

Power to Gas-Electrochemical industry hybrid systems: A case study

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Abstract

Several researchers have proposed in literature different Power to Gas (PtG) hybridizations to improve the efficiency of this energy storage technology. Some of the synergies of this hybrid systems are already being tested under real conditions (e.g. PtG-Amine scrubbing, PtG-wastewater treatment) while others have only been studied through numerical simulations (e.g., PtG-oxyfuel combustion). Here, a novel hybridization between Power to Gas and electrochemical industries is proposed for the first time. This PtG-Electrochemical hybridization avoids to implement the typical water electrolysis stage of PtG since hydrogen is already available in the plant. This study thoroughly analyzes the implementation of Power to Gas in a real electrochemical plant that sub-produces hydrogen from the lines of production of chlorate, chlorine, and potassium hydroxide. It is shown that the required carbon dioxide for methanation can be captured from the flue gas of the factory's boilers without additional energy penalty thanks to energy integration. The methanation plant has been designed according to the H₂ and CO₂ availability, taking into account the number of operating hours and the degree of usage of by-products. Results show that this PtG hybridization could operate more than 6000 hours per year at large scale concepts (nominal H₂ inputs of 2000

m³/h (NTP)), which represents 2000 h more than pilot/commercial demonstrations of classic PtG concepts. Besides, a detailed economic analysis demonstrates the economic feasibility of the system under current scenarios. It is shown that the capital investment would be recovered in 8 years, generating a 4.8 M€ NPV at the end of the project lifetime. Thus, this work presents a suitable way to avoid the subsidy dependency that current PtG research projects have.

Keywords

Power-to-Gas, Methanation, Hybridization, Electrochemical industry

1. Introduction

In 2009, the European Renewable Energy Directive (2009/28/EC) established a global policy to achieve in 2020 a renewable share in the European final energy consumption for at least 20%, together with a 10% share in the field of transport [1]. Beyond 2020, renewables will remain playing a key role since EU countries have already agreed on extending the target up to 27% by 2030. According to the trends to 2050 from the “EU Reference Scenario 2016”, the share of electricity produced from renewables is expected to grow up to 37.2% by 2020, 43% by 2030, and 53% by 2050 [2].

The intermittent nature of these renewable energy sources (RES) produces mismatches between supply and electrical demand that affect the security and stability of the grid. Typically, generators and system operators can only regulate the 5-10% of the output coming from variable renewable sources (wind and solar). For instance, the degree of regulation in Spain is about 5%, in Sweden 6% and in Germany 7% [3]. Hence, the increase of renewable share in the electricity production mix brings along with fluctuating power that limits the operational predictability and flexibility of the energy system, generating a serious challenge

to electrical grid operators. To promote RES deployment, embedding energy storage techniques into conventional power stations and industries result essential to smartly manage renewable intermittent power.

In the last years, Power to Gas (PtG) has been proposed as a very promising and versatile technology to store renewable power surplus. PtG converts electricity into synthetic natural gas via the methanation of CO₂ together with H₂ from water electrolysis [4][5]. This technology widens the application of hydrogen as energy vector, and it makes possible to produce a CO₂ neutral fuel by capturing the carbon emissions from an existing source [6][7]. In addition, it allows the connection between electric and gas network thus increasing the flexibility of the energy supply system. However, significant economic barriers slow down PtG development due to the current high cost of electricity, and the large required investments. These problems could be overcome through hybridizing systems whose synergies increase the global efficiency, improve the resource use, and reduce the investment on new equipment [8].

In 2009, Michael Sterner outlined several configurations that present some synergies depending on the CO₂ source used for the methanation process (biogas, syngas or pure CO₂) [9]. For instance, the use of biogas avoids the necessity of a carbon capture step since biogas is already a mixture of CH₄ (50% – 85%) and CO₂ (50% – 15%) [10]. Besides, it allows the integration of the methanation heat in the digestion processes. For those reasons, the most recently developed PtG pilot plants prefer biogas as source of CO₂ [11]. In 2015, Electrochaea commissioned the largest plant worldwide integrating biogas as resource [12], in which a 1.0 MW alkaline water electrolyzer supplies the hydrogen [13]. They aim to integrate both the by-product oxygen and the methanation heat in the wastewater treatment process that generates the biogas [14]. Technical data from this field experience have not been released yet, but

previous projects showed that 3000 operating hours were achievable under realistic market conditions [15].

Likewise, syngas from gasification does not require a carbon capture process either, and permits the use of the by-produced oxygen during water electrolysis to carry out oxygen-blow gasification. This type of integration is still under development at lab/pilot scale [11], so there are no studies quantifying the benefits of the integration. The cutting-edge research in this topic is carried out by the Karlsruhe Institute of Technology, which has made some methanation tests with input flows of syngas of 14 m³/h (NTP) [16] in a biomass gasification plant belonging to Cortus, in Sweden [17].

Power to Gas plants that make use of pure CO₂ admit different integration configurations. When amine capture technology is employed, methanation heat may be integrated and used for regenerating the solvent. If oxy-fuel combustion capture technique is used, mass flow integration is possible and the by-produced O₂ is used as comburent.

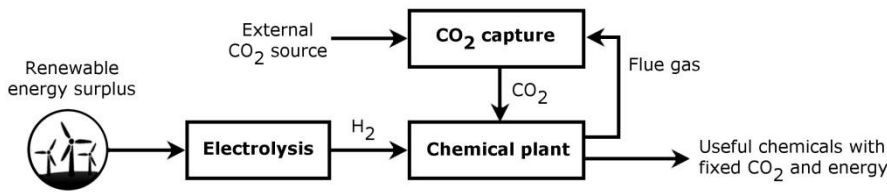
The PtG-Amine integration case is the only one that has a commercial experience, the Audi e-gas plant [18]. It uses three alkaline water electrolyzers of 2.0 MW [19] and produces up to 325 m³/h (NTP) of synthetic natural gas [20]. Besides, the plant is qualified for participating in the electricity balancing market [21], and the availability of the renewable energy consumed gives about 4000 operating hours per year [20]. Specific software had to be developed to optimize the thermal management of the waste heat recovered from electrolysis and methanation, to be later supply in the CO₂ removal plant [21][22]. The objective of the manufacturer, ETOGAS, is to reach PtG systems around 20 MW with efficiencies above 80% thanks to the recovery of the methanation heat [23]. Regarding Power to Gas-oxyfuel combustion hybridization, some studies based on simulations can be found in literature. Bailera et al. characterized these kind of systems and proposed district heating and industries

as preferred applications [24][8]. Besides, they studied the application of PtG-Oxy hybridization in a combined cycle power plant, and showed that the 88% of the methanation heat can be integrated increasing the global efficiency of the power plant from 56% to 68% [25].

Another hybrid route to store fluctuating power from renewables is the Power to Chemicals concept. Those chemicals that require hydrogen and carbon dioxide for their production (e.g., methanol, ethylene, propylene, and formic acid) act as hybrid storage of energy and CO₂ when H₂ is renewably produced with electricity surplus. In these cases, there is no investment related to the methanation stage of the classic PtG concept, since this stage is substituted with an already existing line of production of chemical products [26]. This kind of hybridization puts together the water electrolysis stage of classic Power to Gas concept with an existing chemical line of production that substitutes methanation (Figure 1). For instance, the CO2RRECT project produced hydrogen with renewable energy to reduce CO₂ and obtain carbon monoxide, which is later used as precursor of other chemical products [27].

In this paper, we propose for the first time the Power to Gas-Electrochemical industry hybridization, a new type of integration that implements methanation in chemical plants whose lines of production are based on chemical electrolysis. Whenever a chemical electrolytic process generates hydrogen as by-product, it can be integrated in a PtG process (Figure 1). Thus, the PtG-Electrochemical hybridization avoids implementing the classical water electrolysis stage of PtG since hydrogen is already available in the plant. At the same time, the CO₂ emissions from the electrochemical plant can be used in the methanation process.

POWER-TO-CHEMICALS



PtG-ELECTROCHEMICAL HYBRIDIZATION

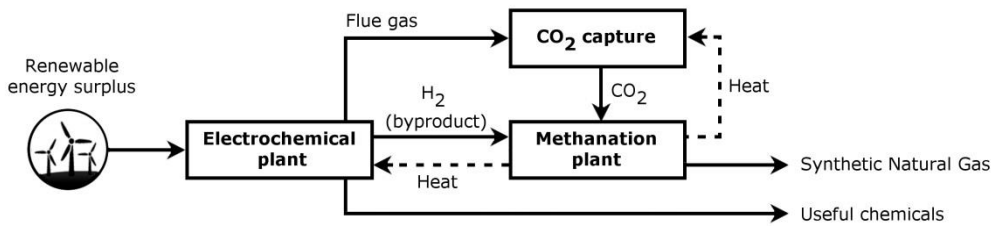


Figure 1. Comparison between the classical Power-to-Chemical route and the novel PtG-Electrochemical hybridization.

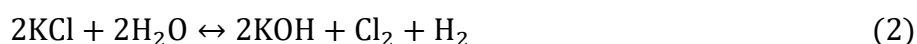
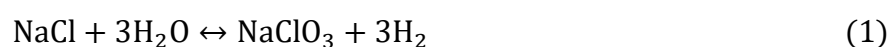
The overall objective of the paper is to size a hybrid PtG-Electrochemical plant through its simulation under real operating data from a Spanish factory. The system includes an amine-based CO₂ capture plant, a TREMP methanation plant, and an optimized heat exchanger network to energetically integrate both facilities. The relation between the operating hours of the different sub-systems is a key parameter when sizing the Power to Gas plant, and it determines the degree of H₂ and CO₂ utilization, as well as the size of the required buffer of H₂ to manage the resource. The study concludes with an economic analysis of the proposed hybrid system.

2. Case study: Power to Gas-Electrochemical hybridization

In PtG-Electrochemical hybridizations, the electricity used is no longer considered as consumption in the factory but as stored energy (it should be noted that the conversion of electricity to hydrogen will have lower efficiency than conventional water electrolyser). This hybrid concept avoids most of the large investment costs (water electrolysers) and an important part of the operational costs (electricity) associated to classical Power to Gas plants.

These costs are removed since hydrogen is directly provided –i.e., by-produced– through other already existing electrochemical processes in the plant. In addition, carbon dioxide could be supplied from the boilers present in the electrochemical plant with low energy penalties thanks to the integration of the heat released in the methanation reaction.

We present here a case study of an existing plant with a significant amount of byproduct hydrogen coming from two electrolytic production lines: sodium chlorate (NaClO_3), Eq. (1), and chlorine (Cl_2) and potassium hydroxide (KOH), Eq. (2).



Currently, both sources of by-produced hydrogen are purified and mixed for further use. The 50% of the produced hydrogen is destined to ammonia (NH_3), the 25% to hydrochloric acid (HCl), and the 20% to hydrogen peroxide (H_2O_2); the remaining 5% are losses (Figure 2).

The proposed hybridization consists of replacing ammonia production with synthetic natural gas production, since the latter is a more profitable product. In addition, the methanation process could consume CO_2 emissions from a boiler installed in the plant.

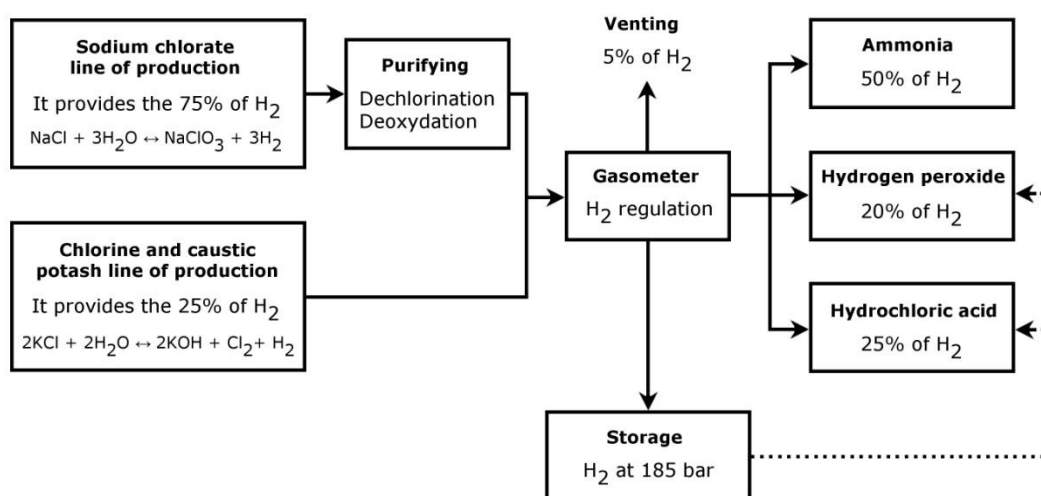


Figure 2. Scheme of the hydrogen routes in the electrochemical plant.

The availability of hydrogen in the plant fluctuates following the electricity market in order to operate the chemical electrolysis during the periods of low electricity prices. This operating strategy limits the amount of CO₂ that can be used in every period of time (Table 1). In this sense, January and February present potential CO₂ utilizations below 60%, whilst August usage capability is above 90%. The maximum potential yearly consumption of CO₂ reaches the 68% of total emissions, although this will be limited due to partial load operation restrictions in the methanation plant (periods of low H₂ productions) and situations in which there is no enough CO₂ to convert the temporarily available hydrogen.

In this work, we have analyzed the hourly production pattern of H₂ to determine the actual potential of integrating Power to Gas in the selected electrochemical plant, with the aim of simulating the optimal-sized plant and performing a detailed economic assessment.

Table 1. Available H₂, emitted CO₂ and potential CO₂ usable in PtG.

Month	H ₂ available [km ³ (NTP)]	CO ₂ emitted [km ³ (NTP)]	Max. CO ₂ usable [%]
January	1058	512	51
February	1067	465	57
March	1253	457	68
April	1260	466	67
May	1175	446	66
June	1116	312	89
July	949	387	61
August	1670	452	92
September	1179	483	61
October	1303	367	89
November	1078	353	76
December	1007	471	53
Total	14115	5171	68

3. Methodology

The developed study comprises three main issues which have been sequentially approached: (i) the characterization of the hourly distribution of the H₂ availability, (ii) the simulation of the hybrid plant, and (iii) the development of an economic evaluation.

3.1 Evaluation of H₂ availability, and plant sizing

The chemical electrolysis lines of the plant present intensive energy consumptions, so their operations must follow the power market to reduce the operational costs. The electricity price varies among 6 time periods (P1 to P6) that are established by legislation [28][29]. It divides the year in 650 hours of P1, 3126 hours of P2-P5, and 4984 hours of P6 (Figure 3). Thus, the plant accordingly adapts the holidays and maintenances to mostly operate in Period 6 (the cheapest one), as well as diminishes the production load during periods P1 to P5. Finally, the hourly availability of H₂ along the year is completely defined by also considering the unplanned shutdowns. The operating hours of the electrochemical plant throughout periods P1 to P6 are summarized in Table 2.

The largest by-production occurs when both chemical electrolysis lines simultaneously operate at Period 6 (the most economic period) thus giving a maximum of 4926.0 m³/h (NTP) (Table 2). However, only the amount that would be consumed in ammonia can be used in methanation, which is equal to the 50% of the by-produced H₂. In addition, during Period 1 the by-produced hydrogen is very limited due to the high cost of electricity, and it is preferred to entirely dedicate it to the production of Hydrochloric acid and Hydrogen peroxide, instead of ammonia. Therefore, we also consider that during P1 there is no hydrogen available for methanation.

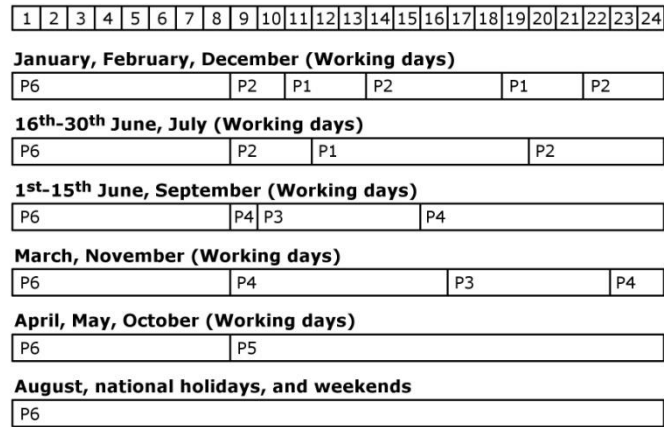


Figure 3. Hourly distribution of pricing period [28].

Table 2. Rates of by-production of H₂, and chemical electrolysis parameters, for the six market periods.

	NaCl electrolysis			KCl electrolysis		
	P1	P2-P5	P6	P1	P2-P5	P6
\dot{V}_{H_2} [m ³ /h (NTP)]	0.0	2333.0	3629.1	486.3	689.0	1296.9
$\dot{V}_{H_2, ammonia}$ [m ³ /h (NTP)]	0.0	1166.5	1814.5	0.0	344.5	648.4
h [h/year]	0	1581	4584	570	2846	4584

The boiler of the electrochemical plant (the CO₂ source) is operative 24 h per day, except those dates in which the facility is completely closed. Hence, the monthly emissions (Table 1) are equally divided between the operating days, what results in hourly emissions in the range 464 – 726 m³/h (NTP).

3.2 PtG-Electrochemical hybrid plant model

The proposed hybrid plant has been modelled and simulated in Aspen Plus[®], and then thermally integrated with Aspen Energy Analyzer through the Pinch analysis technique [30][31].

3.2.1 CO₂ capture plant model

Chemical absorption was considered the most suitable technology for CO₂ capture to be integrated in the electrochemical plant. Thus, a MEA absorption facility was designed and modelled in Aspen Plus® [32][33][34]. Figure 4 shows the CO₂ capture process flowsheet.

Flue gas from the boiler is cooled down to 70 °C before entering the absorber at the bottom (A2). The solvent is introduced at the top of the column (A9). Reactions take place in the absorber with MEA and CO₂ flowing at countercurrent. Vent gas leaves absorber at the top (A10) and a solution of CO₂ and aqueous MEA (rich amine solution) leaves the column at the bottom (A3). Then, the temperature of the rich amine solution is increased from 64 to 80 °C in a heat exchanger (rich/lean exchanger) before entering at the top of the stripper (A11). Steam is required in the MEA regeneration (reboiler) and to separate the solvent and the CO₂. Steam reboiler temperature is limited to 120 °C, in order to prevent high MEA degradation rates and corrosion problems. The lean amine solution (A19) leaves stripper at 103 °C and then goes through the heat exchanger to transfer energy to the rich amine solution flow decreasing temperature down to 87°C. To achieve a lower temperature before entering again the absorber (A9), an additional cooler is required for reducing solvent temperature to 37 °C. Finally, most of water content in CO₂ flow is removed in the condenser and high purity CO₂ gas flow leaves flash separator (A14).

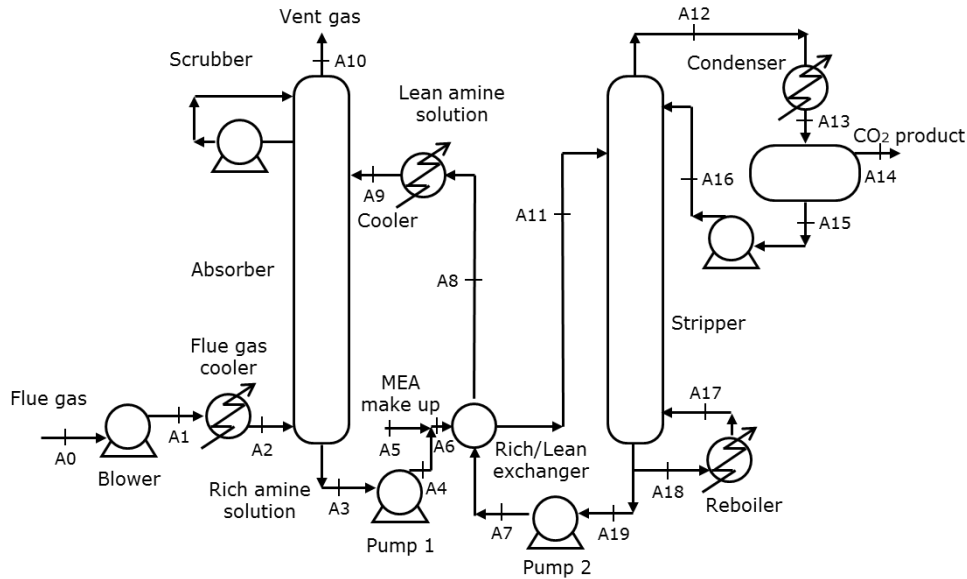


Figure 4. Scheme of the CO₂ separating amine plant

The amine plant was modeled in Aspen Plus[®]. Besides operation temperature levels [35], some additional assumptions according to a quite conservative scenario were considered to accurately run the simulations [36][37]:

- (i) The MEA weight percentage in the absorption solvent was 20% wt.
- (ii) Stripper was designed to require solvent regeneration energy below 6 GJ/t_{CO₂} in any case and to obtain a CO₂ flow with a concentration higher than 94% vol.
- (iii) The amine plant columns were sized to capture more than 90% of CO₂ introduced with the flue gas.
- (iv) The final facility dimension was set according to methanation plant requirements.

These values are collected in following section.

3.2.2 Methanation plant model

The proposed methanation scheme is based on TREMP[™] technology [38]. It is composed by three adiabatic reactors at 30 bar, a recycling loop in the first reactor, and an intermediate water condensation after the second stage (Figure 5). Thus, the obtained SNG reaches 95 vol.% of methane, as the commercial natural gas that can be purchased from the Spanish

natural gas network [39]. We use adiabatic, catalytic methanation due to its greater scalability and energy integration potential [11].

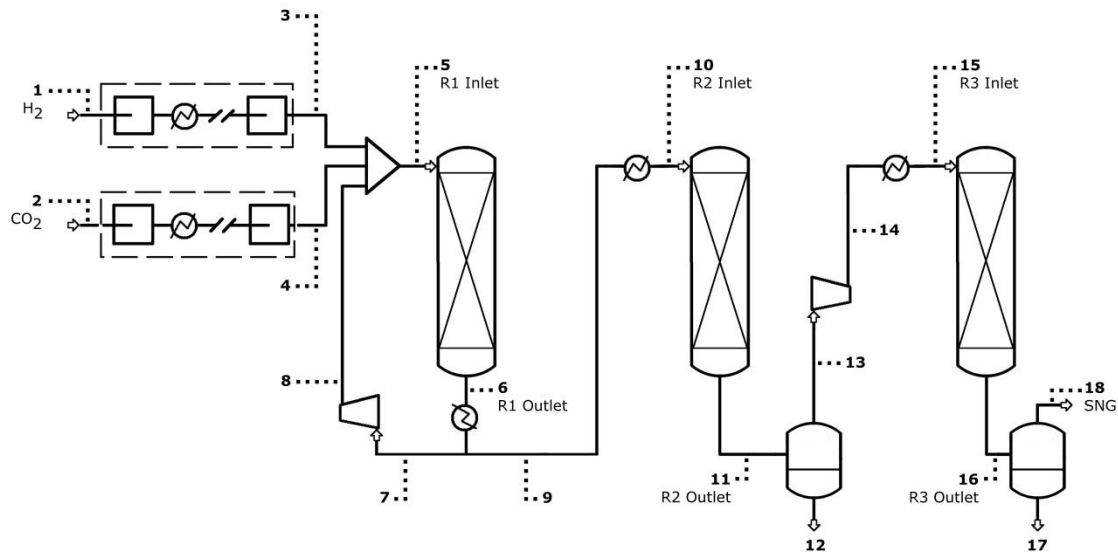


Figure 5. Scheme of the methanation plant.

First, hydrogen (1) and carbon dioxide (2) are pressurized through two multi-stage compressors, what increases the temperature of the gasses up to 300 °C. The outlet gas of Reactor 1 (6) is cooled down to 300 °C and partially recirculated (72 %) with a blower (8). The temperature of the remaining flow is reduced to 250 °C prior entering into the next reactor (10). After this second absorption stage (11), water content normally exceeds the 60 vol.%, what inhibits the reaction; hence, it is reduced to 13 % by condensation (13). Then, the syngas has to be preheated back to 250 °C for the last methanation stage (15). Last, water content is removed again to achieve the required SNG quality. The plant has been simulated in Aspen Plus® considering pressure drops of 0.3 bar at methanation reactors and 0.6 bar at condensation tanks.

4. Results

4.1 H₂ availability and methanation plant size

The hydrogen and CO₂ availabilities (grey area and dashed line in Figure 6, respectively) have been assessed for the year 2014. These graphs are built from the amount of hydrogen known to be available for each type of hour (Section 3.1, Table 2), taking also into account the planned and unplanned shutdowns that the factory reported for each line of production in 2015 (e.g., 1st January). The right axis of Figure 6 is adjusted so that the grey area also indicates the corresponding amount of CO₂ required for methanation in each period. Most of the time, the boiler provides enough CO₂ to consume the produced hydrogen through methanation (dashed line, Figure 6), although the limited emissions during months like November temporally makes CO₂ insufficient at H₂ peaks (it occurred 1344 hours during the year 2014).

These lacks of CO₂ force to set apart some of the available H₂ to maintain the stoichiometry of the methanation reaction. Additionally, there exist periods in which the hydrogen production is too low to reach the minimum operating load of the methanation plant (set at 60% according to literature [4]), so it must be stopped and none of the resources (CO₂, H₂) can be consumed. These two issues limit the maximum potential use of CO₂ and H₂ down to 62.5 % and 91.9 % respectively. This maximum usage, α_i , is calculated according to Equation 3, as the sum of the amount that is used in each hour, $v'_{i,j}$ [m³(NTP)] divided by the sum of the available amount, $v_{i,j}$ [m³(NTP)]. The values of $v_{i,j}$ are those presented in Figure 6 (known data), while $V_{H_2,PtG}$ stands for the nominal hourly H₂ input of the methanation plant. In the case of the evaluation of the maximum usage, $V_{H_2,PtG}$ is set at 2462.9 m³ (NTP), which is the available H₂ when both lines of production operate at P6 (Table 2).

$$\alpha_i = \frac{\sum_j v'_{i,j}}{\sum_j v_{i,j}} \cdot 100 \quad \begin{matrix} i = H_2, CO_2 \\ j = 1, 2, \dots, 8760 \end{matrix} \quad \begin{matrix} i = H_2 \\ i = CO_2 \end{matrix} \begin{cases} \left\{ \begin{array}{ll} v'_{i,j} = 0 & \text{if } v_{H_2,j} \leq 0.6 V_{H_2,PtG} \\ v'_{i,j} = v_{H_2,j} & \text{if } 0.6 V_{H_2,PtG} < v_{H_2,j} \leq 4 v_{CO_2,j} \\ v'_{i,j} = 4 v_{CO_2,j} & \text{if } 4 v_{CO_2,j} < v_{H_2,j} \end{array} \right. \\ \left\{ \begin{array}{ll} v'_{i,j} = 0 & \text{if } v_{H_2,j} \leq 0.6 V_{H_2,PtG} \\ v'_{i,j} = v_{H_2,j}/4 & \text{if } 0.6 V_{H_2,PtG} \leq v_{H_2,j} \leq 4 v_{CO_2,j} \\ v'_{i,j} = v_{CO_2,j} & \text{if } 4 v_{CO_2,j} < v_{H_2,j} \end{array} \right. \end{cases} \quad (3)$$

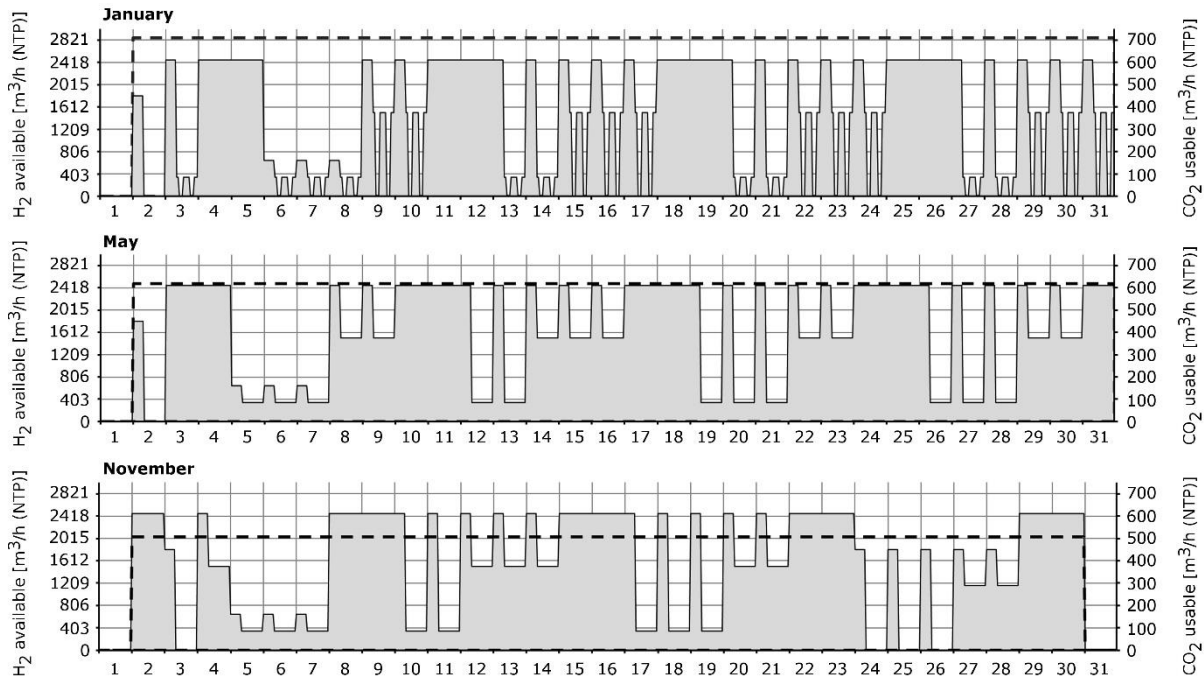


Figure 6. H₂ (grey area) and CO₂ availabilities (dashed line) for January, May and November.

The size of the hybrid plant was selected taking into account the operating hours (Figure 7) and the percentage of the available H₂ that is finally used (Figure 8). We also considered the inclusion of a tank to store the H₂, thus softening the intermittent behavior of the resources. The design criteria to size the facility are a minimum of 6000 operating hours and 85% of H₂ utilization, which give the area hold by the dashed line in Figure 7 and 8. To reduce economic investment on equipment, we select a small H₂ buffer of 1000 m³ (NTP) and a methanation plant of 6 MW_{H₂} input (1998.7 m³/h (NTP)), which leads to 6070 operating hours per year and a 85.9% usage of the available hydrogen. The associated amine plant required to fulfill the requirements of methanation has a nominal output of 500 m³/h (NTP) of CO₂, thus consuming up to the 58.2% of the CO₂ emitted.

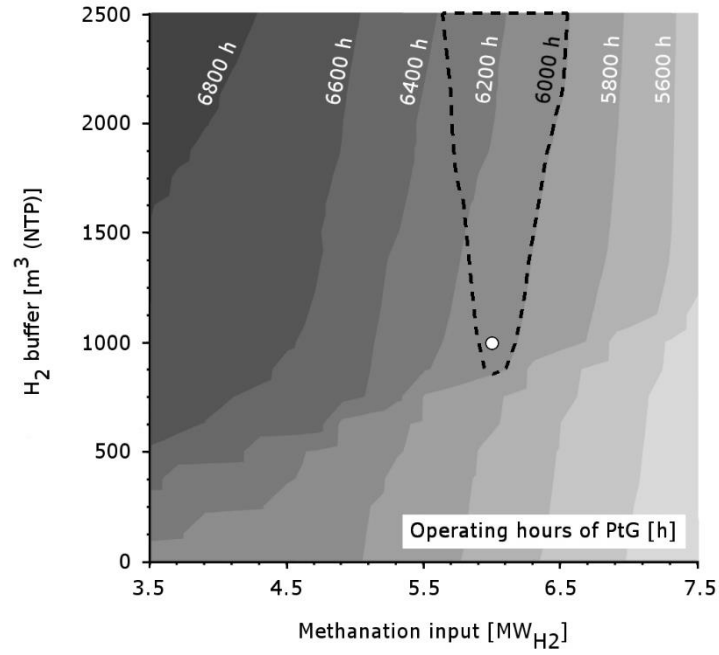


Figure 7. Operating hours as a function of the methanation size and the H₂ buffer.

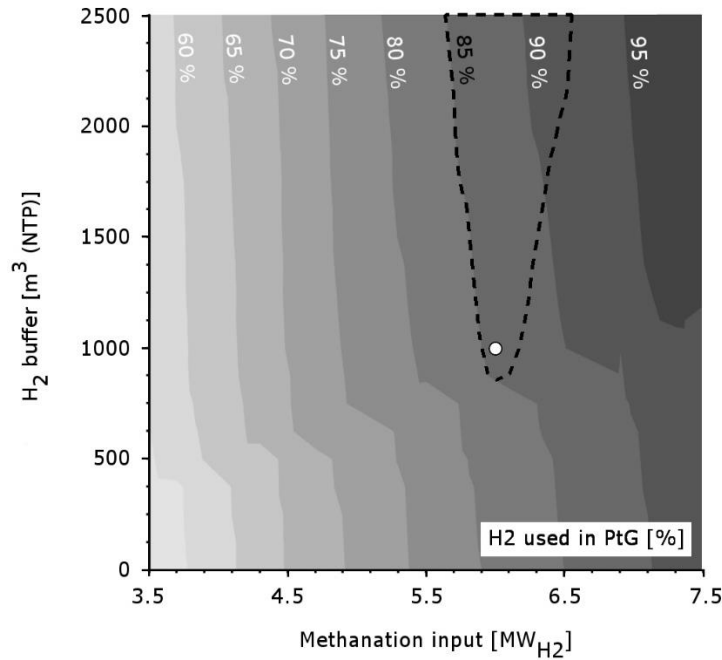


Figure 8. H₂ utilization [%] as a function of the methanation size and the H₂ buffer.

The H₂ usage presented in figure 8 also follows Equation (3), but in this case $v_{i,j}$ depends on the previous step $v_{i,j-1}$ and $v'_{i,j-1}$, since they modify the available H₂ in the buffer $v_{B,j}$. It should be noted that the x-axis determines the value of $V_{H_2,PtG}$, and the y-axis sets the value of $v_{B,max}$. The following rules shall be satisfied:

$$\begin{aligned}
\text{for } i = H_2 \quad & \begin{cases} v'_{i,j} = 0 & \text{if} & v_{H_2,j} + v_{B,j} \leq 0.6 V_{H_2,PtG} \\ v'_{i,j} = v_{H_2,j} + v_{B,j} & \text{if} & 0.6 V_{H_2,PtG} < v_{H_2,j} + v_{B,j} \leq 4 v_{CO_2,j} \\ v'_{i,j} = 4 v_{CO_2,j} & \text{if} & 4 v_{CO_2,j} < v_{H_2,j} + v_{B,j} \end{cases} \\
\text{for } i = CO_2 \quad & \begin{cases} v'_{i,j} = 0 & \text{if} & v_{H_2,j} + v_{B,j} \leq 0.6 V_{H_2,PtG} \\ v'_{i,j} = (v_{H_2,j} + v_{B,j})/4 & \text{if} & 0.6 V_{H_2,PtG} \leq v_{H_2,j} + v_{B,j} \leq 4 v_{CO_2,j} \\ v'_{i,j} = v_{CO_2,j} & \text{if} & 4 v_{CO_2,j} < v_{H_2,j} + v_{B,j} \end{cases}
\end{aligned}$$

where $v_{B,j}$ depends on the previous step in the following way:

- If the available hydrogen is below the minimum partial load ($v_{H_2,j} + v_{B,j} \leq 0.6 V_{H_2,PtG}$), the produced H_2 is stored

$$\begin{cases} v_{B,j+1} = v_{B,j} + v_{H_2,j} & \text{if } v_{B,j} + v_{H_2,j} < v_{B,max} \\ v_{B,j+1} = v_{B,max} & \text{if } v_{B,max} \leq v_{B,j} + v_{H_2,j} \end{cases}$$

- If the available carbon dioxide is enough to consume all the hydrogen ($0.6 V_{H_2,PtG} < v_{H_2,j} + v_{B,j} \leq 4 v_{CO_2,j}$), the buffer is empty

$$v_{B,j+1} = 0$$

- If the hydrogen is enough to consume all the carbon dioxide, but it is necessary to use part of the buffered hydrogen ($4 v_{CO_2,j} < v_{H_2,j} + v_{B,j}$), the stored H_2 will diminish

$$\begin{cases} v_{B,j+1} = v_{B,j} - (4 v_{CO_2,j} - v_{H_2,j}) & \text{if } 0 < v_{B,j} - (4 v_{CO_2,j} - v_{H_2,j}) \\ v_{B,j+1} = 0 & \text{if } v_{B,j} - (4 v_{CO_2,j} - v_{H_2,j}) \leq 0 \end{cases}$$

- If the produced H_2 during the hour j is enough itself to consume all the CO_2 ($4 v_{CO_2,j} < v_{H_2,j}$), the buffer will store more hydrogen up to its limit

$$\begin{cases} v_{B,j+1} = v_{B,j} + (v_{H_2,j} - 4 v_{CO_2,j}) & \text{if } v_{B,j} + (v_{H_2,j} - 4 v_{CO_2,j}) < v_{B,max} \\ v_{B,j+1} = v_{B,max} & \text{if } v_{B,max} \leq v_{B,j} + (v_{H_2,j} - 4 v_{CO_2,j}) \end{cases}$$

Regarding the operating hours, τ , it is given by Equation 4:

$$\tau = \frac{\sum_j v'_{H_2,j}}{V_{H_2,PtG}} \quad (4)$$

4.2 PtG-Electrochemical hybrid plant

Once methanation plant size was defined, the amine plant was designed according to the CO₂ requirements (496 m³/h (NTP) of CO₂ at nominal output). Table 2 shows the main results obtained from the Aspen Plus simulation of the CO₂ capture plant.

Table 3. CO₂ capture plant simulation results

Absorber	
Design stages	14
Pressure (bar)	1.0
Top stage temperature (°C)	63.5
Bottom stage temperature (°C)	64.3
Reflux ratio	3.9
Boilup ratio	0.3
Stripper	
Design stages	14
Pressure (bar)	1.0
Top stage temperature (°C)	88.9
Bottom stage temperature (°C)	102.8
Reflux ratio	0.4
Boilup ratio	0.15
Reboiler type	Kettle
Thermal energy demand (GJ/t _{CO2})	5.5
CO₂ product characteristics	
Temperature (°C)	34.0
Pressure (bar)	1.0
Volume flow (m ³ /h (NTP))	524.3
Mass flow (kg/h)	997.5
<i>Mass composition (kg/h)</i>	
CO ₂	974.6
H ₂ O	22.8
O ₂	0.002
N ₂	0.087
MEA	-
<i>Mole fraction (%)</i>	
CO ₂	94.6
H ₂ O	5.4
O ₂	3 ppm
N ₂	132 ppm
MEA	-

The CO₂ output from the amine plant meets the requirement of the reactors in the methanation plant. A total gas flow of 524.3 m³/h (NTP) is produced from the stripper with a composition of 94.6 vol% CO₂ and 5.4 vol% H₂O. The total auxiliary consumption of the amine plant (14.2 kW) is much lower than the one in the methanation plant. However, heating and cooling

demands are significant, especially in the reboiler (1494.3 kW) and in the additional solvent cooler (-937.6 kW)

The simulated methanation plant produces 518.6 m³/h (NTP) of SNG mainly composed by 95.2 vol% CH₄ and 4.1 vol.% H₂ (Table 3). The technical data of SNG show that it can be used in typical applications (LHV of 49.8 MJ/kg, density of 0.694 kg/m³(NTP), and Wobbe index of 49.76 MJ/m³). Relevant data of temperature, pressure and flows throughout the methanation plant are presented in Table 4.

The total auxiliary consumption of the methanation plant (513.7 kW) mostly comes from the multi-stage compressors (402.9 kW for H₂, and 105.7 kW for CO₂), while blowers' consumption represents less than 1%. Besides, whenever the plant is operating at full load and simultaneously storing H₂, the hydrogen compressor could require up to 495.6 kW.

Table 4. Molar compositions [%] in the methanation plant.

	H ₂ Inlet	CO ₂ Inlet	R1 Inlet	R1 Outlet	R2 Outlet	R3 Inlet	R3 Outlet	SNG
CO ₂	0.0	94.6	9.9	4.3	1.3	3.0	0.2	0.3
H ₂	100.0	0.0	41.5	19.6	6.2	14.3	3.3	4.1
CH ₄	0.0	0.0	15.5	24.5	30.2	69.7	76.8	95.2
H ₂ O	0.0	5.4	32.8	51.1	62.3	13.0	19.7	0.4
CO	0.0	0.0	0.3	0.5	0.0	0.0	0.0	0.0

Table 5. Temperature, pressure and flows in the methanation plant.

Point	Temperature [°C]	Pressure [bar]	Flow [m ³ /h (NTP)]
1	25.0	1.0	1998.7
2	34.0	1.0	524.3
3	305.2	30.0	1998.7
4	287.4	30.0	524.3
5	300.1	30.0	6879.1

6	582.7	29.7	6050.3
7	300.0	29.7	4356.2
8	301.7	30.0	4356.2
9	300.0	29.7	1694.1
10	250.0	29.7	1694.1
11	414.1	29.4	1572.2
12	136.1	28.8	891.0
13	136.1	28.8	681.2
14	141.1	30.0	681.2
15	250.0	30.0	681.2
16	358.0	29.7	643.2
17	40.0	29.1	124.5
18	40.0	29.1	518.6

The overall cooling and heating needs of the hybrid plant (methanation/carbon capture) are 3675.3 kW and 1533.7 kW, respectively (Table 5). Most of the heat requirement takes place during the desorption stage of the captured CO₂ in the amine plant. Nevertheless, this external heating demand can be suppressed by integrating the streams of both systems (Figure 9, empty-dot exchangers), what concurrently diminishes the cooling needs down to 2141.6 kW. Moreover, there are remaining cooling necessities with high temperature level (R1 outlet), that allows producing 238.8 kg/h of steam at 180 °C for the electrochemical plant; the remainder energy can be cooled with water since the temperatures to reach are not lower than 34 °C (Figure 9, solid-dot exchangers). The minimum temperature difference between hot and cold streams for the design of the exchanger network is 10 °C.

Table 6. Streams of the Pinch Analysis.

	Stream	T _i [°C]	T _f [°C]	ΔQ [kW]
Amine capture plant				
Solvent cooler (A8)	Hot	85.0	37.8	-937.6
Gas cooler (A1)	Hot	175.0	70.0	-238.0
Stripper condenser	Hot	88.9	88.7	-270.4
Flash unit (A13)	Hot	89.0	34.0	-443.8
Reboiler	Cold	120.0	120.5	1494.3

Methanation plant				
R1 outlet (6)	Hot	582.7	300.0	-920.9
R2 inlet (9)	Hot	300.0	250.0	-42.6
R2 outlet (11)	Hot	414.1	136.1	-645.5
R3 inlet (14)	Cold	141.1	250.0	39.4
R3 outlet (16)	Hot	358.1	40.0	-176.5
Electrochemical plant				
Cold water	Cold	20.0	25.0	1939.2
Steam	Cold	50.0	180.0	202.4

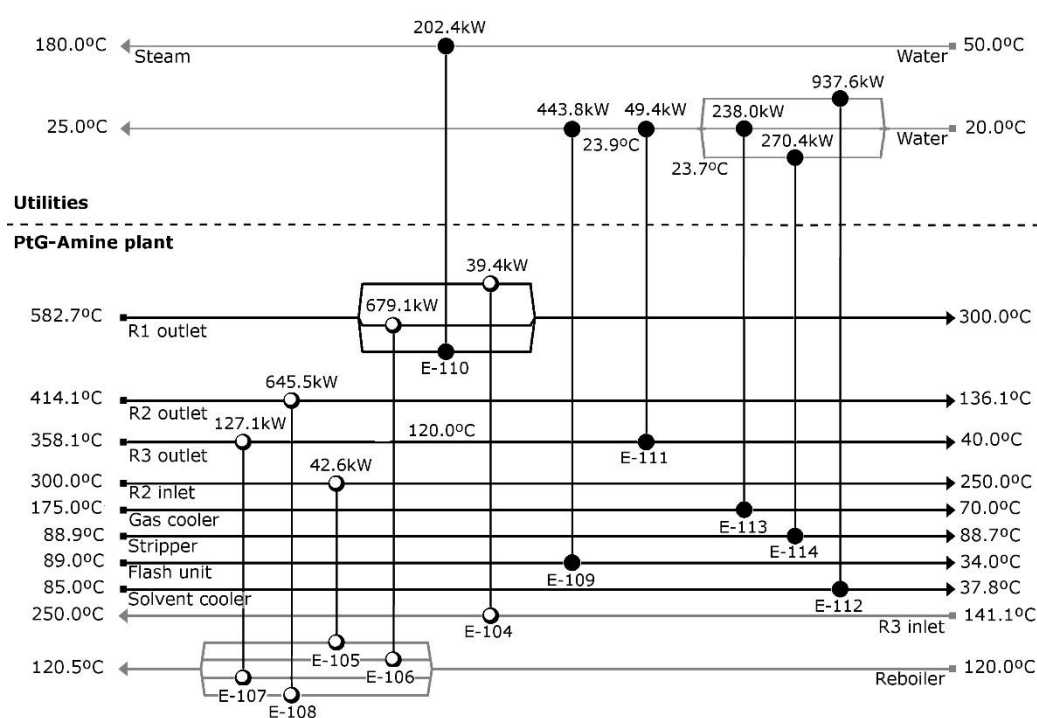


Figure 9. Optimized heat exchanger network (Black lines – Hot streams, Grey lines – Cold streams).

4.3 Economic analysis

To accomplish the economic analysis of the whole facility, the costs of the main equipment for the three processes were obtained: the amine plant, the methanation plant and the optimized heat exchanger network. Then, total capital investment (CAPEX) was completed including other direct and indirect costs as a percentage of the total purchased equipment. Operating cost (OPEX) includes the production costs, which consist of the O&M, electricity,

cooling water, MEA and catalyst renovation. Regarding the economic incomes, two concepts were considered: the Natural Gas (NG) and the additional medium pressure (MP) steam produced in the optimized HEN. This steam is used in the electrochemical industry and hence, can be considered as an input from the network. Meanwhile, natural gas is used in the boiler of the electrochemical plant in order to avoid its purchase from external companies (the selling price would be lower than the purchase price, so thus the income is maximized). The NG price was obtained according to the market (28.99 €/MWh) and the MP steam price was obtained as the NG saving for its generation in conventional gas fired boilers in the baseline scenario (24.64 €/t). Table 6 shows the complete CAPEX and OPEX of the PtG-Electrochemical hybrid plant and the total year incomes of the facility. Some costs regarding the amine plant were included in the HEN disaggregated costs in order not to duplicate equipment costs. Solvent cooler, gas cooler and reflux condenser cooling needs are covered with cooling water and heat exchangers are already included in the HEN (E-112, E-113 and E-114)

Table 7. CAPEX, OPEX and year incomes for the PtG-Electrochemical hybrid plant.

CAPEX				
Direct costs				
Equipment costs				
Reference	Equipment / Process	Cost (€)	Parameter, A	Cost equation (€)
CO2 capture amine plant (Total cost, 523486 €)				
[40]	Amine plant	523486	CO2 captured (t/h)	$26.094 \cdot 10^6 \cdot (A/408)^{0.65}$
Methanation plant (Total cost, 2158644 €)				
[41]	H2 compressor	286978	Power (kW)	$26.7 \cdot 10^4 \cdot (A/445)^{0.67}$
	CO2 compressor	101916		
	Recirculation blower	10390		
	Blower	6150		
[42]	Reactors	1660500	SNG Power (kW)	$300 \cdot A$
[43]	H2 storage tank	50614	H2 (kg, 30bar)	$563 \cdot A$
[41]	Catalyst	42097	Catalyst (m ³)	$187500 \cdot A$
HEN (Total cost, 179642 €)				
Simulation Model	E-108	22992	Area (m ²)	Aspen Energy Analyzer $9016.3 + 721.3 \cdot (A)^{0.8}$
	E-113	45716		
	E-109	13459		
	E-114	9912		
	E-112	14981		
	E-104	10546		
	E-106	14894		
	E-110	11276		
E-111	11822			

	E-105	10135		
	E-107	13908		
Total equipment cost, 2861772 €				
Other direct costs				
[40]	Installation	400648	Total equipment costs (€)	14% · A
	Instrumentation & Control	286177		10% · A
	Piping	457884		16% · A
	Electrical	85853		3% · A
	Building	57235		2% · A
	Land	28618		1% · A
Total direct costs, 4178188 €				
Indirect costs				
[40]	Engineering	292473	Total direct costs (€)	7% · A
	Legal expenses	51387	Total CAPEX (€)	1% · A
	Construction expenses	102774		2% · A
	Contingency	513869		10% · A
Total indirect costs, 960503 €				
Total CAPEX, 5138691 €				
OPEX (€/year)				
[41]	MEA renovation	27679	MEA (t/year)	1520 · A
-	Catalyst renovation	6315	Initial catalyst cost (€)	15% · A
-	Waste management	2000	-	-
[28]	Electricity	25512	kWh	Pricing period
[40]	O&M	154161	Total CAPEX (€)	3% · A
Total OPEX, 215666 €/year				
Incomes (€/year)				
	Natural Gas	976990	SNG (MWh/year)	28.99 (€/MWh) · A
	MP steam	35716	MP steam (t/year)	24.64 (€/t) · A
Total Incomes, 1009706 €/year				
Annual benefit, 794040 €/year				

Considering previous values, total CAPEX of the facility is 5.13 M€, of which 56% correspond with the cost of the equipment. OPEX is about 0.216 M€/year and total incomes are 1 M€/year. To obtain the Net Present Value (NPV), the Internal Rate of Return (IRR) and the Pay-back (PB) of the investment, a 5% discount rate and a 20 years lifetime were considered. Table 7 shows the economic results for the base case and for different discount rates.

Table 8. PB, IRR and NPV evaluation for different discount rate

Discount rate	PB (years)	IRR (%)	NPV (M€)
3.0%	7.3	11.07	6.68
4.0%	7.6	10.00	5.65
5.0%	8.0	8.96	4.76
6.0%	8.4	7.93	3.97

7.0%	8.9	6.92	3.27
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Economic analysis shows positive values that can make attractive the PtG-Electrochemical plant erection. Analyzing the base case scenario (5% of discount rate) it can be observed that capital investment will be recovered in 8 years, generating a 4.8 M€ NPV at the end of the project lifetime with an IRR of 9%. Hence, the present case study avoids the requirement of subsidies to be economically feasible, contrarily to similar PtG research projects that can be found in literature [11]. This is mainly because the H₂ is available in the own industry and no additional water electrolyzers are required. Normally, water electrolyzer represents the highest cost in a PtG facility and it makes very difficult to recover capital investment in a reasonable period of time. Furthermore, the size of the current facility has been carefully chosen after a previous complete analysis of the different processes and taking into account the input gas flows to the methanation plant. In order to extend the economic study, some sensitivity analyses have been performed. Two main parameters were analyzed due to their significant influence on the final revenues of the project: NG price and CO₂ credit price. Firstly, NG price is usually quite unstable and its final value depends on the oil and gas market. In addition, final use of the SNG can be also influenced on the sale price (e.g., transport, gas-fired facilities, NG national network). Regarding CO₂ credit price, there also exists a high uncertainty. Actually, no CO₂ credit revenue has been considered in this study since this particular industry does not have to pay for its emissions. However, if we consider that SNG is fired in the boilers of the chemical facility, CO₂ is always in a loop. It is not emitted since produced CO₂ is the same that is captured and used for SNG production.

In addition, electricity price variation will also have an influence on the cost analysis, especially a change in the pricing system because it will modify not only the OPEX but also the operation hours of the hybrid plant since they directly depend on the billing periods. In

any case, this kind of chemical plants based on electrolyzers follow the same operational procedure and their production depends on the electricity price, working at nominal load when electricity prices are low and diminishing production when electricity prices are higher. This pattern is perfectly adapted to the hybrid concept since it also takes advantage of the lower electricity prices periods when the largest by-production of hydrogen occurs.

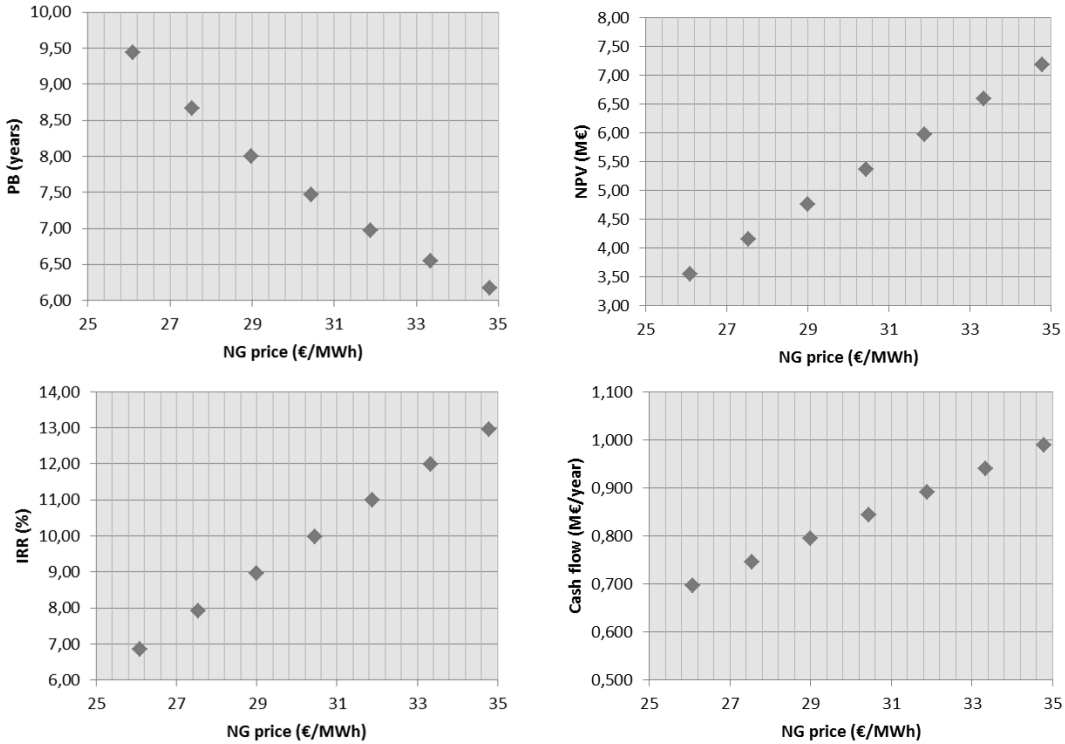


Figure 10. NG price influence on economic parameters

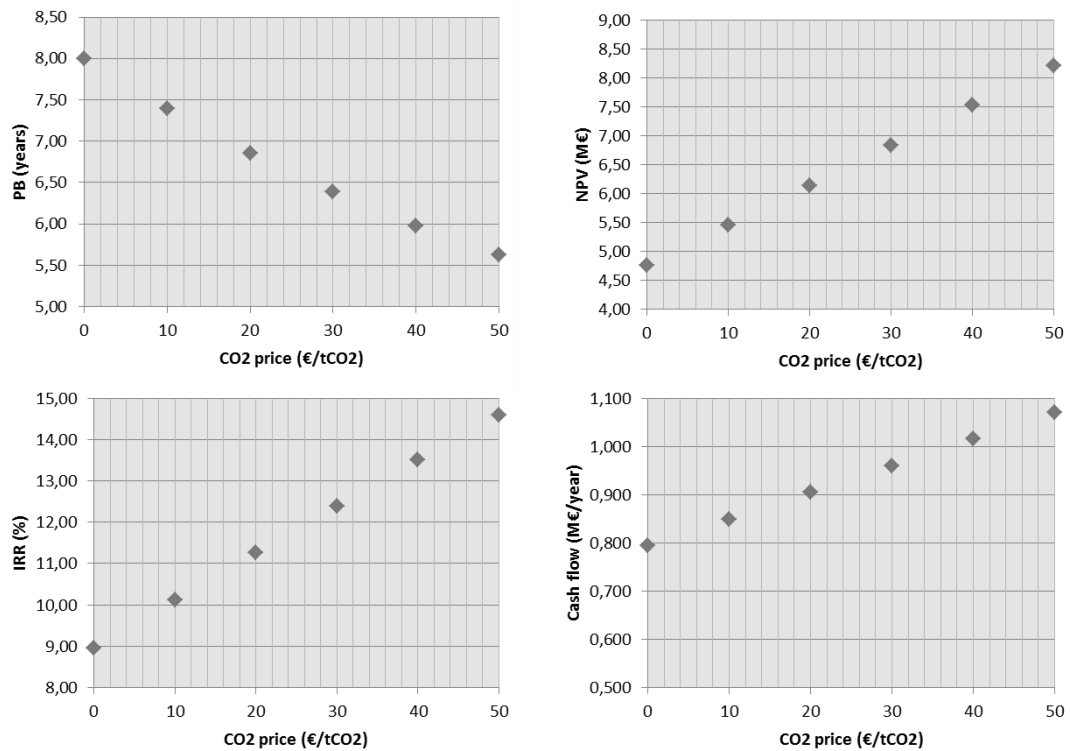


Figure 11. CO₂ credit price influence on economic parameters

Figure 10 and Figure 11 show the influence on economic parameters of both, NG price and CO₂ credit price. The higher NG price is, the more profitable is the investment. It is difficult to predict the evolution of oil and gas fuels, but it is expected a future rise of their prices. For instance, a 15% increase of NG price (from 29 to 33.3 €/MWh) would increase IRR up to 12% with a PB of 6 years and a half achieving very remarkable results for this kind of projects. The case regarding CO₂ credit price is more complex. The lack of a clear regulation or definitive taxes for these singular facilities make difficult to establish a future price. Nevertheless, 30 €/tCO₂ is a reasonable value for making competitive the most CO₂ capture technologies. With this CO₂ credit price, PB is reduced below 6 years and a half and IRR is increased up to 12.4%.

5. Conclusions

We have proposed a novel PtG-Electrochemical hybrid plant that incorporates methanation as a new chemical line of production, thus rising in value substantial amounts of available byproduct hydrogen, and consuming CO₂ emissions from its own gas-fired boilers. The preliminary analysis shows that the products yielding lower profits, like ammonia, are the most suitable to be substituted. The analysis has been carried out using real operating data of an electrochemical factory.

This work shows that PtG-Electrochemical hybrid plant is technical and economically feasible. The plant can be running more than 6000 hours per year consuming more than the 85% of available hydrogen and almost 60% of the CO₂ emitted by the chemical industry. The hybrid plant can achieve a production of 518.5 m³/h (NTP) of SNG and additionally 238 kg/h of MP steam that are used in the industry itself. Since no additional water electrolyzers and consequently, no further electricity consumption is required, economic analysis yield very remarkable figures. Analyzing the base case scenario (5% discount rate) it can be observed that capital investment will be recovered in 8 years, generating a 4.8 M€ NPV at the end of the project lifetime with an IRR of 9%. Moreover, sensitivity analyses have also shown that these values can be even better if CO₂ credit price or NG price increase in a near term.

Although this is a particular case study, some conclusions can be generalized with the aim of speeding up the deployment of PtG at industrial scale. The present PtG-Electrochemical hybrid technology can overcome the economic barriers of erecting a commercial plant, thus allowing gaining operational experience concerning methanation reactors and their performance with variable H₂ and CO₂ flows. In addition, it is expected that equipment cost can be reduced in a future and this reduction could be achieved faster with more industrial scale facilities.

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Nomenclature

Variable	Units	Description
α_i	%	Usage of resource i
$v_{B,j}$	m^3 (NTP)	Amount of H_2 that is present in the buffer at the beginning of hour j
$v_{B,max}$	m^3 (NTP)	Maximum capacity of the H_2 buffer
$v_{i,j}$	m^3 (NTP)	Available amount of resource i at hour j
$v'_{i,j}$	m^3 (NTP)	Used amount of resource i at hour j
$V_{H_2,PtG}$	m^3 (NTP)	Nominal hourly input of the methanation plant
$\dot{V}_{H_2,ammonia}$	$m^3 \cdot h^{-1}$ (NTP)	H_2 by-production destined to ammonia line
\dot{V}_{H_2}	$m^3 \cdot h^{-1}$ (NTP)	H_2 by-production
η		Efficiency of the electrolysis
τ	h	Operating hours of the methanation plant
NPV	€	Net Present Value
IRR	%	Internal Rate of Return
PB	years	Pay-back

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