Future applications of hydrogen production and CO_2 utilization for energy storage: Hybrid Power to Gas-Oxycombustion power plants

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Abstract

Power to Gas (PtG) has appeared in the last years as a potential long-term energy storage solution, which converts hydrogen produced by renewable electricity surplus into synthetic methane. However, significant economic barriers slow down its massive deployment (e.g. operating hours, expensive investments). Within this framework, the PtG-Oxycombustion hybridization can palliate these issues by improving the use of resources and increasing the overall efficiency. In this study we assess the requirements for electrolysis, depending on the size of the oxycombustion plant, the fuel physical and chemical properties and the final application of the hybrid system. Most suitable heat demanding options to implement this PtG-Oxycombustion hybridization are district heating, industrial processes and small combined

Abbreviations: ASU, air separation unit; HEN, heat exchangers network; LHV, lower heating value; M, moisture; Oxy-CC, oxycombustion combined cycle; PtG, power to gas; SNG, synthetic natural gas; Z, ash.

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cycled power plants. The latter case is modelled and simulated in detail and thermally integrated. The global efficiency of this hybrid system increases from 56% to 68%, thanks to avoiding the requirement of an air separation unit and integrating up to 88% of the available heat from methanation in a LP steam cycle.

Keywords

Power-to-Gas, Oxycombustion, Methanation, Integration, Combined cycle

1. Introduction

The constant increase of electricity production from intermittent renewable energy sources has brought to light the necessity of deploying energy storage systems. The management of the surplus power generated by these renewable sources is crucial for developing a sustainable power industry. Power-to-gas has been proposed as one of the promising technologies to overcome these issues [1]. PtG technology uses electricity to produced hydrogen by electrolysis, and then combines CO_2 and the produced H_2 to obtain SNG through methanation. This technology widens the range of application of hydrogen as energy vector, and it makes possible to produce a CO_2 neutral fuel by capturing the carbon emissions from an existing source [2][3]. In addition, it allows connecting the electric and gas network for increasing the flexibility of the energy supply.

The PtG process is conceptually explained as follows: renewable electricity is converted to fuel gas by means of electrolysis, storing electrical energy in form of hydrogen. Oxygen is also obtained as by-product from the electrolyser. Then, the generated hydrogen is combined with carbon dioxide to produce methane through the Sabatier reaction (Equation 1) [4].

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \qquad \Delta H_{298K} = -165\ \mathrm{kJ/mol} \tag{1}$$

The availability of a suitable source of CO_2 can be considered as the main limiting factor for promoting PtG, since it reduces the possible geographic sites for a wide deployment of this

technology [5]. Biogas plants, waste managers, energy-intensive industries and power plants are the largest CO_2 sources and the most interesting partners for integration with PtG [6]. However, the energy consumption required to attain concentrated CO_2 streams leads to efficiency penalties that range between 9-12 efficiency points [7][8], and the associated costs may vary from 50 to 90 €/t_{CO2}, depending on CO_2 concentration in flue gas and capture technology [9]. For this reason, some of the largest PtG projects worldwide directly upgrade biogas to obtain SNG without a previous stage of CO_2 separation [10]. However, this kind of concepts makes useless the byproduct oxygen coming from the electrolysis process.

To this context, oxygen may be used as gasification agent or for the activation of sludge in biomass gasification and sewage plants, respectively [6]. Nevertheless, the hydrogen concentration in syngas from gasification may reach values above 60% and further hydrogen addition is barely needed, what limits the energy storage potential [11]. Sewage plants produce poor biogas and its upgrading is relatively expensive. Thus, it is currently preferred to burn this gas in engines for self-consumption [12]. Hence, a suitable option to take advantage of produced oxygen would be the hybridization of PtG with oxyfuel combustion. In oxyfuel combustion, a mixture of pure oxygen and recycled flue gas (mainly CO_2 and H_2O) acts as comburent [13]. The requirement of an air separation unit (ASU) to produce oxygen would be replaced with the electrolyser which by-produces O_2. Thus, the electrical consumption of the ASU would be reduced, and CO_2 would be taken from flue gas without extra energy penalty in its separation. With an adequate size design of the PtG–Oxycombustion system, the by-produced oxygen from electrolysis could entirely replace the ASU [6][14][15].

This paper deals with some potential applications that include biomass, coal and gas consumption. These applications cover different sizes and technologies but all of them are based on the Oxycombustion-Power to Gas hybridization. Special attention is paid to an advanced oxycombustion combined cycle hybridized with PtG. This technology can achieve higher net electric efficiencies [16] than air-fired coal power plants, so the required capacity of electrolysis

to remove the ASU is lower than in other power plants of the same net electric power. Furthermore, methanation produces extra thermal energy that can be useful. Thus, a preliminary heat integration analysis has been also performed and the maximum potential efficiency after heat integration is also determined.

2. Power to Gas-Oxycombustion hybridizations

As stated above, a suitable option to take advantage of by-produced oxygen is the hybridization of Power to Gas with oxyfuel combustion. During oxycombustion, a mixture of recycled flue gas and pure oxygen is used as comburent instead of air [17]. Thus, the large N_2 content in air is substituted by the combustion products (mainly CO_2 and H_2O), and flue gas can achieve a high carbon dioxide concentration once steam is condensed. Energy penalty associated to this capture process mainly comes from the air separation unit that produces the required oxygen with typical consumptions of 190 kWh/t_{O2} [18]. Therefore, by using the oxygen from electrolysis we could suppress the electrical consumption of the ASU, and we would directly obtain pure CO_2 for methanation from flue gas without energy penalties (Figure 1).

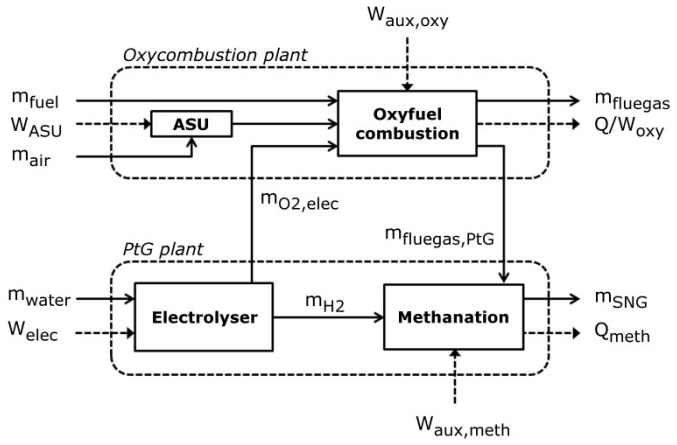


Figure 1. Scheme of the hybrid PtG-Oxycombustion concept.

The key variable in the Power to Gas-Oxycombustion hybridizations is the ratio that relates the chemical energy in the hydrogen from electrolysis and the net energy output of the oxyfuel combustion plant, Equation 2 (thermal outputs for boilers, ξ_{oxy}, and net electric outputs for

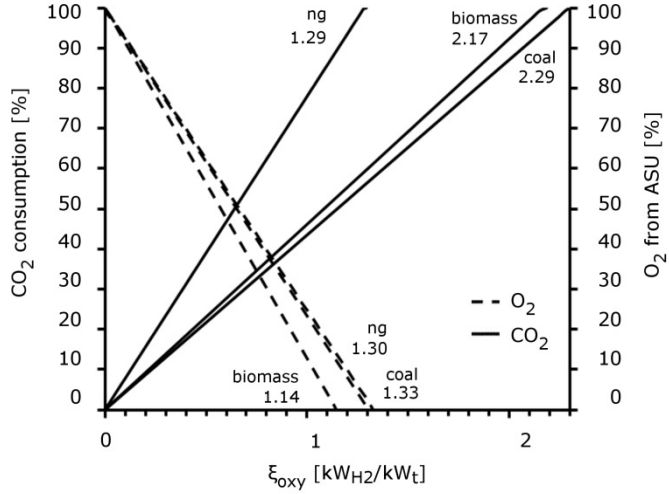
power plants, ξ'_{oxy}) [14][19]. The net electrical output accounts for the consumed electricity by the ASU and the auxiliary equipment in the form of Equation 3.

$$\xi_{oxy} = \frac{LHV_{H2} \cdot \dot{m}_{H2}}{\dot{Q}_{oxy}} \left[\frac{kW_{H2}}{kW_t}\right] \quad \text{or} \quad \xi'_{oxy} = \frac{LHV_{H2} \cdot \dot{m}_{H2}}{\dot{W}_{net,oxy}} \left[\frac{kW_{H2}}{kW_e}\right] \tag{2}$$

$$\dot{W}_{net,oxy} = \dot{W}_{gross,oxy} - \dot{W}_{aux,oxy} - \dot{W}_{ASU} \quad [kW_e] \tag{3}$$

Depending on the size ratio between the electrolyser and the oxyfuel combustion, the byproduced oxygen could cover the oxyfuel process requirements and avoid the air separation unit (situation denoted as ξ_{ASU}). Besides, whenever the installed electrolyser capacity is enough to process the whole flow of flue gas, the size ratio will be denoted as ξ_{CO2}. The type of fuel used in oxycombustion will modify the values of ξ_{ASU} and ξ_{CO2} (Figure 2). Thus, the use of biomass leads to lower values of ξ_{ASU} (1.14) in comparison with coal (1.33) thanks to the greater oxygen content (Table 1). Whilst the smaller C:H ratio of typical biomass fuels also gives minor values of ξ_{CO2} (2.17) than coal (2.29) due to the less amount of CO_2 produced per generated kWh [19]. The latter effect is more pronounce for natural gas oxycombustion, thus decreasing ξ_{CO2} (1.29) down to meet with ξ_{ASU} (1.30). Furthermore, despite of the differences between the compositions of natural gas and coal, both of them require for combustion comparable amounts of oxygen per MJ of fuel (2.80 mol_{O2}/MJ_{fuel} for natural gas, and 2.86 mol_{O2}/MJ_{fuel} for coal, according to our simulations), what implies similar values of ξ_{ASU}.

It should be noted that $\xi_{CO2} < \xi_{ASU}$ for the natural gas case, due to second order effects. Since complete combustion of CH_4 is considered and methanation is forced to be stoichiometric, the parameters ξ_{CO2} and ξ_{ASU} should be equal for natural gas. However, second order effects modify the values of ξ, such as (a) the presence of H_2 in the fuel input (more O_2 required, $\xi_{ASU} \uparrow$), (b) the requirement of an O_2 excess during combustion (more O_2 required, $\xi_{ASU} \uparrow$), and (c) the presence of O_2 in the flow of CO_2 that is directed to methanation (more H_2 required, $\xi_{CO2} \uparrow$). These effects almost cancel each other, and makes ξ_{ASU} slightly greater than ξ_{CO2}.



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119 **Figure 2.** Behaviour of ξ_{oxy} for coal, biomass and natural gas

120 **Table 1.** Ultimate analysis of selected coal and biomass for the study [% w.b.] [14][19].

	C	**H**	**O**	**N**	**S**	**M**	**Z**	**LHV [MJ/kg]**
Coal	66.1	3.6	7.1	1.6	0.6	8.6	12.4	25.4
Biomass	43.9	5.5	41.6	0.3	0.0	5.5	3.2	17.8

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122 The type of the power plant also modifies the values of ξ'_{ASU} and ξ'_{CO2}. Figure 3 shows the
123 behaviour of ξ'_{oxy} for a subcritical power plant with a LHV efficiency of 38.6% (coal and
124 biomass), and for a combined cycle of 64% LHV efficiency (natural gas) [16]. The greater
125 efficiency of the combined cycle allows reducing the amount of fuel used per kWh produced,
126 and therefore the required oxygen for oxycombustion and the size of electrolysis.

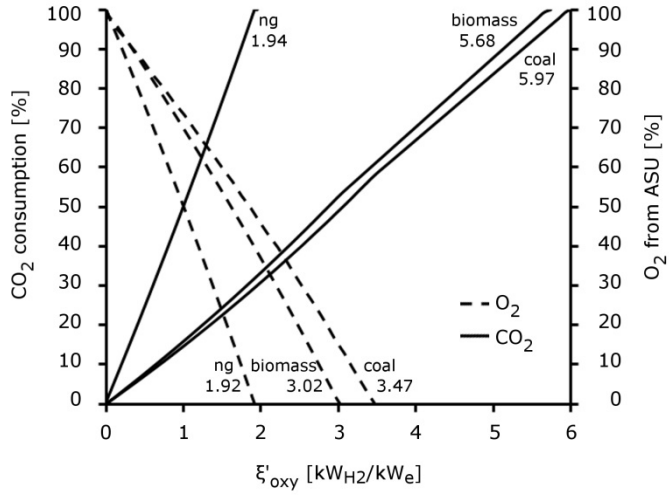

Figure 3. Behaviour of ξ'_{oxy} for a subcritical power plant (coal and biomass) and a combined cycle (natural gas).

The final application of the PtG–oxycombustion hybridization will define the adequate operation point of ξ_{oxy} and ξ'_{oxy}. Five generic applications are analysed to evaluate its technical feasibility. At small and mid-scale, we consider boilers producing thermal output that is applied to households, district heating, or industrial processes. At big scale, we take the production of electricity by combined cycles for natural gas, and by subcritical power plants for coal and biomass (Table 2).

Table 2. Generic applications and characteristics for PtG-oxycombustion systems at different scales (electrolyser efficiency 68.1%) [19]

Thermal output					
Application	$\dot{Q}_{oxy}$ **[MW]**	**Electrolyser [MWe]**			ξ_{oxy}
		Coal	**Biomass**	**Natural gas**	
Households	0.01	0.02	0.02	0.02	$\xi_{ASU} - 1.15 \cdot \xi_{ASU}$
District heating	2	3.9 – 4.5	3.4 – 3.9	3.8 – 4.4	$\xi_{ASU} - 1.15 \cdot \xi_{ASU}$
Industry	20	39.1 – 67.3	33.5 – 63.7	39.1 – 37.9	$\xi_{ASU} - \xi_{CO2}$
Electrical output					
Application	$\dot{W}_{net,oxy}$ **[MW]**	**Electrolyser [MWe]**			ξ'_{oxy}
		Coal	**Biomass**	**Natural gas**	
Subcritical PP	50	350.6 – 438.3	333.6 – 417.0	–	$0.8 \cdot \xi'_{CO2} - \xi'_{CO2}$

Combined cycle	50	–	–	113.9 – 142.4	$0.8 \cdot \xi'_{CO2} - \xi'_{CO2}$

Small scale installations (households and district heating) are not compelled to capture their emissions since the amount of produced CO_2 is not large enough. Hence, an operation point around ξ_{ASU} would be recommended. In medium scale facilities, such as industrial applications, avoiding greenhouse gas emissions might be economically interesting, so they could operate in the range between ξ_{ASU} and ξ_{CO2}. Power plants should be compelled to capture their carbon dioxide; therefore, a range next to ξ_{CO2} would be the most suitable operation for those applications.

The technical feasibility of these applications is strong limited by the high specific cost and the maximum achievable size of electrolysers. Nowadays, electrolysers are commercially available from a few kWe up to 2 MWe [20]. Therefore, coal and biomass power plants are prohibitive because they require more than 160 electrolysers. Industry and district heating are the most suitable applications, since they would combine less than 30 units of 2 MWe size electrolysers. In the following section, we analyse and integrate a small combined cycle power plant as the upper limit case for PtG-Oxy applications.

3. Power to Gas-Oxycombustion combined cycle model

The operation of a Power to Gas-Oxycombustion combined cycle plant makes sense when we use buffers of H_2 and O_2 to separate the storage periods from the electricity generation (the analysis of storage sizing and management is beyond the scope of this paper, although it becomes essential for economic analysis). Whenever renewable energy surplus exists, the electrolyser starts storing this electricity as hydrogen and oxygen. Contrarily, during the periods of high demand, the electrolyser remains unused, and the combined cycle generates electricity using the stored oxygen for the oxycombustion. Simultaneously, the methanation process combines the hydrogen with the CO_2 emissions of the power plant, what allows generating approximately the same amount of SNG that is consumed. Hence, the final electricity

production can be considered as renewable, since methane and carbon dioxide act as the charge and discharged forms of an energy carrier that is continuously recycled. Besides, the exothermal heat from methanation can be integrated as low pressure steam in the steam cycle of the power plant for increasing the overall efficiency.

The hybridization between the combined cycle in oxycombustion and the Power to Gas plant has been modelled with Aspen Plus® under industrial conditions for steady state operation and chemical equilibrium. The simulation of both plants is described in detail in the following sub-sections.

3.1 Combined cycle power plant

To convert the chemical power of the produced SNG back to electric power, a gas and steam cycles are combined in a single oxycombustion power plant (Oxy-CC). By burning the SNG in pure oxygen, the produced flue gas is rich in CO_2 that can be easily separated from water using a condenser. An overall layout of the power plant is shown in Figure 4. Pure oxygen, SNG and recycled flue gas are fed to the stoichiometric combustion chamber (BO) where the temperature is raised up to 1330 °C (see Table 3 for stream details). We assume a complete combustion process and an isentropic efficiency of 90% for all turbines.

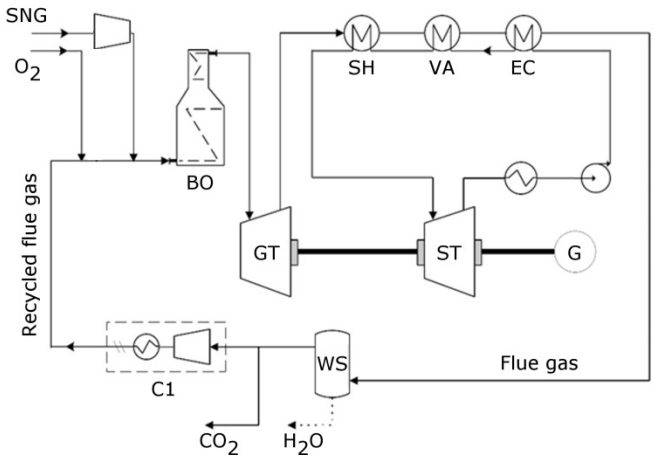

Figure 4. Scheme of the oxycombustion combined cycle.

The resulting flue gas is then expanded in a Gas Turbine (GT) to atmospheric pressure to produce about 35.7 MW_e of electric power. A Rankine cycle is then used to recover the heat from the flue gas. The Steam Turbine (ST) operates at 530°C and 150 bar and generates up to 13.4 MW_e. The used Heat Recovery Steam Generator consists of 3 modules: an Economizer (EC) a Vaporizer (VA) and a Superheater (SH).

Table 3. Main streams of the oxycombustion combined cycle.

	Fuel	**Comburent**		**Flue Gas**	**CO_2 to PtG**
Stream	SNG	O_2	Recycled flue gas	Flue Gas	CO_2
T [ºC]	40.0	27	382.0	1329.5	30.0
P [bar]	26.0	40.0	40.0	40.0	1.0
Flow [Nm^3/h]	5775.9	11210.8	67679.4	84581.4	5859.1
CO_2 [%]	0.8	0.0	94.5	82.2	94.5
H_2 [%]	3.5	0.0	0.0	0.0	0.0
CH_4 [%]	95.3	0.0	0.0	0.0	0.0
H_2O [%]	0.4	0.0	4.3	16.8	4.3
O_2 [%]	0.0	100.0	1.2	1.0	1.2

The total electric consumption of the Oxy-CC is the sum of the ASU consumption (3.0 MW), the multi-staged compressor of the recycle loop (13.8 MW), and the water pump in the Rankine cycle (0.2 MW). Thus, the total 49.1 MW that the plant is able to generate translates into 31.1 MW of net power, assuming a 98% efficient electric generator (G). This leads to an overall plant efficiency of 55.9% defined as the ratio between the net electric output of the Oxy-CC plant (Equation 3 where $W_{aux,oxy}$ includes the consumption of the multi-staged compressor of the recycle loop) and the chemical energy contained in the SNG from PtG unit (LHV based). This value is comparable to the efficiency of NGCC power plants with CO_2 capture found in literature [21]. The Oxy-CC produces 5859.1 Nm^3/h of CO_2 for methanation with 94.5 mol% CO_2 content.

3.2 Power to Gas plant

The modelled methanation facility is based on TREMP™ process from Haldor Topsøe [22], and consists of three adiabatic stages at about 30 bar with recycling on the first reactor, and a steam condenser after the second one (Figure 5). The main target is to achieve methane molar fractions above 95% in the SNG, according to the Spanish legislation [23].

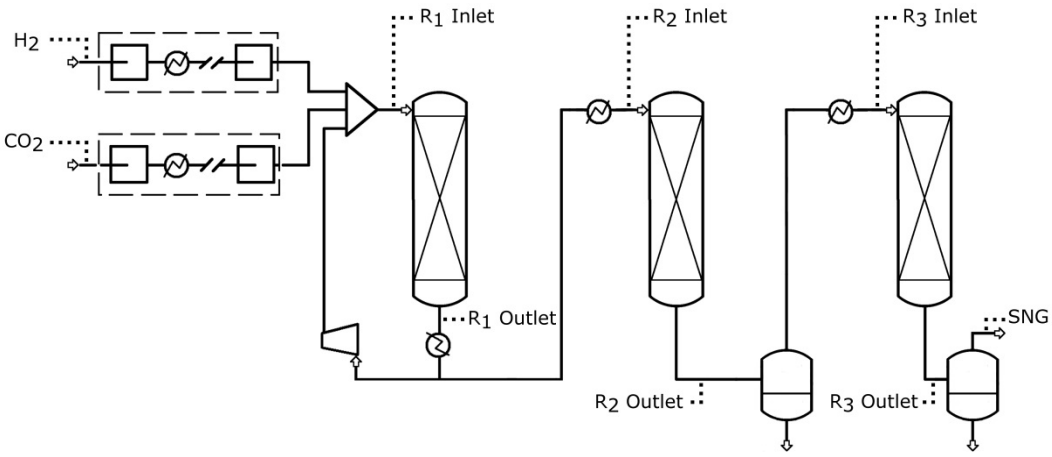

Figure 5. Scheme of the Power to Gas plant.

The flue gas from the Oxy-CC amounts to 5859.1 Nm^3/h at 30ºC and 1 bar. We assume a stoichiometric methanation, so the required amount of hydrogen is 22310.1 Nm^3/h. This is calculated by Equation 4 [14] as a function of the total molar flow of flue gas, $\dot{n}_{FG}$, and its molar concentrations of CO_2, $y_{CO_2,FG}$, and O_2, $y_{O_2,FG}$.

$$\dot{n}_{H_2} = 4 \cdot \left(y_{CO_2,FG} + \frac{1}{2} y_{O_2,FG} \right) \cdot \dot{n}_{FG} \quad (4)$$

This hydrogen comes from alkaline electrolysers fed with renewable electricity, which have been modelled by programming a user-defined subroutine in Aspen Plus®. The inlet electric power and the inlet water stream are the initial variables for the external calculations. This block splits water in two mass flows of pure oxygen and a mixture of hydrogen with unreacted water. Based on literature, the water conversion is assumed to be 99.9% with an electrical consumption of 4.4 kWh/Nm^3H_2 and an outlet temperature of 80 °C [24][25]. These operation conditions lead to an efficiency of the electrolyser unit of 68.1% (LHV basis).

The hydrogen and carbon dioxide are pressurized up to 30 bar prior the methanation plant. At the outlet of both compression trains, the temperature reached allows the removal of any preheating stage before the first reactor. Then, the outlet of Reactor 1 is cooled down to 300 ºC, and partially recycled (72.5%) using a blower. The stream directed to the second stage of methanation enters the reactor at 250 ºC. After this point, steam content strongly inhibits the methanation reaction; therefore water content is reduced to 12% through a condensation stage and the outlet gas is heated back to 250 ºC prior entering the third reactor. Finally, most of the steam at the outlet of Reactor 3 is condensed, and the gas achieves SNG quality (Table 4). In the simulation, the reactor blocks calculate the composition and temperature of outlet gas streams, at equilibrium state, minimizing Gibbs free energy in an adiabatic process. Besides, the pressure drops are assumed to be 3% along the reactors and 2% in the condensation stages.

Table 4. Main streams of the Power to Gas plant.

	H_2	**CO_2**	**R1 Inlet**	**R1 Outlet**	**R2 Inlet**	**R2 Outlet**	**R3 Inlet**	**R3 Outlet**	**SNG**
T [ºC]	80.0	30.0	307.7	592.1	250.0	421.9	250.0	366.3	40.0
P [bar]	1.0	1.0	30.0	29.1	29.1	28.2	27.7	26.8	26.3
Flow [Nm^3/h]	22310.1	5859.1	78318.7	69143.3	18993.7	17579.7	7544.6	7090.9	5756.9
CO_2 [%]	0.0	94.5	9.9	4.5	4.5	1.6	3.6	0.7	0.8
H_2 [%]	99.9	0.0	41.3	20.0	20.0	6.3	14.7	2.9	3.5
CH_4 [%]	0.0	0.0	15.3	24.0	24.0	29.9	69.7	77.3	95.2
H_2O [%]	0.1	4.3	32.9	50.8	50.8	62.2	12.0	19.1	0.4
CO [%]	0.0	0.0	0.5	0.7	0.7	0.0	0.0	0.0	0.0
O_2 [%]	0.0	1.2	0.1	0.0	0.0	0.0	0.0	0.0	0.0

4. Energy integration and efficiency

Based on the Power to Gas plant simulation results a heat integration study is conducted in order to find the optimal Heat Exchangers Network (HEN) for heat recovery purposes. The pinch analysis methodology is integrated into the Power to Gas model in order to determine the minimal hot and cold utilities required by the process. Heat fluxes are integrated with a pinch temperature of $\Delta T=10K$ [26]. The resulting optimal HEN is shown in Figure 6. In this optimal

HEN, part of the heat recovered from the exit of the first reactor is used for internal heating requirements at the inlet of the third reactor (HEX1). The remaining heat is used to generate 24 tonnes of LP steam per hour at 124°C and 2 bar by using 3 heat exchangers placed at the exit of the first reactor and both ends of the second (HEX2, HEX3 and HEX4).

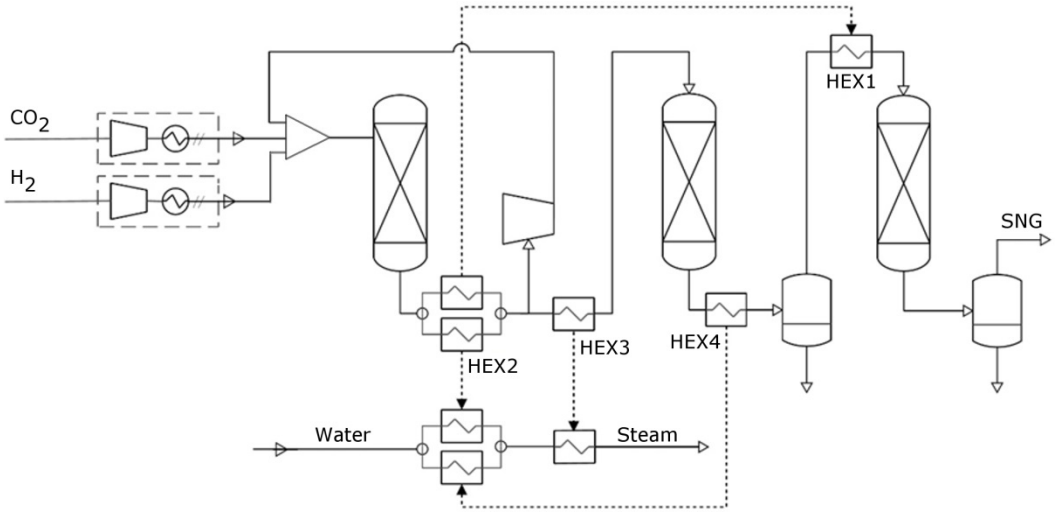

Figure 6. Scheme of the Heat Exchangers Network in the methanation plant.

The heat generated at the exit of the last reactor cannot be efficiently recovered with the considered operating conditions. An external cooling utility is thus used for condensate removal from the final product (e.g. cooling tower).

In order to make use of this generated steam, a low pressure turbine (LP) is introduced into the previous Oxy-CC (Figure 7). The generated LP steam is mixed to the steam exiting the high pressure turbine (HP) at 2 bar before the second expansion process in the following low pressure turbine (LP). The flow exiting the LP turbine is then separated to retrieve the portion which will be pumped back to the HEN in the Power to Gas plant. This configuration allows to run the oxycombustion and Power to Gas processes separately if need be.

Thanks to the external heat source for more power generation (heat integration with PtG plant), the new combined cycle is able to produce 53 MW of electric power (near 8% more power). The removal of ASU unit for O_2 generation avoids 3 MW of extra consumption. But the

requirement of a new compression train to pressurized O_2 coming from the electrolyser penalizes the system with 2.1 MW. This modification finally leads to a net power generation of 35.8 MW. Thus, the total efficiency of the combined cycle rises by 11.6 points, up to 67.5% (LHV based). Moreover, the performance of the plant could still be further improved by means of an exergy analysis to identify the avoidable losses at fixed design [27].

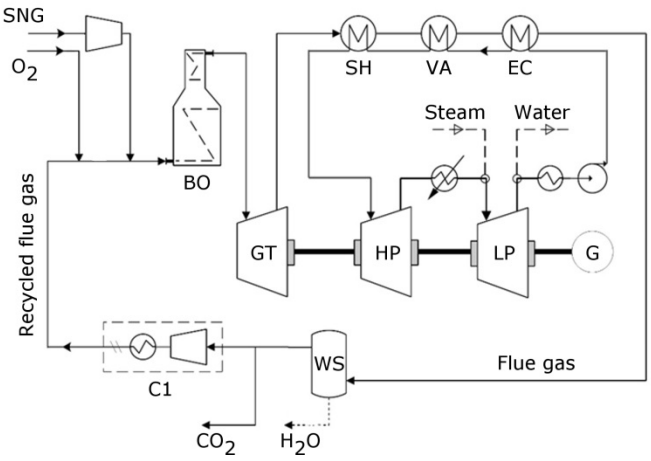

Figure 7. Scheme of the Oxycombustion Combined Cycle heat integration.

5. Conclusions

In this study, the PtG-Oxycombustion hybridization that was presented in previous works has been assessed for different types of Oxycombustion plants. These systems store renewable electricity as hydrogen, taking also advantage of the O_2 by-produced during electrolysis to overcome the energy penalty of the ASU in an oxyfuel combustion facility. Later, the O_2 stored can be used to operate the oxycombustion plant and, in addition, the H_2 stored is used in the methanation plant to generate synthetic natural gas. The parameter used to characterize the systems is the size ratio, ξ_{oxy}, which relates the energy contained in the hydrogen from electrolysis and the net output of the oxyfuel combustion plant (thermal output for boilers, ξ_{oxy}, and net electric output for power plants, ξ'_{oxy}). Depending on the value of ξ_{oxy}, the byproduct oxygen could completely feed the oxyfuel process and avoid the air separation unit (ξ_{ASU}), or the hydrogen may be sufficient for processing the whole flow of flue gas (ξ_{CO2}).

The type of fuel used in oxycombustion modifies the values of ξ_{ASU} and ξ_{CO2}. Natural gas and coal require comparable amounts of oxygen per MJ of fuel, what implies similar ξ_{ASU} (1.30 and 1.33, respectively), whilst biomass has greater oxygen content, thus reducing ξ_{ASU} down to 1.14. Besides, for smaller C/H ratios, the amount of CO_2 produced per generated kWh is lower, so $\xi_{CO2,coal} > \xi_{CO2,biomass} > \xi_{CO2,natural\,gas}$. The type of power plant also modifies the values of ξ'_{ASU} and ξ'_{CO2}. The lower efficiency of subcritical power plants compared to combined cycles implies increasing the amount of fuel per kWh produced, the required oxygen and the size of electrolysis; therefore, $\xi_{CO2,SPP} \gg \xi_{CO2,CC}$.

Five generic applications of the concept have been evaluated, from which industry and district heating result the most suitable options due to their technical feasibility. Small combined cycles are considered as the upper limit for PtG-Oxy applications, whilst subcritical power plants are prohibitive since they require between 330 and 420 MW of electrolysis capacity. Furthermore, a PtG-OxyCC hybrid system has been simulated and thermally integrated with Aspen Plus® software. A total of 88% of the exothermal heat available from methanation is recovered with an optimized heat exchangers network, thus generating low pressure steam that can be introduced in the steam cycle of the power plant. Hence, the absence of ASU unit for O_2 generation and the use of the methanation heat allow increasing the overall efficiency from 55.9% to 67.5%.

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Nomenclature

Variables

LHV	Lower heating value [kJ/kg]
$\dot{m}$	Mass flow [kg/s]
$\dot{n}$	Molar flow [kmol/s]
P	Pressure [bar]
$\dot{Q}$	Thermal power [kWt]
T	Temperature [ºC]
$\dot{W}$	Electric power [kWe]
y	Molar fraction [-]
ξ_{oxy}	Ratio between electrolyser and boiler outputs [kWe/kWt]
ξ'_{oxy}	Ratio between electrolyser and power plant outputs [kWe/kWt]

Subscripts

ASU	Air separation unit
aux	Auxiliary consumption
CC	Combined cycle
CO_2	Carbon dioxide
FG	Flue gas
$gross$	Gross power
H_2	Hydrogen
net	Net power
oxy	Oxycombustion plant
O_2	Oxygen
SPP	Subcritical power plant

References

[1] Scamman D, Newborough M. Using surplus nuclear power for hydrogen mobility and power-to-gas in France. Int J Hydrogen Energy 2016;41:10080–9. doi:10.1016/j.ijhydene.2016.04.166.

[2] Streibel M, Nakaten N, Kempka T, Kühn M. Analysis of an integrated carbon cycle for storage of renewables. Energy Procedia 2013;40:202–11. doi:10.1016/j.egypro.2013.08.024.

[3] Kühn M, Nakaten N, Streibel M, Kempka T. CO2 geological storage and utilization for a carbon neutral "power-to-gas-to-power" cycle to even out fluctuations of renewable energy provision. Energy Procedia 2014;63:8044–9. doi:10.1016/j.egypro.2014.11.841.

[4] Estermann T, Newborough M, Sterner M. Power-to-gas systems for absorbing excess solar power in electricity distribution networks. Int J Hydrogen Energy 2016;41:13950–9. doi:10.1016/j.ijhydene.2016.05.278.

[5] Schneider L, Kötter E. The geographic potential of Power-to-Gas in a German model region-Trier-Amprion 5. J Energy Storage 2015;1:1–6. doi:10.1016/j.est.2015.03.001.

[6] Sterner M. Bioenergy and renewable power methane in integrated 100% renewable energy systems. Kassel university press GmbH, 2009.

[7] Goto K, Yogo K, Higashii T. A review of efficiency penalty in a coal-fired power plant with post-combustion CO2 capture. Appl Energy 2013;111:710–20. doi:10.1016/j.apenergy.2013.05.020.

[8] Thambimuthu K, Soltanieh M, Abanades JC. Capture of CO2. IPCC Spec. Rep. Carbon dioxide Capture Storage, Cambridge University Press; 2005, p. 105–78.

[9] Rubin ES, Davison JE, Herzog HJ. The cost of CO2 capture and storage. Int J Greenh Gas Control 2015;40:378–400. doi:10.1016/j.ijggc.2015.05.018.

[10] Bailera M, Lisbona P, Romeo LM, Espatolero S. Power to Gas projects review: Lab, pilot and demo plants for storing renewable energy and CO2. Renew Sustain Energy Rev 2017;69:292–312. doi:10.1016/j.rser.2016.11.130.

[11] Iskov H, Rasmussen NB. Global screening of projects and technologies for Power-to-Gas and Bio-SNG. Danish Gas Technology Centre; 2013.

[12] Szwaja S, Kovacs VB, Bereczky A, Penninger A. Sewage sludge producer gas enriched with methane as a fuel to a spark ignited engine. Fuel Process Technol 2013;110:160–6. doi:10.1016/j.fuproc.2012.12.008.

[13] Toftegaard MB, Brix J, Jensen PA, Glarborg P, Jensen AD. Oxy-fuel combustion of solid fuels. Prog Energy Combust Sci 2010;36:581–625. doi:10.1016/j.pecs.2010.02.001.

[14] Bailera M, Lisbona P, Romeo LM. Power to gas-oxyfuel boiler hybrid systems. Int J Hydrogen Energy 2015. doi:10.1016/j.ijhydene.2015.06.074.

[15] Spazzafumo G. Storing renewable energies in a substitute of natural gas. Int J Hydrogen Energy 2016;41:19492–8. doi:10.1016/j.ijhydene.2016.05.209.

[16] Climent Barba F, Martínez-denegri Sánchez G, Soler Seguí B, Gohari Darabkhani H, John Anthony E. A technical evaluation, performance analysis and risk assessment of multiple novel oxy-turbine power cycles with complete CO2 capture. J Clean Prod 2016;133:971–85. doi:10.1016/j.jclepro.2016.05.189.

[17] Wall T, Liu Y, Spero C, Elliott L, Khare S, Rathnam R, et al. An overview on oxyfuel coal combustion-State of the art research and technology development. Chem Eng Res Des 2009;87:1003–16. doi:10.1016/j.cherd.2009.02.005.

[18] Hu Y, Li X, Li H, Yan J. Peak and off-peak operations of the air separation unit in oxy-coal combustion power generation systems. Appl Energy 2013;112:747–54. doi:10.1016/j.apenergy.2012.12.001.

[19] Bailera M, Lisbona P, Romeo LM, Espatolero S. Power to Gas–biomass oxycombustion hybrid system: Energy integration and potential applications. Appl Energy 2015. doi:10.1016/j.apenergy.2015.10.014.

[20] Sharma S, Ghoshal SK. Hydrogen the future transportation fuel: From production to applications. Renew Sustain Energy Rev 2015;43:1151–8. doi:10.1016/j.rser.2014.11.093.

[21] Kanniche M, Gros-Bonnivard R, Jaud P, Valle-Marcos J, Amann J BC. Pre-combustion, Post-combustion and Oxy-combustion in thermal power plant for CO capture. Appl Therm Eng 2009;30:53.

[22] Kopyscinski J, Schildhauer TJ, Biollaz SM a. Production of synthetic natural gas (SNG) from coal and dry biomass - A technology review from 1950 to 2009. Fuel 2010;89:1763–83. doi:10.1016/j.fuel.2010.01.027.

[23] BOE-A-2013-185. Resolución de 21 de diciembre de 2012, de la Dirección General de Política Energética y Minas, por la que se modifica el protocolo de detalle PD-01. Ministerio de Industria, Energía y Turismo; 2013.

[24] Tijani AS, Yusup NAB, Rahim a. HA. Mathematical Modelling and Simulation Analysis of Advanced Alkaline Electrolyzer System for Hydrogen Production. Procedia

Technol 2014;15:799–807. doi:10.1016/j.protcy.2014.09.053.

[25] Dieguez P, Ursua a, Sanchis P, Sopena C, Guelbenzu E, Gandia L. Thermal performance of a commercial alkaline water electrolyzer: Experimental study and mathematical modeling. Int J Hydrogen Energy 2008;33:7338–54. doi:10.1016/j.ijhydene.2008.09.051.

[26] De Saint Jean M, Baurens P, Bouallou C, Couturier K. Economic assessment of a power-to-substitute-natural-gas process including high-temperature steam electrolysis. Int J Hydrogen Energy 2015;40:6487–500. doi:10.1016/j.ijhydene.2015.03.066.

[27] Hagi H, Le Moullec Y, Nemer M, Bouallou C. Performance assessment of first generation oxy-coal power plants through an exergy-based process integration methodology. Energy 2014;69:272–84. doi:10.1016/j.energy.2014.03.008.

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