Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: http://ees.elsevier.com

Carbon footprint of synthetic natural gas through biogas catalytic methanation

Jordi Guilera [a,c,*], Mariana Filipe [b], Aleix Montesó [c], Ignasi Mallol [d], Teresa Andreu [a,e]

[a] *Catalonia Institute for Energy Research (IREC), Jardins de Les Dones de Negre 1, 08930, Sant Adrià de Besòs, Spain*
[b] *Inèdit Innovació Sl, C/diputació 37-39, 08015, Barcelona, Spain*
[c] *Department of Chemical, Biological and Environmental Engineering, School of Engineering, Edifici Q, Universitat Autònoma de Barcelona, 08193, Bellaterra, Barcelona, Spain*
[d] *Naturgy, Plaça Del Gas 1-4, 08003, Barcelona, Spain*
[e] *Departament de Ciència de Materials I Química Física, Universitat de Barcelona, Martí I Franquès, 1, Barcelona, 08028, Spain*

ARTICLE INFO

Article history:
Received 10 August 2020
Received in revised form 13 October 2020
Accepted 5 November 2020
Available online xxx
Handling editor: Cecilia Maria Villas Bôas de Almeida

Keywords
Synthetic natural gas
Hydrogen
Biogas
Methanation
Carbon footprint
Global warming potential

ABSTRACT

The carbon footprint of synthetic natural gas production from biogas catalytic methanation was determined. The material and energy data inputs required to produce 1 kWh of synthetic natural gas were experimentally collected from a pilot plant operating in a waste water treatment plant as a relevant environment. The experimental plant had a capacity of 37 kW and consisted of biogas and water conditioning, water electrolysis and 2-step carbon dioxide catalytic methanation unit, by compact technology of micro-reactor and micro-size catalysts al mild pressure conditions. The technology evaluated in this study is ready for scalability to MW-scale. The carbon footprint was evaluated by means of the Global Warming potential impact in kg CO_2-eq/kWh. Life Cycle Assessment methodology was used according to ISO:14040 and ISO:14067 thorough Ecoinvent data. The carbon footprint analysis showed that producing synthetic natural gas using the current electricity mix led to high carbon impact. However, the utilization of renewable electricity sources and a more efficient electrolyzer technology is able to reduce the carbon footprint to 0.100 kg CO_2-eq/kWh. This value represents an interesting reduction of the climate change impact of 57%, using currently available technologies. Therefore, synthetic natural gas from biogas catalytic methanation process represents a feasible option to partially decarbonize the gas grid infrastructure. In this way, synthetic natural gas can support the penetration of random renewable sources by allowing its seasonal storage, as well as, to provide a low-carbon gas alternative.

1. Introduction

Power-to-Gas consists on the storage of renewable energy into hydrogen or methane energy vectors (Blanco et al., 2018). This concept is of special interest in regions that meet two premises, high penetration of wind and photovoltaic energy sources in the electricity mix and the presence of an extensive natural gas infrastructure. In this way, unpredictable renewable energy sources (RES) can be stored, transported, distributed to the costumers using the existing gas infrastructure and consumed when there is demand.

In a first step, hydrogen is generated through water splitting (1) (Gahleitner, 2013; Glenk and Reichelstein, 2019). This hydrogen can be stored and transported either in a dedicated distribution grid or mixed in the existing natural gas infrastructure. As there are some technical barriers of using hydrogen blends in the current gas infrastructure (Marcogaz, 2019), hydrogen compatibility in the gas grid can be overcome by means of a second chemical transformation step, in which hydrogen is converted to methane (2). In this form, the produced synthetic methane is fully compatible with the current gas infrastructure. The electrolytic methane, synthesized from electrolytic hydrogen, is commonly referred to as synthetic natural gas (SNG). This product can be introduced to the natural gas grid if the conversion within the methanation unit is high enough, otherwise a too high hydrogen fraction could disable the injection.

$$H_2O\text{-- }> H_2 + ½\, O_2 \;\; \Delta H = +286 \text{ kJ/mol} \quad (1)$$

$$4\, H_2 + CO_2\text{--}> CH_4 + 2\, H_2O \;\; \Delta H = -165 \text{ kJ/mol} \quad (2)$$

At present, SNG production costs are higher than natural gas and economically unaffordable (Bailera et al., 2019; Chauvy et al., 2020). In future scenarios, technological advances improving energy efficiency and reducing investment costs, together with national policies, could play a determinant role in the economic feasibility of SNG. In this direction, Blanco et al. estimated that up to 75% of the gas demand will be supplied by SNG, including a simultaneous reduction of 70% of the total gas demand, in a EU low carbon economy scenario (80–95% reduction) (Blanco and Faaij, 2018). Analogously, a technical report of the European Commission predicted up to 42% share of SNG in 2050 (European Commission, 2019). Together with H_2, SNG appears to be key element for assisting the continuous penetration of

* Corresponding author. Catalonia Institute for Energy Research (IREC), Jardins de les Dones de Negre 1, 08930, Sant Adrià de Besòs, Spain.
E-mail address: jguilera@irec.cat (J. Guilera)

https://doi.org/10.1016/j.jclepro.2020.125020
0959-6526/© 2020.

renewables, enabling grid balancing, seasonal storage and decarbonisation of natural gas demand (Colbertaldo et al., 2018).

As Power-to-Gas includes electrolytic hydrogen, the carbon footprint of SNG is closely linked to the power source, either renewable or fossil. Indeed, some authors reported that this is the crucial parameter to determine the SNG carbon footprint (Reiter and Lindorfer, 2015; van der Giesen et al., 2014). From an environmental point of view, the most optimistic scenario considers SNG only from electricity surpluses that would otherwise be lost. In that case, the carbon footprint of SNG is very low, even using coal gasification as carbon source (Sternberg and Bardow, 2015). However, the construction of a Power-to-Gas plant solely using surpluses leads nowadays to excessive investment costs for unit of gas produced (Guilera et al., 2018). Accordingly, Power-to-Gas technology seems an alternative to produce SNG seasonally, rather than punctual electricity storage.

Previous works reported the carbon footprint of SNG by CO_2 methanation. Zhang et al. studied many SNG scenarios and they revealed the complexity of several subsystems, power sources, electrolyzer efficiency and CO_2 origin (Zhang et al., 2017). At the end of the study, they suggested that more specific aspects of the methanation technology; namely heat generation, external energy demand and catalyst requirements, should be included in further studies, as soon as more data will be available. Similarly, Collet et al. performed a comprehensive Life Cycle Assessment (LCA) of SNG production using academic resources and internal communications (Collet et al., 2017). Most recently, Zhang et al. performed a LCA of Power-to-Gas strategies, including direct biogas methanation system (Zhang et al., 2020). They considered bubbling fluidized bed reactor models on this study. To the best of our knowledge, all the reported LCA data on the methanation process are based on process models due to insufficient experimental data at relevant environments.

The lack of experimental information is the main weakness to establish precise GHG emissions of the SNG process. Although SNG production is not a widely spread technology, the implementation of Power-to-Gas is under way and mean plant size and number of projects worldwide are exponentially rising (Bailera et al., 2017; Thema et al., 2019). The technical information obtained in those projects, often confidential, should be included in environmental assessments for policy decisions. Recently, the technical feasibility of SNG production for grid injections in a waste water treatment plant (WWTP) by using biogas as carbon source was demonstrated at relevant environment (Guilera et al., 2020a). The produced SNG accomplished with current legislation on gas quality for gas grid injection. It was proposed a 2-step CO_2 methanation process using compact technology, namely micro-structured reactors and micro-size catalysts, under precise temperature profiles at mild operation pressure. The scale-up of the process to the MW-range is feasible and mass production of compact reactors and micro-size catalysts is on the way for industrialization for gas and liquid fuel production (Dittmeyer et al., 2017).

The goal of this study is to provide carbon footprint of SNG production from biogas methanation using a combination of the recent advances in reactor and catalyst technology. To the best of our knowledge, previous works dealing with the environmental impact on the methanation units were based on process modelling, not from real data. The novelty of this work is to carry out the evaluation of the carbon footprint of biogas methanation from experimental data in relevant environment in order to elucidate environmental information for the deployment of future SNG industrial plants. Accordingly, material and energy inventory data of this innovative process were collected and employed to estimate the carbon footprint impact of producing that SNG from biogas in a WWTP. The functional unit selected was 1 kWh of SNG produced. Eventually, the obtained environmental data is compared with respect to fossil natural gas and other electricity storage alternatives.

2. Methodology

2.1. Case of study

The carbon footprint of SNG using biogas as carbon feedstock was evaluated using material and energy data inventory of the demonstration process, located at the premises of the WWTP Riu Sec (Sabadell, Spain). The sewage plant treats the primary and secondary sludges (85 m^3/day of 4.0% dry content and 70% volatile solids) by anaerobic digestion at mesophilic conditions (36-39 °C). Two anaerobic digester units are in operation in the sewage plant and they produce about 100 $Nm^3{\cdot}h^{-1}$ of biogas. Biogas is currently converted to heat in order to maintain the digesters at the mesophilic temperature, the rest of the biogas is burned in a torch. A detailed description of the overall plant can be found elsewhere (Guilera et al., 2020a). Gas analytics exposed that the main impurities of the biogas consist on H_2S (11–31 mg/Nm^3), VOCs (1–32 mg/Nm^3), NH_3 (0–11 mg/Nm^3), BTX (0–9 mg/Nm^3), siloxanes (0.6–1.5 mg/Nm^3).

In the context of an industrial R&D project (CoSin: Synthetic fuels), a CO_2 methanation pilot plant, with a production capacity of 4.25 Nm^3 $SNG{\cdot}h^{-1}$, was built, coupled to biogas generation and operated during the period 2018-19, for approximately 3000 h of operation. The aim of the Cosin project was to obtain technical, economic and environmental data of the process in a relevant environment for further industrialization steps. The SNG demonstration plant consisted in 4 steps i) water treatment and ii) biogas treatment, iii) water electrolysis and iv) methanation. A simplified Process Flow Diagram of the overall process is illustrated in Fig. 1. Biogas treatment consisted on both cleaning and compressing. At first, raw biogas was dried using a water-glycol mixture at 5 °C, then cleaned through two active carbon filters supplied by Prodeval and Bioconservacion, respectively, and finally compressed up

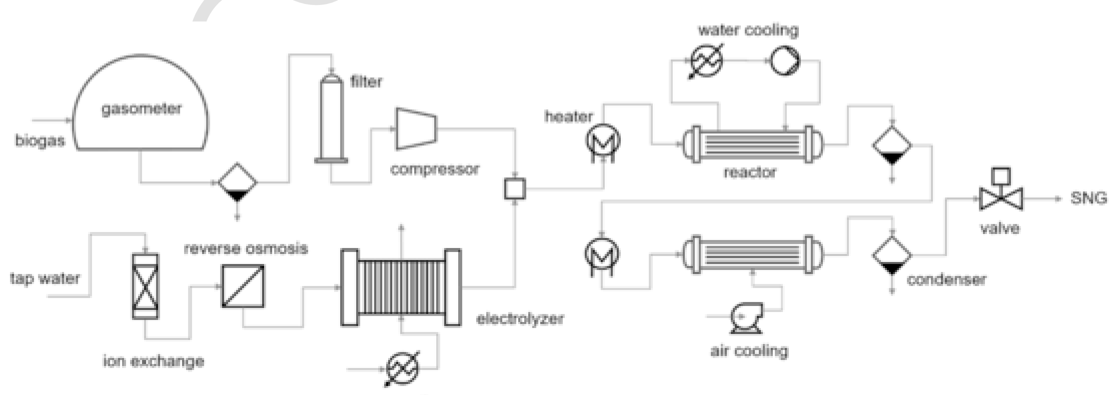

Fig. 1. Simplified Process Flow Diagram of SNG production from biogas.

to 6 bar g by an air-driven piston compressor (Maximator). After compression, an additional filter filled with ZnO based adsorbent (ActiSorb®S2) operated at 250 °C to reach very low H_2S < 0.1 mg/Nm^3 concentration to avoid catalyst poisoning (Alarcón et al., 2020).

Conventional tap water from the local distribution system was used as hydrogen source. Tap water quality was purified by a reverse osmosis demineralizer (Osmodemi 12, Idrotecnica), consisting on a pre-filter (active carbon), ion-exchange resins (DF0402) and reverse osmosis membranes (S181236S). Purified water was supplied to a 37 $kW_{electricity}$ alkaline electrolyzer (G10, Erredue). The electrolyzer was connected to conventional grid electricity and produced 6 Nm^3/h of hydrogen. The main materials of the electrolyzer consisted on steel and nickel and the electrolyte was a NaOH solution (20 wt%). Other minor materials were not considered due to supplier confidentiality. A significant amount of low quality water (T = 10-30 °C) was used to keep the electrolyzer cell below 60 °C and to reduce the moisture of the hydrogen outlet. Two additional coalescent filters were installed to limit the amount of water introduced to the methanation system. At the end of the electrolysis unit, hydrogen at 6 bar g were delivered to the methanation unit without further compression.

Subsequently, biogas (4.25 Nm^3·h^{-1}) and hydrogen (6.00 Nm^3·h^{-1}) gases were mixed and supplied (MFC, Bronkhorst) to the methanation system. Hydrogen to carbon dioxide ratio was precisely adjusted to reaction stoichiometry 4:1 (vol%) in order to obtain a high methane content at the outlet and to not damage the catalyst by carbon poisoning or re-oxidation. The methanation process consisted of a 2-step synthesis unit, including two sequential processes of gas pre-heating, catalytic reaction and water condensation. Detailed engineering and process information can be found in a previous work (Guilera et al., 2020b). In brief, the two catalytic reactors operated in series and the second was fed with the first outlet stream. The reactors operated in decreasing temperature profile from 450 °C to 275 °C, being the maximum temperature at the entrance of the first reactor and the lowest at the exit of the second reactor. The micro-structured reactors were made up by several staking sequences of catalytic micro-beds and cooling foils; in particular, formed by 10 diffusion bonded reaction channels. The first reactor operated at a gas hour space velocity of 75,000 h^{-1} and the second one at 20,000 h^{-1}.

For the methanation unit, a closed water cooling cycle was implemented for two purposes, cooling down of the first reactor and water condensations of the produced gases, whereas compressed-air was used to cool-down the second reactor. Pre-heaters, which were composed of electrical heating cartridges, were installed before and inside each reactor. The reactors were loaded with a micro-size catalyst composed of nickel, ceria and alumina in both reactors (Alarcón et al., 2019). The methanation process was set at 5 bar g by a control valve at the process outlet. The operation pressure was high enough for gas injection into the gas distribution grid. In contrast, an additional compressor should be installed after the methanation unit, if the gas injection point is set at higher pressures (P > 10 bar g), as in the case of national transport pipelines.

Gases were on-line analyzed by a micro-chromatograph (490 Agilent). The composition of the biogas was in the range of 63–65% CH_4 and 35–37% CO_2.CH_4 content was increased to 72.7% after the first reactor and, at least, to 93.5% after the second step. As shown in Table 1, the gas quality of the product, referred to as SNG, accomplished the Spanish gas quality regulations for injection to the existing infrastructure. At present, the absence of a common regulatory framework prevents a generic specification valid for all parts of the European or International gas infrastructure.

Table 1
Experimental gas quality and current legislation on gas grid injection (Miniserio para la Transición Ecológica, 2018; Ministerio de Industria Energía y Turismo; 2013).

component	composition (vol%)		
	biogas	SNG	regulation
CH_4	63–65	93.5	≥90
CO_2	35–37	1.7	≤2.5
H_2	–	4.8	≤5

2.2. Carbon footprint

This study includes definition of the goal and scope, inventory analysis, impact assessment and interpretation of the results. The goal of this work is to identify the SNG carbon footprint through biogas catalytic methanation and to compare it with natural gas. The scope of this study comprises the whole production phase and use of SNG. The function and primary application of the SNG is final energy provision. The functional unit declared is, 1 kWh of consumed energy considering its lower heating value (LHV) of produced SNG. In the present work, SNG is defined as the gas product obtained from biogas methanation with an injectable composition in the gas network. The carbon footprint of SNG is defined as a measure of the total amount of greenhouse gas (GHG) emissions as CO_2-equivalent using the relevant 100-year global warming potential (GWP) (Wright et al., 2011). A process-based, attributional LCA has been developed in order to compare the GWP of alternative products with analogous gas quality, such as fossil natural gas and biomethane. The carbon footprint was the impact category chosen to the analysis of the SNG using LCA method, according to ISO 14040:2006 and ISO 14067:2018.

Fig. 2 shows the system boundaries of the LCA conducted. The production of SNG consisted on 5 steps i) anaerobic digestion ii) water treatment and iii) biogas treatment, iv) electrolysis and v) methanation. In the present WWTP, 20% of biogas is currently converted to heat to maintain the digesters at the mesophilic temperature, the rest of the biogas is burned in a torch. However, in future plant locations the installations, the anaerobic digestion phase should be included as a necessary step of the complete process.

The listed material and energy inputs necessary to produce 1 kWh of SNG in the described case of study are detailed in Table 2. As regards to the energy consumption, data was obtained from real electricity consumption, which was measured during steady state during 1 week of continuous SNG production of 4.25 Nm^3·h^{-1}. Electricity meters allowed to measure electricity consumption from the biogas treatment, electrolysis and the methanation units independently. As an exception, electrical consumption of the ZnO filter, electrically heated, was included in the methanation process, rather than the biogas treatment. Besides, it should be mentioned that the electrical consumption of the methanation steps also included all the auxiliaries such as gas analytics, process control room and safety measures. Water consumption was experimentally measured, whereas the amount of compressed-air was obtained from equipment specifications. The amount of material consumables necessary to produce 1 kWh of SNG was related to the operational hours before maintenance and replacement. It is expected some overestimation of the amount of consumables considered as most of them were not replaced during the project experimental campaign, i.e. thermal oil, activated carbon, ion exchange resin, polymeric membrane and glycol. In the case of the catalyst and the electrolyte, annual replacement during the periodic plant shutdown for equipment maintenance was considered. The lifetime considered the whole plant was 20 years, while 7 years for the electrolyzer electrodes. The extension of

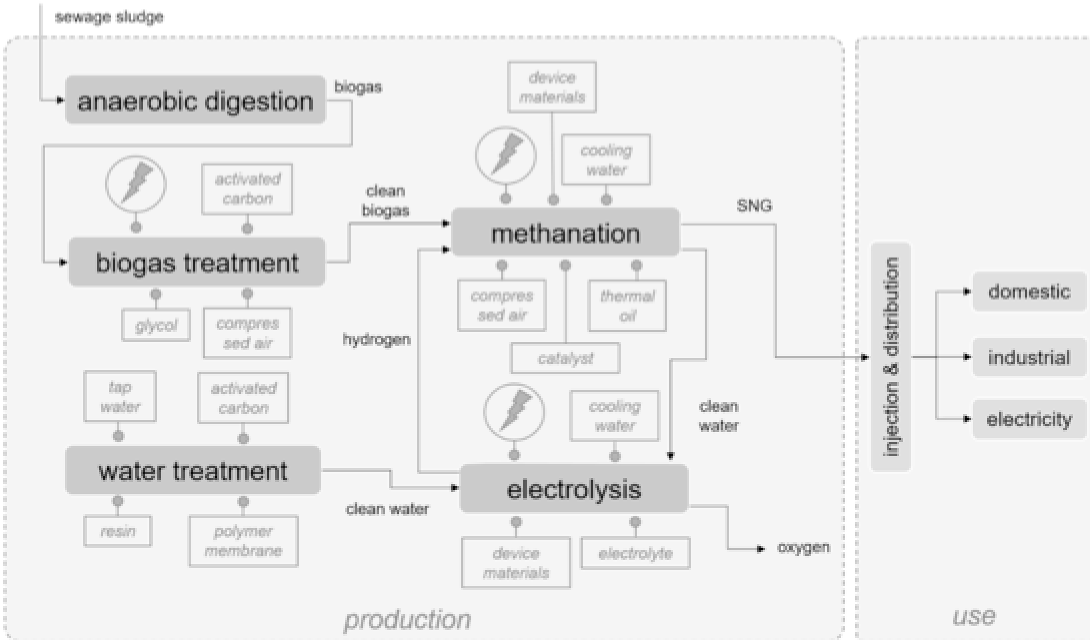

Fig. 2. System boundaries considered in the LCA.

Table 2
Life Cycle Inventory used for 1 kWh SNG production.

step	element	consumption	Unit
anaerobic digestion	biogas	$1.00{\cdot}10^{-01}$	Nm^3
water treatment	tap water	$1.08{\cdot}10^{-01}$	L
	ion exchange resin	$5.18{\cdot}10^{-05}$	kg
	activated carbon	$1.11{\cdot}10^{-05}$	kg
	polymeric membrane	$6.48{\cdot}10^{-05}$	kg
biogas treatment	activated carbon	$4.32{\cdot}10^{-05}$	kg
	Glycol	$1.11{\cdot}10^{-05}$	kg
	compressed air	$1.99{\cdot}10^{-08}$	m^3
	gas dryer	$9.54{\cdot}10^{-06}$	kWh
	Compressor	$1.60{\cdot}10^{-02}$	kWh
electrolysis	cooling water	$7.90{\cdot}10^{+01}$	L
	sodium hydroxide	$1.16{\cdot}10^{-03}$	kg
	Nickel	$5.81{\cdot}10^{-04}$	kg
	Steel	$1.69{\cdot}10^{-03}$	kg
	Electricity	$8.73{\cdot}10^{-01}$	kWh
methanation	cooling water	$2.28{\cdot}10^{-04}$	L
	compressed air	$2.11{\cdot}10^{-02}$	m^3
	thermal oil	$1.16{\cdot}10^{-03}$	kg
	Steel	$5.07{\cdot}10^{-03}$	kg
	Catalyst	$4.24{\cdot}10^{-05}$	kg
	Electricity	$1.11{\cdot}10^{-01}$	kWh

this period can be revised in the future as soon as more information on industrial operation will be experimentally obtained and disclosed. Note that in a previous work, the amount of steel considered was limited to reactor construction, a significant less amount of catalyst was considered, energy required to supplement pressure loss and cooling requirements were not considered due to insufficient data (Zhang et al., 2017). Analogously, the present information should be updated from future information on MW-scale plants.

The endpoint impact category evaluated was the climate change with the GWP in kg CO_2 equivalent (kg CO_2 eq) through the ReCiPe 2016 model for a time frame of 100 years (Huijbregts et al., 2017). As mentioned, the SNG pilot plant was connected to the Spanish electricity grid. In this aspect, as it is presented in Table 3, the national electricity mix was used for calculations (Ecoinvent v3.5 data). During 2019, several technologies were used in Spain to supply electricity; led by nuclear, combined cycle and wind power. The GWP impact obtained in this study for the mix electricity consumption was 0.3469 kg CO_2-eq/kWh, which includes generation and transport to the final user. The impact associated to using solely the available RES, instead of electricity mix, was 87% lower of 0.0442 CO_2-eq/kWh. In this case, the cur-

Table 3
Structure of the Spanish 2019 annual electric balance (Red Eléctrica Española, 2020).

Technology	GWh	(%)
Nuclear	55,824	21.10
Combined cycle	55,239	20.88
Wind [a]	54,212	20.49
Cogeneration	29,591	11.19
Hydro [a]	26,337	9.96
Coal	12,672	4.79
Solar photovoltaic [a]	9223	3.49
International exchanges	6862	2.59
Fuel + Gas	5696	2.15
Solar thermal [a]	5166	1.95
Renewable thermal [a]	3616	1.37
Non-renewable waste	2222	0.84
Renewable waste [a]	890	0.34
Hydro + Wind [a]	23	0.01
Water pumping	−3025	−1.14
Total	264,548	100

[a] RES (37.60%).

rent share of wind, hydro, solar photovoltaic, solar thermal, renewable thermal, renewable waste and hydro-wind generation were considered.

Direct CO_2 emission related to the combustion of SNG, either in domestic, industrial or power applications, was not accounted in the case of SNG in the net result due to the biogenic origin of biogas feedstock. Biogenic GHG emissions and removals shall be included and expressed separately as expressed in ISO 14067:2018 (ISO, 2018)). In contrast, CH_4 and N_2O emissions factors were included in the carbon footprint. They were assumed to be equivalent to those produced by combusting natural gas (UK Government, 2020). Direct CO_2 emissions of fossil natural gas were accounted due to the fossil origin (Dones et al., 2007)) and related to the final use distribution in Spain (2018), 61% industrial, 21% domestic-commercial and 18% electricity production (CNMC Comisión Nacional de los Mercados y la Competencia 2019, 2020).

3. Results and discussion

The carbon footprint of producing SNG using biogas is presented in Table 4, and compared to natural gas. At the present location, the electrolysis of water step contributed almost 75% of the total SNG impact, whereas the methanation step about 17%, followed by the production of biogas by means of anaerobic digestion with a contribution of 6%. In contrast, the GWP impact of water and biogas treatment was very residual. Among both auxiliary processes, higher impact was inferred in biogas conditioning as it requires, besides cleaning, of compression before the methanation step. The selected pre-compression conditions at 6 bar g can be used for SNG production, as well as, for direct injection to the gas distribution grid, typically set at 4 bar in the gas distribution grid.

The LCA study revealed that the current carbon footprint of SNG (0.414 kg CO_2-eq/kWh) was higher than the use of fossil natural gas (0.232 kg CO_2-eq/kWh). In this aspect, SNG technology could provide grid balance for the continuous incorporation of wind and photovoltaic random sources into the electricity mix. However, SNG technology, as implemented in the WWTP plant (i.e. connected to the national electricity mix), does not contribute in the decarbonisation of the gas network. Indeed, the solely contribution of the electrolysis step presented higher GWP impact (0.311 kg CO_2-eq/kWh) than keep using fossil natural gas. The high GWP impact is the result of high power consumption of the electrolyzer ($8.73{\cdot}10^{-01}$ kWh) and high impact of the current Spanish electricity system (0.347 kg CO_2-eq/kWh). The measured consumption of the commercial electrolyzer (electrolytic cell and auxiliaries) was 6.16 kW/Nm^3, which corresponds to 57% of Power-to-Hydrogen efficiency. It is worth mentioning that there are other commercial electrolyzer options, as discussed later.

Table 4
Carbon footprint of SNG using grid electricity with respect to natural gas.

GWP	SNG current case	natural gas
(kg CO_2 eq/kWh)		
anaerobic digestion	0.02534 [a]	
water treatment	0.00056	
biogas treatment	0.00558	
Electrolysis	0.31072	
Methanation	0.07183	
extraction		0.0494 [a]
production		0.0013 [a]
transport and distribution		0.0146 [a]
use	0.00021 [a]	0.1670 [a]
total	0.41424	0.2322

[a] Ecoinvent v3.2 data.

From these results, it can be concluded that the SNG produced from biogas and the current grid electricity mix cannot be considered as a low carbon fuel alternative. Nevertheless, this statement is only valid in the present location and time. Greener national electricity mixes can reduce the carbon footprint of SNG. Specifically, the carbon footprint of SNG is equaled to natural gas impact considering 69% of RES in the electricity mix, without any technology advance in the process of SNG production. For comparison, the presence of RES in the European mix is about 32% and higher RES than 69% is very restricted to some specific countries as Norway (Enerdata, 2020).

The carbon footprint of SNG can be significantly reduced by using available RES, instead of the current electricity mix. The GWP impact of electricity in Spain during 2019 calculated in this study was, on average, 0.347 kg CO_2-eq/kWh_{in}, in which the share of RES, nuclear and fossil fuel sources were considered. The electricity impact is significantly reduced to 0.044 kg CO_2-eq/kWh considering only RES. As a consequence, the consideration of using RES reduces remarkably the carbon footprint of SNG up to 0.111 kg CO_2-eq/kWh (−78%) because Power-to-Gas is an electricity-intense process. In the case that RES is employed only in hydrogen production, the only process that really falls within the Power-to-Gas concept, this reduction already reaches −65%. In any case, the utilization of RES reduced the impact of all the steps but water cleaning.

Despite this significantly improvement, it is important to critically point out that the impact of the producing SNG is still higher than natural gas conditioning to the final user (0.065 kg CO_2-eq/kWh), considering "conditioning of natural gas" as extraction, production, transport and distribution. The difference among fossil and SNG is that no CO_2 emissions are accounted during its combustion as it is provided by biogenic sources. The real CO_2 emissions during the combustion of SNG was 0.199 kg CO_2-eq/kWh (UK Government, 2019). Therefore, it is very important to avoid using fossil carbon dioxide sources for synthetic natural gas production, otherwise the SNG carbon footprint would be higher than fossil natural gas.

The GWP impact of the Power-to-Gas process as emerging technology can be reduced by means of technological advances and process scale-up to industrial scale. To identify the most critical process steps, Fig. 3 displays the GWP impact of each process unit using biogas and RES electricity. The contribution of the water treatment was very low (<1%), while the biogas conditioning was 7%, mainly due to gas compression at 6 bar g. Among the main process, electrolysis remained the main contributor (39%) to the SNG carbon footprint, although RES were considered; closely followed by the methanation process (32%). Without hesitation, the main environmental efforts should be driven to improvement on methanation and electrolysis units.

Fig. 4 presents the contribution of each element of the methanation unit. The main carbon footprint was related to the materials necessary for plant construction. The engineering process allowing to obtain SNG quality at low pressure is complex and it requires of several units as tank buffers, piping, reactors, pumps, controllers, water condensers, heat-exchangers, among others. The present process considers $5.07{\cdot}10^{-03}$ kg of steel per kWh of SNG produced during 20 years. It is expected that plant scaling from 37 kW to several MW would reduce the amount of materials necessary per kWh of SNG produced, and thus, a certain overestimation of these impacts can be expected using the available information. These parameters can be revised in the future using MW-scale information. As an example, a variation −10% of the methanation inputs lead to a global carbon footprint reduction of −3.61%. Among them, a −10% reduction of the amount of steel necessary to build the plant already reduces the final impact by −2.89%, while the power consumption just −0.65%. A reduction of the amount of materials during plant upscaling to MW is definitely feasible. The

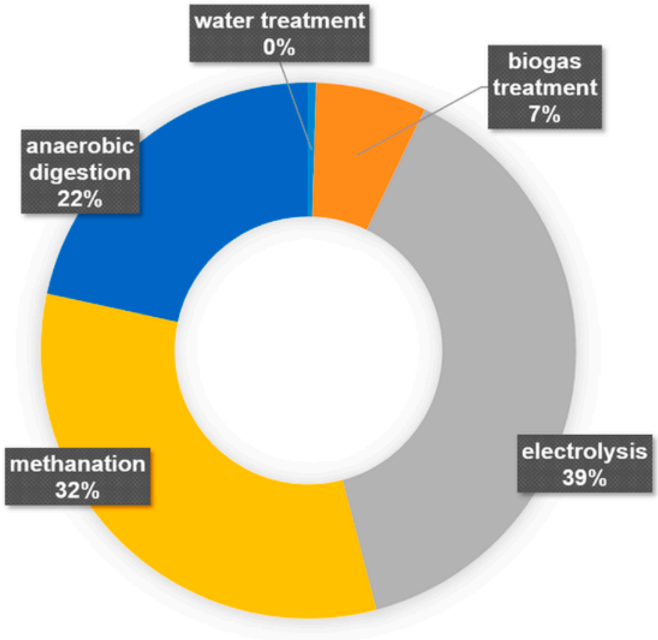

Fig. 3. GWP distribution in SNG production using RES.

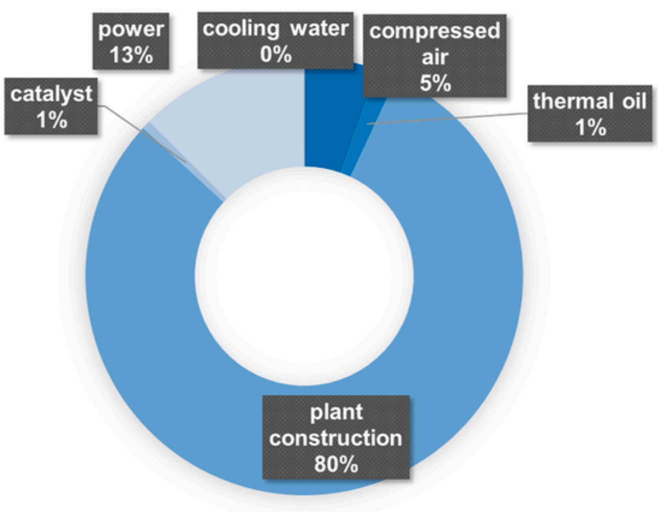

Fig. 4. GWP distribution in the methanation step using RES.

modularity of the reactor technology used in this process does not reduce the amount of materials during scale-up but a significant reduction is expected from the auxiliary units.

On the other hand, an interesting environmental finding was observed as regards to the catalytic reactor cooling strategy. The first reactor was cooled using a closed water cycle and thermal oil, while the second one using compressed air. The amount of heat released in the second reactor was much lower (−0.61 kW) than the first reactor (−2.88 kW), as most CO_2 conversion yield (90%) occurred in the first reactor. On the contrary, the environmental impact of the heat-management of the second reactor was still higher (5%). Therefore, the heat-management strategy of cooling down the reactor by compressed air was not as efficient as water cooling. This environmental information can be useful in future scale-up steps. With respect to the catalyst, the impact associated to the materials necessary for its fabrication was very low (1%), despite 20 catalyst exchanges were considered during the whole Power-to-Gas plant lifetime.

The measured power consumption of the demonstration methanation process was, on average over one week of uninterrupted operation, 0.11 kW_{in}/kW_{SNG}. This amount of energy includes gas heating to 300-350 °C, water pumps, refrigeration systems and auxiliary equipment (process control and analytics). CO_2 methanation reaction is exothermic and it converts 4 mol of hydrogen (12.00 kW/Nm^3) to methane (9.67 kWh/Nm^3). Thus, about 20% of the inlet energy was released to the environment. Accordingly, a proper heat-management, out of the scope of the current demonstration of the technical feasibility of producing SNG, can reduce the power consumption in future scale-up steps. On one hand, internal heat-management integration can prevent of power consumption for gas pre-heating. Simple manufacturing approaches in this direction has been recently reported (Moioli et al., 2019). On the other hand, the released heat can be integrated to external energy-demanding processes, such as high temperature electrolyzer or mesophilic and thermophilic anaerobic digestion (Belimov et al., 2017). Both approaches can potentially reduce the GWP of the methanation step.

Fig. 5 shows that GWP contribution of the individual elements of the electrolysis step. In the present case, the availability of cooling water in the WWTP was very positive in terms of GWP. Thus, the environmental impact of water requirements for the electrolyzer was almost negligible, although a significant amount was necessary to cool-down the electrolyzer and to condensate the gas products. In contrast, the fabrication of the electrolyzer required significant amount of materials, such as 0.58 g nickel/kWh. This amount can be reduced in two directions; a more efficient utilization of metals or by extending the lifetime of the electrodes beyond 7 years. In any case, the power consumption, although renewable, was still the main carbon footprint contributor (83%). This is a direct consequence that the power consumption of the electrolyzer was very high (0.87 kW_{in}/kW_{SNG}). The high contribution of power to the GWP of electrolysis step was expected as the Power-to-Gas process it is, by nature, an energy intensive process. It is worth noting that if the electricity mix is considered the 83% of power contribution would be increased to 97%, due to the different impact associated (0.044 kg CO_2-eq/kWh and 0.368 kg CO_2-eq/kWh, respectively).

In the present pilot plant, Alkaline Electrolysis Cell (AEC) electrolysis technology was installed. Experts estimate (Schmidt et al., 2017) that AEC is currently the most mature and economic technology, followed by Proton Exchange Membrane (PEM) technology. Solid Oxide Electrolyzer Cell (SOEC) systems could reach the cost and lifetime

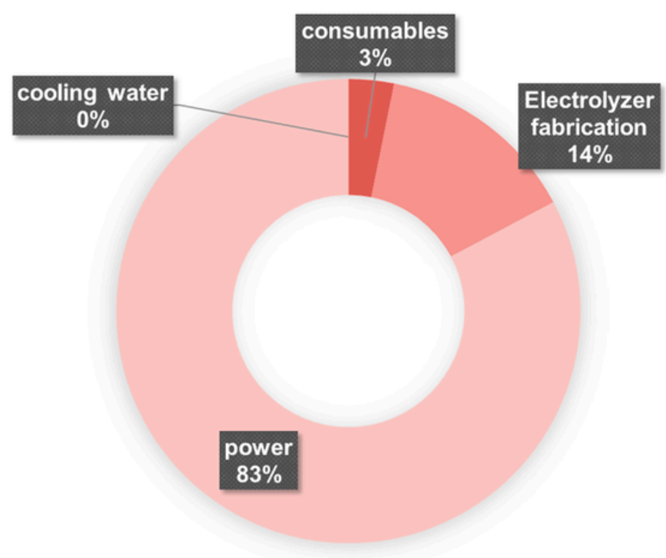

Fig. 5. GWP distribution in the electrolysis step using RES.

regime of AEC and PEM systems by 2030. Regardless of the current investment costs, SOEC technology already offers 81% of energy efficiency according to manufacturer's specifications, which is an important advantage with respect to the 56% of the device used in the project (Sunfire, 2019). By using advanced commercial electrolysis technology, the energy consumption of SNG production can be potentially reduced from 0.873 to 0.604 kWh_{in}/kW_{SNG}. In this case, the carbon footprint of SNG is accordingly reduced to 0.100 kg CO_2-eq/kWh.

Fig. 6 compares the carbon footprint of the presented options, all commercially available. It is worth noting that the impact of biogas and water treatment is almost negligible. At first sight, it can be observed that SNG is not always the greenest option. SNG can support the continuous penetration of wind and photovoltaics sources to the electricity mix; otherwise, restricted due to problems with grid balance. However, the production of SNG using the current electricity mix is not an option to decarbonize the gas grid. Indeed, SNG increases the GWP impact of the gas by 78%. As soon as the power source is shifted to RES, the GWP impact definitely decreases. However, SNG production is still a very energy demanding process, thus, the impact of SNG using biogas and RES is 48% with respect to the natural gas of fossil origin. It is interesting to note that the carbon footprint of SNG will decrease year after year, without any technological improvement, because wind and photovoltaics are the main new power generation capacity worldwide (IRENA, 2020). Thus, the electricity impact (kg CO_2-eq/kWh) will be progressively reduced. Another option is direct coupling of SNG plant to RES generation. This option is technically feasible, for example, hydrogen production in photovoltaic installations (ELY4OFF, 2020). Nevertheless, the number of annual operation hours would be reduced and the GWP impact of materials for building the plant increased. Besides, possible impact on biogas transport should be considered. An alternative option is to use non-coupled tradable green certificates to foster the penetration of renewables in suitable locations (Bertoldi and Huld, 2006; Ciarreta et al., 2017).

Finally, shifting from AEC electrolysis to a more advanced technology such as SOEC electrolyzer reduces an additional 5% of the carbon footprint to 0.100 kg CO_2-eq/kWh. In summary, production of SNG using RES and an advanced electrolyzer technology, SNG reduces significantly the carbon footprint of the current fossil gas by −57%. In some locations, the sludge treatment by anaerobic digestion can be considered as a part of the water treatment, rather than a biogas production plant. In that case, the carbon footprint of SNG is reduced by −68% to 0.074 kg CO_2-eq/kWh. Very optimistic scenarios considering negligible impact from electricity from the hypothesis of consuming only excesses of electricity production were not considered in this work because, to the best of our knowledge, building a Power-to-Gas plant using only electricity surpluses is far to be profitable.

The emissions associated to the production of SNG using biogas as carbon feedstock, advanced electrolysis technology and renewable energy sources was estimated in 0.100 kg CO_2-eq/kWh. With respect to alternative Power-to-Gas decarbonisation strategies, comparable results were obtained in the BioCat plant through biological methanation technology. Authors reported a reduction of −59% of GWP using current data, and up to −79% in optimistic scenarios (Energiforskning, 2014). Another way to obtain renewable methane is by means of carbon dioxide removal from biogas, i.e. biogas upgrading to biomethane. The reported carbon footprint of biomethane is about 0.045–0.082 kg CO_2-eq/kWh (Adelt et al., 2011; Buratti et al., 2013; Lozanovski et al., 2014). Thus, the carbon footprint of biomethane is lower than that of SNG. Unfortunately, biomethane cannot replace the entire demand for gas, neither current nor at medium term (European Commission, 2019). Besides, biogas upgrading does not allow chemical storage of renewable energies. Accordingly, both routes capable of substituting natural gas, to biomethane and SNG, seems complementary options to decarbonize the gas grid.

The continuous penetration of RES should be inevitably complemented by massive storage methods as Power-to-Gas, hydro pumping reservoirs or even low-cost battery technologies. Hydro-pumping is definitely a low-carbon solution but with important land-use and geographical limitations (Lu et al., 2018). For electrolytic stationary grid storage, Hiremath et al. recommend lithium-ion batteries with high round-trip efficiency (Hiremath et al., 2015). Assuming 20 years of operation in the German grid, they reported a total impact of 0.759 kg

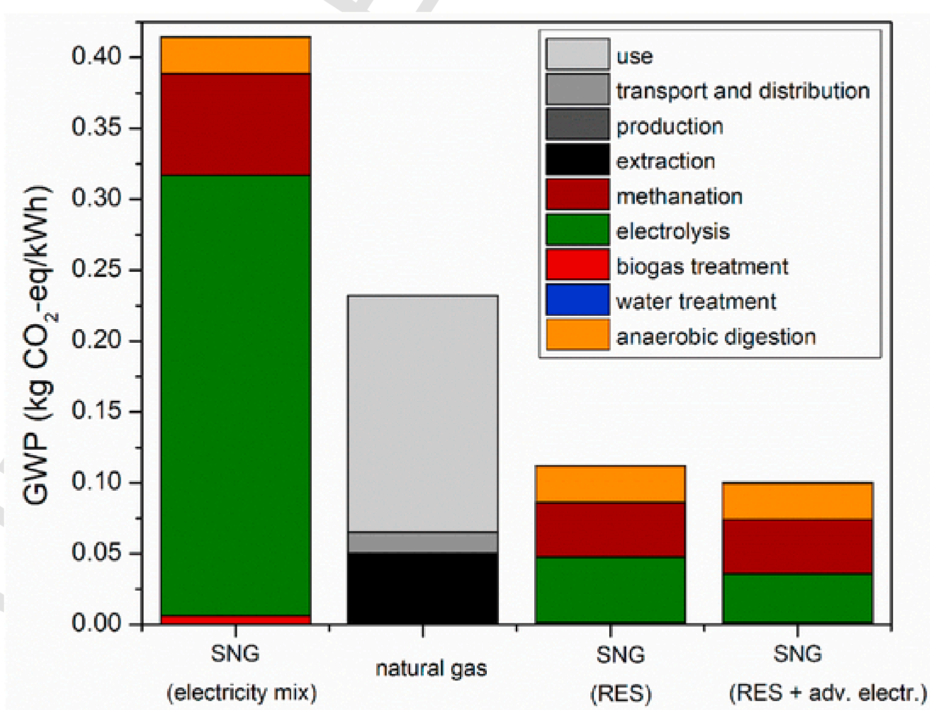

Fig. 6. Comparison of the carbon footprint of the different available alternatives.

CO_2-eq/kWh. Among them, 0.020–0.079 kg CO_2-eq/kWh intended for the cradle-to-gate battery device, as a function of the number of cycles considered. In another work, Baumann et al. reported 0.052–0.271 kg CO_2-eq/kWh for the battery production step (Baumann et al., 2017). Thus, it seems that the carbon footprint of using batteries for massive storage is higher than SNG technology. However, the reutilization of electric vehicle batteries for stationary grid storage applications can be an opportunity to reduce the carbon footprint of these alternative (Rallo et al., 2020). In general, there is a consensus that no individual option can decarbonize the energy system and that a broad portfolio of solutions will be needed. In this aspect, SNG offers an interesting reduction of 59–68% of the carbon footprint of the natural gas grid.

4. Conclusions

The carbon footprint of SNG through a compact 2-step biogas methanation process was evaluated from experimental data obtained in a relevant environment. Results indicate that the SNG carbon footprint is higher (0.414 kg CO_2-eq/kWh) than fossil natural gas (0.232 kg CO_2-eq/kWh) when the national electricity (38% RES) mix is used. Thus, the production SNG from the current electricity mix is not an option to reduce the impact of gas consumption.

As soon as the electricity source is shifted to 100% RES, the carbon footprint is highly reduced to 0.111 kg CO_2-eq/kWh. In that case, the electrolysis step remained the main GWP contributor, closely followed by the methanation unit; while the biogas and water conditioning were minor contributors. The substitution of alkaline electrolyzer technology for a more advanced one, such as solid oxide one, can reduce an addition 5% of the carbon footprint to 0.100 kg CO_2-eq/kWh.

Accordingly, the use of currently available options allows a reduction of, at least, 57% of the carbon footprint of SNG with respect to the use of fossil natural gas. The carbon footprint impact of SNG is higher than that of biomethane from upgrading and lower than batteries for stationary applications. In this sense, SNG within the Power-to-Gas concept can support the continuous penetration of RES sources to the electricity mix by allowing seasonal storage and can help to decarbonize the gas grid.

CRediT authorship contribution statement

Jordi Guilera: Conceptualization, Methodology, Investigation, Validation, Writing - original draft, Data curation. **Mariana Filipe:** Conceptualization, Methodology, Software, Validation, Writing - review & editing. **Aleix Montesó:** Investigation. **Ignasi Mallol:** Conceptualization, Resources, Supervision, Funding acquisition. **Teresa Andreu:** Conceptualization, Formal analysis, Project administration, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Authors acknowledge the support of this work by the LCAeneroost ("tool for eco-innovation in innovative technologies in the energy sector") and the Cosin ("synthetic fuels") projects of the RIS3CAT Energy Community, which has been co-founded by ACCIO and the European Regional Development Fund under the ERDF Operational Program of Catalonia 2014–2020 (COMRDI15-1-0037 and COMRDI15-1-0042). We thank the water treatment operator Ajuntament de Sabadell and Companyia d'Aigües de Sabadell for giving us the space and the biogas for the realization of this project. We are grateful to Cetaqua, especially to Núria Basset, Adriana Romero and Paula Gómez, for material and energy inventory of biogas cleaning and compression. We thank Alois Preishuber from ErreDue spa and Dr. Tim Boltken from Ineratec GmbH for providing us with inventory data on their electrolysis and methanation processes, respectively.

List of abbreviations

AEC
Alkaline Electrolysis Cell
BTX
Benzene Toluene Xylene
GHG
Greenhouse Gas
GWP
Global Warming Potential
ISO
International Organization for Standardization
LCA
Life Cycle Assessment
LHV
Lower Heating Value
MFC
Mass Flow Controller
PEM
Proton Exchange Membrane
RES
Renewable Energy Sources
SNG
Synthetic Natural Gas
SOEC
Solid Oxide Electrolyzer Cell
VOC
Volatile Organic Carbon
WTTP
Waste Water Treatment Plant

References

Adelt, M., Wolf, D., Vogel, A., 2011. LCA of biomethane. J. Nat. Gas Sci. Eng. 3, 646–650. doi:10.1016/j.jngse.2011.07.003.
Alarcón, A., Guilera, J., Díaz, J.A., Andreu, T., 2019. Optimization of nickel and ceria catalyst content for synthetic natural gas production through CO2 methanation. Fuel Process. Technol. 193, 114–122. doi:10.1016/j.fuproc.2019.05.008.
Alarcón, A., Guilera, J., Soto, R., Andreu, T., 2020. Higher tolerance to sulfur poisoning in CO2 methanation by the presence of CeO2. Appl. Catal. B Environ. 263, 118346. doi:10.1016/j.apcatb.2019.118346.
Bailera, M., Hanak, D.P., Lisbona, P., Romeo, L.M., 2019. Techno-economic feasibility of power to gas–oxy-fuel boiler hybrid system under uncertainty. Int. J. Hydrogen Energy 44, 9505–9516. doi:10.1016/j.ijhydene.2018.09.131.
Bailera, M., Lisbona, P., Romeo, L.M., Espatolero, S., 2017. Power to Gas projects review: lab, pilot and demo plants for storing renewable energy and CO2. Renew. Sustain. Energy Rev. 69, 292–312. doi:10.1016/j.rser.2016.11.130.
Baumann, M., Peters, J.F., Weil, M., Grunwald, A., 2017. CO2 footprint and life-cycle costs of electrochemical energy storage for stationary grid applications. Energy Technol. 5, 1071–1083. doi:10.1002/ente.201600622.
Belimov, M., Metzger, D., Pfeifer, P., 2017. On the temperature control in a microstructured packed bed reactor for methanation of CO/CO2 mixtures. AIChE J. 63, 120–129. doi:10.1002/aic.15461.
Bertoldi, P., Huld, T., 2006. Tradable certificates for renewable electricity and energy savings. Energy Pol. 34, 212–222. doi:10.1016/j.enpol.2004.08.026.
Blanco, H., Faaij, A., 2018. A review at the role of storage in energy systems with a focus on Power to Gas and long-term storage. Renew. Sustain. Energy Rev. 81, 1049–1086. doi:10.1016/j.rser.2017.07.062.
Blanco, H., Nijs, W., Ruf, J., Faaij, A., 2018. Potential of Power-to-Methane in the EU energy transition to a low carbon system using cost optimization. Appl. Energy 232, 323–340. doi:10.1016/j.apenergy.2018.08.027.
Buratti, C., Barbanera, M., Fantozzi, F., 2013. Assessment of GHG emissions of biomethane from energy cereal crops in Umbria. Italy. Appl. Energy 108, 128–136. doi:10.1016/j.apenergy.2013.03.011.
Chauvy, R., Dubois, L., Lybaert, P., Thomas, D., De Weireld, G., 2020. Production of synthetic natural gas from industrial carbon dioxide. Appl. Energy 260, 114249. doi:10.1016/j.apenergy.2019.114249.
Ciarreta, A., Espinosa, M.P., Pizarro-Irizar, C., 2017. Optimal regulation of renewable energy: a comparison of Feed-in Tariffs and Tradable Green Certificates in the Spanish electricity system. Energy Econ. 67, 387–399. doi:10.1016/j.eneco.2017.08.028.

CNMC Comisión Nacional de los Mercados y la Competencia 2019 The natural gas market in Spain2018https://www.cnmc.es/sites/default/files/2647322_0.pdf2020
Colbertaldo, P., Guandalini, G., Campanari, S., 2018. Modelling the integrated power and transport energy system: the role of power-to-gas and hydrogen in long-term scenarios for Italy. Energy 154, 592–601. doi:10.1016/j.energy.2018.04.089.
Collet, P., Flottes, E., Favre, A., Raynal, L., Pierre, H., Capela, S., Peregrina, C., 2017. Techno-economic and Life Cycle Assessment of methane production via biogas upgrading and power to gas technology. Appl. Energy 192, 282–295. doi:10.1016/j.apenergy.2016.08.181.
Dittmeyer, R., Boeltken, T., Piermartini, P., Selinsek, M., Loewert, M., Dallmann, F., Kreuder, H., Cholewa, M., Wunsch, A., Belimov, M., Farsi, S., Pfeifer, P., 2017. Micro and micro membrane reactors for advanced applications in chemical energy conversion. Curr. Opin. Chem. Eng. 17, 108–125. doi:10.1016/j.coche.2017.08.001.
Dones, R., Bauer, C., Bolliger, R., Burger, B., Faist Emmenegger, M., Frischknecht, R., Heck, T., Jungbluth, N., Röder, A., Tuchschmid, M., 2007. Life Cycle Inventories of Energy Systems: Results for Current Systems in Switzerland and Other UCTE Countries. Final Rep. Ecoinvent Data V2. 0 5.
ELY4OFF PEM Electrolysers for operation with offgrid renewable installationshttp://ely4off.eu/project/2020
Enerdata Global energy statistical yearbook 2020[WWW Document]. URLhttps://yearbook.enerdata.net/2020
Energiforskning, 2014. Life Cycle Analysis of BioCat Plant. ANNEX 1 ForskEL 2014-1-12164.
European Commission, 2019. Impact of the Use of the Biomethane and Hydrogen Potential on Trans-European Infrastructure.
Gahleitner, G., 2013. Hydrogen from renewable electricity: an international review of power-to-gas pilot plants for stationary applications. Int. J. Hydrogen Energy 38, 2039–2061. doi:10.1016/j.ijhydene.2012.12.010.
Glenk, G., Reichelstein, S., 2019. Economics of converting renewable power to hydrogen. Nat. Energy 4, 216–222. doi:10.1038/s41560-019-0326-1.
Guilera, J., Andreu, T., Basset, N., Boeltken, T., Timm, F., Mallol, I., Morante, J.R., 2020. Synthetic natural gas production from biogas in a waste water treatment plant. Renew. Energy 146, 1301–1308. doi:10.1016/j.renene.2019.07.044.
Guilera, J., Boeltken, T., Timm, F., Mallol, I., Alarcón, A., Andreu, T., 2020. Pushing the limits of SNG process intensification: high GHSV operation at pilot scale. ACS Sustain. Chem. Eng. 8, 8409–8418. doi:10.1021/acssuschemeng.0c02642.
Guilera, J., Ramon Morante, J., Andreu, T., 2018. Economic viability of SNG production from power and CO2. Energy Convers. Manag. 162, 218–224. doi:10.1016/j.enconman.2018.02.037.
Hiremath, M., Derendorf, K., Vogt, T., 2015. Comparative life cycle assessment of battery storage systems for stationary applications. Environ. Sci. Technol. 49, 4825–4833. doi:10.1021/es504572q.
Huijbregts, M.A.J., Steinmann, Z.J.N., Elshout, P.M.F., Stam, G., Verones, F., Vieira, M., Zijp, M., Hollander, A., van Zelm, R., 2017. ReCiPe2016: a harmonised life cycle impact assessment method at midpoint and endpoint level. Int. J. Life Cycle Assess. 22, 138–147. doi:10.1007/s11367-016-1246-y.
IRENA, 2020. Global Renewables Outlook: Energy Transformation 2050.
ISO 14067, 2018. Greenhouse Gases — Carbon Footprint of Products — Requirements and Guidelines for Quantification.
Lozanovski, A., Lindner, J.P., Bos, U., 2014. Environmental evaluation and comparison of selected industrial scale biomethane production facilities across Europe. Int. J. Life Cycle Assess. 19, 1823–1832. doi:10.1007/s11367-014-0791-5.
Lu, B., Stocks, M., Blakers, A., Anderson, K., 2018. Geographic information system algorithms to locate prospective sites for pumped hydro energy storage. Appl. Energy 222, 300–312. doi:10.1016/j.apenergy.2018.03.177.
Marcogaz, 2019. Overview of Available Test Results and Regulatory Limits for Hydrogen Admission into Existing Natural Gas Infrastructure and End Use.
Miniserio para la Transición Ecológica, 2018. BOE-A-2018-14557.
Ministerio de Industria Energía y Turismo, 2013. BOE-A-2013-185.
Moioli, E., Gallandat, N., Züttel, A., 2019. Model based determination of the optimal reactor concept for Sabatier reaction in small-scale applications over Ru/Al2O3. Chem. Eng. J. 121954. doi:10.1016/j.cej.2019.12195.
Rallo, H., Canals Casals, L., De La Torre, D., Reinhardt, R., Marchante, C., Amante, B., 2020. Lithium-ion battery 2nd life used as a stationary energy storage system: ageing and economic analysis in two real cases. J. Clean. Prod. 272, 122584. doi:10.1016/j.jclepro.2020.122584.
Red Eléctrica Española Electric balance (Spain)[WWW Document]. URLhttps://www.ree.es/es/datos/balance/balance-electrico2020
Reiter, G., Lindorfer, J., 2015. Global warming potential of hydrogen and methane production from renewable electricity via power-to-gas technology. Int. J. Life Cycle Assess. 20, 477–489. doi:10.1007/s11367-015-0848-0.
Schmidt, O., Gambhir, A., Staffell, I., Hawkes, A., Nelson, J., Few, S., 2017. Future cost and performance of water electrolysis: an expert elicitation study. Int. J. Hydrogen Energy 42, 30470–30492. doi:10.1016/j.ijhydene.2017.10.045.
Sternberg, A., Bardow, A., 2015. Power-to-What? – environmental assessment of energy storage systems. Energy Environ. Sci. 8, 389–400. doi:10.1039/C4EE03051F.
Sunfire, 2019. Clean hydrogen for sector integration.
Thema, M., Bauer, F., Sterner, M., 2019. Power-to-Gas: electrolysis and methanation status review. Renew. Sustain. Energy Rev. 112, 775–787. doi:10.1016/j.rser.2019.06.030.
UK Government, 2020. 2019 Government Greenhouse Gas Conversion Factors for Company Reporting.
UK Government, 2019. Greenhouse Gas Reporting: Conversion Factors 2019.
van der Giesen, C., Kleijn, R., Kramer, G.J., 2014. Energy and climate impacts of producing synthetic hydrocarbon fuels from CO2. Environ. Sci. Technol. 48, 7111–7121. doi:10.1021/es500191g.
Wright, L.A., Kemp, S., Williams, I., 2011. 'Carbon footprinting': towards a universally accepted definition. Carbon Manag. 2, 61–72. doi:10.4155/cmt.10.39.
Zhang, X., Bauer, C., Mutel, C.L., Volkart, K., 2017. Life Cycle Assessment of Power-to-Gas: approaches, system variations and their environmental implications. Appl. Energy 190, 326–338. doi:10.1016/j.apenergy.2016.12.098.
Zhang, X., Witte, J., Schildhauer, T., Bauer, C., 2020. Life cycle assessment of power-to-gas with biogas as the carbon source. Sustain. Energy Fuels 4, 1427–1436.