of solar and wind energy. This is an attractive fact since the operation is more flexible depending in the demand. Under these expected conditions solar and wind the prices are competitive with current natural gas but also between the two places since the production and investment costs will be reduced below 5 €/MMBTU.

Table 2.- Summary of production and investment costs.

Table 3.- Projections in production and investment costs. 2050

Figure 6.-Case of study of Spain. Continuum operation: a) Operating costs breakdown; b) Plant section contribution to equipment cost. Variable operation: c) Operating costs breakdown; d) Operating costs breakdown;

Figure 7.-Case of study of the UK. Continuum operation: a) Operating costs breakdown; b) Plant section contribution to equipment cost. Variable operation: c) Operating costs breakdown; d) Operating costs breakdown;

6.-Conclusions.

In this work biogas has been upgraded to natural gas composition via methanation using renewable hydrogen. The plant uses solar and/or wind energy for the production of hydrogen via electrolysis. In parallel waste has been anaerobically digested into biogas. Finally, the CO_2 within the biogas is converted into methane using the renewable hydrogen. The excess is separated using a membrane and recycle. Two allocations, Spain and UK, and two modes of operation, optimal usage of solar or wind and continuum upgrading of biogas are evaluated. To address each mode of operation, different models and optimization procedures are developed.

The optimization allows determining the optimal operating conditions in all the units. In terms of operation, the high cost of wind turbines and solar panels suggest the temporary storage of biogas and the optimization of the use of wind and solar. The comparatively higher cost of the solar panels results in the fact that upgrading in the UK is cheaper than in Spain under current prices. However, the expected decrease in about 90% of the cost of PV panels over the next 30 years compared to the relatively small 25% decrease in the wind turbine costs is expected to equalize the costs.

Acknowledgments

Authors thank PSEM3 group for software licenses and JCYL project SA026G18

7.-Nomenclature

a: Parameter of the power curve (m/s)
$BioCH4_{(per)}$: Flow of biomethane produced during a period (kg/s)
C_i : Cost €/kg of species i
Cp: Heat capacity (kJ/kg K)
fc_i: Flow rate of component i (kg/s)
kp: Equilibrium constant
$K_{H2/BG}$: Ratio of kg of hydrogen required per kg of biomethane produced
$ElectroH2_{(per)}$: Flow of hydrogen produced during a period (kg/s)
m: Parameter of the power curve (s/m)
n_i: Flow of component i (kmol/s)
n_{panels}: Number of panels
$n_{panelsused}$: Number of panels actually used.
$n_{turbines}$: Number of turbines
$n_{turbinesused}$: Number of turbines actually used.
Norg; Organic nitrogen
p_{air}: Atmospheric pressure (Pa)
p_v: Vapor pressure (Pa)
P_i: Partial pressure of species i (Pa)
P_{H2}: ratio of power required per flow of hydrogen produced (kJ/kg)
Per: Period of time.
Q: Thermal energy (kW)
Rest: Other components in the waste
t_{yr}: Seconds in a year
t_{month}: Seconds in a month
T: Temperature (K) unless otherwise specified
W: Electrical energy (kW)
z: Polytropic coefficient.
Z: Objective function (€/s)

Symbols

ω: Panels efficiency
η: Compressor efficiency
φ: Relative humidity
ΔH_f : Formation enthalpy (kJ/kg)

Units

Compress: Compressor.
CD: Condensation vessel.
HX: Heat Exchanger
MS: Molecular Sieve
MEM: Membrane
Src: Source;

Subindexes

C : Carbon
CO: Carbon Monoxide
CO_2 : Carbon dioxide
H_2: Hydrogen.
H_2O: Water
Steam
Electricity
Per: Period of 1 month

8.-References.

Almena, A. Martín, M . 2015. Techno-economic analysis of the production of epiclorhidrin from glycerol. Ind. Eng. Chem. Res . 55 (12); 3226-3238.

Bader, A., Bauersfeld, S., Brunhuber, C., Pardemann, R., Meyer, B., 2011. Modelling of a Chemical Reactor for Simulation of a Methanisation Plant. Presentation 063:064. Proceedings of the 8th International Modelica Conference, March 20th-22nd, Technical University, Dresden, Germany https://modelica.org/events/modelica2011/Proceedings/pages/papers/44_4_ID_202_a_fv.pdf

Davies, J., Lihou, D. 1971. Optimal design of methane steam reformer. Chem. Proc. Eng., 52, 71-80.

Davis, S.J., Lewis, N.S., Shaner, M., Aggarwal, S., Arent, D., Azevedo, I.L., Benson, S.M., Bradley, T., Brouwer, J., Chian Y.M., Clarck, C.T.M., Cohen, A., Doig, S., Edmonds, J., Fennell, P., Field, C.B., Hannegan, B., Hodge, B.M., Hoffers, M.I., Ingersoll, E., Jaramillo, P., Lackner, K.S., Mach, K.J., Mastrandrea, M., Ogden, J., Peterson, P.F., Sanchez, D.L., Sperling, D., Stagner, J., Trancik, J.E., Yang, C-J., Caldeira, K. 2018. Net-zero emissions energy systems. Science 360, 1419

Davis, W., Martín, M. 2014. Optimal year-round operation for methane production from CO_2 and Water using wind energy. Energy. 69, 497-505

Davis, W., Martín, M. 2014. Optimal year-round operation for methane production from CO_2 and Water using wind and/or Solar energy. J. Clean Prod. 80, 252-261.

De la Cruz, Martin, M. 2016. Turbine characterization selection and optimal design under uncertainty. J Clean Prod. 133, 1302-1311.

Ferella, F., Puca, A., taglieri, G., Rossi, L., Gallucci, K. 2017. Separation of carbon dioxide for biogas upgrading to biomethane. J. Clean. Prod. 164, 1205-1218.

Gassner, M., Marechal, F. 2009. Thermo-economic process model for thermochemical production of Synthetic Natural Gas (SNG) from lignocellulosic biomass. Biomass Bioenergy 33, 1587 – 1604

Goodrich, A., James, T., Woodhouse, M., 2012. Residential, Commercial, and Utility-Scale Photovoltaic (PV) System Prices in the United States: Current Drivers and Cost-Reduction Opportunities NREL/TP-6A20-53347, February 2012. http://www.nrel.gov/docs/fy12osti/53347.pdf

Görke O., Pfeifer, P., Schubert, K. 2005. Highly selective methanation by the use of a microchannel reactor. Catalysis Today 110, 132–139

GPSA Engineering_Data_Book FPS VERSION 21-10, 2004

Gunaseelan, V.N. 1997 Anaerobic digestion of biomass fro methane production: A review. Biomass and Bioenergy. 13 (12): 83-114

Hauchhum, L., Mahanta, P. 2014. Carbon dioxide adsorption on zeolites and activated carbon by pressure swing adsorption in a fixed bed Int J Energy Environ Eng., 5:349–356

Hasan, M.M.F, Balibam R.C., Elia, J.a., Floudas, C.A. 2012. Modeling, Simulation, and Optimization of Postcombustion CO_2 Capture for Variable Feed Concentration and Flow Rate. 1. Chemical Absorption and Membrane Processes. Ind. Eng. Chem. Res., *51* (48), 15642–15664

Hasan, M.M.F, Balibam R.C., Elia, J.a., Floudas, C.A. 2012. Modeling, Simulation, and Optimization of Postcombustion CO_2 Capture for Variable Feed Concentration and Flow Rate. 2. Pressure Swing Adsorption and Vacuum Swing Adsorption Processes. Ind. Eng. Chem. Res., *51* (48), 15665–15682

He, X., Chu, Y., Lindbrathen, A., Hillestad, M., Hagg, M-B. 2018. Carbon molecular sieve membranes for biogas upgrading: Tecno-economic feasibility analysis. J. Clean. Prod. 194, 584-593

Kirchbacher, F., Miltner, M., Lehner, M., Steinmuller, H., Harasek, M. 2016. Demonstration of a Biogas Methanation Combined with Membrane Based Gas Upgrading in a Promising Power-to-Gas Concept. Chem. Eng. Trans. 52, 1231-1236

Korhonen, J., Honkasalo A., Seppala J (2018) Circular Economy: The concept and its limitations. Ecological Economics. 143, 37-46.

Hernández, B, León, E., Martín, M. 2017. Bio-waste selection and blending for the optimal production of power and fuels via anaerobic digestion. Chem. Eng. Res. Des. 121, 163–172

Hernández, B., Martin, M. 2017. Optimal integrated plant for waste to biodiesel production ACS Sust. Chem Eng., *5* (8), 6756–6767,

INE (2018) http://www.ine.es/jaxi/Datos.htm?path=/t26/e068/p01/serie/l0/&file=02003.px. Last accessed September 2018.

León E., Martín, M. 2016. Optimal production of power in a combined cycle from manure based biogas Energ. Conv. Manag. 114 89–99.

Maaßen, M., Rübsamen, M., Perez, A. 2011. Photovoltaic Solar Energy in Spain SEMINAR PAPERS IN INTERNATIONAL FINANCE AND ECONOMICS *Seminar Paper 4/2011.*

Martín, M. 2016. Industrial Chemical process analysis and design. Elsevier. Oxford.

Martín, M., Grossmann, I.E. 2011. Energy optimization of Hydrogen production from biomass. Comp. Chem. Eng., 35, 9, 1798-1806

Martín, M., Grossmann, I.E. 2012 BIOpt: A Library of models for Optimization of Biofuel Production Processes. Computer Aid. Chem. Eng. Vol 30, 16-20

Martín, M., Davis, W. 2015 Integration of wind, solar and biomass over a year for the constant production of CH_4 from CO_2 and water Comp Chem Eng 84: 314-325

Matche, 2014. http://www.matche.com/prod03.htm, 2003 (last accessed Feb. 2018).

Moreno, B., Groppelli, E.S., Campanella, E.A., (2018) Evaluation of biogas upgrading technologies using a response surface methodology for process simulation. J. Clean Prod. 141, 978-988

NEL Hydrogen, 2012. Technical Data. http://www.nel-hydrogen.com/home/?pid=75 Last accessed November 2013

NREL, 2013a. System advisor Model (SAM) https://sam.nrel.gov/ Last Accessed February 2014

Sinnot. R.K., 1999. Coulson and Richardson, Chemical Engineering. 3ªEd. Butterworth Heinemann, Singapore, Malaysia

Walas, S. M., 1990. Chemical Process Equipment: Selection and Design,3rd ed.; Butterworth-Heinemann. Oxford, UK.

Rykebosch, E., Brouillon, M., Vervaeren, H. 2011. Techniques for transformation of biogas to biomethane. Biomass Bioenergy; 35, 1633–1645.

Sánchez A, Martín M. 2018. Optimal renewable production of ammonia from water and air, J. Clean Prod. 178, 325-342.

Schidhauer, TJ, Biollaz, SMA Reactors for Catalytic Methanation in the Conversion of Biomass to Synthetic Natural Gas (SNG) . ThE SWISS COmpETEnCE CEnTER fOR EnERgy RESEaRCh On BIOEnERgy CHIMIA 2015, 69, No. 10, 603-607

Schlömer S., T. Bruckner, L. Fulton, E. Hertwich, A. McKinnon, D. Perczyk, J. Roy, R. Schaeffer, R. Sims, P. Smith, and R. Wiser, 2014: Annex III: Technology-specific cost and performance parameters. In: Climate Change 2014: Mitigation of Climate Change. Contribution of Working Group III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Edenhofer, O., R. Pichs-Madruga, Y. Sokona, E. Farahani, S. Kadner, K. Seyboth, A. Adler, I. Baum, S. Brunner, P. Eickemeier, B. Kriemann, J. Savolainen, S. Schlömer, C. von Stechow, T. Zwickel and J.C. Minx (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Stangeland, K., Kalai, D., Li, H., Yu, Z. 2017. CO_2 methanation: The effect of catalyst and reaction conditions. Energy Procedia 105, 2022-2027

Tynjala, T. 2015. Biological methanation of hydrogen: a way to increase methane yield in biogas plants http://www.neocarbonenergy.fi/wp-content/uploads/2016/02/06_Tynjala.pdf

World Energy Council (2016) World Energy Resources Waste to Energy | 2016 https://www.worldenergy.org/wp-content/uploads/2017/03/WEResources_Waste_to_Energy_2016.pdf

Appendix

Table A.1.- Parameters of the surrogate model

Parameter	Value
Power_op (kW)	19457
CH4_prod (kg_{CH4}/s)	0.665
H2_prod (kg_{H2}/s)	0.103
Waste (kg/s)	10
P_{H2}	Power_op/H2_prod
$K_{H2/BG}$	H2_prod/CH4_prod
$K_{CH4/Was}$	Waste/CH4_prod

Table 1.- Main operating and design parameters

	Spain		UK	
	Continuum CH_4	Variable CH_4	Continuum CH_4	Variable CH_4
$n_{turbines}$	20	0	8	9
$n_{electrolizers}$	9	9	9	9
n_{panels}	31250	20610	8630	0
$n_{digesters}$	5	8	5	8
T(ºC) Methanation	140	140	140	140
P(bar) Methanation	15	15	15	15

Table 2.- Summary of production and investment costs.

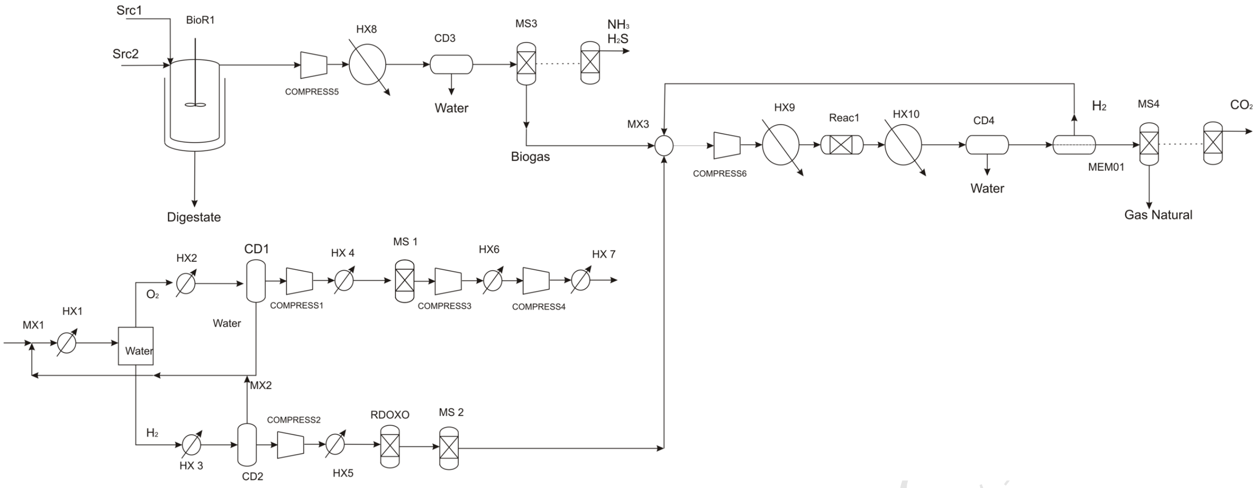
	Spain		UK	
	Continuum CH_4	Variable CH_4	Continuum CH_4	Variable CH_4
Prod. Cots (€/Nm3)	0.57	0.27	0.25	0.21
Investment cost (M€)	229	116	108	94

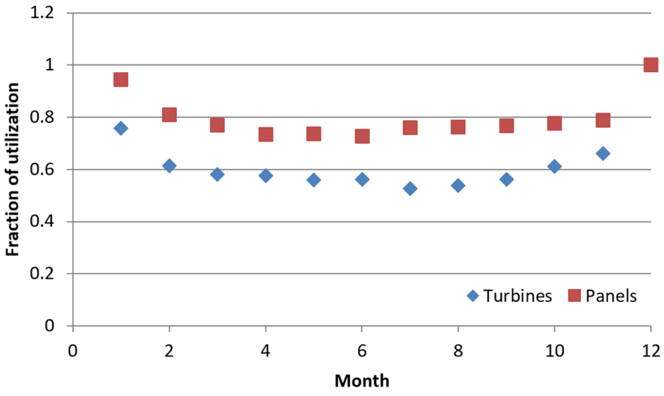
Table 3.- Projections in production and investment costs. 2050

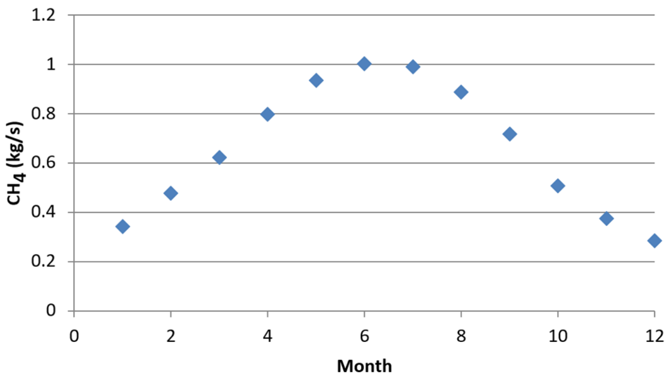
	Spain		UK	
	Continuum CH_4	Variable CH_4	Continuum CH_4	Variable CH_4
Prod. Cots (€/Nm3)	0.31	0.14	0.17	0.18
Investment cost (M€)	131	68	78	83

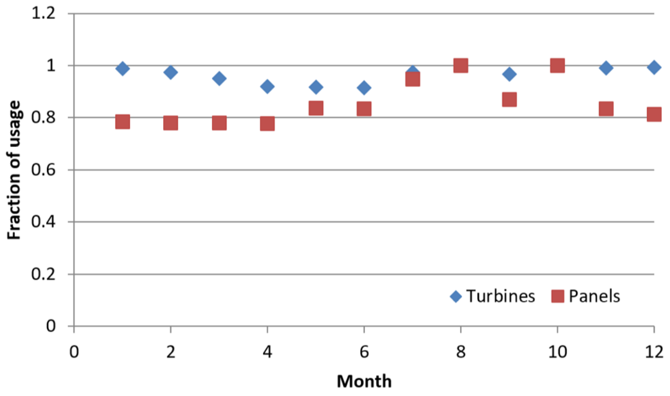
Table A.1.-Operating parameters of the plant

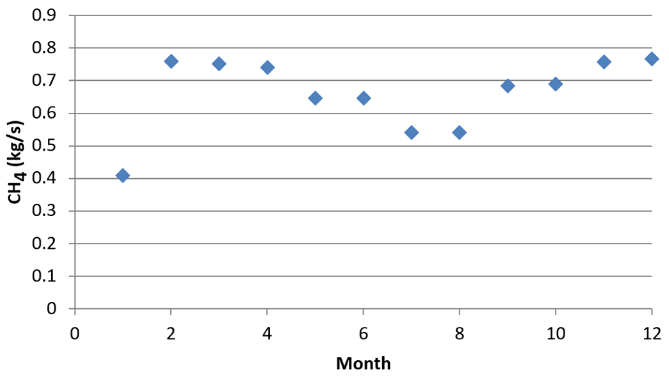
Parameter	Value
Power_op (kW)	19457
CH4_prod (kg_{CH4}/s)	0.665
H2_prod (kg_{H2}/s)	0.103
Waste (kg/s)	10
P_H2	Power_op/H2_prod
K_H2_BG	H2_prod/CH4_prod
K_CH4_Was	Waste/CH4_prod

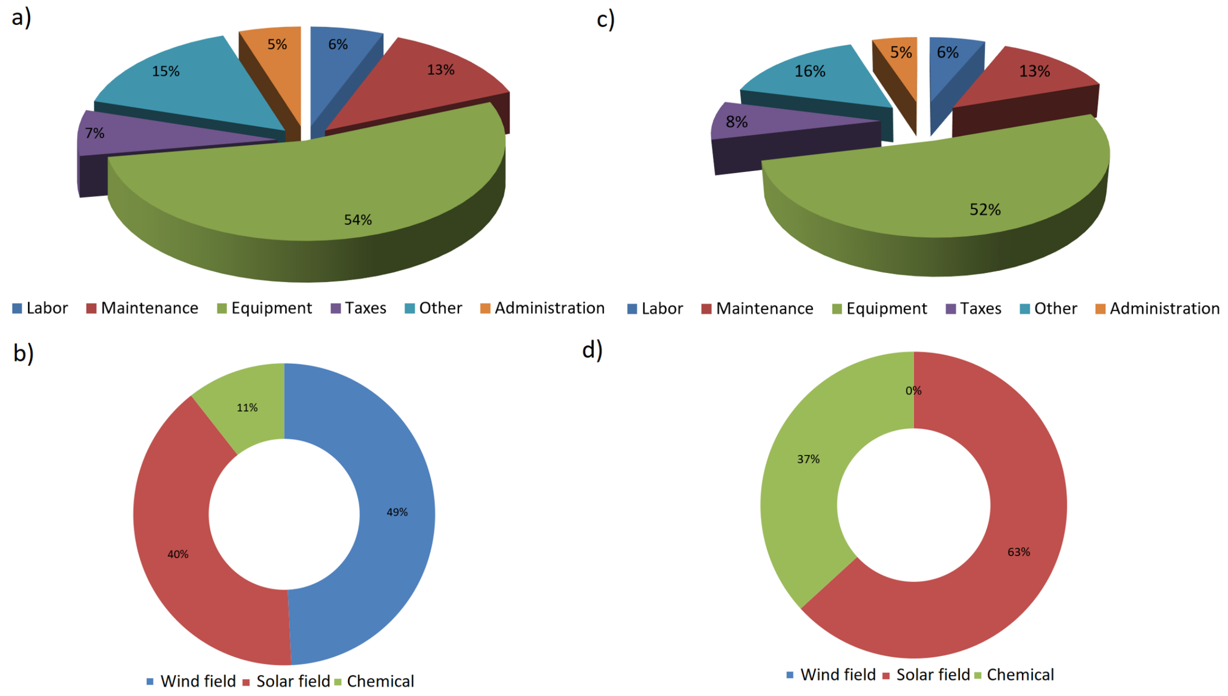

Src1
Src2
BioR1
Digestate
COMPRESS5
HX8
CD3
Water
MS3
NH_3
H_2S
Biogas
MX3
COMPRESS6
HX9
Reac1
HX10
CD4
Water
H_2
MEM01
MS4
CO_2
Gas Natural
MX1
HX1
Water
O_2
HX2
CD1
Water
COMPRESS1
HX 4
MS 1
COMPRESS3
HX6
COMPRESS4
HX 7
MX2
H_2
HX 3
CD2
COMPRESS2
HX5
RDOXO
MS 2

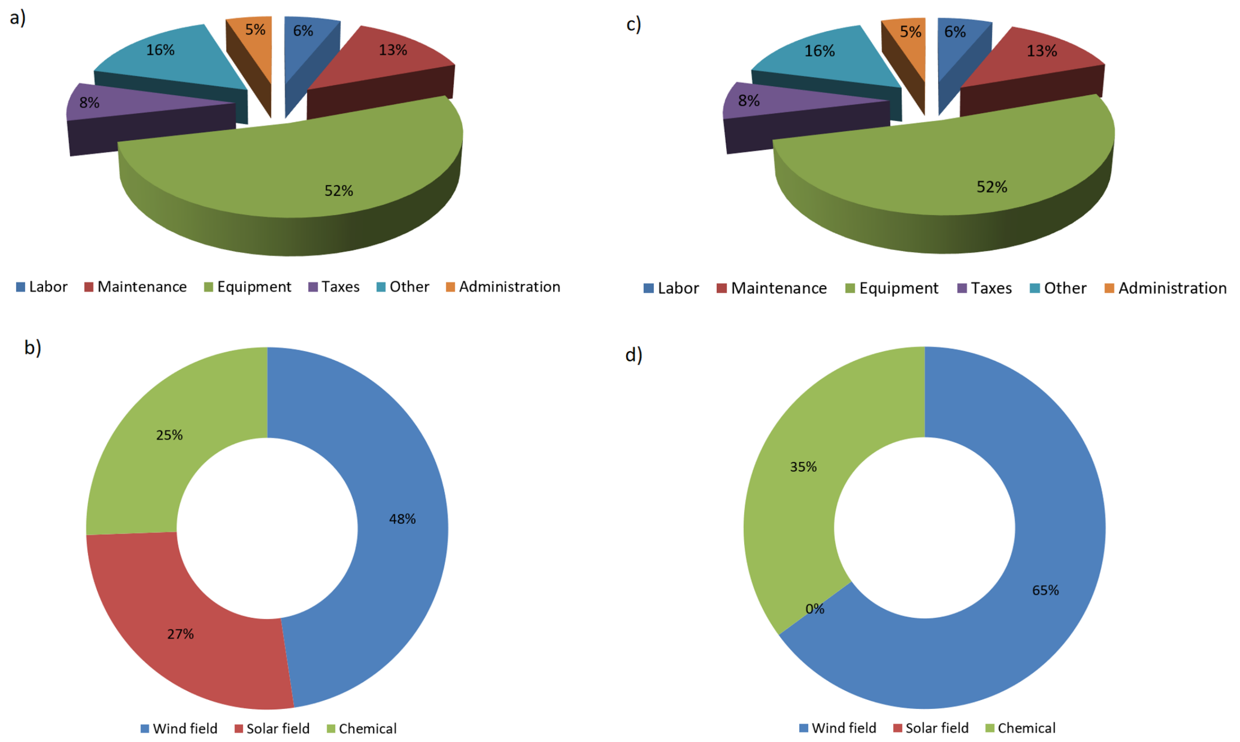

1.2
1
0.8
0.6
0.4
0.2
0
Fraction of utilization
0
2
4
6
8
10
12
Month
Turbines
Panels


1.2
1
0.8
0.6
0.4
0.2
0
CH_4 (kg/s)
0
2
4
6
8
10
12
Month


1.2
1
0.8
0.6
0.4
0.2
0
Fraction of usage
0
2
4
6
8
10
12
Month
Turbines
Panels


0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
CH_4 (kg/s)
0
2
4
6
8
10
12
Month


a)
6%
13%
54%
7%
15%
5%
Labor
Maintenance
Equipment
Taxes
Other
Administration
c)
6%
13%
52%
8%
16%
5%
Labor
Maintenance
Equipment
Taxes
Other
Administration
b)
11%
49%
40%
Wind field
Solar field
Chemical
d)
0%
37%
63%
Wind field
Solar field
Chemical


a)
5%
6%
16%
13%
8%
52%
Labor
Maintenance
Equipment
Taxes
Other
Administration
c)
5%
6%
16%
13%
8%
52%
Labor
Maintenance
Equipment
Taxes
Other
Administration
b)
25%
48%
27%
Wind field
Solar field
Chemical
d)
35%
0%
65%
Wind field
Solar field
Chemical

Biogas CO_2 methanation is evaluated to produce synthetic natural gas

Renewable hydrogen is produced via electrolysis using solar or wind energy

Multiperiod optimization for continuum and variable methanation rates are studied

Spain and UK cases of study are evaluated for prevailing solar and wind resources

Variable biogas upgrading makes the most of renewable resources