

CO₂ recycling for Oxy-Power-to-Gas and Oxy-Power-to-Methanol. Clean alternatives for energy storage

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Abstract:

Carbon dioxide is the largest single contributor to global warming and current atmospheric concentrations are increasing at the fastest ever observed rate. Carbon capture and storage (CCS) and carbon capture and utilization (CCU) have been proposed as essential alternatives to reduce CO₂ emissions. Unfortunately, there are important energy penalties when CO₂ is separated from flue gases, as well as social issues concerning underground storage. Besides, most of the CCU methods actually release the captured CO₂ after the lifetime of the generated product. Other possibility to reduce global CO₂ emissions is the massive deployment of renewable energy. The main challenge that arises in this scenario is the management of the fluctuating renewable production. To tackle this problem, Power-to-X technologies (PtX) store surplus electricity in form of an energy vector by using H₂ from electrolysis as precursor. In particular, Power-to-Methane and Power-to-Methanol combine H₂ coming from electrolysis with CO₂ to produce synthetic methane and methanol. Both options are classified as energy storage and CCU methods as they use CO₂ to produce synthetic fuels. The conventional concepts release again the CO₂ when synthetic fuels are used. In this work we present novel and clean alternatives combining oxyfuel combustion and Power-to-X technologies to keep CO₂ in closed loops. These options make use of the oxygen produced in the electrolysis to feed, with recirculated CO₂, an oxyfuel boiler that satisfies a thermal demand and produces a flue gas mainly composed by CO₂ and H₂O. CO₂ is recycled, together with H₂, to produce valuable fuels in Power-to-X. This work overviews the state-of-the-art of these technologies and presents some examples for the application of these systems.

Keywords:

Energy storage, Power to gas, Power to methanol, Oxyfuel combustion

1. Introduction

The necessity of decarbonizing the current energy system has acted as the driving force to promote the penetration of renewable sources in electricity production. Mainly in Europe, but also in most of the countries, there are ambitious plans about a massive deployment of renewable energy. The “EU Reference Scenario 2016. Energy, transport and GHG emissions. Trends to 2050” [1] quantifies the contribution of renewable net electricity generation to 44% by 2030 and 56% by 2050.

However, the management of intermittency of renewable energy sources (with variable excess power derived from highly renewable energy future scenarios) has brought to light the necessity of deploying energy storage systems. Matching energy production and consumption has become a critical challenge for future energy systems. Current energy storage technologies present disadvantages when applied at large scale (e.g., low energy density or limited storage potential). The use of Power to Fuels technology is an option to overcome these limitations [2].

At the same time, carbon capture from fossil-based power plants is under development. One of the main barriers for carbon capture is the need of recycling and valorising CO₂ stream, which otherwise must be compressed and stored with the consequent energy and economic cost. The CCS technologies can be classified in post-combustion capture (based on the sorption of CO₂ from the

combustion gases), pre-combustion capture (separation of CO₂ from CO and H₂-rich gas before its use), and oxy-combustion technology (combustion in an atmosphere of CO₂/O₂ instead of N₂/O₂). Carbon capture faces the challenge of using CO₂ as valuable by-product, since CO₂ underground storage has not been completely regulated by governments and institutions around the world.

In this scenario, Power-to-X (PtX) has been proposed in the last years as one of the promising technologies to overcome both problems [3–5]. In general terms, PtX converts electricity surplus into synthetic fuels –e.g., methanol, ethanol, dimethyl ether (DME) and methyl tert-butyl ether (MTBE)– by combining water electrolysis and CO₂ reaction [6,7].

This technology may use captured CO₂ to produce a ‘CO₂ neutral’ fuel, while facilitates the temporal displacement of renewable energy. Thus, the interconnection of the electric and fuel networks would allow increasing the flexibility of the energy supply. However, depending on the application, the captured CO₂ is released again when synthetic fuels are used. This partially reduces the interest on the technology because it loses its carbon neutral behaviour as has been demonstrated [8,9]. Nevertheless, it remains interesting as energy storage alternative.

As Fig. 1 depicts, when fossil fuels are used as the main energy input and then the produced synthetic fuel is used in decentralized applications, there will be net CO₂ emissions. Therefore, the energy penalty and associated cost of carbon captures make non-sense since CO₂ is finally emitted to the atmosphere. Only when biomass (renewable) is used as main energy input, the overall process is neutral regarding CO₂ emissions. So, the consequences of the application of Power-to-X technology regarding CO₂ emissions depend on the fuel used as main input. The additional energy penalty and costs associated with carbon capture will be only worthy if the goal of using renewable energy is producing a specific fuel because excess power cannot be used in an application (storage).

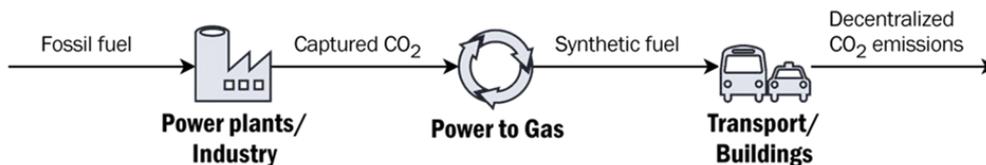


Fig. 1. Effect of production of fuels (PtX) on CO₂ emissions

Only when the fuel is used again in the original process (power plant or industry), CO₂ emissions are avoided. In this case there is a CO₂ recycle and CO₂ is used as an “energy carrier”. The process is fuelled just by renewable energy in order to produce hydrogen in electrolyser.

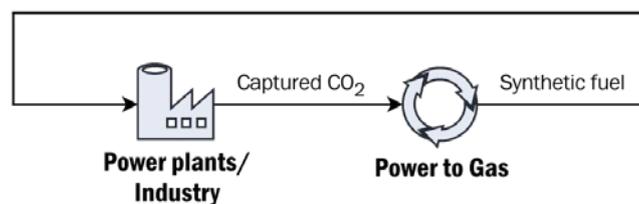


Fig. 2. Production of fuels (PtX) with CO₂ recirculation

Due to the oxygen by-production in the electrolysis process, the most suitable alternative for carbon capture is oxyfuel process. In oxyfuel process, fuel is burnt with O₂ (generally produced in an Air Separation Unit, ASU), free of N₂, which is diluted with CO₂ seeking the control of the boiler temperature. The amount of recycled flow gas is a fundamental parameter to determine the O₂ concentration in the comburent. It allows obtaining a high CO₂ concentration at the exhaust gas.

So, an appropriate option for taking advantage of oxygen by-produced in electrolysis would be the hybridization of PtX with oxyfuel combustion [10,11]. Thus, oxygen from electrolyser would importantly reduce (even avoid) the power consumption of the required air separation unit, and CO₂ would be taken from the boiler flue gas without extra energy penalty in its separation. This papers overviews the state-of-the-art of oxyfuel combustion, oxy-Power-to-Methane and oxy-Power-to-Methanol, and presents some examples for the application of these systems.

Despite the expectations and some past prospective, the scale for oxy-fuel combustion plants has not advanced to full commercial sizes, and some projects have been decommissioned worldwide due to unclear economic and regulation constrains. The main units now available are all in a similar demonstration scale (Table 1).

Table 1. Oxy-fuel combustion power plants in the world

<i>Location</i>	<i>Thermal power, MW</i>	<i>Fuel / Boiler</i>	<i>Output</i>	<i>CO₂ emissions</i>
Lacq (France)	35	Natural gas / Thermal production	Thermal energy	Storage in depleted gas field
Schwarze Pumpe (Germany)	30	Pulverized coal	Electricity	Without permanent disposal of CO ₂
Ciuden (Spain)	30	Pulverized coal / Fluidized bed	n.a.	Without permanent disposal of CO ₂
Yingcheng (China)	30	Coal / Retrofit	Combined heat and power	Without permanent disposal of CO ₂
Callide (Australia)	30	Pulverized coal	Electricity	Storage in depleted gas field

New horizons for oxy-fuel combustion, aiming at increasing the flexibility of power plants along with integrating renewable energies, could result in an outstanding leap for their wide application.

3. Oxy-Power-to-Gas

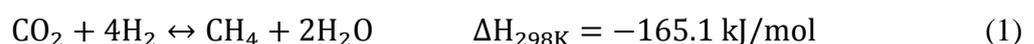
There exist in literature some relevant reviews regarding Power-to-Methane (PtM), which are focused on technical aspects of the methanation, such as operating conditions, reactor configurations or catalysts performance [5,24,25]. Besides, Bailera et al. recently reviewed the existing worldwide PtM projects at different scales [3]. First, a brief summary of these reviews on conventional Power-to-Methane process is presented, in order to introduce the technology. Then, then specific literature on Oxy-Power-to-Methane is reviewed (subsections 3.2, 3.3 and 3.4).

3.1. Conventional Power-to-Gas concept

The Power to Gas concept, understood as an option to store renewable energy and carbon dioxide in the form of methane, was first proposed by Koji Hashimoto in 1994 [26]. The difficulties associated to long-distance electricity transport in Japan inspired the research on energy carriers. The combination of electrolysis –driven by solar energy– and Sabatier reaction (Eq. 1) allowed the synthesis of methane and, thus, the distribution of renewable electricity without requiring new infrastructures [27]. Later, in 2009, Michael Sterner refreshed the PtG concept to focus on the management and long-term storage of renewable power surplus.

The main purpose of Power to Gas concept is to establish a connection between the electric and gas networks, through which renewable energy surplus can be stored and later used to satisfy backup or end-use demand (Fig. 4). Whenever RES oversupply the electricity network, the excess may feed electrolyzers to dissociate water in hydrogen and oxygen. Then, captured CO₂ is recycled via methanation thanks to the renewably-produced hydrogen. The resulting methane can be reconverted to electricity by gas-fired turbines, natural gas combined cycles, CHP or fuel cells, to substitute the fossil-based backup power. Besides, it can be directly consumed in end-use necessities (industry, households, buildings and transport) using the existing gas network, to displace fossil fuels in applications that are hardly penetrable by renewable energies.

The methanation is an exothermic reaction that combines H₂ and CO₂ to produce CH₄ and H₂O (Eq. 1) [5]. This synthetic methane can be obtained through catalytic or biological via (Table 2).



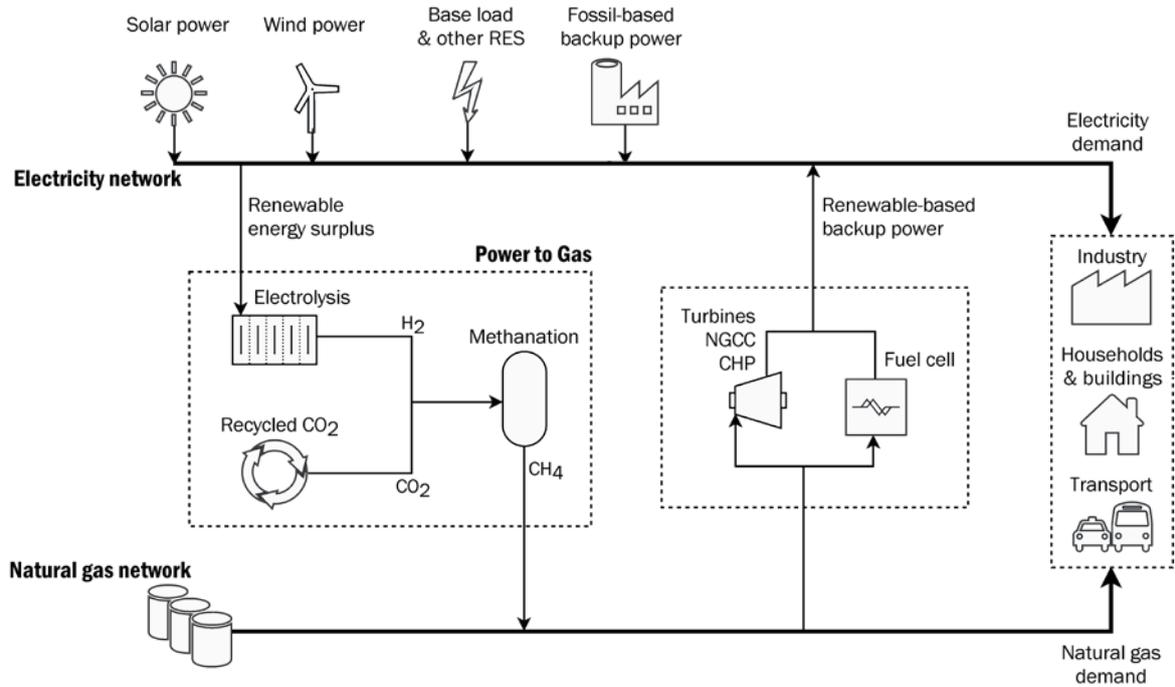


Fig. 4. Conceptual scheme of conventional Power-to-Gas technology

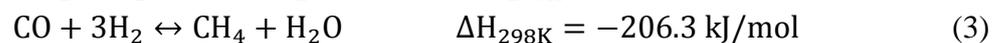
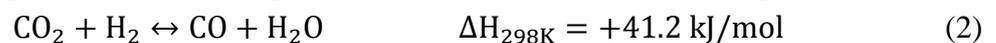
Table 2. Characteristics of biological and catalytic methanation [5],[3]

	Biological methanation	Catalytic methanation
Status	Laboratory / Pilot	Pilot / Commercial
Typical size [MW]	< 1	< 6
Temperature [°C]	20 – 70	250 – 700
Pressure [bar]	1 – 3	1 – 100
GHSV [h ⁻¹]	< 10	2000 – 5000
Impurity tolerance	High	Low
Heat integration	Low	Regular / High
Minimum load [%]	10	40
Load variation flexibility	High	Low / Regular

Biological methanation uses methanogenic archaea that grow by obtaining energy from CO₂-reducing/H₂-consuming metabolic routes. The process takes place in aqueous solution, at 20 – 70 °C and 1 – 3 bar. As the reaction occurs in liquid phase, the system presents high thermal inertia. This allows controlling changes in temperature caused by load variations that modify the released exothermal energy. Besides, archaea tolerate impurities that are commonly present in biogas or syngas (e.g., H₂S, NO_x, and NH₃). Its main drawbacks are the low reaction rate (GHSV < 10 h⁻¹) and therefore the requirement of big reactor volumes, what limits the industrial scalability [5][3].

To perform biological methanation, continuous stirred-tank reactors are commonly used. Since methanation takes place in an aqueous solution, and H₂ has a poor solubility in water, improving the gas liquid mass transfer is the main challenge on reactor design. Greater stirring rates increase the transfer of H₂ to the liquid, but the power consumption for the agitation becomes a strong energy penalty. Other kind of reactors, such as trickle-bed are also used in lab-scale [5].

Catalytic methanation uses active materials like Ni, Ru or Co to promote the Sabatier reaction. It is widely accepted that the catalytic process comprises two intermediate reactions. CO₂ is reduced through a reverse water-gas shift reaction (Eq. 2), followed by CO methanation (Eq. 3) [5].



The catalytic process is favoured by high pressures and low temperatures, although it can operate between 250 °C and 750 °C, and at pressures between 1 and 100 bar [5]. This operating conditions are suitable for heat integration with industries, while the higher reaction rate ($GHSV = 2000 - 5000 \text{ h}^{-1}$) makes easier its scalability. Drawbacks are the low tolerance against the presence of impurities, and the limited flexibility to manage temperature fluctuations [5][3].

In the case of catalytic methanation, five types of reactors have been proposed in literature to carry out this process: adiabatic fixed-bed, cooled fixed-bed, structured reactor, fluidized bed reactor, and three-phase reactor. In adiabatic fixed-bed reactors, inlet gases react passing through fixed catalyst layers located inside the reactor. Since high temperature inhibits the process, from 2 to 5 reactors in series (with intermediate cooling or recycling loops), are needed to reach CH_4 concentrations above 90% vol. The large amount of energy released inside the reactor also produces hot-spots that can damage the catalyst, and limits the operability under load fluctuations. Its main advantages are the low residence times and the high potential for heat integration (Table 3) [5][25].

Cooled fixed-bed reactors use internal cooling based on air, water or oil (without direct contact with gases), to favour the reaction and avoid sharp gradients of temperature [3]. Hence, the operation is less complex, but the possibilities of heat integration are reduced and the cost increases [5][25].

Structured reactors can mitigate drawbacks of fixed-bed reactors (i.e., hot-spots and pressure drops). In these reactors the gas passes through an internal multichannel structure impregnated with catalyst. Thus, heat transfer can be two orders of magnitude greater than in fixed-bed reactors. However, if catalyst is deactivated, the whole structure has to be re-impregnated [5][25].

Fluidized bed reactors present high mix ratios between catalyst particles and gas, leading to isothermal operation. This allows working at lower temperatures and, therefore, reduces the number of required reactors. Nevertheless, the lifetime of the system is notably reduced, due to the mechanical stress over both the catalyst and the walls of the reactor [5][25].

Lastly, three-phase reactors use liquid with high heat capacity to precisely control the temperature inside the reactor and guarantee an isothermal process. The particles of catalyst are suspended in the liquid, and the gas bubbles through it. As it occurs in biological methanation, the mass transfer from the gas to the medium controls the reaction rate. Besides, some residual liquid in vapour form can appear in the final synthetic natural gas (SNG) [5][25].

Costs of Power-to-Gas facilities widely vary because the technology has not reached the commercial stage yet. Typical cost may range between and 1000 € and 2000 € per kW of electrolyzer, in which 86.3% are allocated to the electrolysis stage [28].

Table 3. Characteristics of catalytic reactors [3][5][25]

	<i>Adiabatic fixed-bed</i>	<i>Cooled fixed-bed</i>	<i>Structured reactor</i>	<i>Fluidized bed</i>	<i>Three-phase reactor</i>
Status	Commercial	Pilot	Laboratory	Pilot	Laboratory
Operating mode	Adiabatic	Polytropic	Polytropic	Isothermal	Isothermal
Stages	2 - 7	1 - 2	1 - 2	1 - 2	1 - 2
Recycling	Usually	Sometimes	No	Sometimes	No
Temperature [°C]	250 - 700	250 - 500	250 - 300	300 - 400	300 - 350
Pressure [bar]	5 - 100	5 - 100	1 - 20	1 - 12	20
GHSV	High	High	High	Regular	Low
Catalyst arrangement	Fixed	Fixed	Impregnated	Fluidized	Suspended
Catalyst size	mm - cm	mm - cm	< 200 μm	< 500 μm	< 100 μm
Mechanical stress	Low	Low	Low	High	Regular
Thermal stress	High	Regular	Low	Low	Low
Complexity	High	Low	Low	Low	Regular
Cost	Regular	High	Very high	Low	Regular

3.2. Oxy-Power-to-Gas concept

As stated, Oxyfuel-PtG systems store renewable electricity as methane, taking also advantage from the O₂ by-produced during the electrolysis stage. This O₂ acts as comburent in the oxycombustion plant, overcoming the energy penalty of the ASU (Fig. 5). Besides, if the system includes a boiler, the exothermal heat from methanation can be integrated as a useful output. If the concept is applied to a power plant, the heat can be integrated in the power cycle to increase the generated electricity.

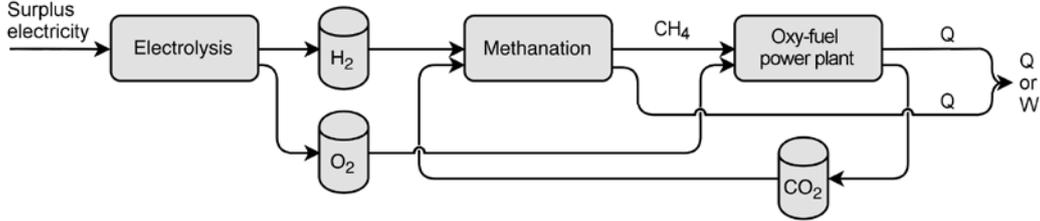


Fig. 5. Conceptual scheme of Oxy-Power-to-Gas technology

Aiming to characterize this concept, Bailera et al. proposed to use the ratio between the sizes of electrolysis and oxy-fuel combustion [10,11]. This parameter was defined as the quotient, ξ_{oxy} (Eq. 4), that relates the chemical energy contained in the H₂ from electrolysis ($LHV_{H_2} \cdot \dot{m}_{H_2}$), and the net energy output of the oxy-fuel application (\dot{Q}_{oxy} for boilers, and $\dot{W}_{net,oxy}$ for power plants) [29].

$$\xi_{oxy} = \frac{LHV_{H_2} \cdot \dot{m}_{H_2}}{\dot{Q}_{oxy}} \left[\frac{kW_{H_2}}{kW_t} \right] \quad \text{or} \quad \xi'_{oxy} = \frac{LHV_{H_2} \cdot \dot{m}_{H_2}}{\dot{W}_{net,oxy}} \left[\frac{kW_{H_2}}{kW_e} \right] \quad (4)$$

The selection of these factors facilitates the sizing of Oxy-PtG systems for specific applications. The numerator makes ξ_{oxy} independent of the electrolysis technology (alkaline, PEM or SOEC), while the denominator corresponds to the thermal or electrical demand that shall be satisfied in a given situation (\dot{Q}_{oxy} or $\dot{W}_{net,oxy}$). Hence, the selected operation point (ξ_{oxy}) allows to directly determine the required amount of hydrogen for a given application, from which the corresponding power consumption can be calculated under the technical characteristics of any electrolyzer.

These Oxy-PtG systems are characterized by two relevant values of ξ_{oxy} . The first, ξ_{ASU} , corresponds to an electrolysis large enough to cover the oxyfuel process by only using the byproduct O₂. Hence, for $\xi_{oxy} > \xi_{ASU}$, the ASU is not required. The other characteristic point is reached when the electrolyser produces enough H₂ to process the whole flue gas (ξ_{CO_2}) [30].

The type of fuel used in oxycombustion modifies the values of ξ_{ASU} and ξ_{CO_2} (Fig. 6). The use of biomass leads to lower values of ξ_{ASU} in comparison with coal, due to its greater O₂ content. Besides, the typically smaller C:H ratio of biomass also gives minor values of ξ_{CO_2} than coal due to the less amount of CO₂ produced per generated kWh [11]. The latter effect is more pronounced for natural gas oxycombustion, thus decreasing ξ_{CO_2} down to meet with ξ_{ASU} [29].

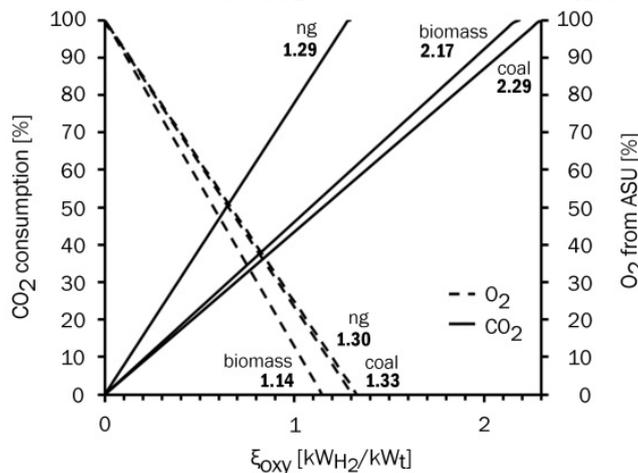


Fig. 6. Behaviour of ξ_{oxy} for coal, biomass and natural gas [30]

Whatever is the application for which the Oxy-PtG system is designed, and the selected operation point (ξ_{ASU} or ξ_{CO_2}), the overall system must avoid net CO₂ emissions. It means that either the produced SNG is reused in the oxy-fuel system or the initial fuel (from which the CO₂ is captured) is neutral on carbon dioxide (e.g., biomass).

3.3. Studied applications of Oxy-Power-to-Gas technology

In the following, CO₂-neutral Oxy-PtG applications that were studied in literature are summarized.

3.3.1. District heating based on biomass Oxy-PtG

The application of Oxyfuel-Power to Gas systems to district heating was studied by Bailera et al. [11]. They combined a biomass oxyfuel boiler (2 MW thermal output) with a methanation plant composed by three adiabatic reactors at 30 bar. The district heating infrastructure was assumed to have an end user distribution network made by rigid plastic jacket pipes at 140 °C and 25 bar.

Since the initial fuel is already CO₂ neutral, the selected operation point was ξ_{ASU} (not all produced CO₂ is recycled), in order to reduce the required electrolyser capacity (3.4 MW). The analysis of the system showed that 81.2% of the available heat in methanation becomes useful for integration. The overall efficiency was 78.7%, which is defined as the useful thermal energy from the boiler, plus the exothermal heat from methanation and the energy contained in the produced synthetic natural gas, divided by the chemical energy of the burnt biomass, plus the electricity consumed in the electrolyser and the auxiliary equipment [11].

3.3.2. Oxyfuel Combined cycle and PtG as renewable back-up power

The University of Zaragoza (Spain) in collaboration with the Centre Efficacité énergétique des Systèmes (France) studied the application of Oxy-PtG systems in combined cycles to act as renewable back-up power. In this case, CO₂ is continuously recycled and emissions avoided [29].

They quantified the increase in efficiency on a conventional oxyfuel combined cycled of 31.1 MW of net power (55.9% efficiency) after hybridizing with PtG technology. The system was simulated in Aspen Plus® and thermally integrated through Pinch analysis. The results showed that the required electrolyser power capacity is 98.2 MW. The removal of the ASU avoids the consumption of 3.0 MW, but the compression of the O₂ coming from the electrolyzer penalized the system with 2.1 MW. Besides, a total of 88% of the exothermal heat available from methanation may be recovered with an optimized heat exchangers network, thus generating low pressure steam that can be introduced in the steam cycle of the power plant. Thus, modifications finally lead to a net power generation of 35.8 MW, what means that the total efficiency of the combined cycle rises up to 64.3% (8.4 points increment, LHV based). The avoided flue gas was 5859.1 Nm³/h [29,30].

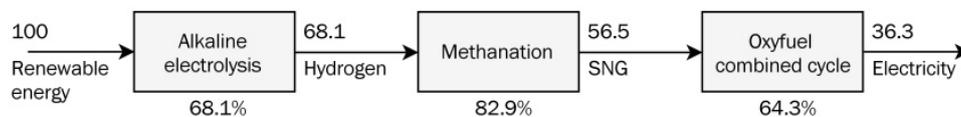


Fig. 7. Round-trip efficiency of the Oxy-PtG system studied by Bailera et al. [30]

3.3.3. Heating and domestic hot water by integrating PV and Oxy-PtG

Bailera et al. have recently proposed a novel integration of photovoltaic power and Oxy-Power-to-Gas systems in buildings with large roof areas of the tertiary sector [31]. The surplus electricity coming from PV is managed and stored through PtG technology in the form of methane to be later used in an oxyfuel boiler and partially cover thermal demand (CO₂ is completely recycled). They proposed several scenarios depending on the ratio between PV production, electricity demand and thermal demand of the building. It was found that the percentage of thermal demand that can be renewably covered by the PV-Oxy-PtG system varies between 12.0% and 64.7% depending on the scenario. It was found that the long-term energy storage capabilities of PtG were better used when electricity demand is 0.8 times the electric production coming from PV (in annual terms) and thermal demand is 0.6 times the electric demand. In that case, surplus electricity from PV is stored along August and then recovered as thermal energy during September and October.

3.4. Oxy-Power-to-Gas projects

Only two research projects focused on Oxy-PtG systems were found in literature. The first one corresponds to the Brandenburg University of Technology, which studied the stability of methanation catalysts against SO_x and NO_x in the context of oxyfuel processes (2011 – 2013) [32]. The lab facility comprised a reactor tube (8 mm in diameter and 100 mm in length) mounted into an oven that supplied homogeneous temperature distribution. The studied catalysts were (i) NiO supported on silica gel and (ii) RuO_2 supported on alumina. The Federal Ministry of Education and Research financially supported this research, in which also participated the German Research Centre for Geosciences and the University of Potsdam [33][34]. Later, they scaled up the lab facility into a pilot plant [35][36] that comprised two methanators of 153 mm in diameter, 870 mm high [37]. Total volume reactor is 30 dm^3 and contains 2 kg of catalyst. The pilot plant works at 350 °C and 10 bar, and produces $200 \text{ Nm}^3/\text{day}$ of CH_4 [35]. This second stage (2011 – 2014) was funded with 605 k€ from the European Regional Development Fund [38]. A third stage took place, in which they performed a 3 month trial operation at Schwarze Pumpe power plant [39][40].

The second research project regarding Oxy-PtG systems is the MERCURIA project, developed in the Mechanical Engineering Department of the University of Zaragoza (Spain). This project started in January of 2017 and comprises the designing, building and operating of a lab-scale methanation system (5 kW of H_2 input). It will analyse the methanation of flue gas typical in oxyfuel combustion, by using premixed flows of CO_2 , CO, and H_2O coming from bottles. A multi-fixed bed reactor is being developed for the first methanation stage, with intermediate cooling between beds. Besides, the reactor will have a glass window to perform thermographic measures with an infrared camera in the range of 0 °C to 650 °C. The project was co-funded by the Spanish Ministry of Economy and Competitiveness and the European Regional Development Funds.

4. Oxy-Power-to-Methanol

Several studies can be found in literature in which amine scrubbing is integrated with the Power-to-Methanol concept [41–43]. Only Trudewind et al. performed a life cycle assessment of the PtMeOH method comparing the different carbon capture methods that can be used [44]. He found that oxycombustion is the less harmful technology regarding primary energy demand and global warming potential. Besides, he showed that the environmental improvement compared to the conventional production processes is greater in the case of Oxy-PtMeOH than in Oxy-PtMethane.

In this section, we briefly summarize the conventional Power-to-Methanol concept, and then propose some ideas about potential applications of Oxy-PtMeOH. Due to the scarce information in literature about the concept, related studies and projects cannot be presented.

4.1. Conventional Power-to-Methanol concept

Methanol has been one of the most studied fuels in the framework of Power-to-Fuel technologies because it acts as feedstock for the chemical industry to produce dimethyl ether, acetic acid, formaldehydes, etc. [6,7,45,46]. Moreover, methanol produced from CO_2 could reach volumes as large as 1.5 or 3.0 Gt per year if fossil fuels are replaced [47].

The chemical reactions in the synthesis of methanol from CO_2 and H_2 are presented in Eq. 5, 6 and 7. Methanol can be obtained through the direct hydrogenation of CO_2 (Eq. 5) or by the reverse water gas shift reaction (Eq. 6) and the subsequent hydrogenation of CO (Eq. 7) [48].



The methanol synthesis process occurs at pressures that range from 50 to 250 bar and temperatures between 200 and 350 °C. It takes place in presence of catalysts such as copper/zinc/aluminium oxides, and is highly exothermic. Like in PtMethane, the challenges regarding the development of reactors are related with the heat removal and stability of the process [48].

As Artz et al. describe in their review [48], the first commercial Power-to-Methanol plant was commissioned in Iceland in 2011, and uses geothermal electricity to feed the electrolysis stage. It can produce up to 4000 t of methanol per year, what corresponds to the 2.5% of the fuel demand of the country. Now, it is intended to integrate the PtMeOH facility with a coal-fired power plant in Lünen. Other recent pilot experiences are the one developed by Mitsui Chemicals in 2009 (100 t/y), and the CAMERE process of the Korean Institute of Science and Technologies (100 kg/day).

4.2. Proposed applications of Oxy-Power-to-Methanol technology

Most of applications of PtMeOH are focused on producing fuels for transport or feedstock for chemical industries. In both cases, the CO₂ emissions are actually not avoided. When methanol is used as fuel, CO₂ is emitted through multiple decentralized sources. Moreover, chemical industries do not re-capture CO₂ after using the feedstock, so CO₂ is not cyclically used.

An option to make Oxy-PtMeOH sustainable is to capture CO₂ from the consumption of a biomass fuel. This could take place in pulp and paper manufacturers, since they generate bark and sawdust as by-product that is commonly used as biofuel for producing steam that is self-consumed [49]. Besides, they are one of the main medium temperature steam consumers that could take advantage of the exothermal heat from CO₂ hydrogenation. Paper industry uses indeed the 84% their entire energy expenditure for producing steam (steam is required at 170.0 °C for digesting, 144.4 °C for chemical recovery, and 126.7 °C for bleaching and drying) [50]. Hence, paper mills are one of the best candidates for a big scale Oxy-PtMeOH development.

Other interesting option is to use methanol as fuel in maritime transport. It has the advantage that is liquid at ambient temperature and therefore it can be used in current infrastructure. The main handicap is the low energy density of methanol compared to other fuels. The METHAPU project already tested the utilization of a 20 kW SOFC in a ship, and studied the implications of international regulations on MeOH as marine fuel [51]. This should be complemented with on-board carbon capture [52] to avoid net emissions. The captured CO₂ would be gathered at the harbour and used to produce the synthetic fuel again.

5. Conclusions

This paper presents an overview of the integration of Oxy-fuel combustion with Power-to-Fuels concepts. Both technologies have pilot scale experiences at the MW scale, but none of them have been commercially deployed because remaining technical issues. Besides, a legislative framework is needed to promote carbon capture and synthetic fuel production.

The most studied hybridization in literature is the Oxyfuel-Power-to-Gas technology for the production of synthetic methane: (i) a district heating application was studied in the range of 2 MW, based on biomass fuel to achieve neutral CO₂ emissions. It was found that 81.2% of the available heat in methanation becomes useful for integration. Moreover, (ii) the conversion of an oxy-combined cycled to a renewable based back-up power facility (CO₂ as energy carrier) was studied. In this case, the efficiency of the conventional oxy-combined cycle may be increased 8.4 points. Lastly, (iii) the application of Oxy-PtG systems in buildings with installed photovoltaic panels was also evaluated in literature. The surplus electricity from PV may cover up to the 64.7% of the thermal demand of the building, in the case of sport centers.

The Oxy-Power-to-Methanol concept has not been studied yet in literature. Novel applications are proposed, such as maritime fuel with on-board carbon capture, and integration in paper industry.

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Nomenclature

LHV	Lower heating value, kJ/kg
\dot{m}	Mass flow rate, kg/s
\dot{Q}	Heat power, kW
\dot{W}	Electric power, kW

Greek symbols

ξ	Design ratio for PtG-Oxy systems
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Subscripts and superscripts

ASU	Avoidance of Air Separation Unit
CO ₂	Complete consumption of flue gas
H ₂	Hydrogen
net	Net power
oxy	Oxycombustion

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