

Design configurations to achieve an effective CO₂ use and mitigation through Power to Gas

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Abstract

Power to gas energy storage is usually conceived as a carbon utilisation technology, as it consumes CO₂ for the production of synthetic fuels. However, some authors put in doubt its potential for mitigating global warming, since CO₂ is released to the atmosphere when the synthetic fuel is used. In this paper, we demonstrate that power to gas can be an effective mitigation option under certain design configurations. When synthetic fuels are used in the same installation where the CO₂ is captured (industry or power plant) then CO₂ could be effectively recycled. This “CO₂ recycle concept” allows the use of renewable energy to satisfy thermal demands of industry or other sectors avoiding carbon emissions. This proposal is useful for decarbonising industrial processes based on fossil-fuels that cannot be decarbonised by direct renewable electrification. The paper provides key aspects to define a catalytic power-to-gas system where the CO₂ is captured (through amine scrubbing or oxyfuel technology) and recycled. It analyses system efficiency, overall emissions and economic feasibility of the concept.

Keywords:

CCU; Power-to-Gas; Carbon capture; Global warming; oxyfuel.

Nomenclature

AC	CO ₂ Avoided Cost	E	Electrolyser
B	Boiler	FCF	Fixed Charge Factor
C	Cost	Oxy-PtG	Oxyfuel boiler and PtG
CF	Capacity Factor	PtF	Power-to-Fuels
CCS	Carbon Capture and Storage	PtG	Power-to-Gas
CCU	Carbon Capture and Utilization	LCA	Life Cycle Analysis
COE	Cost of Electricity	SNG	Synthetic Natural Gas

1. INTRODUCTION

Despite the efforts and developments made by the scientific community in the field of carbon capture and storage (CCS) the technology has not been fully deployed. The lack of global legislation and international agreements has delayed the implementation of this technology to fight against global warming. This fact, together with the urgent environmental concern, has stimulated the research about carbon capture and utilization technologies (CCU) to avoid or reduce the carbon storage necessities and relaunch carbon capture as a feasible option for global warming mitigation.

Considering the huge quantities of CO₂ that are needed to be captured and used, carbon utilization technology is in its earlier stages. In recent years, there have been several proposals to use carbon as precursor in fuel synthetization through electricity [1][2][3]. These processes, denoted as power-to-gas (hydrogen, synthetic methane) or power-to-liquid (diesel, gasoline, jet fuel), are conceived as energy storage technologies in future scenarios in which renewable energy sources are fully deployed [4][5]. In power-to-hydrogen, excess grid electricity is converted to hydrogen through electrolyzers. If hydrogen is used together with CO₂ in a methanation reactor, synthetic methane could be obtained. Other chemical reactions could be used to obtain liquid synthetic fuels through H₂ and CO₂.

However, the effective recycling of this CCU method has been recently called into question by several authors in literature [6][7]. These authors demonstrated the limited mitigation potential of using significant amounts of primary energy both to capture CO₂ from flue gases and to produce synthetic fuels. The main concern is the emission of the captured CO₂ into the atmosphere when the fuel is used. Instead, they promote the underground storage of CO₂ to completely avoid emissions. Other works [8][9] claims that PtG and Pt-Syngas could achieve lower Global Warming impact than fossil-fuel based processes, even if CO₂ was supplied by a coal-fired power plant. This question is not currently solved. Even, in the EU Directive 2015/652 [10] it is not clear if greenhouse gas intensities of methanation reaction with non-renewable energy electrolysis is 3.3 or 12.4 gCO₂-eq/MJ [11].

The use of CO₂ for producing synthetic fuels is controversial. One approach believes that producing fuels from captured CO₂ neglects the primary goal of carbon

sequestration [12]. There is not CO₂ utilization as CO₂ emissions are not really avoided [12][13]. This is the case of synthetic fuels used in decentralized applications that release CO₂ again to the atmosphere. Other approach has tried to support with data the Global Warming impact of PtG and PtF. Life Cycle Analysis (LCA) has been presented in recent years to quantify the Global Warming Impact and Primary Energy Demand [8][9][13][14][15][16] but initial assumptions and functional units vary in each analysis. One common conclusion of LCA is that the impact and environmental performance of PtG or PtF strongly depends on the electricity generation source for the electrolyser that generates the hydrogen [8][9][14][15][16]. The threshold of emitted CO₂ per kWh to consider improvements compared with current situation is very challenging. Values about 72-113 gr CO₂-eq/kWh [8] or 48-82 gr CO₂-eq/kWh [9] have been calculated. Even in a practical case in Canada, only electricity with impact below 50 gr CO₂-eq/kWh was considered sustainable for H₂ production through electrolysis [16].

In general, these limited numbers of papers with PtG carbon balance [14], agree in relatively low energy necessities for CO₂ capture compared with H₂ production [8]. However, when the impacts in Global Warming and CO₂ emissions are calculated, those values are larger than the H₂ production. This is due to the assumption that H₂ is produced by renewable energy, and energy necessities for CO₂ capture are supplied by additional fuel without carbon capture [8][9][14][15]. In this literature, the energy for CO₂ separation is usually produced in a fossil fuel power plant with: (i) outdated solvents; (ii) high separation necessities, (iii) low energy integration [8][9][14]; (iv) lack of integration between methanation and CO₂ capture and, in some cases, (v) with additional combustion without CO₂ capture. All of these reasons increase the negative impacts of carbon capture in PtG. Only in a limited number of works [11][14][17] the energy from the methanation is used for carbon capture. Based on calculations, it is assumed that between 60 and 79% of the catalytic methanation heat could be recoverable for carbon capture [14][17][18][19]. It would contribute to reduce the global impact and CO₂ emissions of PtG application. Moreover, the consideration of using a boiler and not a power plant to provide the CO₂ for methanation is also lack in literature.

Our proposal is that CO₂ from fossil-fuel power plants should be stored underground providing real carbon mitigation. CO₂ from smaller sources than power plants should be used for PtG applications and energy storage. It is related with the recommendation of using H₂/CH₄ in industry or mobility rather than to produce power again [8] that increase the energy penalization

Other novelty of our work is to consider the integration of carbon capture and methanation, avoiding the use of power plants as CO₂ source after demonstrating the unfeasibility of using the CO₂ from these installations for catalytic PtG. It may justify the interest of industry (boilers) and biogas plants for PtG have previously demonstrated.

Finally, only a few works consider the multiple reuses of CO₂ [11][20]. That means the utilization of the fuel produced in the same installation to capture again the CO₂ produced in the fuel combustion. With this idea, the impact in Global Warming and CO₂ emissions reduces up to 70% when renewable electricity surpluses are used for H₂ generation. It is even possible to obtain a near complete carbon recirculation if direct air CO₂ capture is used to supply the lack of CO₂ in carbon capture [11].

The use of other options for CO₂ capture and its integration in PtG systems is lack in literature. Oxyfuel technology has only been considered in a limited number of works [21][22][23][24][25][26]. It has a potential interest as oxygen, that is a by-product of electrolysis, is used in the boiler and avoid the CO₂ capture energy penalization. The energy integration of and oxyfuel boiler (CO₂ capture) and a methanation reactor avoids the necessity of additional combustion without carbon capture and it will reduce the CO₂ emissions of PtG. If there is reutilization of synthetic fuel in the same industry it will make possible a complete carbon sequestration with low environmental impact. This should be done in relatively small installations to avoid large investments and provide real carbon sequestration.

This is the aim of this work, to demonstrate that catalytic power to gas can be an effective mitigation option under configuration with a closed CO₂ generation and utilization loop. Based on a theoretical and rigorous approach the proposed design configurations allow a technical and, under some hypothesis, economic feasibility of power to gas with near zero or negative CO₂ emissions. To demonstrate this goal

several assumptions has been made: (i) the utilization of amine scrubbing or oxyfuel technologies (using oxygen from electrolysis) for CO₂ capture applied to boilers and not to power plants; (ii) the proposal of energy integration to use methanation heat to supply thermal energy to the CO₂ capture or industrial processes; (iii) the proposal of multiple reuses of CO₂ using the synthetic fuel in a centralized application (industry) with associated CO₂ capture and (iv) using renewable energy or electricity surpluses to produce hydrogen in the electrolyser.

2. POWER-TO-GAS AND CARBON CAPTURE AND UTILIZATION

There are four main variables that define the role of catalytic PtG as a CCU technology: (i) the quantity of CO₂ to process; (ii) the efficiency of energy storage; (iii) the end-use of the synthetic fuel and (iv) the water demand. These variables constrain the implementation of PtG processes to a limited, but very interesting, number of designs, dimensions and applications.

2.1. QUANTITY OF CO₂ TO PROCESS

It is necessary to take in mind the order of magnitude of CO₂ emissions when applying CCU in coal or natural gas power plants. Table 1 shows the yearly CO₂ emissions for two different coal and natural gas power plants depending on power plant efficiency (specific CO₂ emissions) and full load operational hours per year. These data are approximate and conservative. Part loads, start-up and shut-downs have not been considered and they reduce power plant efficiencies and increase specific and global emissions. In any case, the CO₂ production rate is in the range of hundred thousand tons per year. If 90% of carbon emissions are captured, quantities remain too large to be processed. Especially if several power units are running in the same installation, as these figures are for only one coal or natural gas power plant.

Table 1. Yearly CO₂ emissions for two different coal and natural gas power plants depending on power plant efficiency

	Carbon emissions (tCO ₂ /y)			
	Operational hours (h/y)			
	2000	4000	6000	8000
Coal power plant (500 MWe) 900 kgCO₂/MWh	900,000	1,800,000	2,700,000	3,600,000
Coal power plant (500 MWe) 800 kgCO₂/MWh	800,000	1,600,000	2,400,000	3,200,000
NG combined cycle (400 MWe) 500 kgCO₂/MWh	400,000	800,000	1,200,000	1,600,000
NG combined cycle (400 MWe) 400 kgCO₂/MWh	320,000	640,000	960,000	1,280,000

For example, if power-to-methane is proposed as an alternative to use this CO₂, the required hydrogen for the Sabatier's reaction should be firstly put in context. Table 2 shows the hydrogen needed to produce synthetic methane consuming the hourly CO₂ emissions rates, assuming stoichiometric reaction (i.e., 5.5 kgCO₂/kgH₂) to produce synthetic methane. Table also shows the required power supply for the electrolyser, assuming an electrolyser efficiency of 70% and a LHV of 120 MJ/kgH₂. This lead to power capacities of electrolysis between 1 and 4 GW, showing that is unlikely to be feasible to use PtG to mitigate CO₂ at large scale. These calculations show that if electrolyser is running at the same time that power plant, the power provided to the electrolysis process should be 3.5 to 7.8 times greater than the power produced in the power plant, and such quantities of electricity surplus should be available (for every power plant). In case of reducing the electrolysis power capacity it is necessary to increase its operational hours above the power plant's hours. Moreover, it would be required an excessively large CO₂ storage to perform methanation according to the hydrogen availability. In the case of coal power plants, if electrolyser size is reduced to around 345 to 389 MW (10% of the initial power requirements) the operational hours of the power plant have to be reduced in the same magnitude. That means a low power plant capacity factor if the electrolyser operated with surplus renewable energy or low price electricity. In any case it does not seem reasonable to use power to gas for CCU at large scale power plants. For example, in an analysis of the future role of PtG in the energy transition of a German region, the required energy input to use the yearly total amount of CO₂ from fossil fuel power plants amounts 114-184 TWh_{el} that was twice the final electricity consumption in the region [17]. These figures highlight the

conclusion that is not reasonable to use CO₂ captured in power plants to run PtG systems.

It has more sense to reduce the size of the system (for biogas applications or industry) and try to use a relatively small quantity of CO₂ emissions for PtG. In this case: the renewable energy surplus is affordable; the size of the PtG system would be technically feasible; it would lead to the utilization of the CO₂ (depending on the design an avoided CO₂ emissions as it will be shown later); and energy storage is a feasible alternative.

Considering specific emissions of 330 kgCO₂/MWh_{th} in a coal-fired boiler (equivalent to 900 kgCO₂/MWh in a power plant), a CO₂ removal efficiency of 90% and 5.5 kgCO₂/kgH₂ needed for methanation, the necessity of hydrogen would be 54 kgH₂/MWh_{th}. The energy to produce this hydrogen is 2.57 MWh_e/MWh_{th}. As the biggest electrolyser plant planned at present has a power capacity of 100 MW_e [27], the maximum size of the coal-fired boiler from which CO₂ is captured should be around 39 MWh_{th}. This conclusion has already stated in previous detailed studies [28], which proposed industry applications as the upper-limit case for PtF. If natural gas, with specific emissions of 200 kgCO₂/MWh_{th}, is used instead of coal the electricity consumption required is 1.56 MWh_e per MWh_{th} produced in the boiler.

Table 2. Hourly CO₂ emissions rates for two different coal and natural gas power plants and hydrogen needed for PtG

	Hourly carbon emissions (t/h)	H ₂ needed for PtG (t/h)	Renewable power to produce H ₂ (MW)
Coal power plant (500 MW _e) 900 kgCO ₂ /MWh	450	81.8	3896.1
Coal power plant (500 MW _e) 800 kgCO ₂ /MWh	400	72.7	3463.2
NG combined cycle (400 MW _e) 500 kgCO ₂ /MWh	200	36.4	1731.6
NG combined cycle (400 MW _e) 400 kgCO ₂ /MWh	160	29.1	1385.3

The first conclusion about the size of the PtG system for CCU is that if both system run simultaneously, the electricity consumption of the PtG system should be in the range of 2.5 MWh_e/MWh_{th} or 1.5 MWh_e/MWh_{th} depending on the fuel used for carbon emissions. Evidently, the power to gas installation will have smaller power capacities,

but operational hours would be larger than the operating hours of the CO₂ emitter installation. This idea, to find a balance between size and full load hours, has been previously reported [14]. A suitable application in which PtG could act as CCU technology is the production of biogas in gasification plants [29][30][31][32] which are within the range previously proposed or in industry or mobility sector [8].

2.2. EFFICIENCY OF ENERGY STORAGE

From an energetic point of view, 171.4 MJ/kgH₂ are necessary to produce 1 kgH₂ in an electrolyser with an efficiency of 70%. This energy should be covered with renewable energy to use green-H₂ for PtG. To this consumption it should be added the energy required for carbon capture, since CO₂ is consumed in methanation. Considering amine scrubbing with heat necessities of 3 - 4 GJ/tCO₂ in the regenerator [11][33][34][35], and assuming that 5.5 kgCO₂ are consumed per kgH₂, the energy requirement for carbon capture is about 16.5 - 22.0 MJ/kgH₂. It represents a 13% of the electrolyser consumption as much, and it is required in the form of heat instead of electricity, so its impact in the overall efficiency is limited. This result proves that CCS is not the most relevant energy consumption in PtG. Moreover, the heat released in the methanation exothermic reaction can be used to provide this heat requirement to the carbon capture process, thus minimizing or avoiding the energy penalisation. Some methanation plant configurations may produce up to 34.8 MJ/kgH₂ of useful heat for district heating [28], what is in the range of the energy necessities for amine regeneration. Amine scrubbing is the most preferred technology to produce CO₂ for Power to Gas processes [36][37][38], and the energy requirements for CCS are at lower temperature (110-120 °C) [33] than methanation's available temperatures (>250-300°C) [11][39].

As the LHV of methane is 50 MJ/kgCH₄, and 2 kgCH₄ are produced per kgH₂ (complete conversion), the chemical energy stored is 100 MJ/kgH₂. Then, the efficiency of the energy storage (electricity to SNG) may range between 44.7% and 58.3% depending on the energy requirements considered for carbon capture and the available heat from methanation. The minimum value corresponds to a situation in which 22 MJ/kgH₂ have to be provided to the carbon capture process, and this cannot be covered with the

heat coming from methanation. In that case, we assume that the thermal requirements are covered consuming part of the SNG in a boiler with a 94% thermal efficiency (Eq. 1).

$$\eta_{st,min} = \frac{\text{energy stored} - \frac{\text{available methanation heat}}{\text{efficiency of utilization}}}{\text{renewable energy input}} = \frac{100 \left[\frac{\text{MJ}}{\text{kgH}_2} \right] - \frac{22 \left[\frac{\text{MJ}}{\text{kgH}_2} \right]}{0.94 [-]}}{171.4 \left[\frac{\text{MJ}}{\text{kgH}_2} \right]} \quad (1)$$

The maximum efficiency corresponds to the case in which there is no energy penalisation coming from the carbon capture process (second addend in the numerator of the right side of Equation 1 vanishes). This may take place when the available heat from methanation is enough to satisfy the thermal energy requirements, or when it is used biogas as CO₂ source for methanation. In any case, these efficiencies are in the range of other energy storage alternatives [40], with the advantage that PtG is the only technology without limitation in quantity of stored energy or duration of the storage.

2.3. END-USE OF SYNTHETIC FUEL

The consideration of PtG as technology for CCU depends on the design and the use of final synthetic fuel. Generally, in literature, power to gas is considered as a valid CCU technology that uses hydrogen coming from renewable electricity [41][42] (green H₂) and this is positive advantage of the PtG technology. However, some authors have recently called into question this concept, as CO₂ is released to the atmosphere when the synthetic fuel is consumed, thus limiting the mitigation potential [6][7]. Besides, the additional energy consumed to capture the CO₂ (prior the methanation process) becomes meaningless in practice, since emissions are not avoided. Only in scenarios with a very high renewable energy penetration there may be a reduction in CO₂ emissions when applying PtG as CCU within the industry sector.

When CO₂ originally comes from a fossil source, and SNG is used in decentralized applications, there is a net carbon emission to the atmosphere (Fig. 1a). The only advantage of this overall scheme is that renewable electricity that would otherwise

have been curtailed can be used. If biomass is used as primary energy input instead fossil fuels (Fig. 1b), then it is clear that CO₂ emissions are neutral in the overall (renewable) concept.

If SNG is used in the same or other centralised emitting source from which CO₂ is captured (industry or power plant), then CO₂ is really recycled (Fig. 1c). It acts, thanks to the hydrogen, as an “energy carrier” of the system. This is called multiple reuses [11]. Thus, the consideration of power to gas as a valid technology for CCU depends on the overall design and the end-use of the synthetic methane. Several positive aspects can be highlighted in the latter case:

1. The use of primary fossil fuel is reduced close to zero, so there is an important CO₂ emissions reduction (avoided emissions).
2. CO₂ is constantly recirculated and it is not released to the atmosphere.
3. The whole system mainly works with renewable energy. There is a small fossil (carbon) contribution due to the impossibility (economical) of capturing 100% CO₂.

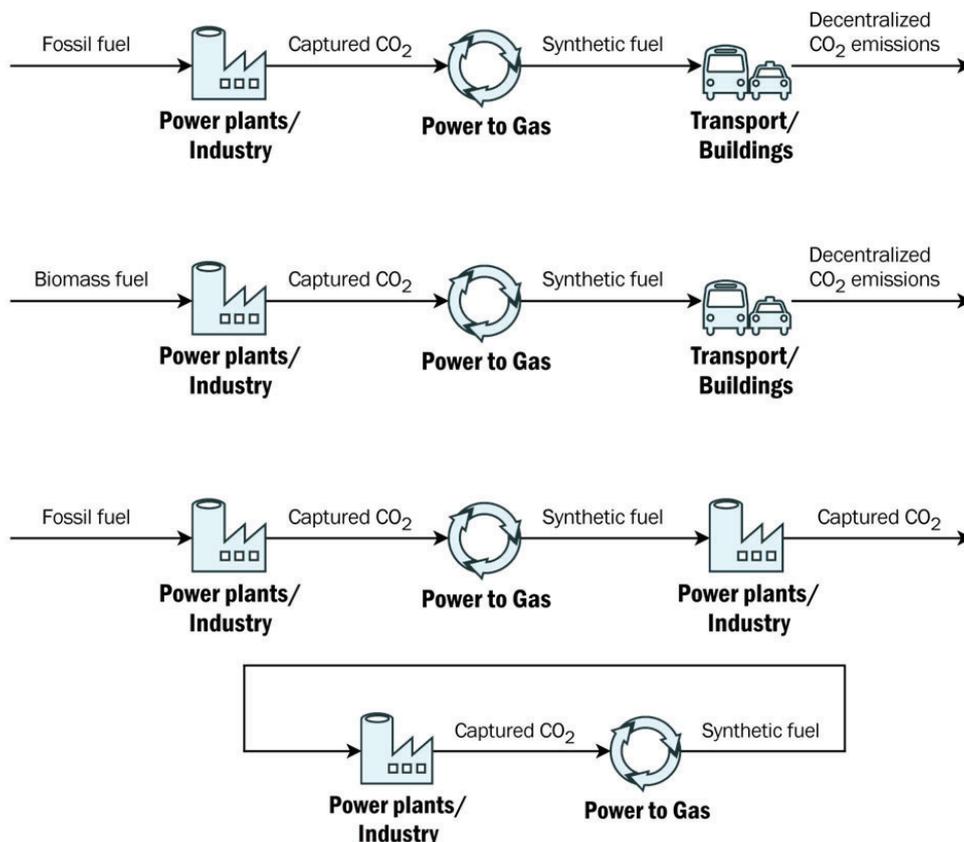


Figure 1. Power to Gas and carbon net emissions relationship

Several authors have also proposed the concept of CO₂ cycle based on power to gas systems [11][20][43][44]. This is the only concept with which it is possible to avoid CO₂ emissions, store energy and use PtG in an efficient, environmental and economic feasible way. It should be noted that under this configuration the SNG is not sold but used for self-consumption. The saving of purchasing fuel may lead to feasible business models, as already showed in the chemical industry [36].

This reveals that some previous analysis [6] although right, do not consider all the possibilities of PtG. This “recycling CO₂ concept” for PtG applications allows the use of renewable energy to satisfy thermal demands of industry or other sectors avoiding carbon emissions. This proposal is useful for global warming mitigation and for the deployment of renewable energy and green hydrogen.

2.4. WATER UTILIZATION.

Regarding water demand, it is necessary (at least) 4 mol H₂O to obtain 4 mol H₂ through electrolysis, which are required to produce 1 mol CH₄ through methanation. Assuming, optimistically, that water from methanation is recovered completely, the water necessities reduce to 2 mol H₂O per mol CH₄. So, 36 kgH₂O are required to produce 16 kgCH₄. The energy content (LHV) of this SNG produced is around 800 MJ (16*50 MJ/kg). So, between 0.05 and 0.08 [16] kgH₂O are needed per MJ of energy produced. For a PtG plant with 100 MW_e of electrolysis it would be required 2.9 kgH₂O/s. It is not a limitation but it should be considered when designing an installation. If it is possible to recover H₂O from combustion of CH₄ in a condensing boiler for example, a near-zero H₂O necessities could be achieved.

3. ENERGY BALANCES AND AVOIDED EMISSIONS WITH CO₂ RECYCLING PTG.

There are several potential synthetic fuels that can be produced through PtG and power-to-liquids. Table 3 shows some of these fuels, together with their energy content (LHV) per kg, mole, and emitted CO₂. Methanol and natural gas are the fuels with higher energy content per carbon emissions. Besides, natural gas has a 10%

higher energy content per mole of CO₂ produced than methanol. Thus, methane is selected as the preferred synthetic fuel for the calculations in this section.

Table 3. Main potential synthetic fuels and their energy contents.

Substance	Formula	kJ/kg	kJ/kmol	kJ/kmol CO ₂
Methane	CH ₄ (g)	50,000	800,000	800,000
Ethane	C ₂ H ₆ (g)	47,800	1,434,000	717,000
Propane	C ₃ H ₈ (g)	46,360	2,039,840	679,947
Butane	C ₄ H ₁₀ (g)	45,750	2,653,500	663,375
Pentane	C ₅ H ₁₂ (g)	45,360	3,265,920	653,184
Octane	C ₈ H ₁₈ (g)	44,430	5,065,020	633,128
Methanol	CH ₃ OH(g)	22,700	726,400	726,400
Ethanol	C ₂ H ₅ OH(g)	29,700	1,366,200	683,100

3.1. REFERENCE CASE

In Figure 2 the reference case is illustrated for future comparisons. Here, 1 kg of methane (LHV 50 MJ/kgCH₄) is used as energy input. Assuming 94% boiler efficiency, there are 47 MJ to be used as thermal energy in industrial processes per kgCH₄. The carbon emissions of the methane consumed are 2.74 kgCO₂ if complete combustion is assumed. Table 4 details the main assumption in these calculations.

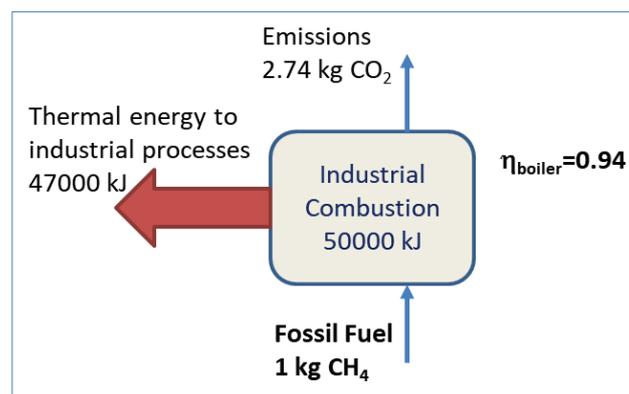


Figure 2. Reference case to analyse PtG systems.

3.2. CONVENTIONAL POWER TO GAS WITH AMINE CARBON CAPTURE

Figure 3 shows a complete catalytic PtG process, in which the thermal energy output of the boiler is kept at 47000 kJ for comparison purposes.

Carbon capture system needs thermal energy for amine regeneration. This requirement has been assumed in 3 GJ/tCO₂, so 7.41 MJ are needed. This energy is supplied by an additional CH₄ consumption of 0.148 kgCH₄. The carbon emission of this additional fuel consumption, together with the emissions of the boiler, totalized 2.469+0.681=3.150 kgCO₂. If 90% carbon capture efficiency is assumed in the boiler, 2.469 kg CO₂ are sent to the methanation, releasing the remaining to the atmosphere (the 10% not captured, 0.274 kgCO₂, and the CO₂ from the extra fuel consumption, 0.407 kgCO₂).

Assuming stoichiometric methanation, 5.5 kgCO₂ are required per kgH₂. Therefore, 0.449 kgH₂ are necessary for the 2.469 kgCO₂ that are directed to the methanation process. Methanation reaction combines CO₂ and H₂ producing 0.898 kgCH₄ and 8.696 MJ of exothermal energy. Assuming an electrolyser efficiency of 70%, 76.94 MJ of renewable electricity is required for the production of the hydrogen. Additionally, there is an oxygen production of about 3.590 kgO₂.

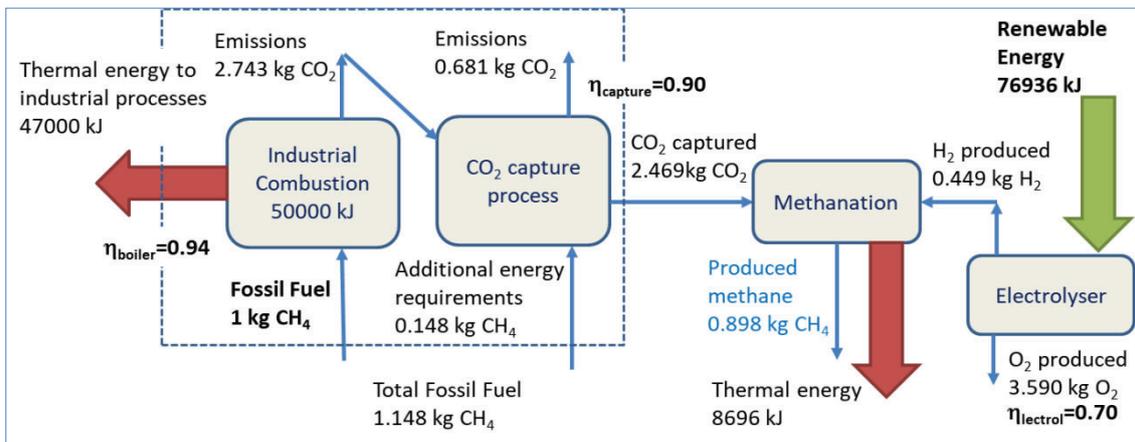


Figure 3. Conventional PtG with amine carbon capture used in industrial processes.

Table 4. Main assumptions for energy calculations of catalytic power to gas systems.

Main assumptions	
Main boiler efficiency	94%
CO ₂ carbon capture efficiency	90%
Heat duty in regenerator (CO ₂ capture)	3 GJ/tCO ₂
Electrolyser efficiency	70%
Heat from methanation reaction	3.75 MJ/kgCO ₂
Efficiency of heat from methanation	94%

Excess oxygen in oxyfuel combustion	1.05
ASU requirement	200 kWh/tO ₂

It is evident that, if the synthetic methane is used in decentralized applications, the 2.469 kgCO₂ captured will be emitted to the atmosphere (Fig. 3) with a thermal efficiency that will depend on the utilization. The input energy includes the natural gas (57.4 MJ) and the renewable energy (76.9 MJ), totalising 134.3 MJ. The energy output is the thermal energy from the boiler (47 MJ) plus the energy from methanation reaction and the energy demand satisfied with the SNG produced. Detailed energy calculation depends on the end-use of SNG (44.9 MJ) and the efficiency of recovering the heat from methanation (8.7 MJ). In the latter, it is expected a high efficiency as the energy is released at constant temperature about 300°C. However, the use of SNG opens a wide range of possibilities. In the ideal case (efficiency equals to 1 in SNG consumption), the maximum overall efficiency of the scheme (Fig. 3) would be 74.9%, with global CO₂ emissions amounting to 3.024 kgCO₂. This means 30.06 gr CO₂ per MJ used. It should be noted that efficiency is electrical plus chemical to heat.

3.3. CO₂ RECYCLING POWER TO GAS WITH AMINE CARBON CAPTURE

Figure 4 shows the case of recycling the carbon emissions into SNG, to be later used as primary fuel in the original boiler. Moreover, the methanation heat (9.4 MJ) is used in the carbon capture process (8.0 MJ) reducing and avoiding additional input energy required. Under the same assumptions, the methane production of 0.968 kgCO₂ is recirculated and it is only necessary to add 0.108 kgCH₄ to compensate carbon capture losses (capture efficiency 90%). As there is not additional fuel in the carbon capture, the emissions are reduced compared with the previous case. The electricity from renewable sources has increased due to the augmentation of the carbon emissions captured up to 82.9 MJ. In this case it is necessary 0.484 kgH₂.

Input energy to the system includes the natural gas (5.4 MJ) to compensate carbon losses in the capture equipment and the renewable energy (82.9 MJ) and totalises 88.3 MJ. Energy output is the thermal energy form boiler (47 MJ) that includes the excess energy from methanation. Overall efficiency in this case is 53.2% but the fossil fuel necessities has decreased from 1.148 to 0.108 kg and global carbon emissions drop

from 3.024 kgCO₂ to 0.296 kgCO₂ that represents 6.30 gr CO₂ per MJ used. Efficiency could be improved up to 54.8% if excess energy from methanation to stripper could be used in other processes.

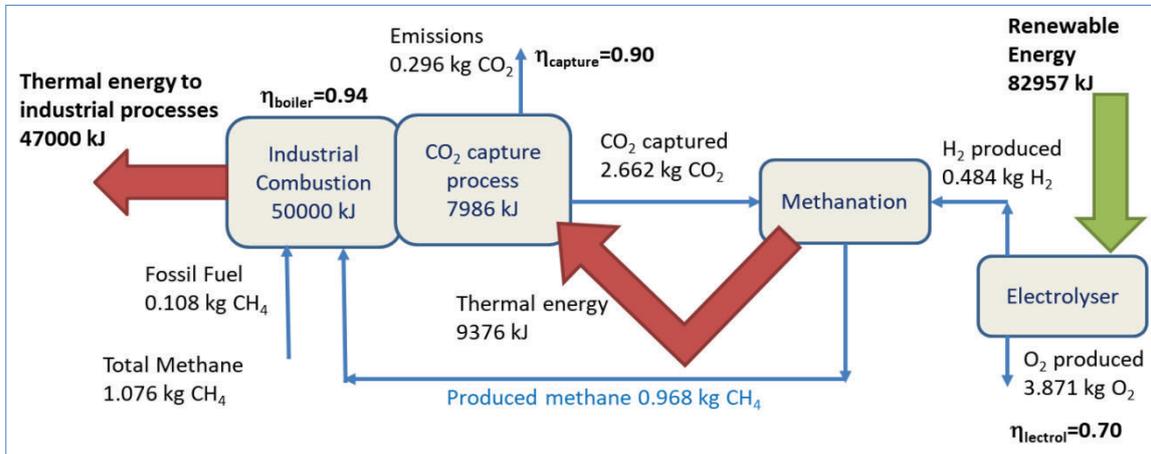


Figure 4. CO₂ recycling PtG with amine carbon capture used in industrial processes.

3.4. CO₂ RECYCLING POWER TO GAS WITH OXY-FUEL COMBUSTION

There is another option of carbon capture that leads to better energy results. In the case of oxy-fuel technology, the energy penalisation of carbon capture comes from the air separation unit (ASU) and the CO₂ compression to 110 bar for CO₂ transportation and storage. In a power plant, the ASU may lead to a loss around 6 percentage points (consumption ranges from 160 to 220 kWh/tO₂ [45][46][47]), while the CO₂ compression to 3 percentage points. In PtG applications, there is not compression stage for the CO₂, since it is used in the methanation reactor. Besides, the electrolyser by-produces O₂, so the ASU becomes unnecessary. Taking advantage of the O₂ from the electrolyser and designing an oxy-fuel boiler to satisfy thermal demands [24], the penalty caused by carbon capture is reduce practically to zero. In addition, the heat from exothermic methanation reaction can be used to satisfy process necessities and reduce natural gas input energy. The integration of catalytic PtG and oxy-fuel boilers (oxy-PtG) has been previously proposed [24][28][48][21][49] and represent the most interesting option if thermal demands are required.

In Fig. 5, the oxy-fuel power to gas system is presented. There is a small additional requirement for O₂ of about 0.165 kg of a total of 3.474 kg. It represents the 5%, due

to the 90% carbon capture efficiency. It is assumed an ASU specific consumption of 200 kWh/tO₂, so the energy requirement (electricity from renewable source) is 119 kJ. Also, in this case the thermal energy from methanation is used in the oxy-fuel boiler to reduce the primary natural gas consumption. As a results, the use of natural gas input is reduced to 0.092 kgCH₄, which is mixed with the recycled SNG (0.827 kgCH₄) to deliver 47 MJ in a 94% efficiency oxy-fuel boiler. The CO₂ produced is 2.528 kgCO₂, which is lower than in previous cases as the fuel consumption has diminished. With the assumption of 90% capture efficiency, 0.253 kgCO₂ are emitted and 2.275 kgCO₂ are used in the methanation stage. The CO₂ sent to the methanation has decreases in comparison with previous cases and less H₂ (0.414 kgH₂) is required from renewable sources. In this case the renewable electricity necessities are 71.0 MJ. In summary, the energy input amounts to 75.6 MJ and the energy output to 47 MJ, leading to an overall efficiency of 62.2%, including the boiler. Specific CO₂ emissions are 5.38 gr CO₂ per MJ produced in the boiler.

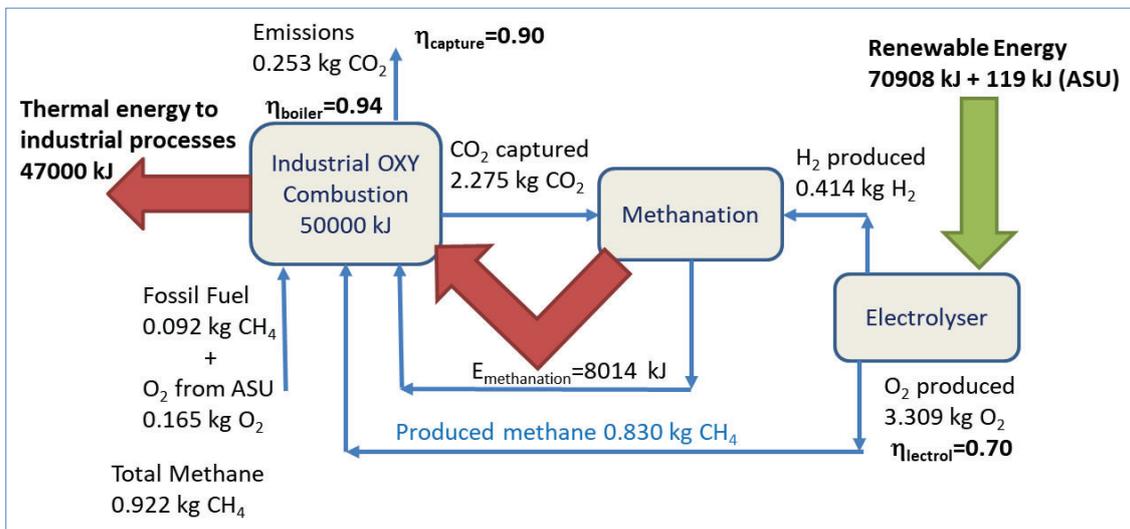


Figure 5. CO₂ recycling PtG with oxy-fuel combustion used in industrial processes.

Table 5 compares main variables in the reference case and in the other three cases studied. With CO₂ recycling PtG and oxy-fuel combustion, the system is smaller (lower CAPEX required) and has better figures in energy efficiency, curtailed renewable energy necessities for the H₂ production and CO₂ emissions. Compared to the reference case, the CO₂ recycling configurations are able to satisfy thermal demands of

industrial process without CO₂ emissions and reducing dependency of external fossil fuels. It will allow:

- Deployment of renewable energy utilization and storage.
- Deployment of H₂ as energy vector and energy storage vector.
- Deployment of carbon capture technologies to have a feasible carbon source.
- Use of excess renewable energy with high efficiency.
- Decarbonisation of industry sector based on thermal energy (as power sector will be decarbonised in a medium term due to high renewables penetration).
- Reduction of OPEX from fossil fuels necessities.

Table 5. Main results obtained for the different cases analysed.

	Reference case	Conventional PtG amine based	CO ₂ recycling PtG amine based	CO ₂ recycling PtG oxy-fuel based
Original fuel, kg	1.000	1.000	0.108	0.092
Additional fuel (for CCS), kg	-	0.148	-	-
CO ₂ produced, kg	2.743	2.743+0.406	2.958	2.528
CO ₂ emitted, kg	2.743	0.681	0.296	0.253
CO ₂ captured, kg	-	2.469	2.662	2.275
H ₂ needed, kg	-	0.449	0.484	0.414
Oxygen produced, kg	-	3.590	3.871	3.309
RREE needed, kJ	-	76,936	82,957	70,908+119
Thermal energy methanation, kJ	-	8,696	9,376	8,014
CO ₂ energy requirement, kJ	-	7,400	7,986	-
CH ₄ produced, kg	-	0.898	0.968	0.830
H ₂ /REE efficiency, %	-	70.03	70.01	69.94
CH ₄ /H ₂ efficiency, %	-	83.33	83.33	83.48
CH ₄ /REE efficiency, %	-	58.36	58.34	58.39
Thermal energy/(REE+fuel) efficiency, %	-		53.19	62.15

4. ECONOMIC CONSIDERATIONS

Besides showing the carbon mitigation potential of the CO₂ recycling concept for power to gas, some economic considerations must be made to position the concept as a promising alternative. It should be noted that, at the end, economic incomes will

determined if a technology is deployed or not, independently of its environmental performance. This is the cause of the delay on deploying renewable energy and CCS, and consequently the stunting in the fight against climate change.

A preliminary cost analysis is presented in this section to evaluate the feasibility of the concept, including figures from carbon capture, H₂ production and PtG. The avoided carbon cost, AC (€/kg CO₂ avoided), is defined as the difference between the cost of the system proposed (CO₂ recycling PtG) and the cost of the reference case, divided by the difference of their corresponding specific emissions (Eq. 2). The cost of each system is the sum of the annualized capital costs (CAPEX) and the operational cost (OPEX) (Eq. 3). The latter are composed by the fuel costs (natural gas) and the electricity cost.

$$AC_{Oxy-PtG} = \frac{C_{Oxy-PtG} - C_{boiler}}{(CO_2)_{boiler} - (CO_2)_{Oxy-PtG}} \quad (2)$$

$$C_{Oxy-PtG} = CAPEX_{Oxy-PtG} + COE * Electricity + Fuel\ costs_{Oxyfuel-boiler} \quad (3)$$

$$C_{boiler} = CAPEX_{boiler} + Fuel\ costs_{boiler} \quad (4)$$

It should be noticed that this definition is conservative as the reference case is not the production of natural gas by reforming or other types of alternatives for energy storage. The reference case is the same boiler of 94% efficiency (Eq. 4). The aim of the economic analysis is to obtain the primarily energy cost at which the system is competitive. The proposed system should be economically feasible to avoid carbon emissions and provide energy storage.

Table 6 shows the main economic assumptions for calculations of oxy-fuel power to gas systems with CO₂ recycling. The fixed charge factor (FCF) is the annual equivalent cost of the revenue requirements which are related to the capital investment of the equipment. It has been fixed in 0.08. This value corresponds to a plant life of 30 years and an effective after-tax annual cost of money of 7%. The capacity factor (CF) has been assumed in 0.80 (7008 h) for the boiler. In a first approach, both systems boiler and PtG, operate simultaneously these hours. However, as it has been illustrated in Table 2, a continuous operation of the electrolyser to run the PtG system has non-

sense as the power necessities are huge. For this reason, a sensitivity analysis of CF will be developed below.

Primary energy cost is 8 €/GJ for natural gas [50] and variable prices for electricity. A sensitivity analysis is done for the electricity costs required for operating the system. Regarding the CAPEX for the main equipment, 300 €/kW_{th} has been selected for a common natural gas boiler, a 33% higher cost for oxy-fuel gas boiler, as the differences compared with usual boilers (when the boilers were completely developed) do not justify higher figures. In any case, as it is shown below, this value has a marginal effect in overall results and further analysis is not required. It is assumed an electrolyser specific cost of 700 €/kW_e (600-700 €/kW_e are expected for the year 2030 [51][52]) and a methanation reactor specific cost of 800 €/kW_e [51] taken the electrolyser power as a reference for the cost and size of the methanation.

Table 6. Main assumptions for economic calculations of catalytic power to gas systems.

Main assumptions	
Fixed charge factor (FCF)	0.08
Capacity factor (CF)	0.80
Natural gas cost	8 €/GJ
Cost of electricity (COE)	variable
Boiler specific cost	300 €/kW _{th}
Oxy-fuel boiler specific cost	400 €/kW _{th}
Electrolyser specific cost	700 €/kW _e
Methanation reactor specific cost	800 €/kW _e (electrolyser)

To use similar values to the energy analysis presented previously, it has been assumed a boiler of 50 MW_{th} that consumes 1 kg/s of natural gas. It means that is necessary to translate from energy to power in the above Figs. 2 to 5. For the reference case, a boiler yearly cost of 11.29 M€ is calculated. Annualized CAPEX represents 10.6% and fuel cost represents 89.4% (10.09 M€) of the total costs. The CO₂ emissions are 69,379 tCO₂ per year.

In the case of Fig. 4 (CO₂ recycling PtG with amine carbon capture), the fuel (natural gas) cost strongly diminishes from 10.09 M€ to 1.09 M€ thanks to the methane

production that represents the 90% of the energy input necessities. Accordingly, the CO₂ emissions are reduced in the same quantity.

Key variables are the electrolyser power that defines the annualized CAPEX, and the electricity cost to run the electrolyser. Under this condition, the price of electricity makes completely unfeasible any PtG application. In the case of Fig. 4 and 50 MW_{th} boiler, it is required near 83 MW_e of electricity to run the electrolyser. Moreover, as previously commented the electrolyser power is very large and increase the annualized CAPEX.

The relationship between the boiler and electrolyser capacity factors (CF) determines the size of the electrolyser and then the CAPEX of the installation. Table 7 shows the electrolyser power as a function of this variable. For a boiler capacity factor (B-CF) of 1 (8760 boiler operational hours), it is impossible to reduce the electrolyser power below 1 without increasing the power above the 83 MW_e. These values are shadowed in the table. Those values with lower electrolyser capacity factor (E-CF) than boiler B-CF make unfeasible the system due to an important increment in the CAPEX of the installation.

When boiler B-CF decreases there are more room for reducing the size of the electrolyser and the CAPEX of the system. For example, if boiler B-CF is 0.5, if there are enough electricity (at low price) to run electrolyser with an E-CF of 0.7, the size of the electrolyser down to 59.3 MW_e. If renewable or curtailed energy have to be used to run electrolyser the E-CF would be low and force to reduce the boiler B-CF to maintain a reasonable CAPEX. This conclusion reinforces the idea of using power to gas as energy storage (and CCU) technology and not for continuous operation.

Assuming an 83 MW_e electrolyser with the same CP of the boiler, 0.8, the yearly CAPEX increases from 1.20 M€ to 12.36 M€, which is a higher quantity than the difference in fuel cost. Only in the case of free electricity, the system is feasible and obtain a CO₂ AC of 34.9 €/tCO₂ (Table 8). Due to the size of the electrolyser, the annualized CAPEX of the installation represent an important part of the total costs. When COE exceeds 0.02 €/kWh, the electricity costs are the most relevant contribution to total costs and, together with TCR, make unfeasible the system.

Table 7. Electrolyser power as a function of boiler capacity factor and electrolyser capacity factor. (a) dimensionless; (b) for example in table 4.

$\frac{CF_{\text{boiler}}}{CF_{\text{electrolyser}}}$	1.00	0.90	0.80	0.70	0.60	0.50	0.40	0.30	0.20	0.10
1.00	1.00	1.11	1.25	1.43	1.67	2.00	2.50	3.33	5.00	10.0
0.90	0.90	1.00	1.13	1.29	1.50	1.80	2.25	3.00	4.50	9.0
0.80	0.80	0.89	1.00	1.14	1.33	1.60	2.00	2.67	4.00	8.0
0.70	0.70	0.78	0.88	1.00	1.17	1.40	1.75	2.33	3.50	7.0
0.60	0.60	0.67	0.75	0.86	1.00	1.20	1.50	2.00	3.00	6.0
0.50	0.50	0.56	0.63	0.71	0.83	1.00	1.25	1.67	2.50	5.0
0.40	0.40	0.44	0.50	0.57	0.67	0.80	1.00	1.33	2.00	4.0
0.30	0.30	0.33	0.38	0.43	0.50	0.60	0.75	1.00	1.50	3.0
0.20	0.20	0.22	0.25	0.29	0.33	0.40	0.50	0.67	1.00	2.0
0.10	0.10	0.11	0.13	0.14	0.17	0.20	0.25	0.33	0.50	1.0
$\frac{CF_{\text{boiler}}}{CF_{\text{electrolyser}}}$	1.00	0.90	0.80	0.70	0.60	0.50	0.40	0.30	0.20	0.10
1.00	83.00	92.22	103.75	118.57	138.33	166.00	207.50	276.67	415.00	830.0
0.90	74.70	83.00	93.38	106.71	124.50	149.40	186.75	249.00	373.50	747.0
0.80	66.40	73.78	83.00	94.86	110.67	132.80	166.00	221.33	332.00	664.0
0.70	58.10	64.56	72.63	83.00	96.83	116.20	145.25	193.67	290.50	581.0
0.60	49.80	55.33	62.25	71.14	83.00	99.60	124.50	166.00	249.00	498.0
0.50	41.50	46.11	51.88	59.29	69.17	83.00	103.75	138.33	207.50	415.0
0.40	33.20	36.89	41.50	47.43	55.33	66.40	83.00	110.67	166.00	332.0
0.30	24.90	27.67	31.13	35.57	41.50	49.80	62.25	83.00	124.50	249.0
0.20	16.60	18.44	20.75	23.71	27.67	33.20	41.50	55.33	83.00	166.0
0.10	8.30	9.22	10.38	11.86	13.83	16.60	20.75	27.67	41.50	83.0

Table 8. Economic variables for a 50 MW_{th} boiler, amine scrubbing for CO₂ capture and PtG with a CF of 0.8 in boiler and electrolyser as function of COE.

COE (€/kWh)	COST (€/y)=	TCR+	ELECT COST+	FUEL COST	CO ₂ emissions (tCO ₂)	Avoided cost (€/tCO ₂)
0.000	13.45	12.36	0.00	1.09	7,493	34.9
0.005	16.36	12.36	2.91	1.09	7,493	81.85
0.010	19.26	12.36	5.81	1.09	7,493	128.82
0.020	25.08	12.36	11.63	1.09	7,493	222.76
0.040	36.70	12.36	23.25	1.09	7,493	410.64
0.070	54.15	12.36	40.70	1.09	7,493	692.46
0.100	71.59	12.36	58.14	1.09	7,493	974.28

As Figure 9 illustrates, results improve when oxy-fuel technology is considered as in Fig. 5. In this case, and under the same assumptions as in the previous analysis, there is a profit in the case of free electricity due to lower CAPEX, fuel costs and CO₂ emissions. In the case of 0.10 €/kWh, that is one order of magnitude below the usual COE, the CO₂ AC is around 75 €/tCO₂ and the system becomes feasible.

Table 9. Economic variables for a 50 MW_{th} oxyfuel boiler and PtG with a CF of 0.8 in boiler and electrolyser as function of COE.

COE (€/kWh)	COST (€/y)=	TCR+	ELECT COST+	FUEL COST	CO ₂ emissions (tCO ₂)	Avoided cost (€/tCO ₂)
0.000	11.04	10.12	0.00	0.93	6383	-3.92
0.005	13.53	10.12	2.49	0.93	6383	35.57
0.010	16.02	10.12	4.98	0.93	6383	75.06
0.020	21.00	10.12	9.95	0.93	6383	154.04
0.040	30.95	10.12	19.90	0.93	6383	312.01
0.070	45.87	10.12	34.83	0.93	6383	548.96
0.100	60.80	10.12	49.76	0.93	6383	785.91

These results are in agreement with previous works that consider power to gas [6] economically feasible only in the case of low price of electricity. To maintain the CO₂ AC below 100 €/tCO₂ the COE to run the electrolyser have to be in the range of 0.005 to 0.010 €/kWh that is one order of magnitude below the average COE. It is supposed that in a future renewable scenario, the COE would have more variability and together with variation in natural gas price there will be a chance for economic feasibility, especially if energy storage is considered in the economic calculation.

There is no doubt about the interest of the technology as a CCU technology due to carbon cycle, the minimum CO₂ emissions (in the range of other carbon capture technologies with energy integration), the energy storage that avoid the misuse of curtailed energy and the reduction of the dependency of primary energy.

5. CONCLUSIONS

Power-to-gas and power-to-liquid are conceived as energy storage technologies that make use of CO₂ emissions and have been proposed also as CCU alternatives. Nevertheless, it is not clear their potential advantages as carbon utilization

technologies as the CO_2 is released to the atmosphere after the synthetic fuel utilization.

In this paper, it has been demonstrated that catalytic power to gas can be an effective mitigation option under certain design configurations. The key element of PtG for carbon mitigation is the recycling of SNG to be used in the same installation. In this case, renewable energy and CCU are required to work in a complementary role, not competing for being the main approach to decarbonise, at least, the industrial sector.

It has been demonstrated that if catalytic PtG and CCU systems run simultaneously, the electricity consumption of the PtG system should be in the range of 2.5 $\text{MWh}_e/\text{MWh}_{\text{th}}$ or 1.5 $\text{MWh}_e/\text{MWh}_{\text{th}}$ depending on the fuel. It forces to avoid the application in large installations and it focuses the interest in small applications as industrial sites or biogas production in gasification plants.

The efficiency of the energy storage (electricity to SNG) may range between 44.7% and 58.3%, this value is similar to other energy storage systems but with the advantage that this storage is not limited in time or quantity. The main penalty is caused by hydrogen production, and the carbon capture stage represents a value below 15% of the energy requirements. In some cases the heat released in methanation compensates these energy necessities.

If SNG is used in the same installation from which CO_2 is captured (industry or power plant), CO_2 is “recycled” and it allows the use of renewable energy to satisfy thermal demands of industry or other sectors avoiding carbon emissions. This idea is useful for global warming mitigation and for the deployment of renewable energy and green hydrogen. CO_2 is used in a closed loop without being emitted to the atmosphere.

It has been shown that the case of CO_2 recycling PtG with oxy-fuel combustion used in industrial processes has outstanding energy and economic results. From an energetic point of view there a reduction in the system size and energy necessities compared with amine scrubbing case or PtG alone. The oxyfuel boiler can take advantage of the methanation heat release and reduce the natural gas necessities around 10%. This demand is near completely covered by the production of synthetic methane. Renewable energy requirements are 70.9 MJ per a methane production of 0.83 kg that is the necessary to have a thermal demand of 47 MJ in the oxyfuel boiler.

Economically, it has been quantified the COE needed for the electrolyser and hydrogen production that makes feasible the concept. The range 0.005 to 0.01 €/kWh is the price to obtain CO₂ avoided costs below 100 €/tCO₂ with the additional advantage of energy storage. These prices are high today and economically unaffordable. Further research is needed to reduce the costs associated with electrolyser that represents the main concept. Moreover, it is necessary to propose operational strategies that increase economic feasibility with the future link between electricity and natural gas.

Acknowledgments

The work described in this paper is supported by the R+D Spanish National Program from Ministerio de Ciencia, Innovación y Universidades (Spanish Ministry of Science, Innovation and Universities) and the European Regional Development Funds (European Commission), under project ENE2016-76850-R. This work has also been supported by the Government of Aragón (Research Group DGA T46_17R) and co-financed by FEDER 2014-2020 "Construyendo Europa desde Aragón".

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