OxyMES. A combination of oxy-fuel technology and microbial electrosynthesis for sustainable energy storage

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ABSTRACT

Advances in renewable energy generation technologies entail the necessary deployment of associated energy storage technologies. One of them is *power-to-gas* technology, which make use of the surplus electricity from the system for its conversion and storage in the form of synthetic natural gas. These systems enable to convert the current fossil fuel-based gas system into a system that operates with biological origin gases (bioenergy). In this context, locally generated *power-to-gas* schemes based on biological subprocesses are of great interest. Microbial electrosynthesis (*MES*) cells are biological systems that produce biogas via microbial action and the supply of electrical energy. The *MES* subsystem can be integrated as a fundamental part of an energy storage and utilization system. The *OxyMES* scheme proposed is a *power-to-gas* system that seeks to neutralize the emissions of a standard industrial process through the hybridization of oxy-fuel combustion and bioelectrochemical processes. The energy balance analysis yielded a *power-to-gas* efficiency in the *MES* cell close to 51% and a global performance of the *OxyMES* integrated system close to 60%, for a cell with a faradaic efficiency of 80%, CO_2-to-CH_4 conversion rate of 95% and ΔV_{cell} = 1.63 V.

Keywords: Power to Gas; renewable energy surplus; CO_2 conversion; energy storage; biogas; oxycombustion, microbial electrosynthesis; hybrid and integrated processes.

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1. INTRODUCTION

According to the IEA, the *net-zero emissions* target for 2050 is to achieve a 45% reduction in total CO_2 emissions by 2030 compared 2010 [1]. The Paris Agreement and European recent commitments also force to implement an important increase of the contribution of renewable energy sources (RES) for the next years. In the case of EU of at least 40% of the final gross energy consumption [2, 3, 4].

For the rapid implementation of renewable energies in the electrical system to be viable, they need to be deployed alongside energy storage technologies that enable their integration into the electrical system, minimizing the electricity surplus and ensuring the operability of the system [5, 6]. *Power-to-gas* technologies (PtG), which make use of the renewable electricity surplus of the system for storing it in the form of gas through electrolysis [7, 8], is a sound alternative for energy storage. It allows the interconnection and transfer of energy between the electrical and the gas systems [9, 10], providing both with the possibility of increasing their capacity factor and flexibility and improving their ability to adapt to demand, expanding the profitability options by participating in other electricity market services [11].

Moreover, in 2016, emissions from energy use in industry accounted for 24.2% of the total of 49.4 $GtCO_{eq}$ [12]. Certain carbon-based industries will need to adapt their processes to neutralize them. The *power-to-gas* systems allow converting the current fossil fuel-based gas system into a system that operates with biologically derived gases generated with renewable sources, thus getting closer to a more environmentally sustainable energy model and circular economy [13, 14, 15].

In this context, local generated *power-to-gas* schemes based on biological subprocesses have been identified as being of great interest. Among them, one of the most promising options for converting electrical energy surplus is the use of microbial systems. Microbial electrosynthesis (*MES*) cells are biological systems that produce biogas as a result of microbial action and the supply of electrical energy. They are based on the fact that some microorganisms, such as methanogens, have the natural ability to use CO_2 to produce organic compounds [16]. It has been found that genera such as *Geobacter*, *Clostridium* and *Sporomusa* act as biocatalysts by accepting electrons from a solid electrode to reduce CO_2 directly or indirectly into organic compounds such as methane [17], according to Eq. 1:

$$CO_2 + 8H^+ + 8e^- \Longrightarrow CH_4 + 2H_2O \qquad E0' = -0.24\text{V vs SHE} \qquad \text{[Eq. 1]}$$

The transfer of electrons between microbes and electrodes can be via direct electron transfer (DET), indirect (IET) or through soluble electron acceptors acting as mediators (MET) [17, 18, 19]. The ability of microorganisms to produce methane from reducing CO_2 by using an electrode acting as a direct electron donor was first referenced by Cheng et al. [20]. During the electrochemical interactions of the cathode, hydrogen is produced, either by bioelectrochemical processes of certain microorganisms or by electrolysis reactions when applying a potential in the cathode immersed in an aqueous electrolyte. Hydrogen can act as an electron donor in CO_2 reduction reactions, thus promoting indirect electron transfer (IET). Depending on the potential applied to the cathode, one of the electron

transfer mechanisms (DET vs. IET) is favoured, although this parameter also influences the methane production obtained [17]. Villano et al. [19] and Gomez et al. [21] observed that a biocathode improves current densities compared to an abiotic cathode that only produces hydrogen.

Thus, *MES* cells mainly consist of two electrodes (anode and cathode) immersed in an electrolyte (water) and an electroactive biofilm on the cathode (biocathode) with microorganisms that electrocatalyse the CO_2 reduction reaction. A proton-exchange membrane (PEM) is also used to separate the anodic and cathodic chambers. The electrode in the anodic chamber is usually a mesh or sheet of some metallic material, such as Ti/IrO_2. Fig. 1 shows a basic diagram of an *MES* cell.

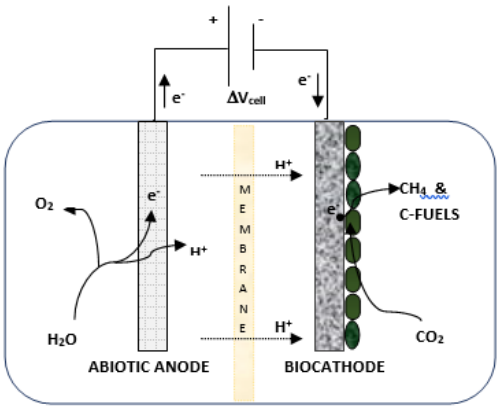


***Fig. 1**. Schematic representation of MES. Adapted from Bajracharya, et al [17]*

The *MES* system can be integrated as a fundamental part of an energy storage and utilization system. The *OxyMES* scheme proposed below is a *power-to-gas* system that seeks to neutralize the emissions of an industrial process through the hybridization of oxy-fuel combustion and bioelectrochemical processes. In this work, the integrated operation of units that work in oxy-fuel mode is studied to achieve the capture and conversion of their CO_2 emissions that, until now, have not been analysed jointly. There are references of studies of hybridization schemes of oxyboilers, clinker kilns and MSW incinerator in *power-to-gas* systems, [22], [23], [24], [25], all of them based on industrial systems of non-biological origin. In the *P2G-BioCat* project [26], hydrogen from an electrolyzer and CO_2 are methanized by microorganisms in a biological reactor; the biomethane produced is injected in the gas grid [27].

The design of the *OxyMES* system has been developed as a result of searching for emissions neutralization in industries that carry out oxy-fuel combustion processes. The use of these emissions in biological systems that convert them into products with an energetic value (biogas) is pursued. Certain designs of *MES* cells, such as the one proposed, allow obtaining pure oxygen as a byproduct in the anodic chamber, which is precisely what is used in the boiler during the oxycombustion [28].

This work presents the concept and the basic sizing of the main necessary equipment. Although the technological development of the *MES* cell is less advanced than the rest of the proposed processes, the study shows the potential of this technology when its

development accelerates and its technology readiness level (TRL) increases. The integration of conventional energy production systems (boilers) with novel bio-based systems (microbial electrosynthesis cells) presumes the main challenges to be addressed in this type of hybrid schemes.

2. DESCRIPTION OF THE PROPOSED PROCESS: OXYMES

The process integrates an oxycombustion plant (oxyboiler) with a microbial electrosynthesis system (*MES*). The diagram of the proposed process is schematically illustrated in Figure 2. The process combines the use of renewable electricity surplus with the capture of CO_2 emissions generated in industrial processes through the integration of biomethanization and oxy-fuel combustion processes. With this, it is possible to store the electricity surplus in the form of a biogas for its subsequent storage and delivery to the natural gas network or any other use.

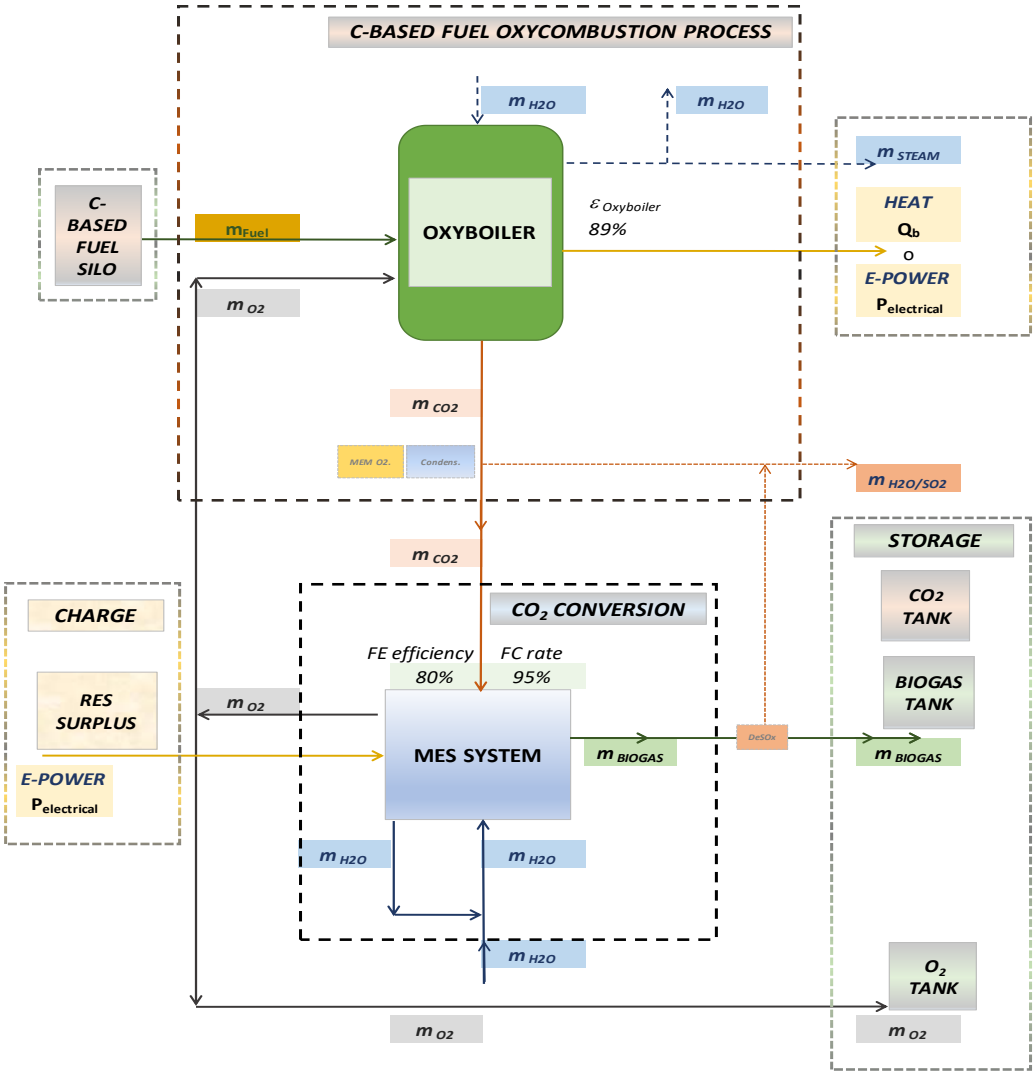


***Fig. 1**. Basic scheme for novel process proposed 'OxyMES', integrated by three main sub-units: Oxyboiler, MES cell and tanks system (boundary limits marked in dashed lines).*

The oxy-fuel boiler provides gases with a high concentration of CO_2 to the *MES* cell while generating steam for heating purposes and/or electricity production. In the cathodic chamber of the *MES* cell, CO_2 is converted into CH_4 which, together with the rest of the minor compounds of the oxycombustion gas stream, form what we will call *biogas*. Likewise, the anodic chamber produces a stream of pure oxygen that is used in the boiler for oxy-fuel combustion, thus avoiding the air separation unit (ASU), present in the typical designs for this type of industry [29].

The CO_2 gases from the industrial oxy-fuel combustion process are thus recovered as methane, forming a biogas fuel that can be totally or partially injected into the network once its composition has been adjusted to the quality requirements of the gas system [30]. The system includes oxygen storage tanks and biogas.

2.1. Oxyfuel boiler

The study is based on the design of a semi-industrial demonstration plant, which has a pulverized coal boiler with a nominal power of 20 MW_{th}, as well as the rest of the auxiliary systems necessary for its operation (preparation fuel train, oxidizers, etc.). This plant is located in the Technology Development Center of the *Fundación Ciudad de la Energía* (CIUDEN), located in Cubillos del Sil (León, Spain) [31]. The operating data of the oxycombustion plant were obtained during the tests carried out in the framework of the FP7 European co-funded project, *RELCOM* Project [32]. The experimental tests used bituminous coal of South African origin, whose characteristics are reflected in Table 1 of supplementary material. The plant performed tests both in conventional combustion with air as oxidizer, as well as in oxycombustion mode with different degrees of flue gases recirculating towards the boiler, mixed with pure oxygen (> 99.5% purity) supplied from cryogenic liquefied oxygen tanks.

2.2. MES system

In the *OxyMES* scheme, the inlet flows to the cathodic chamber of the *MES* cell are the combustion gases produced in the oxyboiler, the make-up water for the *MES* cell and the electricity to maintain the potential between the electrodes, which will come from the RES surpluses. Oxycombustion gases are mainly composed of CO_2, water vapour and N_2. The outlet streams of the *MES* cell, in the form of products, are a stream of high purity oxygen produced in the anode and another of biogas with a methane concentration greater than 50% by weight, produced in the cathode. Part of the oxygen produced in the *MES* cell is introduced into the oxyboiler to perform oxycombustion and replace the ASU oxygen supply. The remaining oxygen is stored in the tank.

MES systems, designed from the perspective of *power-to-gas bioelectrochemistry* (BEP2G), combine the production of energy carriers (CH_4) with the sequestration of CO_2 [21, 33]. The model that simulates what happens inside the *MES* cell considers that the oxygen evolution reaction (OER) that generates molecular oxygen (O_2) takes place at the

anode. Meanwhile, in the cathode, CO_2 is reduced to organic compounds due to the catalytic action of microorganisms. The protons (H^+) cross the membrane separating the two half-cells from the anodic chamber to the cathodic chamber. The redox half-reactions are:

Anode half-reaction:

$$2H_2O \rightarrow O_2^- + 4e^- + 4H^+ \qquad E^0 = -1.23\ V\ (E^0\ vs.\ NHE\ at\ pH\ 0) \qquad [Eq.\ 2]$$

Biocathode half-reaction:

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \qquad E^0 = 0.169\ V\ (E^0\ vs.\ NHE\ at\ pH\ 0) \qquad [Eq.\ 3]$$

where E^0 are the standard potentials related to CO_2 reduction and water oxidation with reference to Normal Hydrogen Electrode (NHE) at pH=0.

The process requires the contribution of energy from an external source, in the form of electrical energy, through the application of a potential to the electrodes, sufficient to trigger the reduction–oxidation reactions (redox) and overcome the losses of the process itself. This external energy will come from the surpluses of the electrical system. One of latest published works of *MES* cells designed for the simultaneous production of oxygen in the anode and methane in the cathode [21] uses a cell in which the potential applied between anode and cathode is 2.8 V. In addition, it should be noted that there are studies in which it has been shown that microorganisms are still active after an electricity supply interruption [34].

As seen in the redox half-reaction (Eq. 3), for the reduction of 1 mole of CO_2 to methane, 8 moles of electrons are needed, which implies that the gas flow to be treated from the oxyboiler stream involves a higher number of electrons to transfer through the external electrical circuit of the electrochemical cell compared to what would be required to produce other compounds such as hydrogen (supplementary material). Both the redox potential of the electrode and the pH of the electrolyte influence the species obtained in the cell [17].

Regarding electrode potentials, Villano et al. [19] observed that methane was produced in cathodic potentials more negative than −0.7 V (vs. Ag/AgCl), which corresponds to −0.5 vs. SHE at pH 7, and at −0.8 vs. SHE, the efficiency in the conversion of electrical current into methane reached 96%. Later, Villano et al. [35] reported methane production of 9.7 ± 0.6 mmol/l day in a two-chamber *MEC* cell, with a conversion efficiency of electrical current to methane of 84-90% and a conversion efficiency of acetate to current at the anode of 72-80%. The cathodic efficiency in methane production in most studies reaches 95-99% with biocathode potentials between -0.7 V and -0.8 V vs. SHE, [17]. Similarly, Batlle-Vilanova [36] reported a biocathode potential of -0.8 V vs. SHE, obtaining a faradaic conversion of 89.7% and a conversion ratio of CO_2 to methane of 95.8%. Gómez et al. [21] recently demonstrated the continuous production of methane in a cell with and without a membrane with a cathode potential between -0.9 V and 0.7 V vs. NHE, with an average cathodic efficiency of 84%.

In addition, in the *MES* cell during microbial electrosynthesis, a certain amount of thermal energy is produced that can be used in another part of the process. In this study, it was considered negligible.

2.3. Integrated process. Balance of Plant (BOP)

Fig. 3 identifies the main streams of the study. The gas stream to be introduced into the *MES* cell is taken from the outlet of the dust particle filter of the oxycombustion plant, normally set at 180 °C. At this point, the flue gases have the composition shown in Table 1. The flow and composition values of the fuel and the flue gases leaving the oxycombustion plant are obtained from the experimental tests performed in the reference demonstration plant [31], Table 1. The model is simulated by performing the mass and energy balances of each of the process streams. In this study, a base case of oxyboiler operation is considered, feeding 2550 kg/h of bituminous coal with the characteristics shown in supplementary material. This operational scenario remains fixed for the entire study, so that the flow rate of oxycombustion gases entering the *MES* cell is also constant for all cases and, therefore, the biogas produced.

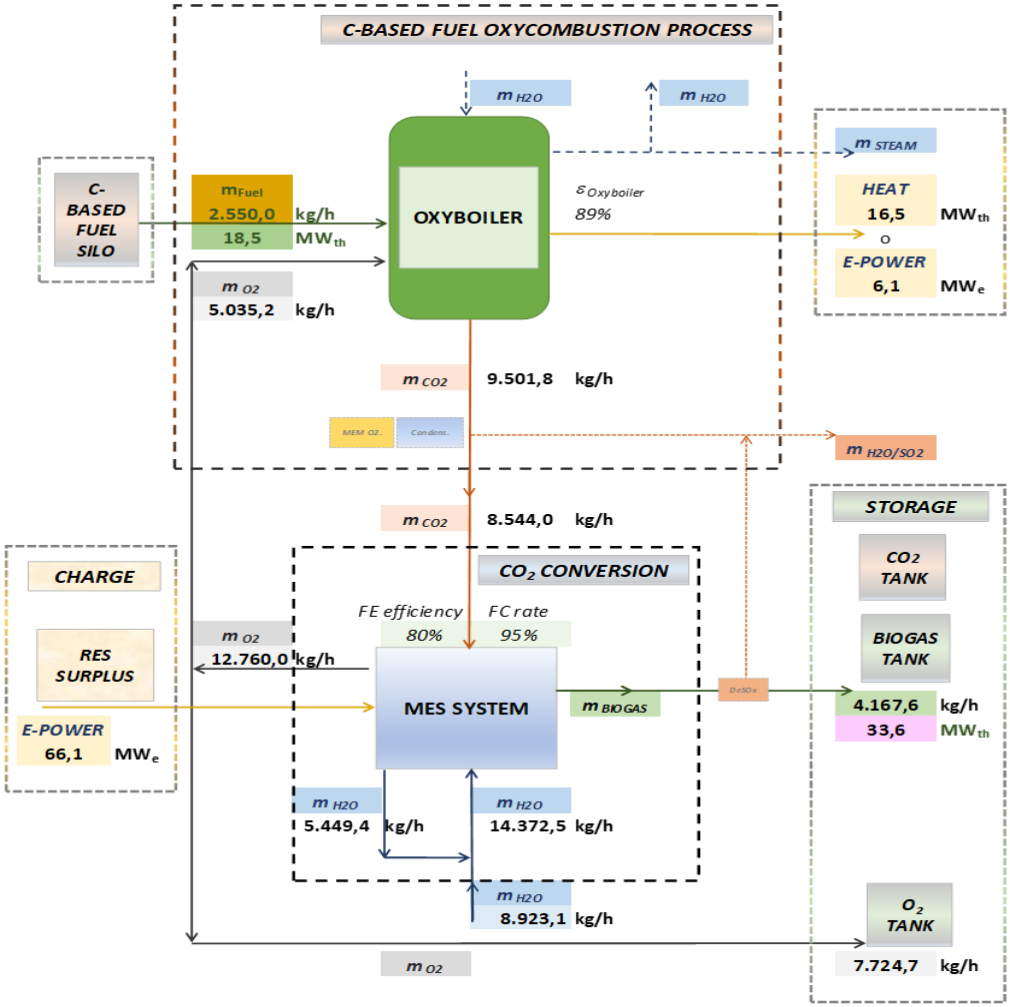


***Fig. 3**. Conceptual layout of the analysed OxyMES system, including main mass and energy flow data.*

	Oxyboiler plant outlet (%w_{th}, w.b.)	MES cell inlet (%w_{th}, w.b.)	MES cell outlet (%w_{th}, w.b.)
CH_4	-	-	57.96
CO_2	73.79	82.06	8.39
H_2O	10.38	2.91	2.91
N_2	11.56	12.86	26.29
O_2	3.54	1.57	3.22
SO_2	0.33	0.15	0.30
Ar	0.40	0.45	0.92

Table 1. *Flue gases composition at oxyboiler plant outlet and biogas composition at inlet/outlet of the MES cell.*

To avoid affecting the microorganisms of the *MES* cell, the temperature of the gas stream is set at 32 °C [37]. In addition, since the process must be anaerobic, the oxygen content is limited to a maximum of 2% by volume in the flue gas stream, however there are recent studies that indicate the possibility of reaching higher values, although methane production is reduced [38]. Staying oxygen below 2%$_{vol}$ involves incorporating a gas conditioning train ahead of the cell for cooling and condensing its moisture as well as part of the SO_2 and O_2 content. If in practice the oxygen content requirement is not met, a dedicated equipment (deOxo or similar) should be included to ensure this condition (out of the scope of this work). According to calculations, the biogas generated in the *MES* cell has the composition shown in Table 1.

Oxyboiler plant inlet/outlet	MES cell inlet/outlet
Fuel (pulverized coal) flow, m_f: 2.55 t/h LHV_{fuel}: 26137 kJ/kg Input thermal power, LHV, P_{in}: 18.5 MW_{th} Oxyboiler thermal efficiency, LHV, $\mu_{oxyboiler}$: 89% Output thermal power, LHV, P_{out} (Q_b): 16.5 MW_{th} Oxygen flow (fresh): 5.0 t/h Oxycombustion flue gases flow: 9.5 t/h ;180 °C *	Oxycombustion flue gases flow: 8.5 t/h ** CO_2 flow (contained in oxy-flue gases): 7.0 t/h O_2 content in oxy-flue gas: < 2%$_{vol}$ Net water consumption: 8.9 t/h Electrical power consumption: 66.1 MWe *** Biogas flow, m_{biogas}: 4.17 t/h CH_4 flow (contained in biogas), F_{CH4}: 2.4 t/h LHV_{CH4}: 50000 kJ/kg Biogas power, LHV: 33.64 MW Faradaic efficiency, FE: 80% CO_2-to-methane conversion rate, FC: 95% Operational temperature: 30-35 ° C

Table 2. *Main technical characteristics for units and subunits. Simulation assumptions and operational parameters for sizing main units OxyMES system.*

* *Oxycombustion flue gases at oxyboiler plant outlet, after recirculation (before stack).*

** *Oxycombustion flue gases after water condensation, at MES cell inlet.*

*** *The electrical power input for the MES is* calculated considering ΔV_{cell}:1.63 V, FE: 80%; FC: 95%.

The energy stored by the *OxyMES* is a function of the operating hours of the aforementioned system and these, in turn, of the storage tank capacity of the biogas produced in the *MES* cell. Initially, the design assumes that these operation hours will correspond to the number of hours in which the renewable electricity surpluses are produced, although this is a criterion that can vary according to the final application and the degree of autonomy sought. In this case, 10 hours of *MES* cell operation have been considered, with which the chemical energy stored in the form of biogas is 336 MWh_{th}. In turn, the operation of the oxyboiler is directly conditioned by the capacity of the oxygen tank, since this must be sufficient to cover the hours that the plant is in operation. In short, the system of tanks for storage of process fluids is a key element that directly affects the operation of the whole and must be properly designed so that they meet the expected stored energy (MWh) and autonomy objectives of the plant.

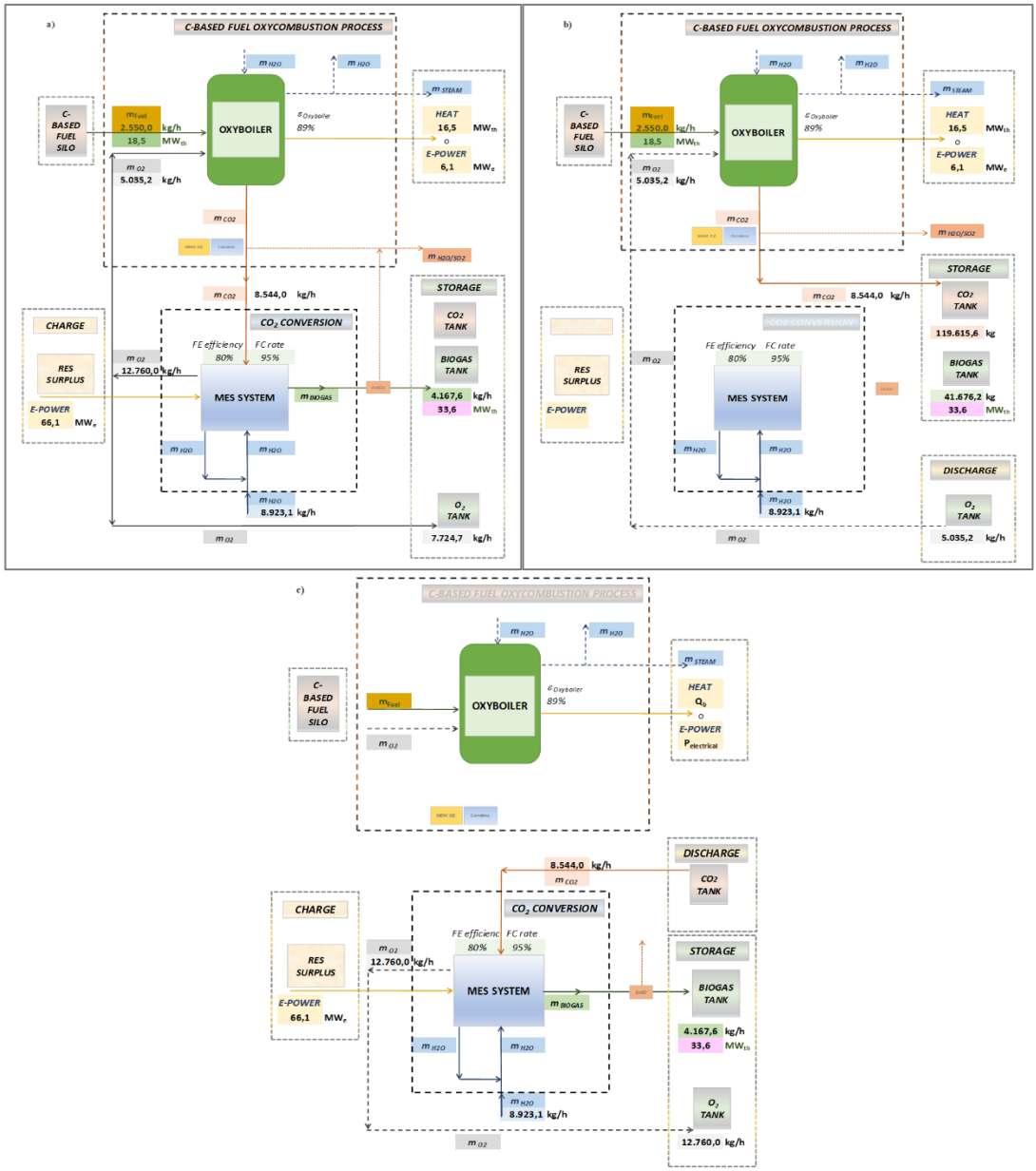


Fig. 4*. Charge, discharge and storage cycles in the OxyMES system standard operation profile. a) Oxyboiler and MES are ON: CO_2 from oxyboiler feeds the MES cell and it is converted to biogas and stored during a*

RES surplus period (RES charge, biogas and O_2 storage); b) Oxyboiler ON and MES OFF: CO_2 from oxyboiler is led to its storage tank during high-demand periods with no RES surplus; O_2 is fed to the oxyboiler to maintain the oxycombustion (CO_2 charge, O_2 discharge); c) Oxyboiler OFF and MES ON: during oxyboiler shutdowns when RES surplus occurs, CO_2 from tank feeds the MES cell to convert it into biogas (RES charge, CO_2 discharge, biogas and O_2 storage).

The *OxyMES* system can be parameterized as an energy storage one: 33.6 MW/336 MWh. Without going into detail considerations, the capacity and autonomy of the CO_2 tank are the parameters that will define the maximum power of the *OxyMES* system (33.6 MW), while the capacity of the biogas tank is the stored energy (336 MWh).

To size the complete *OxyMES* system, we begin by defining a daily operating profile of the *MES* cell considering that it operates during the hours in which the RES surpluses occur. For this work, an average of 10 h per day concentrated in the central hours of the day has been considered [39]. This assumption has been made by analysing the expected *oversupply* of renewable energies in scenarios projected to 2030 with high penetration of renewable energies (mainly solar and wind) and without storage systems (Fig. 5). It is during the operation of the *MES* cell that the biogas produced and the oxygen left unconsumed in the oxyboiler will be stored. Therefore, the oxygen stored during the charging process (Fig. 4.a) must be sufficient to cover the oxygen consumption of the oxyboiler during the next period, in which the *MES* cell is no longer coupled to the oxyboiler because there is no renewables surplus (Fig. 4.b). The final capacity of the tank system will depend on the hourly, daily or even weekly scope, defined by the operator of the industry or, in other words, the stored energy (MWh) that is to be made available to the system.

MES cell, inlets streams (consumptions)	
Oxyboiler flue gas flow after cooling, kg/h	8544
CO_2 flow (contained in oxy-flue gas) after cooling, kg/h	7011
Water net flow, kg/h	8923
(RES) Electrical power, MWe	66
MES cell outlets streams (products)	
Raw biogas flow, kg/h	4178
Methane flow (contained in the biogas flow), kg/h	2422
Oxygen flow, kg/h	12760

***Table 3**. Hourly flows of CO_2 consumed and oxygen and biogas produced in the MES cell from the mass balance calculations.*

MES cell, 10-hour operation profile	
Biogas stored*, kg//tank autonomy, h	41676//10 h
Biogas chemical energy stored, MWh_{th}	579
Oxygen store, kg//tank autonomy, h	77247//10 h
Oxygen net store (stock), kg	6754
CO_2 store, kg//tank autonomy, h	119615//14 h

***Table 4**. Minimum capacity of CO_2, O_2 and biogas tanks for 10 hours of MES cell operation. * Note: biogas is stored after a deSOx treatment (Fig. 3).*

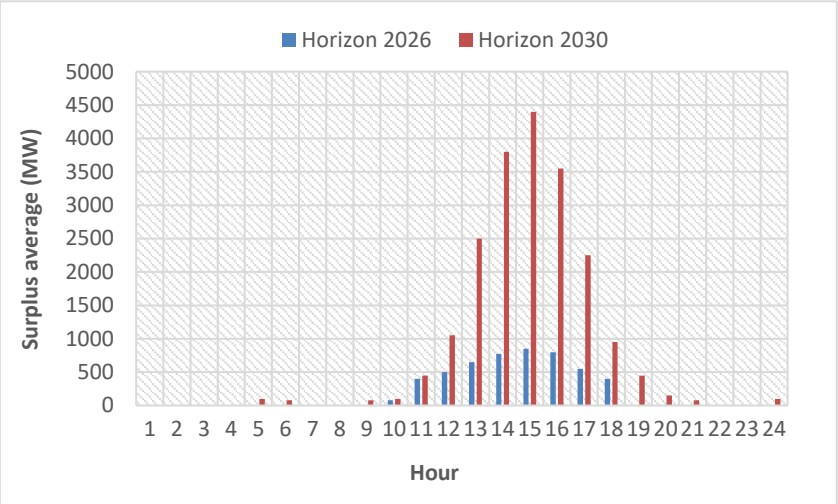


***Fig. 5**. Pattern of hourly oversupply associated with photovoltaic (PV) production in Spain (central hours of the day). In 2030, it will be able to reach values above 4000 MW. Adapted from [5]*

2.4. Analysis of partial performance and global performance of the OxyMES hybrid process

To evaluate the *OxyMES* process, the efficiency of the two main subsystems (oxyboiler and *MES* cell) that make up the hybrid system has been defined. These performances are calculated by the relationship between the energy produced and the energy supplied to operate the subsystem, according to their respective boundary limits (black dashed lines in Fig. 3). Then, the global *OxyMES* system performance can be obtained.

The thermal energy generated in the oxyboiler Q_b (MW_{th}) is a function of the performance of the oxycombustion boiler, $\mu_{oxyboiler}$, which has been calculated from the experimental data gathered in [32], resulting in an average value of 89% LHV basis, which is close to that reported in various studies on oxyfuel power plants (> 87.37% HHV, [29]; > 90% - 93% LHV, [40]). This Q_b is the thermal energy of the steam produced and it is available for thermal uses of the plant or for its conversion to electrical energy through a Rankine cycle in a steam turbine.

$$\mu\ Oxyboiler, LHV\ basis\ (\%) = \frac{Qb\ Oxyboiler}{LHVf \cdot \dot{m}f} x100 \qquad \text{[Eq. 4]}$$

In relation to the *MES* system, the electrical energy consumed comes from the *RES* surplus of the network. This is used to maintain the potential in the electrodes of the electrochemical cell, which is necessary to promote the transport of electrons that convert the CO_2 molecules into CH_4 ones. In turn, the chemical energy of the methane produced in the biocathode, E_{biogas}, can be considered as energy produced by the *MES* cell. The **electrical energy consumed** in the *MES* cell, required to reduce the CO_2 to methane, is:

$$E_{MES}=\Delta V_{cell}\cdot I \quad [MJ/tCH_4] \qquad [Eq. 5]$$

where ΔV_{cell} is the external applied voltage to the cell and I is the current intensity calculated as the specific flow of electrons from the anode to the cathode through the external electrical circuit.

$$\Delta V_{cell} = \Delta V_{theoretical\ cell} + E_{overpotentials} = E^0_{cathode} - E^0_{anode} + E_{overpotentials} \qquad [V] \qquad [Eq. 6]$$

Due to the losses of the electrochemical process in both electrodes, $E_{overpotential}$, it is necessary to apply a potential ΔV_{cell} greater than that theoretically necessary according to the thermodynamics of the global redox reaction, with $\Delta V_{theoretical\ cell} = E^0_{cathode} - E^0_{anode} = 0.169 - (-1.23) = -1.06$ V vs. NHE, pH 0 [Eq. 7], where E^0 are the standard potentials of the electrodes. The negative sign indicates that the reaction is not spontaneous.

To obtain the efficiency of the global microbial electrosynthesis process in the cell, the actual conversion of CO_2 to methane (FC or CO_2-to-CH_4 ratio) must be considered, thus expressing the carbon captured and converted into product. It is also necessary to consider a factor that indicates the efficiency in the electrical conversion towards that product, in the electrodes (mainly, cathode) of the cell (faradaic efficiency, FE) [36]. With these parameters, the specific flow of electrons per ton of methane produced, I, is calculated (Fig. 1):

$$I = (n_{CO2}\cdot n\cdot F\cdot 100/FE)\cdot(M_{CO2}/M_{CH4})\cdot(100/FC) \qquad [C/tCH_4] \quad [Eq. 8]$$

where n_{CO2}, is moles of CO_2/tCO_2, n is moles of electrons per mole of CO_2-to-CH_4, F is the Faraday constant, 96485 C/mol e-, and M *i*s the molecular weight. The electrical power consumed by the *MES* cell is:

$$P_{e\_MES} = E_{MES}\cdot F_{CH4} \quad [MW] \qquad [Eq. 9]$$

where F_{CH4} is the methane flow rate in t/h produced in the MES cell. The supplementary material includes the development of the calculation to obtain the specific current intensity, I, and the electrical consumption E_{MES} in the MES cell.

In experimental studies, it has been found that to achieve interesting results in the operating parameters of the cells, the potential applied to the cell (ΔV_{cell}) varies, in practice, between values close to 4 V [41] and 2.6 V [21], although it is expected to be able to reduce these values to approximately 1.7 V, in view of the lower value of biocathode potential reported thus far (-0.4 V vs. SHE) by Beese-Vasbender et al. [42], which also reached a cathodic efficiency of 80%.

Based on the bibliographic references [17] and [21], for the calculation of the electrical consumption of the *MES* cell in this study, a faradaic efficiency value, FE, of 80% and a

CO_2 to methane conversion factor, FC, of 95% were used. Applying the previous equations, the results of the electrical power consumed, P_{e_MES}, are presented in Table 5 for four assumptions of the external applied voltage (ΔV_{cell} = 1.23 V, 1.63 V, 2.8 V and 3.5 V).

With all of the above, the energy efficiency of the *power-to*-gas conversion is calculated in the *MES* cell (μ_{PtG_MES}) as the ratio between the energy obtained in the form of chemical energy from biogas (E_{biogas}) and the electrical energy supplied to produce the aforementioned biogas (E_{MES}):

$$\mu\, PtG_{MES}(\%) = \frac{Ebiogas}{EMES} x100 = \frac{LHVCH4 \cdot \dot{m}CH4}{\Delta Vcell \cdot I} x100 \qquad \text{[Eq 10]}$$

The value obtained from this *power-to*-gas efficiency, μ_{PtG_MES}, for the case ΔV_{cell} = 1.63 V is 50.88%, as shown in Table 5.

Finally, once the energy balances are performed for each subunit, the **global efficiency of the oxyMES process** is calculated ($\mu_{PtGtHeat\_OxyMES}$) taking as inputs to the boundaries of the global system, the chemical energy contained in the oxyboiler fuel ($LHV_f \cdot m_f$) and the electrical energy that feeds the *MES* cell (E_{MES}) and, as outputs, the thermal energy of the steam produced in the oxyboiler ($Q_{bOxyBoiler}$) and the chemical energy of the biogas (E_{biogas}) generated in the biocathode of the *MES* cell:

$$\mu\, PtGtHeat_{OxyMES}(\%) = \frac{Qb\ OxyBoiler + Ebiogas}{LHVf \cdot \dot{m}f + EMES} x100 = \frac{Qb\ OxyBoiler + LHVCH4 \cdot \dot{m}CH4}{LHVf \cdot \dot{m}f + \Delta Vcell \cdot I} x100 \text{ [Eq. 11]}$$

If the global performance is calculated for the selected base case of the oxyboiler operation (18.51 MW_{th} LHV, Table 5, corresponding to the 2550 kg/h of bituminous coal selected) and an external potential applied in the MES cell of ΔV_{cell} = 1.63 V, the result obtained is 59.22%, Table 5.

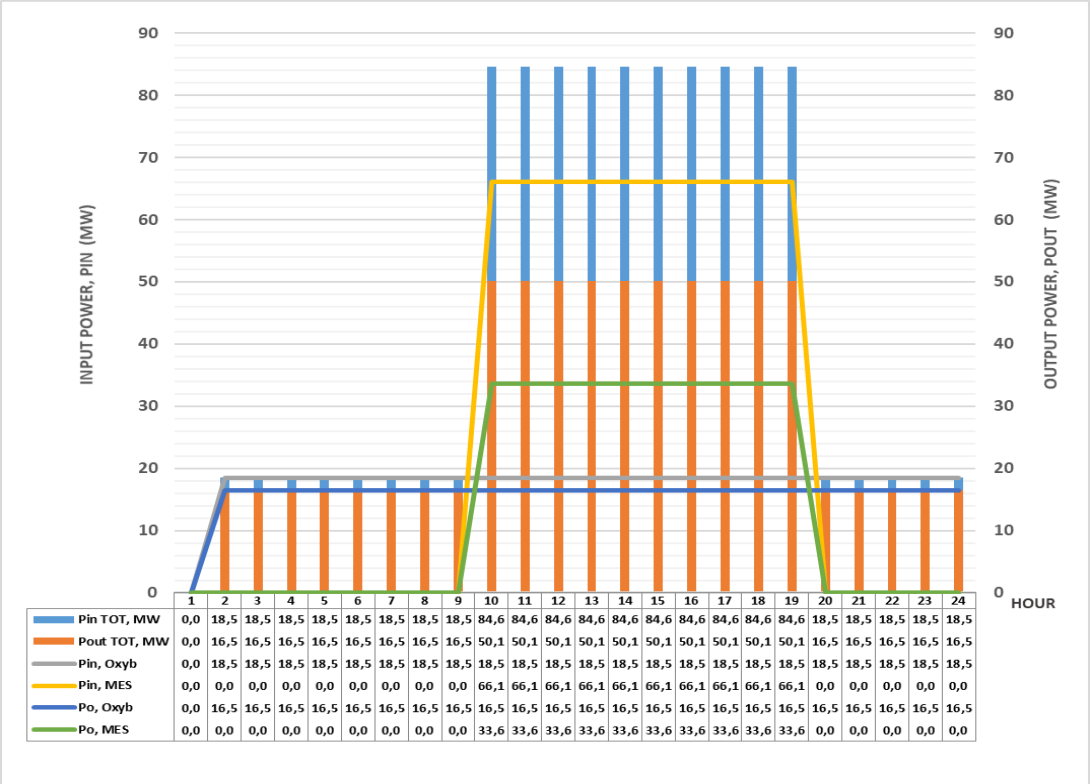
3. RESULTS AND DISCUSSION

3.1. Operating profile

As mentioned initially, it has been chosen as basic conditions for the *OxyMES* design that global emissions are zero and that the system is as self-sufficient as possible. These two conditions influence the design and sizing of the different main units that make up the *OxyMES* scheme. The condition of a self-sustaining system necessarily implies the use of tank storage for the process fluids (oxygen and biogas) and eliminates their external supplies, especially oxygen. In addition, the tank system allows the transfer of energy in the successive cycles of charging and discharging to/from the electrical and gas system, with oxygen acting as *feedstock* and biogas as an *energy carrier*.

To carry out these charging and discharging cycles, the oxygen and biogas tanks are sized so that they can cover the demand of the boiler during the periods in which the *MES* cell is inactive. In these periods (Fig. 6, 12 am-8 am and 7 pm-12 pm), the oxycombustion gas stream is stored in its corresponding tank (Fig. 4.b). Table 4 shows the minimum tanks capacity for 10-hours continuous cell operation. However, the final sizing of the tank

system will be determined not only by the duration of the product charging and discharging cycles but also by its operation profile (continuous/discontinuous) and by the planning of its final discharge in each cycle of plant operation. We will understand the *cycle of operation* of the plant as the time between two discharges to the external network of the accumulated stock of oxygen, CO_2 and biogas.



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Pin TOT, MW	0,0	18,5	18,5	18,5	18,5	18,5	18,5	18,5	18,5	84,6	84,6	84,6	84,6	84,6	84,6	84,6	84,6	84,6	84,6	18,5	18,5	18,5	18,5	18,5
Pout TOT, MW	0,0	16,5	16,5	16,5	16,5	16,5	16,5	16,5	16,5	50,1	50,1	50,1	50,1	50,1	50,1	50,1	50,1	50,1	50,1	16,5	16,5	16,5	16,5	16,5
Pin, Oxyb	0,0	18,5	18,5	18,5	18,5	18,5	18,5	18,5	18,5	18,5	18,5	18,5	18,5	18,5	18,5	18,5	18,5	18,5	18,5	18,5	18,5	18,5	18,5	18,5
Pin, MES	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	66,1	66,1	66,1	66,1	66,1	66,1	66,1	66,1	66,1	66,1	0,0	0,0	0,0	0,0	0,0
Po, Oxyb	0,0	16,5	16,5	16,5	16,5	16,5	16,5	16,5	16,5	16,5	16,5	16,5	16,5	16,5	16,5	16,5	16,5	16,5	16,5	16,5	16,5	16,5	16,5	16,5
Po, MES	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	33,6	33,6	33,6	33,6	33,6	33,6	33,6	33,6	33,6	33,6	0,0	0,0	0,0	0,0	0,0

***Fig. 6**. OxyMES daily operation profile. Adjusted to the RES discharge profile in Spain. $P_{in\ TOT}$ (blue) refers to the total power input (MW) to the global system per hour: sum of chemical coal-fuelled power consumed by the oxyboiler (grey) and electric power consumed by the MES cell (yellow). $P_{out\ TOT}$ refers to the total power produced (MW) by the global system per hour: sum of steam heat power (MW) generated in the oxyboiler (dark blue) and biogas chemical power produced (MW) by the MES cell (green).*

Fig. 7 shows the influence of the operating profile of the plant on the number and size of the final tanks to be installed. If the discharge cycle is a daily one, the size of the oxygen storage tank can be optimized by proposing a discontinuous intraday cell operation, Fig. 8. The greater the time lag between the two start-ups of the *MES* cell, the lower the required maximum value of the oxygen tank capacity.

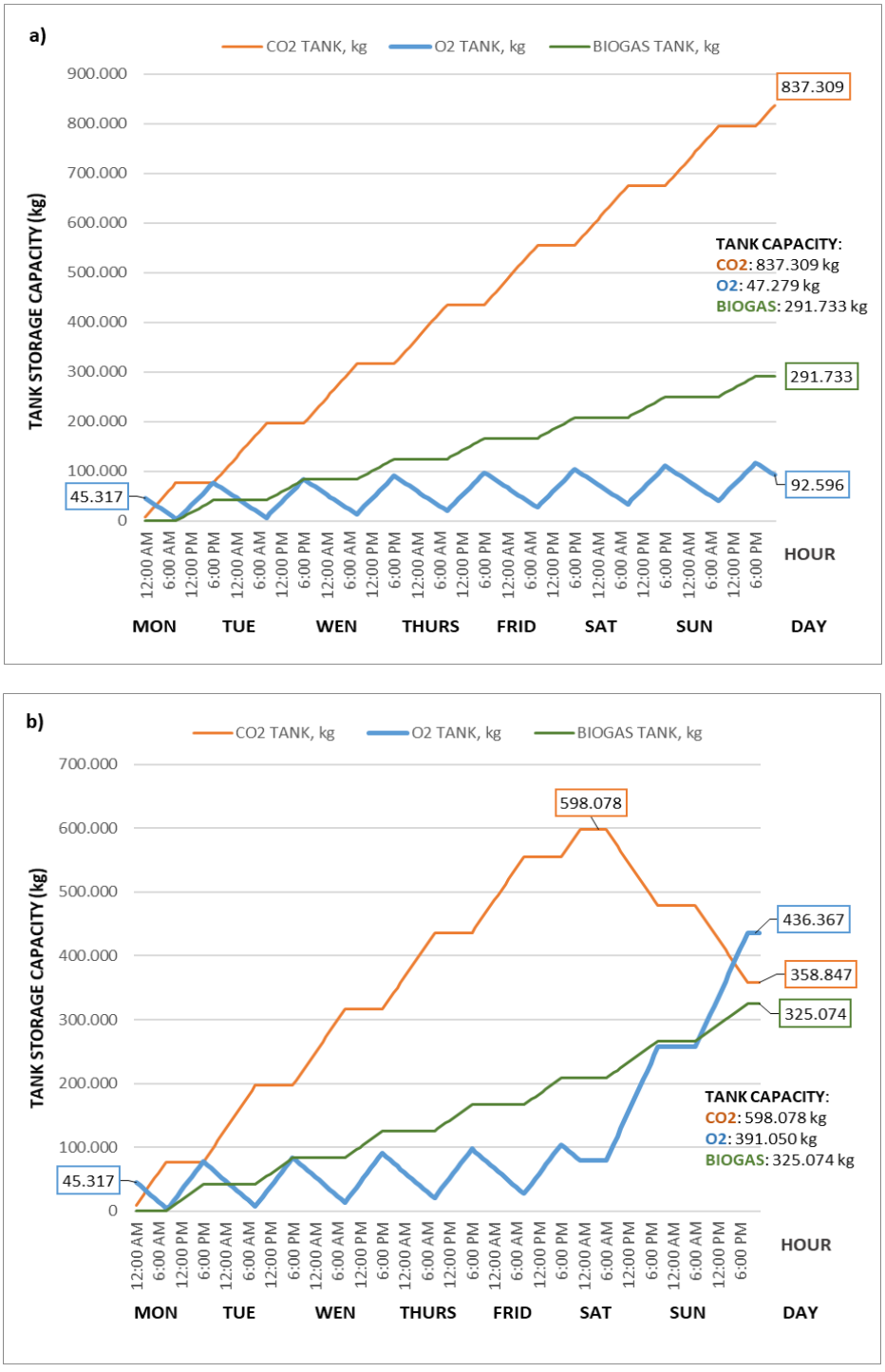


***Fig. 7 a, b**. Daily operation of the OxyMES system in the weekly operation cycle: a) Continuous operation from Monday to Sunday, 24 h/day for oxyboiler and 10 h/day for MES cell; b) Continuous operation from Monday to Friday, 24 h/day for Oxyboiler and 10 h/day for MES cell; from Saturday to Sunday, 14 h/day for MES cell (assuming higher surplus hours during the weekend). In each operation scenario a) and b), the minimum weekly storage capacity necessary for the CO_2, O_2 and biogas tanks is obtained according to the plant operation cycle.*

Fig. 8 a, b, c*. Tank storage capacity operating with a daily discharge cycle: a) continuous operation of 10 hours of MES cell; b) discontinuous operation in two 5-hour periods of MES cell with two hours of lag between each period; c) discontinuous operation in two 5-hour periods of MES cell with three hours of lag between each period. The peak capacity value of the oxygen tank decreases as the offline period of the MES cell increases between operating periods.*

From an application perspective in new decentralized energy models, the *OxyMES* schemes will better optimize their design and operation if they are integrated into networks connecting various industries, forming an *industrial hub*, so that they can transfer their surplus energy pre-carriers and carriers (CO_2, oxygen and biogas). In this way, the interconnection network itself will act as a buffer of the whole system and this would be a matter of advancing in the construction of a "*system of systems*" aimed at the effective implementation of circular and sustainable economy models [43].

3.2. Comparison of efficiency according to different scenarios of MES cells

For the same biogas production, four scenarios have been proposed in the sensitivity analysis of the efficiencies μ_{PtHeat_OxyMES} as a function of the cell potential (ΔV_{cell}), which is directly related to the energy consumed by the cell (Table 5). The four scenarios analysed are based on data and initial assumptions reported by different research groups mentioned

throughout the article. In this sense, it seeks to cover a reasonable range of *MES* cell operation in terms of the external potential to be applied. The most unfavourable potentials selected for the study are those that assume a greater electrical consumption in the cell: ΔV_{cell} = 3.5 V, a case similar to that reported by Zhou et al. [41] and ΔV_{cell} = 2.8 V by Gomez et al. [21], and represent the current state of the art (TRL3-4).

On the other hand, an optimistic scenario is proposed with lower cell overpotentials, and according to the trend in the results obtained by the different research teams, it is predicted that it can be achieved in the short term; in this case, the applied voltage would be ΔV_{cell} = 1.63 V, and assumption reached based on the lowest biocathode potential reported by Beese-Vasbender et al. [42] (-0.4 V vs. SHE). Finally, the fourth scenario simulates the theoretical minimum cell potential to be applied (ΔV_{cell} = $\Delta V_{theoretical\ cell}$ = 1.23 V) when considering no overpotentials losses; this scenario would represent the theoretical upper limit of the performance value that *OxyMES* could be aim for. In all scenarios, it is considered the same flow of oxycombustion gases entering to the *MES* cell.

	ΔV_{cell} = 1.23 V	**ΔV_{cell} = 1.63 V**	**ΔV_{cell} = 2.8 V**	**ΔV_{cell} = 3.5 V**
Chemical energy of inlet fuel fed to oxyboiler (LHV), MW_{th}	18.51	18.51	18.51	18.51
$\mu_{Oxyboiler}$, Oxyboiler efficiency (LHV), %	89.00	89.00	89.00	89.00
Q_b, heat absorbed by steam, MW_{th}	16.48	16.48	16.48	16.48
Chemical energy of biogas (LHV), MW_{th}	33.64	33.64	33.64	33.64
P_{e_MES}, MES electric consumption, MW_e	**49.89**	**66.11**	**113.57**	**141.96**
μ_{PtG_MES} MES efficiency, %	**67.43**	**50.88**	**29.62**	**23.70**
$\mu_{PtGtHeat\_OxyMES}$, OxyMES global efficiency, %	**73.26**	**59.22**	**37.94**	**31.23**

Table 5*. Summary of energy produced, consumed and efficiencies obtained for four ΔV_{cell} scenarios.*

Table 5 shows the influence on the performance of the electrical cell overpotentials [44] due to their direct relationship with the *MES* cell electrical consumption. Reducing these losses to a minimum is a fundamental objective to advance the development of *MES* technologies and their integration into different processes. The results obtained indicate achievable values of *power-to-gas* performance (μ_{PtG_MES}) of 51% in the *MES* cell and 60% for the *OxyMES* integrated global system ($\mu_{PtGtHeat\_OxyMES}$). These data are in line with those reported for other *power-to-gas* schemes, such as [22, 45, 46]. This gives us an idea of the perspectives and applicability of the hybridization proposed in this work.

3.3. Comparison of *OxyMES* with conventional CO_2 capture plants

Another interesting advantage of OxyMES process is that the production of the oxygen necessary for the oxycombustion is carried out '*in situ*' in the *MES* reactor. This represents a significant advantage in that it avoids the CAPEX and the OPEX of the oxygen

generation units used in conventional oxycombustion plants with CO_2 capture (ASU) [47]. The ASU facilities assume between 5% and 6% penalties in the global energy efficiency of CO_2 capture plants [40, 48]. Similarly, the CO_2 compression and purification unit (CPU) is necessary for the delivery of CO_2 captured for transport and deep geological storage. In this case, the global efficiency penalty introduced by these units is between 4.5 % and 5% [40].

If we analyse the specific energy consumption W_{ASU} and W_{CPU} (kWh_e/kWh_{th}) of the ASU and CPU facilities that no longer need to be installed in the *OxyMES* scheme, expressed over the thermal energy of the steam produced in the oxyboiler, and compare them to the new units that need to be installed W_{MES} (*MES*), it can be done an approximate quantification of the relative energetic improvement against an oxycombustion plant with conventional CO_2 capture (see supplementary material). As a first option, it is proposed to store the biogas for subsequent delivery to the gas system, so this would require a prior treatment of upgrading to biomethane. For the calculation of $W_{Upgrading}$ (kWh_e/kWh_{th}), the specific energy consumption of the upgrading plant considered is 0.28 kWh_e/kg biogas (0.25 kWh_{th}/Nm^3 biogas) [49, 50].

Table 6 shows the results of this comparative study, which is carried out on the scenario of ΔV_{cell} = 1.63 V. In option A, the specific energy consumption of the *MES* cell (W_{MES}) has been included, while in options B and C, this consumption is considered negligible because it comes from surpluses of the electrical system. Option C reflects the improvement when the biogas is used as fuel for the oxyboiler ($W_{Upgrading}$ = 0).

[Energy saved (E_s) + Energy produced (E_p)] vs. [Energy consumed (E_c)] [Eq. 12]

	W_{ASU} (kWhe/kWht Q_b)	W_{CPU} (kWhe/kWht Q_b)	W_{Biogas} (kWhe/kWht Q_b)	W_{MES} (kWhe/kWht Q_b)	$W_{Upgrading}$ (kWhe/kWht Q_b)	ENERGY GAIN / LOSS (kWhe/kWht Q_b)
IMPROVEMENT OPTION A: ASU & CPU avoided, MES and Upgrading biomethane to network						
A.1	0.0581	0.0511	0.7437	4.01244	0.0712	-3.2308
A.2	0.0581	0.0511	0.0000	4.01244	0.0712	-3.9745
IMPROVEMENT OPTION B: ASU & CPU avoided, MES 100% surplus RES and Upgrading biomethane to network						
B.1	0.0581	0.0511	0.7437	0.00000	0. 0712	0.7816
B.2	0.0581	0.0511	0.0000	0.00000	0. 0712	0.0379
IMPROVEMENT OPTION C: ASU & CPU avoided, MES 100% surplus RES, biogas for self-consumption						
C.1	0.0581	0.0511	0.7437	0.00000	0.00000	0.8528
C.2	0.0581	0.0511	0.0000	0.00000	0.00000	0.1091

Table 6. Relative specific consumption: results of the comparison with the reference plant (oxycombustion plant with CPU). Note: W_{Biogas} calculated considering a thermal to electric conversion efficiency of 36.43% (efficiency from a small-size CCGT plant). W_{ASU} calculated considering 190 kWhe/tO_2 [22] and W_{CPU}, 120 kWhe/CO_2 [51].

The improvements obtained according to options B.1 and B.2 indicate that, depending on the chosen biogas upgrading technology, the avoided specific energy consumption of ASU and CPU (W_{ASU} and W_{CPU}) could alone compensate the specific energy consumption ($W_{Upgrading}$) of the upgraded installation, even without considering the thermal energy contained in the biogas (option B.2). The best energy improvement is achieved when upgrading is not required (options C.1 and C.2) replacing the original fossil fuel by the *MES* biogas for self-consumption purposes.

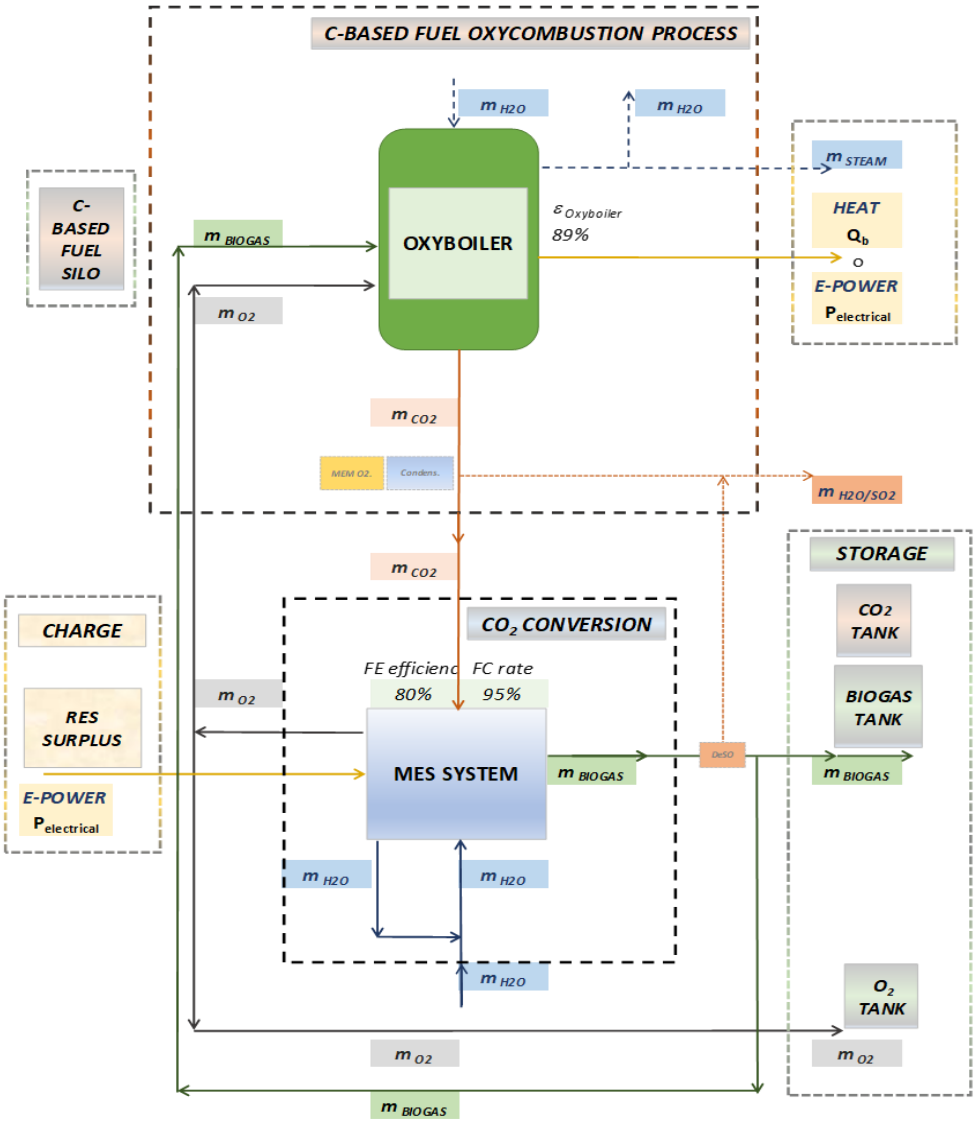


Fig 9. 100% self-sustaining "OxyMES" scheme, fed with the biogas produced in the MES (option C Table 6).

After this preliminary comparative analysis, it is concluded that **an *OxyMES* system provides the energy storage function without energetically penalizing the process** if it is compared with an oxycombustion plant with conventional CO_2 capture. From the energy point of view, the best option for the implementation of the *OxyMES* scheme would be to

apply it as a measure to decarbonize an industry, switching the original fuel of the oxycombustion boiler to the biogas generated in the *MES* cell (future study). This also allows this industry to store RES surplus (see Figure 9) and consider new business models that generate benefits derived from the energy storage market, which is currently undergoing not only technical but also regulatory development [52, 53]. The second most favourable option for the *OxyMES* implementation would be to use it as a system for neutralizing the emissions of an industry recovering the CO_2 to biomethane for its network injection, without having to substitute its primary fuel.

In any case, the *OxyMES* system has intrinsic advantages in that it produces biogas and oxygen in a single piece of equipment ('*all-in-one*'), while other *power-to-gas* systems require two intermediate steps with their corresponding equipment each (electrolyzer and methanizer) [24, 54, 55]. Regardless, the production of oxygen in microbial systems represents one of the greatest challenges facing *MES* technologies due to the high CAPEX required to achieve stable membranes and anodes [56].

4. CONCLUSIONS

In this study, a novel scheme has been proposed for the storage of renewable electrical energy surplus for its conversion to biogas through the hybridization of a microbial electrosynthesis (*MES*) system with an industrial process operating in oxycombustion. The *MES* cell is capable of treating the flue gases from the oxycombustion boiler and converting them into biogas while providing it with the necessary oxygen for the oxycombustion. The biogas can be stored and, later, purified to be discharged to the natural gas network. This is an advantage over other *power-to*-gas schemes when valorizing CO_2 and producing oxygen in a single piece of equipment (*MES* cell).

The *OxyMES* system process has been simulated by integrating the gas flows from the oxycombustion boiler to the *MES* cell and the biogas generated in it according to four operating scenarios of the *MES* cell. These four cases are a function of the external applied voltage to the electrodes: 1.23 V, 1.63 V, 2.8 V and 3.5 V. From the energy balance analysis of the set, the *power-to-gas* efficiency in the *MES* cell is obtained, reaching a value close to 51%; the global performance of the integrated *OxyMES* system resulted in nearly 60%, for a cell with an FE 80%, FC 95% and ΔV_{cell} = 1.63 V.

Another possible route for the use of the *MES*-cell biogas is its utilization within the industrial process itself as a primary fuel, displacing the existing fossil fuel-based one. At this point, the range of possible uses for self-consumption is extensive and will depend on the characteristics of each industry. In this work, its self-consumption in the oxyboiler is proposed so that it replaces the original fossil-fuel with a bio-renewable origin one. This possibility is very interesting since it is possible to adapt the process to a circular economy one and convert it into a *net-negative-emissions technology* system (*NET* system). With the proper sizing of the O_2, biogas and CO_2 process tank system, it is possible to achieve 100% autonomy and self-sustainability of the original industrial process. The influence on the tank system design of the duration chosen for energy storage has been studied, that is, of

the operating cycles of the plant and of the daily charging and discharging cycles of the O_2, biogas and CO_2 fluids. These fluids act as energy *pre-carriers* and *carriers*. It is seen how for the new models of distributed generation with energy storage based on *power-to-gas* systems, such as the proposed *OxyMES*, they are better positioned if they are integrated into larger systems forming hubs of different industrial processes ('*system of systems*' concept), forming local networks to transfer their surplus energy *pre-carriers* and adapted to their environment.

Future studies could address the coupling of bottom cycles to the OxyMES process to produce dispatchable electricity in a *power-to-power* scheme. This would enable the industrial operator to participate in new electricity market models.

Finally, it is worth highlighting the great advantage of the *OxyMES* system, based on microbial electrosynthesis, compared to other proposed *power-to-gas* solutions: it is an *all-in-one* system, which means that it converts CO_2 to biogas and produces oxygen for oxy-fuel combustion, all within a single system, with the consequent savings in CAPEX and OPEX.

CRediT authorship contribution statement

Ruth Diego: Formal analysis, Investigation, Methodology, Writing- Original draft preparation, Writing - Review & Editing, Visualization. **Antonio Morán**: Conceptualization, Methodology, Supervision, Funding acquisition and Review. **Luis M. Romeo**: Conceptualization, Methodology, Supervision and Review.

Declaration of competing interest

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

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Appendix A. Supplementary material

PDF file.

NOMENCLATURE

Abbreviations

ASU: Air Separation Unit

CAPEX: Capital Expenditures

CCS: CO_2 capture and storage

CO_2-to-CH_4 ratio = FC

CPU: Compression and Purification Unit

Current-to-methane efficiency = Faradaic efficiency = FE

kWh: Kilowatt hour

MEC: Microbial Electrolysis Cell

MES: Microbial Electrosynthesis System

MWh: Megawatt hour

MSW: Municipal Solid Waste

OPEX: Operational Expenditures

PEM: Proton Exchange Membrane

PtG: Power to Gas

PV: Photovoltaic

RES: Renewable Energy Sources

Symbols

F: Faraday constant, 96485 C/mol e^-

HHV: Higher Heating Value [kJ/kg]

LHV: Lower Heating Value [kJ/kg]

M: molecular weight [g/mol]

m: mass flow [kg/h] or [t/h]

μ: efficiency (%)

NHE: Norμal Hydrogen Electrode (V)

Q: thermal power [MW_{th}]

SHE: Standard Hydrogen Electrode (V)

ΔV: external applied voltage [V]

W: specific energy consumption [kWh_e/kWh_{th}]

Subscripts:

b: boiler

e: electricity

649 f: oxycombustion plant fuel (coal)

650 d.b.: dry basis

651 w.b.: wet basis

652 vol: by volume

653 th: thermal

654 wth: weight

655

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