CARBON CAPTURE AND UTILIZATION VIA CALCIUM LOOPING, SORPTION ENHANCED METHANATION AND GREEN HYDROGEN: A TECHNO-ECONOMIC ANALYSIS AND LIFE CYCLE ASSESSMENT STUDY

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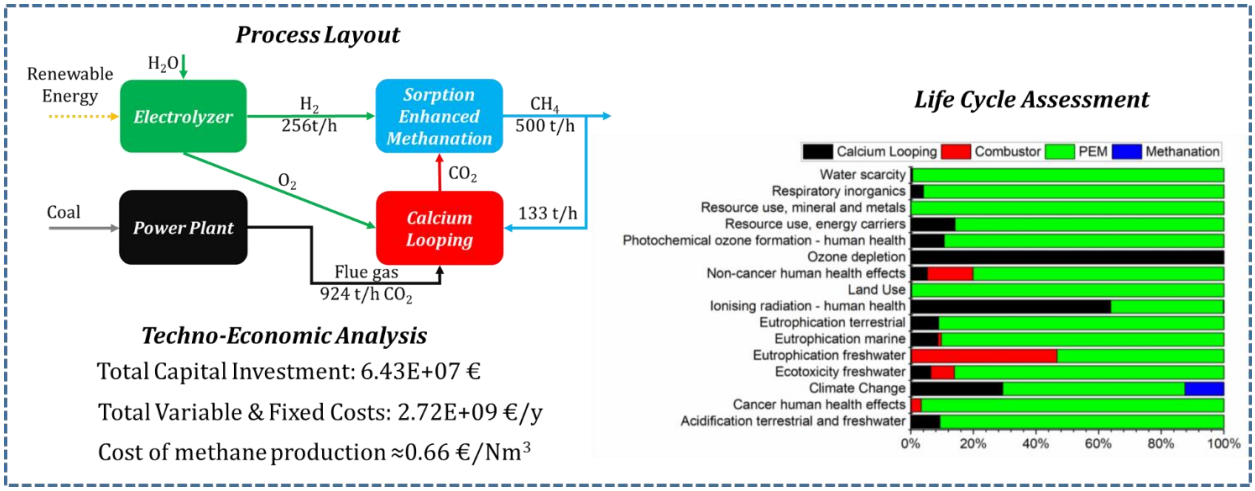
Graphical Abstract



ABSTRACT

The production of synthetic methane using CO_2 from flue gases and green hydrogen appears to be a promising way to combine the concepts of renewable energy, chemical storage, and utilization of CO_2. Recently, a new reactor configuration for catalytic methanation has been proposed, integrating sorption-enhanced methanation and chemical looping in interconnected fluidized bed systems. This configuration would ensure high methane yields while keeping good temperature control and low operating pressure. In this work, such novel system layout for the catalytic production of methane was combined with a calcium looping unit for CO_2 capture from flue gases of a coal-fired power plant, and with a water electrolyzer sustained by renewable energy. The integrated layout offers a series of advantages deriving from the integration of different mass and energy flows of the different sections of the plant. The performance of this latter was assessed in terms of construction and production costs, as well as from an environmental point of view: a life cycle assessment was carried out to quantify the environmental impact of all process units. Results of the techno-economic analysis indicated that the production cost of methane is higher than that of natural gas (0.66 vs 0.17 €/Nm^3), but lower than that of biomethane (1 €/Nm^3). The largest impact on such costs comes from the PEM electrolyzer. The LCA analysis showed that the environmental performance is better in some categories and worse in others with respect to traditional scenarios. Again, the PEM electrolyzer appears to account for most of the environmental impacts of the process.

Keywords: Techno-Economic Analysis; Life Cycle Assessment; CO_2 Capture; Carbon Capture and Utilization; Calcium Looping; Sorption Enhanced Methanation**.**

Nomenclature

C1	Cyclone 1	LCA	Life Cycle Assessment
C2	Cyclone 2	N_{np}	Number of non-particulate processing steps
C3	Cyclone 3	N_{OL}	Number of operators per shift
C4	Cyclone 4	P	Number of processing steps
CaL	Calcium Looping	PEM	Polymer Electrolyte Membrane electrolyzer
C_{OL}	Cost of operating labor	S1	Blower 1
C_{RM}	Cost of raw materials	S2	Blower 2
C_U	Cost of utilities	S3	Blower 3
C_{WT}	Cost of waste treatment	S4	Blower 4
DPC	Direct Plant Cost	SEM	Sorption Enhanced Methanation
EC	Equipment Cost	TCI	Total Capital Investment
FC	Fixed Costs	TEA	Techno-Economic Analysis
FCI	Fixed Capital Investment	TPC	Total Product Cost
H1	Heat exchanger 1	VC	Variable Costs
H2	Heat exchanger 2	WC	Working Capital
IPC	Indirect Plant Cost		

1. INTRODUCTION

The most attractive solution to rapidly reduce CO_2 emissions and the consumption of fossil fuels, responsible for 85% of the greenhouse gas emissions, is the implementation of renewable energy systems, mostly based on solar and wind energy. However, these technologies will not be ready to totally replace the fossil energy systems in the short/medium term, especially because of their intermittent energy production mode [1,2]. Thus, a short-term solution to contain CO_2 emissions generated by fossil fuel consumption may be represented by Carbon Capture and Utilization (CCU) technologies. Among all the possible final products obtainable with these technologies [3,4], synthetic methane is one of the most attractive, due to the existence of a well-developed infrastructure for distribution, and to the wide demand and acceptance of this fuel for industrial and domestic usage. In addition, methane represents a smart energy carrier that can store significant amounts of renewable energy in the natural gas grid. Global methane market is expected

to reach $151.27 billion by 2026 growing at a Compound Annual Growth Rate (CAGR) of 6.1% during the period from 2017 to 2026.

From an industrial point of view, the exothermic catalytic methanation of CO_2 is typically carried out at high pressure in a reactor arrangement composed by a cascade of fixed bed reactors with intermediate cooling; the arrangement enables controlling peak temperature of the system and hence preventing the deactivation of the catalyst [5,6]. A sufficiently high methane purity is needed for injecting synthetic methane into the natural gas grid. The concept of Sorption-Enhanced Methanation (SEM), first formulated by Borgschulte et al. [7] and Walspurger et al. [8], on the basis of the Le Chatelier principle, would allow the process to achieve high degrees of methane conversion at lower pressures, leading to savings in compression energy up to 40%. Specifically, the steam generated by the methanation reaction can be removed from the catalytic bed by adding a suitable sorbent material, in order to push the equilibrium reaction towards methane formation [7,8].

Recently, Coppola et al. [9–11] proposed a novel reactor configuration which combines the concepts of SEM and of chemical looping in dual interconnected fluidized bed systems. Such configuration would ensure good temperature control and lower operating pressure, and most importantly the possibility to carry out a steady process, contrary to fixed bed arrangements. One reactor, the methanator, is used for the catalytic methanation and simultaneous steam capture by means of a suitable sorbent. While the regeneration of the sorbent takes place in another reactor (dehydrator) where H_2O is released from the sorbent by increasing the temperature (or by decreasing the H_2O partial pressure). The two reactors are connected to each other in a dual-interconnected fluidized bed configuration as shown in Fig.1, allowing for the continuous circulation of the solid sorbent between the two reactors.

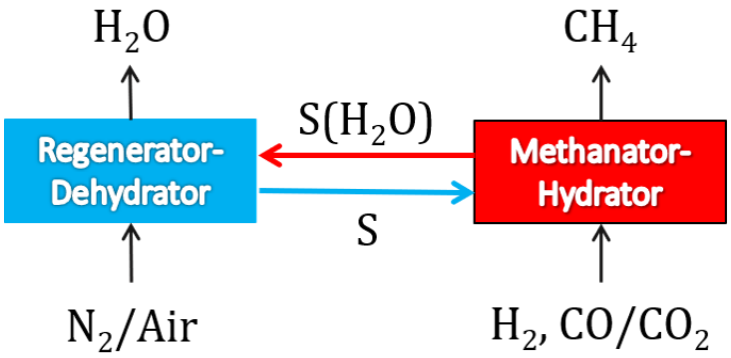


Figure 1. Scheme of the chemical looping sorption-enhanced methanation concept (S=sorbent).

In this work, we propose a new system layout for catalytic methane production that integrates the above SEM concept with a Calcium Looping unit (CaL) for CO_2 capture from flue gas of a coal power plant, and with a water electrolyzer based on polymeric membranes (PEM) sustained by renewable energy. We investigated both techno-economic and environmental performance referring to the Italian scenario, where large amounts of renewable electricity are wasted (i.e. they are not dispatched, nor stored), as a direct consequence of the Italian transmission grid [12,13]. The economic performance was assessed in terms of the €/Nm^3 of methane produced via a techno-economic analysis (TEA). The environmental performance was assessed using the Life Cycle Assessment (LCA) methodology. While many articles in the literature report techno-economic [1,2,13–20] or environmental [22–24] analysis of traditional power-to-methane (PtM) configurations, we could not find any work in the literature assessing a similar configuration which integrates Calcium Looping and Sorption-Enhanced Methanation.

2. METHODOLOGY

Figure 2 shows a flowsheet of the proposed plant layout consisting of three main units able to retrofit a typical power plant with high CO_2 emissions:

i. Calcium Looping (CaL) unit – in orange.
ii. Proton Exchange Membrane (PEM) unit – in light blue.
iii. Sorption-Enhanced Methanation (SEM) unit – in green.

The flue gas - mainly composed of CO_2, H_2O, O_2, and N_2 - leaves the power plant and through a blower enters the carbonator reactor, operated at 650°C, where the CO_2 capture step takes place according to the following gas-solid reaction:

$$CaO + CO_2 \rightarrow CaCO_3 \qquad \text{Eq. 1}$$

According to [25] the CO_2 capture efficiency was chosen to be equal to 95% (molar). Two streams leave the carbonator reactor: the solid carbonated sorbent and the cleaned flue gas. The carbonated sorbent is transferred to the calciner reactor where the reverse reaction (namely calcination) takes place at around 940°C for regenerating the CaO. To thermally sustain the calcination reaction, which is an endothermic reaction, part of the produced methane is burnt in the calciner. The methane is burnt with an excess of oxygen of 50%, which is provided by the PEM. From mass and energy balances, about 35% in volume of the produced synthetic methane is necessary to maintain the temperature of the calciner. We chose this plant layout to avoid utilization of an energy-intensive air separation unit [26]. Furthermore, to account for sorbent deactivation and attrition, a fresh sorbent make-up stream and an exhausted sorbent purge stream were considered at the inlet and at the outlet of the calciner, respectively. The gas leaving the calciner, mainly composed of CO_2, O_2 and H_2O, is partially recycled to the reactor both to support its fluidization and to act as a thermal buffer for the methane combustion reaction.

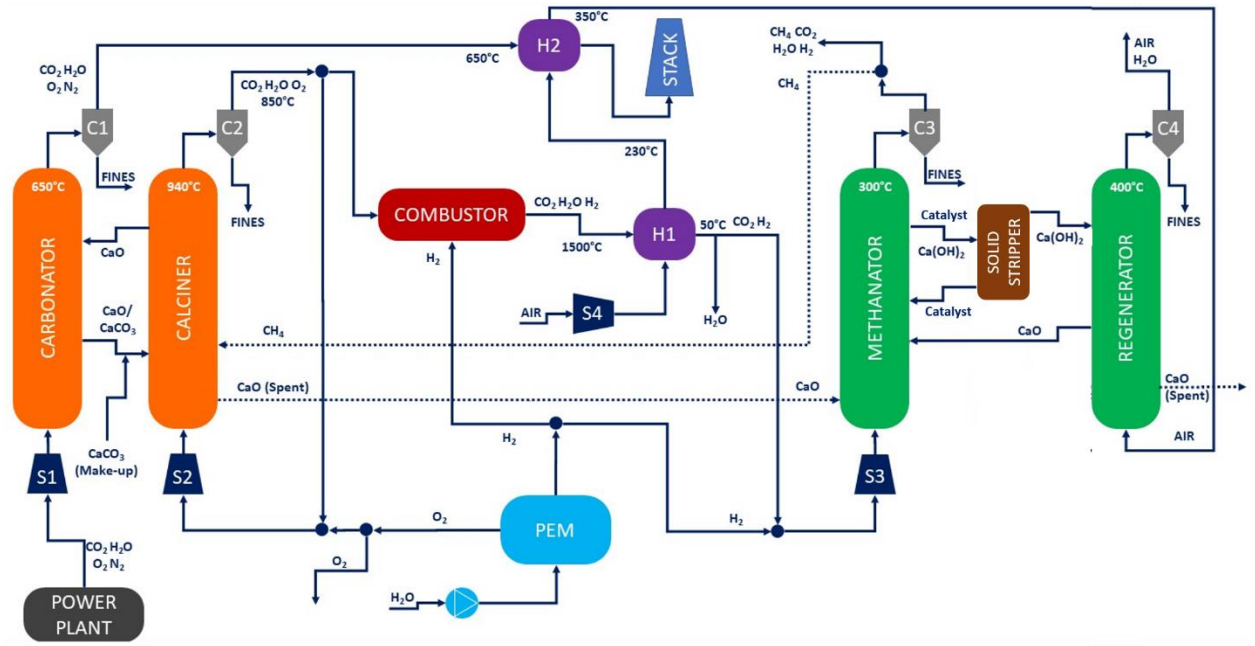


Figure 2. Layout of the Calcium Looping, PEM and Sorption Enhanced Methanation integrated system.

The remaining gas flow leaving the calciner requires an additional purification step to remove residual oxygen before entering the methanator. To avoid the use of expensive solutions for the stream purification, we propose a post-combustor burning hydrogen coming from the PEM. The excess of hydrogen adopted is around 20% with respect to stoichiometric combustion conditions. At the exit of the combustor, the hot gas - mainly composed of CO_2, H_2O and H_2 – is cooled in a heat exchanger (H1) to enable condensation of water, before entering the methanator, and to recover heat, which is used to heat up the air used for the regeneration reactor of the SEM unit.

The purified stream of CO_2 enters the methanator, through a blower, which is operated at 300°C and 1 atm, together with an additional stream of H_2 coming from the PEM to obtain the appropriate stoichiometric H_2/CO_2 ratio equal to 4. Commercial Ni-based catalyst is used in the methanator reactor to promote the methanation reaction:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$ Eq. 2

In the methanation reactor the produced steam is captured by the spent CaO coming from the calciner purge stream: the spent sorbent in terms of CO_2 capture still has a good reactivity towards water vapor, as demonstrated in previous studies [10], therefore it is suitable for the SEM process. The hydration reaction is:

$$CaO + H_2O \rightarrow Ca(OH)_2$$ Eq. 3

In addition to the methanator, the SEM unit includes a regenerator reactor operated at 400°C for sorbent regeneration. The hydrated sorbent stream exiting the methanator passes through a solid-solid stripper (based on density/size difference) to separate the Ni-based catalyst from the sorbent. The catalyst, which is recirculated back to the methanator, in fact should not enter the regenerator since it would be deactivated by oxygen.

3. TECHNO-ECONOMIC ANALYSIS

We considered CO_2 emissions from a real power plant for our analysis. The reference plant was the "As Pontes Coal Power Plant", located in As Pontes de Garcia Rodriguez in Spain and managed by Endesa Generation Spain: designed for a maximum power of 1400 MW_e with a sub-critical steam cycle, it uses as primary fuel lignite and sub-bituminous coal, and as secondary fuel natural gas. The plant comprises four boilers and four turbines connected to the national electric grid, with about 5.5 Mt CO_2 emissions in 2019[*]. The electrolyzer considered in this study was a proton exchange membrane (PEM) system powered by renewable energy. The whole system can generate about 500 t/h of methane (about 7000 MW_{th}). Complete mass balances are reported in Table A1 in the appendix section.

[*] http://globalenergyobservatory.org/geoid/43758

The methodology proposed by Turton et al. [27] was used for the evaluation of the Total Capital Investment (TCI) and the Total Product Cost (TPC). The former is calculated according to equation 4.

$$TCI = DPC + IPC + StC \quad \text{Eq. 4}$$

Where DPC, IPC and StC are the direct plant cost, indirect plant cost and start-up cost respectively. In particular, DPC includes equipment costs (EC), piping, auxiliary system and services, electrical instrumentation and control, and civil work. Remarkably, except for EC all the other DPC items were calculated as a percentage of the equipment cost ([27]). IPC which includes engineering and supervision activities, contingency and contractor fee were calculated as a percentage of direct costs and equipment cost. StC were estimated as a percentage of the fixed capital investment (FCI). The latter was calculated as the sum of DPC and IPC.

Furthermore, the Total Product Cost (TPC) is calculated according to equation 5.

$$TPC = 0.245FCI + 1.21C_{OL} + 1.03\ (C_{UT} + C_{WT} + C_{RM}) \quad \text{Eq. 5}$$

where, C_{OL} is the cost of operating labor, C_{UT} is the cost of utilities (i.e. the electricity needed for the PEM, pumps and blowers), C_{WT} is the cost of waste treatment and C_{RM} is the cost of raw materials. Moreover Eq. 5 takes into account of the depreciation of FCI.

In particular, the C_{OL} is based on the number of workers needed for each work shift, obtained from the following equation:

$$N_{OL} = (6.29 + 31.7P^2 + 0.23N_{np})^{0.5} \quad \text{Eq. 6}$$

where N_{OL} is the number of operators per shift, N_{np} is the number of non-particulate processing steps (compression, heating and cooling, mixing, and reaction) and P is the number of processing steps that require physical effort (transportation and distribution, particulate size control, and particulate removal).

Once we estimated the TPC, by dividing it for the total production of standard cubic meters (smc) of methane per year with the proposed layout, we obtained a preliminary estimation for the production cost of one smc of methane.

C_{RM} C_{WT} and C_{UT} represent the main contributors to the variable costs (VC), while C_{OL} to fixed costs (FC). The others FCs, i.e. Direct Supervisory, Maintenance, Tax & Insurance and Overhead have been calculated as $0.18\,C_{OL}$, 0.06FCI, 0.032FCI and $0.6(1.18\,C_{OL}+0.06\text{FCI})$, respectively, as suggested by [27].

4. LIFE CYCLE ASSESSMENT

The environmental performance and the main sources of environmental impacts (i.e., the "hot-spots") of the proposed plant layout were evaluated by means of the Life Cycle Assessment methodology (LCA) [28,29]. Furthermore, its environmental performance was compared with similar reference systems that provide the same function. The study was based on an attributional approach, and it was framed in the Italian context. The proposed process produces synthetic methane while we assumed that the plant does not produce excess of energy. The functional unit adopted was equal to 1kg of methane and the analysis adopted a "cradle to gate" perspective, including all activities from the extraction of raw materials to the production of methane before its injection into the distribution infrastructure.

The reference systems compared with the proposed one comprise the traditional pathways to produce fossil methane and bio-methane from maize silage. We assume that hydrogen is produced from water using waste electricity from onshore wind farms. Fig.3 shows a simplified diagram of the comparison. The life-cycle inventory is based on the mass and energy balances developed in this study and on literature data.

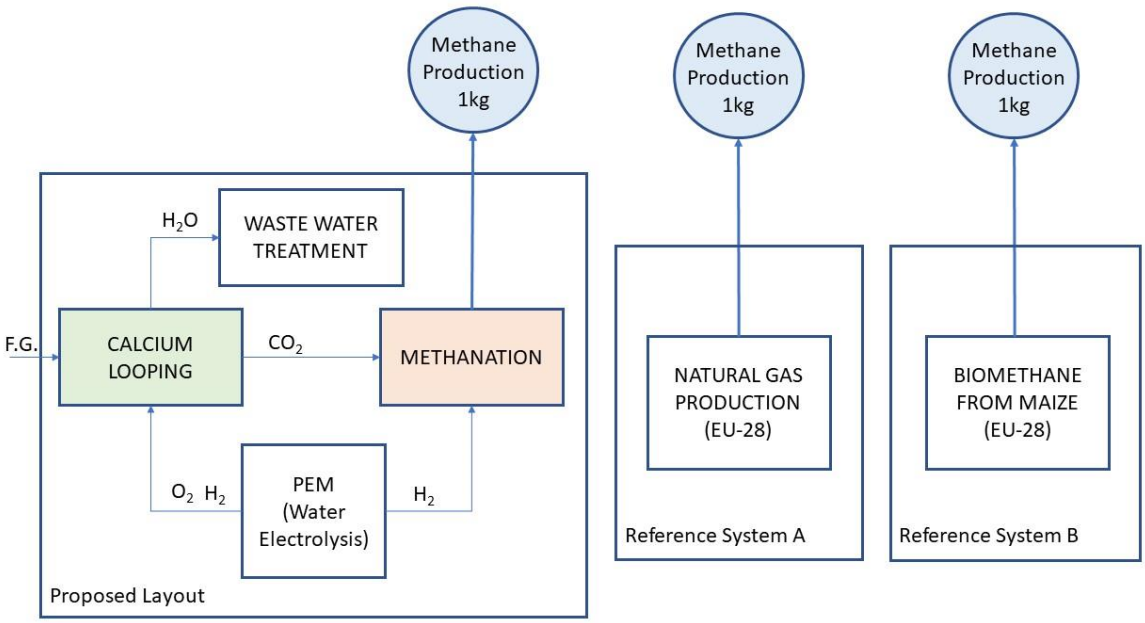


Figure 3. Comparison between the novel process proposed in this study (Proposed Layout) and the reference systems (A and B).

Life-cycle inventory data for the PEM unit and for the remaining activities such as Ni-based catalyst production (for Methanation), calcium carbonate supply, electricity production (Italian electricity mix), and comparative systems (i.e. methane from natural gas and bio-methane from maize silage) were obtained from the Ecoinvent database, version 3.5 cut-off model [32,33]. We did not consider the construction/decommissioning phase because it was found to be negligible in a previous study of a similar plant [24].

The Environmental Footprint (EF) 2.0 method developed by the Joint Research Centre (JRC) of the European Commission [32] was used for quantifying the environmental impacts. All impact categories were included. The environmental impacts were normalized to the reference impact per person of EU-28 using the EF 2.0 normalization factors [33]. We evaluated all the impact categories proposed in the EF2.0 method, which are reported in Table 1.

231 **Table 1**. Environmental impact categories analysed

IMPACT CATEGORY	METRIC
Acidification	Mole of H^+ eq.
Cancer human health effects	CTUh
Climate change	kg CO2 eq.
Ecotoxicity freshwater	CTUe
Eutrophication freshwater	kg P eq.
Eutrophication terrestrial	Mole of N eq.
Ionizing radiations	kBq U235 eq.
Non-cancer human health effects	CTUh
Photochemical ozone formation - human health	kg NMVOC eq.
Resource use, energy carriers	MJ
Resource use, mineral and metals	kg Sb eq.
Respiratory inorganics	Deaths

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5. RESULTS

Techno-Economic Analysis

The main economic assumptions used in this study are reported in Table 2.

Table 2. Economic Assumptions

Average Labour Cost	38000 €/y per person[†]
Depreciation	10% [27]
Stream Factor	95% (working for 8300 h/y) [27]
Electricity price	25 €/MWh [34]
$CaCO_3$ price	20€/ton [35]
Water price	0.01€/ton [35]

The equipment costs (EC) are reported in Table 3. Data for conventional devices like heat exchangers, pumps, blowers, and cyclones were obtained from the Matches website (www.matche.com) and updated via the CEPCI 2020 index to account for inflation. ECs for the Calcium Looping unit and PEM were extrapolated from the literature ([36] and [37], respectively). Costs data for the SEM unit are not available in the scientific literature because this specific configuration envisaging two interconnected fluidized beds was only recently proposed by Coppola et al. [11]. However, since the reactor configuration of the SEM unit is similar to that of the CaL unit (which also comprises two interconnected fluidized beds), we estimated the EC of the SEM unit on the basis of that of the CaL unit, taking into account differences in size. Notably, we estimated the volume of each fluidized bed reactor considering the fluidizing gas and the fluidization regime. The cost of each reactor was estimated from its volume using the relation provided by [36].

[†] From EuroStat: Average personnel costs by NACE Rev. 2 (online data code: TIN00154) (https://ec.europa.eu/eurostat/databrowser/view/tin00154/default/table?lang=en)

Table 2. Equipment Cost.

Equipment cost	[€]	%
CaL unit	2.17E+06	7.98%
SEM unit	2.95E+05	1.09%
PEM	2.42E+07	89.01%
Combustor	2.34E+05	0.86%
Heat exchangers	1.19E+05	0.44%
Pumps & Blowers	4.50E+04	0.17%
Cyclones	1.25E+05	0.46%
Total	**2.72E+07**	**100%**

As shown in Table 3, the highest cost is represented by the PEM electrolyzer, which accounts for about 90% of the whole equipment costs (EC). It must be noted that the PEM technology is more expensive and less mature than alkaline electrolyzers (AEC); the AEC cost is about 1000-1200 €/kW_{el} compared to 1860-2320 €/kW_{el} for PEMs [38]. However, PEMs yield a higher purity of the produced gas, a faster system response and a lower cold-start time which make them more suitable for their combination with intermitted renewable energy systems. Moreover, technology projections estimate that PEM will reach similar costs to AEC in the next ten years, and also that its lifetime will be significantly improved [38].

Table 4 reports estimations of direct and indirect costs of the plant configuration calculated according to the methodology of Turton et al. [27]. The TCI is around 6.4 M€ which corresponds to 8.4 k€ per MW_{th} of methane‡.

‡ $HHV_{methane}$ = 55MJ/kg

272 **Table 3**. Direct and Indirect Costs of the plant configuration.

Direct plant cost (DPC)			**[€]**
Equipment cost (EC)	100%	EC	2.72E+07
Piping	8%	EC	2.16E+06
Auxiliary system and services	12%	EC	3.23E+06
Electrical	10%	EC	2.69E+06
Instrumentation and control	10%	EC	2.69E+06
Civil work	20%	EC	5.39E+06
Total DPC	160%	EC	4.34E+07
Indirect plant cost (IPC)			
Engineering and supervision	12%	EC	3.23E+06
Total DPC & IPC	172%	EC	4.66E+07
Contingency	10%	DPC+IPC	4.66E+06
Contractor fee	10%	DPC+IPC	4.66E+06
Fixed Capital Investment (FCI)			5.59E+07
Working Capital (WC)	15%	FCI	8.39E+06
Total Capital Investment (TCI)		FCI+WC	**6.43E+07**

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275 Table 5 lists the fixed and variable costs of the whole plant. Among the variable costs (VC) the
276 highest value comes from the cost of electricity for PEM operation which accounts for over 99%
277 of the total operation costs. This means that the economic competitiveness of our proposed plant
278 layout is highly dependent on future reductions in the cost of electricity and/or the exploitation of
279 waste energy.

280 The treatment of wastewater, which is mainly produced from the condensation of steam in the
281 methanation section, has a low impact on VC: it accounts for only about 0.1% of the operation
282 costs. However, it could be possible to re-utilize such wastewater as a feed to the electrolyzer, after
283 an appropriate purification step to eliminate any pollutant that could jeopardize the correct
284 functioning of the device. This option could represent a benefit not only from an economic but
285 also from the environmental point of view, reducing the impact of freshwater consumption of the
286 plant. Concerning the fixed costs (FC), it is worth noting that costs related to maintenance account
287 for only about 0.12% of the total operating costs. However, this value, which was estimated as

10% of the equipment costs, could be higher due to the short lifetime of electrolyzers [38]; this aspect should be investigated in more detail in future studies.

Table 4. Fixed and variable costs.

Variable Costs (VC)	**[€]/y**	**%**
Utilities Costs (C_U)		
PEM	2.71E+09	99.58%
Pumps & Blowers	2.85E+05	0.01%
Waste treatment (C_{WT})	2.84E+06	0.10%
Raw material cost (C_{RM})		
$CaCO_3$	3.17E+05	0.01%
Water	2.35E+04	0.00%
Total VC	**2.71E+09**	**99.71%**
Fixed Costs (FC)	[€]/y	
Cost operating labour (C_{OL})	5.70E+04	0.00%
Direct supervisory	1.03E+05	0.00%
Maintenance	3.34E+06	0.12%
Tax & Insurance	1.78E+06	0.07%
Overhead	2.69E+06	0.10%
Total FC	**7.97E+06**	**0.29%**
Total VC & FC	**2.72E+09**	**100%**

The total product cost (TPC), considering the depreciation of the plant, is around $3.35x10^3$ M€/y. The methane cost production was calculated as the ratio between TPC and the total amount of produced methane per year. The proposed system results in a cost of methane production of about 0.66 €/Nm^3 [(§)]. In Europe the cost of natural gas exploration and production corresponds to 0.17 €/Nm^3 in 2020 (ENI, financial report 2020 [39]), while that of methane produced with traditional methanation systems to about 0.51 €/Nm^3 not including the cost of electricity [34]. In addition, bio-methane produced from anaerobic digestion has a production cost of around 1 €/Nm^3 [40]. As recognized by other authors, the cost of electricity is the 'control knob' for the success of these technologies [34]. To reach the parity grid, in terms of methane production cost, for the

§ 15.9 €/kmol; 0.99 €/kg; 0.018 €/MJ; 64.92 €/MWh

configuration proposed in this work the electricity should have a price lower than 0.005 €/KWh_{el}. In particular, for the limiting case where the electricity cost becomes zero (i.e. when considered waste electricity) the cost of methane would be of about 0.02€/Nm^3, that is on order of magnitude lower than the cost of natural gas.

Life Cycle Assessment.

Table 6 reports the inventory data for the proposed plant layout. We assumed that the sorbent ($CaCO_3$) used in the CaL unit can be reused in the SEM unit, thus reducing additional consumption. We also assumed a make-up of around 5% of the mass flow of the sorbent ($CaO+CaCO_3$) cycled between reactors. Literature data is used to describe the operation of the PEM unit in terms of efficiency and electricity consumption; in particular, the electric requirement for the PEM is 46.6 kWh/kgH_2 [30]. Note that we considered the environmental impacts associated with the production of electricity from wind even if we assumed that this electricity would otherwise be wasted [13]. The inventory data for the remaining activities that supply energy and materials to the plant and for the reference systems (i.e. conventional and bio-based methane) are obtained from the Ecoinvent database.

328 **Table 6**. Inventory used for this study.

Calcium Looping			
input			
	CO_2, flue gas	kg	2,10E+00
	H_2O, flue gas	kg	5,71E-01
	O_2, flue gas	kg	3,04E-01
	N_2, flue gas	kg	6,15E+00
	$CaCO_3$ bed	kg	2,74E-03
	$CaCO_3$ make-up	kg	7,71E-01
	electricity mix	kWh	4,10E-04
output			
	CO_2, emission to air	kg	1,05E-01
	H_2O, emission to air	kg	5,71E-01
	O_2, emission to air	kg	3,04E-01
	N_2, emission to air	kg	6,15E+00
Combustor			
output			
	H_2O, wastewater treatment	kg	1,05E-01
PEM			
input			
	H_2O	kg	4,90E+00
	electricity, wind	kWh	2,54E+01
	electricity mix	kWh	1,20E-08
Methanation			
input			
	H_2O	kg	4,90E+00
	electricity renewable	kWh	2,54E+01
	electricity mix	kWh	1,20E-08
output			
	CO_2, emission to air	kg	5,15E-02
	H_2O, emission to air	kg	1,81E+00
	O_2, emission to air	kg	1,16E+00
	N_2, emission to air	kg	7,62E+00
	CaO, solid waste	kg	4,31E-01
	$H_{2,}$, emission to air	kg	9,39E-03

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331 Figure 4 reports the normalised environmental impacts of the proposed plant layout and those
332 of the reference systems. The comparative analysis shows that methane production from the
333 proposed layout yields lower environmental impacts than both reference systems in the categories
334 terrestrial acidification, photochemical ozone formation, marine and terrestrial eutrophication,
335 resource use – energy carriers, and respiratory inorganics impact categories. In addition, the

proposed layout outperforms methane production from maize silage in the following categories: climate change, ecotoxicity freshwater, ionizing radiation, land use and non-cancer human health. The proposed layout is environmentally disadvantageous in the remaining environmental categories.

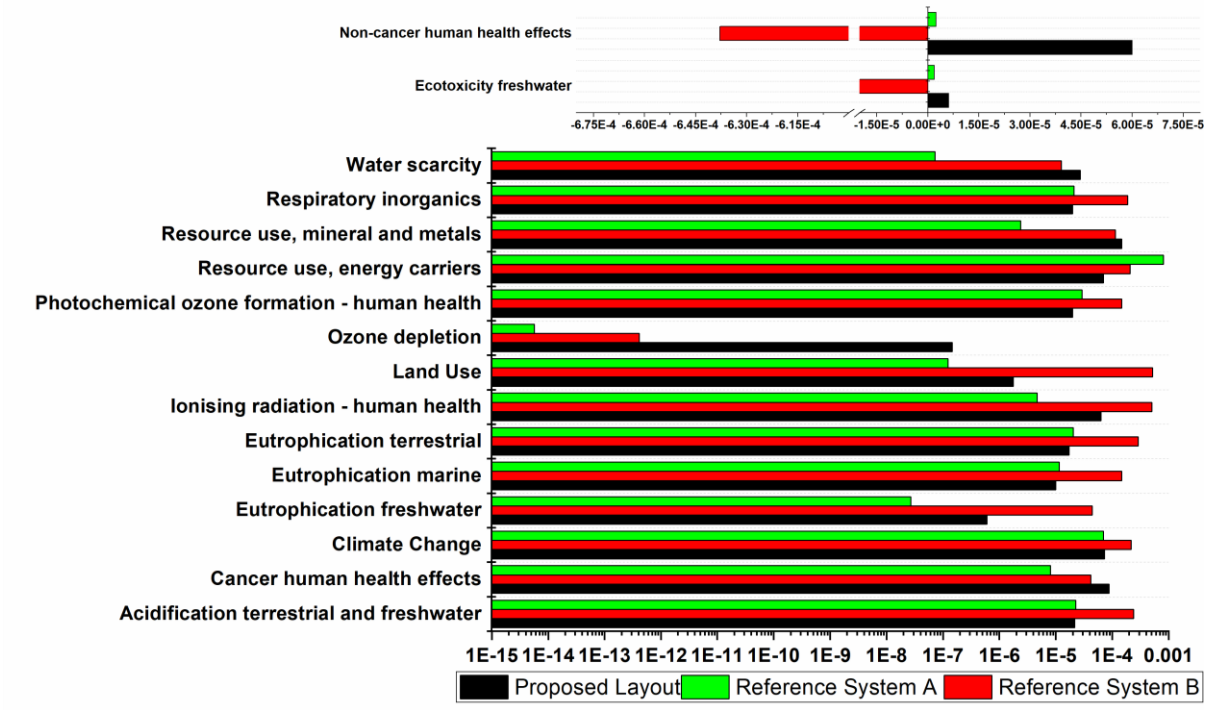

Figure 4. Normalized environmental impacts of the proposed process layout and the reference systems.

Figure 5 reports a hot-spot analysis for the plant layout proposed in this work. The results show that the largest portion of the environmental impacts in nearly all impact categories originate from the PEM unit and, specifically, from the electricity wind production, with contributions ranging from 35% in the category ionizing radiation and up to ~100% in the category water scarcity, resource use-mineral and metal, land use and cancer human health. The CaL unit has significant contributions in a limited number of categories including climate change (~30%), eutrophication terrestrial and marine (~40%), ionizing radiation (~62%) and ozone depletion (~100%). The results from the analysis show that the impacts of the CaL unit are mostly attributable to the production

of the calcium oxide (to capture CO_2). Similarly to what found in the techno-economic analysis, the LCA study indicates that the environmental impacts of electricity consumption heavily affect the environmental performance of the proposed plant layout. As previously reported, these results include the environmental impacts associated with the production of electricity from wind even if this electricity would otherwise be wasted. Table A1 in the appendix reports the environmental performances for the proposed layout without including the wind electricity production. The comparison shows that the new proposed scenario outperforms conventional methane and bio-methane productions in almost all the impact categories except for eutrophication marine and terrestrial, ozone depletion and water scarcity.

A reduction in the electric consumption of the PEM unit will significantly reduce the environmental impacts of the proposed layout, which could make it environmentally advantageous across a larger number of environmental categories. The above also suggests that our results are heavily dependent on the assumed energy source; future studies should investigate the environmental performance when electricity is obtained from other sources such as solar, geothermal or nuclear.

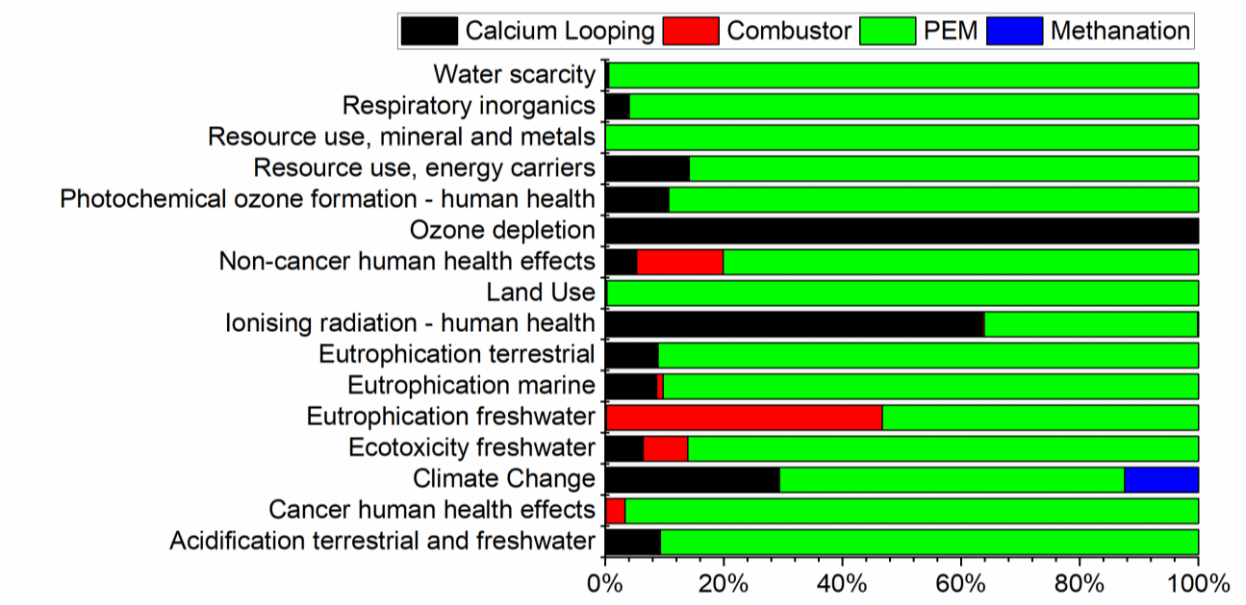

Figure 5. Hot-spot analysis of the proposed plant layout.

6. CONCLUSIONS

In this work, we investigated the technical, economic and environmental performance of a novel plant layout for the production of synthetic methane using CO_2 captured from combustion flue gas. The layout integrates sorption-enhanced catalytic methanation with CO_2 capture via calcium looping, and renewable H_2 production via PEM electrolyzer. The advantages of this configuration include good temperature control and low operating pressure of the methanation step, and the avoidance of a costly air separation unit for the calcium looping step.

The economic and environmental performances of the proposed layout were compared with those of traditional natural gas production, and of biomethane production from maize silage. Our results show that the production cost of methane per unit Nm^3 is higher than that of natural gas, but lower than that of bio-methane. The largest impact on these costs comes from the PEM electrolyzer, and in particular from the consumption of electricity. The PEM is currently an expensive technology but its cost is forecasted to decrease significantly in the coming years. In addition, it is worth highlighting that the possible future introduction of significant carbon taxes would increase the economic attractiveness of synthetic methane production with respect to natural gas. The results of the LCA analysis indicates the existence of several environmental trade-offs, with no systems outperforming the other across all environmental categories. Notably, from a climate change perspective the proposed layout is not advantageous when compared to the conventional pathway for methane production, yielding an increase of ~ 5%. Like for economic costs, the electricity consumption of the PEM electrolyzer accounts for most of the environmental impacts. Overall, our analysis indicates that the high electricity consumption of the PEM electrolyzer is the most critical aspect. Future improvements in the PEM efficiency will significantly improve the economic and environmental performance of the proposed plant layout.

ACKNOWLEDGEMENTS

The help of Ms. Giulia Paone is gratefully acknowledged.

APPENDIX

Table A1. Mass balances of the whole plant in kg/h.

CALCIUM LOOPING							
CARBONATOR				**CALCINER**			
INPUT		**OUTPUT**		**INPUT**		**OUTPUT**	
$CaCO_3$	0.00E+00	$CaCO_3$	2.00E+06	$CaCO_3$	2.34E+06	$CaCO_3$	0.00E+00
CaO	3.82E+06	CaO	2.70E+06	CaO	2.70E+06	CaO	3.82E+06
Flue Gas	4.02E+06	Flue Gas	3.14E+06				
CO_2	9.24E+05	CO_2	4.62E+04	CO_2	0.00E+00	CO_2	1.39E+06
H_2O	2.52E+05	H_2O	2.52E+05	H_2O	0.00E+00	H_2O	2.99E+05
O_2	1.34E+05	O_2	1.34E+05	O_2	3.18E+05	O_2	5.30E+04
N_2	2.71E+06	N_2	2.71E+06	N_2	0.00E+00	N_2	0.00E+00
				CH_4	1.33E+05	CH_4	0.00E+00
COMBUSTOR				**PEM**			
INPUT		**OUTPUT**		**INPUT**		**OUTPUT**	
CO_2	1.39E+06	CO_2	1.39E+06	H_2O	2.42E+06	H_2O	0.00E+00
H_2O	2.99E+05	H_2O	4.18E+05	H_2	0.00E+00	H_2	2.69E+05
O_2	5.30E+04	O_2	0.00E+00	O_2	0.00E+00	O_2	1.08E+06
H_2	1.59E+04	H_2	2.65E+03				
SORPTION ENHANCED METHANATION							
METHANATOR				**REGENERATOR**			
INPUT		**OUTPUT**		**INPUT**		**OUTPUT**	
H_2	2.56E+05	H_2	4.72E+03	H_2		H_2	
CO_2	1.39E+06	CO_2	2.57E+04	CO_2		CO_2	
H_2O	0.00E+00	H_2O	5.71E+05	H_2O	0.00E+00	H_2O	3.50E+05
CaO	2.87E+06	CaO	1.09E+06	CaO	0.00E+00	CaO	2.87E+06
CH_4	0.00E+00	CH_4	4.98E+05	CH_4		CH_4	
O_2		O_2	0.00E+00	O_2	5.87E+05	O_2	5.87E+05
N_2		N_2	0.00E+00	N_2	3.87E+06	N_2	3.87E+06
$Ca(OH)_2$	0.00E+00	$Ca(OH)_2$	2.35E+06	$Ca(OH)_2$	2.35E+06	$Ca(OH)_2$	
CO	0.00E+00	CO	3.01E+01	CO		CO	
CaO_{mup}	1.91E+05					CaO_{sp}	1.91E+05

Table A2. Normalized environmental impacts of the proposed process layout without considering the wind electricity production and the reference systems.

	Proposed layout (no electricity)	Reference system A	Reference System B
Acidification terrestrial and freshwater	1,20E-04	1,33E-02	1,26E-03
Cancer human health effects	1,10E-10	1,61E-09	3,09E-10
Climate Change	2,38E-01	1,68E+00	5,39E-01
Ecotoxicity freshwater	1,25E-02	-3,03E-01	2,20E-02
Eutrophication freshwater	7,93E-07	1,12E-04	6,91E-08
Eutrophication marine	2,21E+00	4,17E-03	3,28E-04
Eutrophication terrestrial	2,49E+02	5,11E-02	3,60E-03
Ionising radiation - human health	1,73E-02	2,12E-01	1,97E-03
Land Use	-6,00E-02	6,95E+02	1,63E-01
Non-cancer human health effects	4,70E-09	-3,03E-07	1,15E-09
Ozone depletion	3,42E-09	9,64E-15	1,33E-16
Photochemical ozone formation - human health	9,10E-05	5,98E-03	1,18E-03
Resource use, energy carriers	6,90E-01	1,36E+01	5,25E+01
Resource use, mineral and metals	0,00E+00	6,56E-06	1,38E-07
Respiratory inorganics	5,00E-10	1,19E-07	1,34E-08
Water scarcity	2,38E-01	1,44E-01	8,30E-04

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CARBON CAPTURE AND UTILIZATION VIA CALCIUM LOOPING, SORPTION ENHANCED METHANATION AND GREEN HYDROGEN: A TECHNO-ECONOMIC ANALYSIS AND LIFE CYCLE ASSESSMENT STUDY

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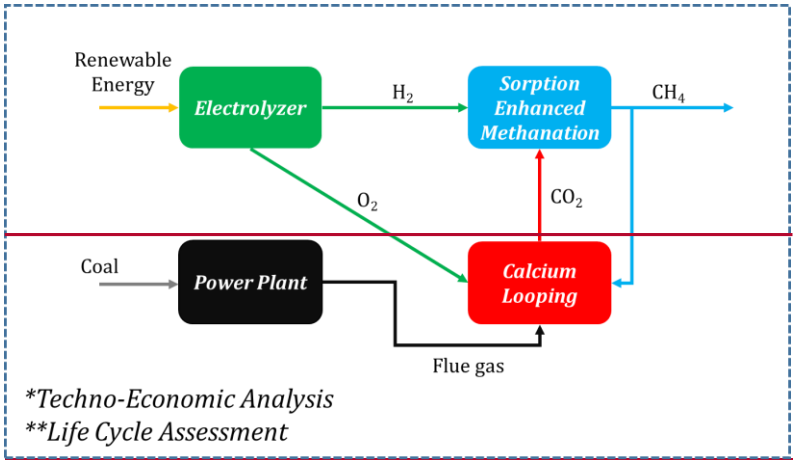
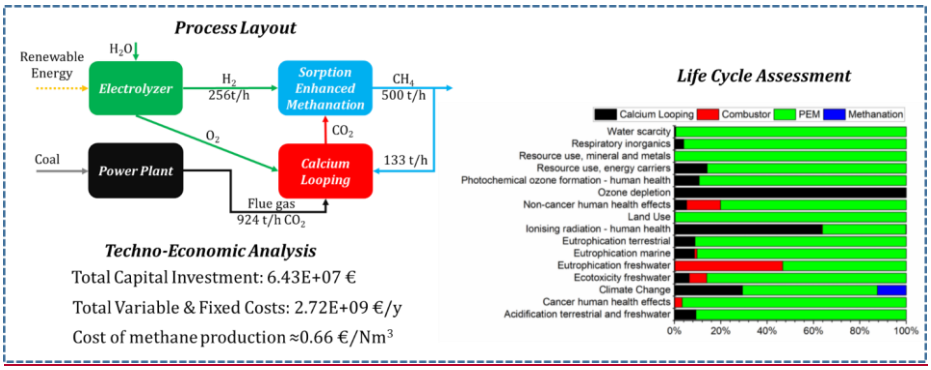
Graphical Abstract





ABSTRACT

The production of synthetic methane using CO_2 from flue gases and green hydrogen appears to be a promising way to combine the concepts of renewable energy, chemical storage, and utilization of CO_2. Recently, a new reactor configuration for catalytic methanation has been proposed, integrating sorption-enhanced methanation and chemical looping in interconnected fluidized bed systems. This configuration would ensure high methane yields while keeping good temperature control and low operating pressure. In this work, such novel system layout for the catalytic production of methane was combined with a calcium looping unit for CO_2 capture from flue gases of a coal-fired power plant, and with a water electrolyzer sustained by renewable energy. The integrated layout offers a series of advantages deriving from the integration of different mass and energy flows of the different sections of the plant. The performance of this latter was assessed in terms of construction and production costs, as well as from an environmental point of view: a life cycle assessment was carried out to quantify the environmental impact of all process units. Results of the techno-economic analysis indicated that the production cost of methane is higher than that of natural gas~~,~~ (0.66 vs 0.17 €/Nm^3), but lower than that of biomethane~~.~~ (1 €/Nm^3). The largest impact on such costs comes from the PEM electrolyzer. The LCA analysis showed that the environmental performance is better in some categories and worse in others with respect to traditional scenarios. Again, the PEM electrolyzer appears to account for most of the environmental impacts of the process.

Keywords: Techno-Economic Analysis; Life Cycle Assessment; CO_2 Capture; Carbon Capture and Utilization; Calcium Looping; Sorption Enhanced Methanation**.**

Nomenclature

C1	Cyclone 1	LCA	Life Cycle Assessment
C2	Cyclone 2	N_{np}	Number of non-particulate processing steps
C3	Cyclone 3	N_{OL}	Number of operators per shift
C4	Cyclone 4	P	Number of processing steps
CaL	Calcium Looping	PEM	Polymer Electrolyte Membrane electrolyzer
C_{OL}	Cost of operating labor	S1	Blower 1
C_{RM}	Cost of raw materials	S2	Blower 2
C_U	Cost of utilities	S3	Blower 3
C_{WT}	Cost of waste treatment	S4	Blower 4
DPC	Direct Plant Cost	SEM	Sorption Enhanced Methanation
EC	Equipment Cost	TCI	Total Capital Investment
FC	Fixed Costs	TEA	Techno-Economic Analysis
FCI	Fixed Capital Investment	TPC	Total Product Cost
H1	Heat exchanger 1	VC	Variable Costs
H2	Heat exchanger 2	WC	Working Capital
IPC	Indirect Plant Cost		

~~1.0~~1. INTRODUCTION

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The most attractive solution to rapidly reduce CO_2 emissions and the consumption of fossil fuels, responsible for 85% of the greenhouse gas emissions, is the implementation of renewable energy systems, mostly based on solar and wind energy. However, these technologies will not be ready to totally replace the fossil energy systems in the short/medium term, especially because of their intermittent energy production mode [1,2]. Thus, a short-term solution to contain ~~the~~ CO_2 emissions generated by fossil fuel consumption may be represented by Carbon Capture and Utilization (CCU) technologies. Among all the possible final products obtainable with these technologies [3,4], synthetic methane is one of the most attractive, due to the existence of a well-developed infrastructure for distribution, and to the wide demand and acceptance of this fuel for industrial and domestic usage. In addition, methane represents a smart energy carrier ~~able to~~that can store ~~large~~significant amounts of ~~energy from~~ renewable ~~sources~~energy in the natural gas grid.

Global methane market is expected to reach $151.27 billion by 2026 growing at a Compound Annual Growth Rate (CAGR) of 6.1% during the period from 2017 to 2026.

From ~~the~~an industrial point of view, the exothermic catalytic methanation of CO_2 is typically carried out at high pressure in a reactor arrangement composed by a cascade of fixed bed reactors with intermediate cooling~~, in order to control~~; the arrangement enables controlling peak temperature of the system and~~,~~ hence~~, to prevent~~ preventing the deactivation of the catalyst [5,6]. A sufficiently high methane purity is needed ~~to allow the injection of~~for injecting synthetic methane into the natural gas grid. The concept of Sorption-Enhanced Methanation (SEM), first formulated by Borgschulte et al. ~~[7] and Walspurger et al.~~[7] and Walspurger et al. [8], on the basis of the Le Chatelier principle, would allow the process to achieve high degrees of methane conversion at lower pressures, ~~implying~~leading to savings in compression energy ~~saving~~ up to 40%. Specifically, the steam generated by the methanation reaction can be removed from the catalytic bed by adding a suitable sorbent material, in order to push the equilibrium reaction towards methane formation ~~[7,8]~~[7,8].

Recently, Coppola et al. ~~[9–11] proposed a novel reactor configuration, which combines the concepts of SEM and of chemical looping in dual interconnected fluidized bed systems. Such configuration would ensure both~~[9–11] proposed a novel reactor configuration which combines the concepts of SEM and of chemical looping in dual interconnected fluidized bed systems. Such configuration would ensure good temperature control and lower operating pressure, and most importantly the possibility to carry out a steady process, contrary to fixed bed arrangements. One reactor, the methanator, is used for the catalytic methanation and simultaneous steam capture by means of a suitable sorbent. While the regeneration of the sorbent takes place in another reactor (dehydrator) where H_2O is released from the sorbent by increasing the temperature (or by decreasing the H_2O partial pressure). The two reactors are connected to each other in a dual-

interconnected fluidized bed configuration as shown in Fig.1, allowing for the continuous circulation of the solid sorbent between the two reactors.

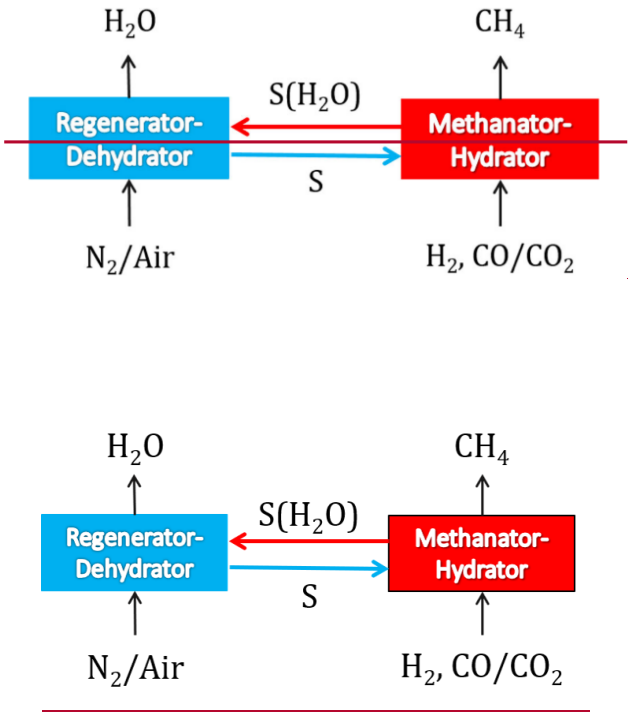

Figure 1. Scheme of the chemical looping sorption-enhanced methanation concept (S=sorbent).

~~In this work, we propose a new system layout for catalytic methane production, integrating the above SEM concept with a Calcium Looping unit (CaL) for CO_2 capture from flue gas of a coal power plant, and with a water electrolyzer based on polymeric membranes (PEM) sustained by renewable energy. We investigated both techno-economic and environmental performance with specific reference to the Italian context where vast amounts of electricity from renewable sources~~

~~are wasted as direct consequence of the Italian transmission grid (i.e. not dispatched nor stored [12]). The economic performance was assessed in terms of the €/Nm³ of methane produced thought a techno-economic analysis (TEA). The environmental performance was evaluated using the Life Cycle Assessment (LCA) methodology. While many papers are available in the literature reporting techno-economic [1,2,13–20] or environmental [21–23] analysis of traditional power-to-methane (PtM) configurations, to the best of the authors' knowledge, there is no previous work in the literature proposing a similar configuration integrating Calcium Looping and Sorption-Enhanced Methanation.~~

In this work, we propose a new system layout for catalytic methane production that integrates the above SEM concept with a Calcium Looping unit (CaL) for CO_2 capture from flue gas of a coal power plant, and with a water electrolyzer based on polymeric membranes (PEM) sustained by renewable energy. We investigated both techno-economic and environmental performance referring to the Italian scenario, where large amounts of renewable electricity are wasted (i.e. they are not dispatched, nor stored), as a direct consequence of the Italian transmission grid [12,13]. The economic performance was assessed in terms of the €/Nm^3 of methane produced via a techno-economic analysis (TEA). The environmental performance was assessed using the Life Cycle Assessment (LCA) methodology. While many articles in the literature report techno-economic [1,2,13–20] or environmental [22–24] analysis of traditional power-to-methane (PtM) configurations, we could not find any work in the literature assessing a similar configuration which integrates Calcium Looping and Sorption-Enhanced Methanation.

~~2.0~~2. METHODOLOGY

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Figure 2 shows a flowsheet of the proposed plant ~~analyzed in this work~~layout consisting of three main units able to retrofit a typical power plant with high CO_2 emissions:

i. Calcium Looping (CaL) unit – in orange.

ii. Proton Exchange Membrane (PEM) unit – in light blue.

iii. Sorption-Enhanced Methanation (SEM) unit – in green.

The flue gas~~, -~~ mainly composed of CO_2, H_2O, O_2, and N_2 ~~-~~ leaves the power plant and ~~is sent by~~through a blower ~~to~~enters the carbonator reactor, operated at 650°C, where the CO_2 capture step takes place according to the following gas-solid reaction:

$$CaO + CO_2 \rightarrow CaCO_3 \quad \text{Eq. 1}$$

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According to ~~[24] the CO_2 capture efficiency was chosen equal to 95% (molar).~~[25] the CO_2 capture efficiency was chosen to be equal to 95% (molar). Two streams leave the carbonator reactor: the solid carbonated sorbent and the cleaned flue gas. The carbonated sorbent is transferred to the calciner reactor where the reverse reaction (namely calcination) takes place at around 940°C for regenerating the CaO. To thermally sustain the calcination reaction, which is an endothermic reaction, part of the produced methane is burnt in the calciner. The methane is burnt with an excess of oxygen of 50~~% -~~%, which is provided by the PEM. From mass and energy balances, about 35% in volume of the produced synthetic methane is necessary to maintain the temperature of the calciner. ~~This~~We chose this plant ~~solution was chosen in order~~layout to avoid ~~the~~ utilization of ~~a high~~ an energy~~-~~-intensive air separation unit ~~[25].~~

[26]. Furthermore, to account for sorbent deactivation and attrition, a fresh sorbent make-up stream and an exhausted sorbent purge stream were considered at the inlet and at the outlet of the calciner, respectively. The gas leaving the calciner, mainly composed of CO_2, O_2 and H_2O, is partially recycled to the reactor both to support its fluidization and to act as a thermal buffer for the methane combustion reaction.

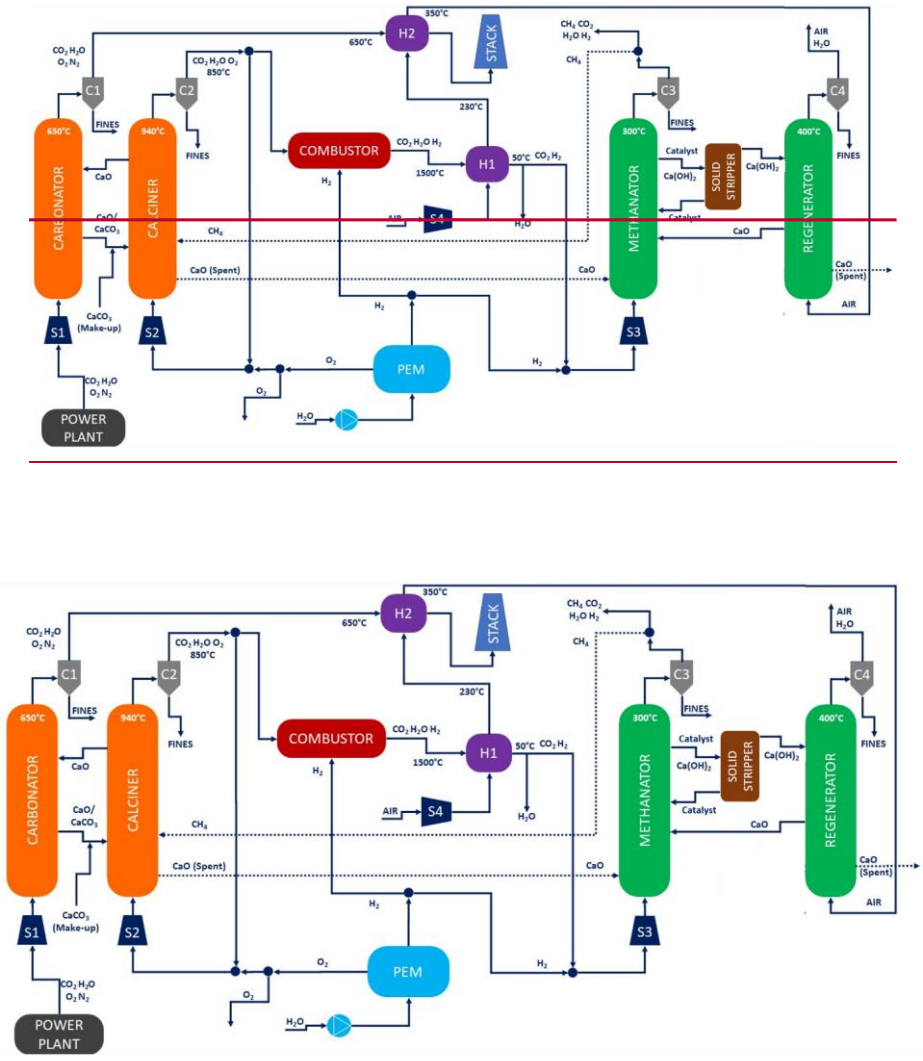

Figure 2. Layout of the Calcium Looping, PEM and Sorption Enhanced Methanation integrated system.

The remaining gas flow leaving the calciner requires an additional purification step to remove residual oxygen~~,~~ before entering the methanator. To avoid the use of ~~somewhat~~ expensive solutions for the stream purification, we ~~proposed~~propose a post-combustor burning hydrogen coming from the PEM. The excess of hydrogen adopted is around 20% with respect to ~~the~~ stoichiometric combustion conditions. At the exit of the combustor, the hot gas - mainly composed ~~by~~of CO_2, H_2O and H_2 – is cooled in a heat exchanger (H1) ~~both~~ to ~~permit the~~enable condensation of water, before entering the methanator, and to recover ~~the~~ heat ~~duty~~, which is used to heat up the air used for the regeneration reactor of the SEM unit.

The purified stream of CO_2 ~~reaches~~enters the methanator, through a blower, which is operated at 300°C and 1 atm, together with an additional stream of H_2 coming from the PEM~~,~~ to obtain the ~~right~~appropriate stoichiometric H_2/CO_2 ratio equal to 4~~, and passing through a blower which injects them at a temperature of 100°C~~. Commercial Ni-based catalyst is used in the methanator reactor to promote the methanation reaction:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad \text{Eq. 2}$$

~~In the methanation reactor the produced steam is captured by the spent CaO coming from the calciner purge stream: the spent sorbent in terms of CO_2 capture still has a good reactivity towards water vapor, as demonstrated in previous studies [10], therefore it is suitable for the SEM process. The hydration reaction is:~~

In the methanation reactor the produced steam is captured by the spent CaO coming from the calciner purge stream: the spent sorbent in terms of CO_2 capture still has a good reactivity towards water vapor, as demonstrated in previous studies [10], therefore it is suitable for the SEM process. The hydration reaction is:

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$$CaO + H_2O \rightarrow Ca(OH)_2$$ Eq. 3

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~~The SEM unit includes, in~~In addition to the methanator, the SEM unit includes a regenerator reactor operated at 400°C for sorbent regeneration. The hydrated sorbent stream exiting the methanator passes through a solid-solid stripper (based on density/size difference) to separate the Ni-based catalyst from the sorbent. The catalyst, which is recirculated back to the methanator, in fact should not enter the regenerator since it would be deactivated by oxygen.

~~3.0~~3. TECHNO-ECONOMIC ANALYSIS

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We considered CO_2 emissions from a real power plant for ~~the~~our analysis. The reference plant was the "As Pontes Coal Power Plant", located in As Pontes de Garcia Rodriguez in Spain and managed by Endesa Generation Spain: designed for a maximum power of 1400 MW_e with a sub-critical steam cycle, it uses as primary fuel lignite and sub-bituminous coal, and as secondary fuel natural gas. ~~It is composed of~~The plant comprises four boilers and four turbines connected to the national electric grid, with about 5.5 Mt CO_2 emissions in 2019*. The electrolyzer considered in this study was a proton exchange membrane (PEM) system powered by renewable energy. The whole system can generate about 500 t/h of methane (about 7000 MW_{th}). Complete mass balances are reported in Table A1 in the appendix section.

~~The main economic assumptions used in this study are collected in Table 1. The methodology proposed by Turton et al. [26] was used for the evaluation of the Total Capital Investment (TCI) and the Total Product Cost (TPC).~~

* http://globalenergyobservatory.org/geoid/43758

Table 1. The methodology proposed by Turton et al. [27] was used for the evaluation of the Total Capital Investment (TCI) and the Total Product Cost (TPC). The former is calculated according to equation 4.

Economic Assumptions		
Average Labor Cost	$TCI = DPC + IPC + StC$	38000 €/y per person Eq. 4
Depreciacion		10%
Start-up period		3 years
Plant Lifetime		20 years
Stream Factor		95% (working for 8300 h/y)
Electricity price		25 €/MWh [27]

The costs of conventional devices, such as heat exchangers, pumps, blowers, and cyclones, were collected on the Matches website (www.matche.com) and updated by CEPCI 2020 index to account for inflation.

The cost of the PEM was estimated from the literature [28,29]. Conversely, reactors were designed basing mainly on the fluidizing gas, the fluidization regime and TDH estimation, to evaluate the volume of each reactor. Finally, the volume of each unit was related to its cost [30]. The relation between the reactor volume and cost was extrapolated from literature [31].

Total Capital Cost, including equipment cost and startup cost, and Total Product Costs were evaluated. Where DPC, IPC and StC are the direct plant cost, indirect plant cost and start-up cost respectively. In particular, DPC includes equipment costs (EC), piping, auxiliary system and services, electrical instrumentation and control, and civil work. Remarkably, except for EC all the

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other DPC items were calculated as a percentage of the equipment cost ([27]). IPC which includes engineering and supervision activities, contingency and contractor fee were calculated as a percentage of direct costs and equipment cost. StC were estimated as a percentage of the fixed capital investment (FCI). The latter was calculated as the sum of DPC and IPC.

Furthermore, the Total Product Cost (TPC) ~~was obtained from the following~~ is calculated according to equation~~:~~ 5.

$$TPC = 0.245FCI + 1.21C_{OL} + 1.03\,(C_{UT} + C_{WT} + C_{RM}) \quad \text{Eq. } 4\text{5}$$

where ~~FCI is the fixed capital investment~~, C_{OL} is the cost of operating labor, C_{UT} is the cost of utilities~~,~~ (i.e. the electricity needed for the PEM, pumps and blowers), C_{WT} is the cost of waste treatment and C_{RM} is the cost of raw materials.

~~All these costs were evaluated according to the assumptions outlined before and to~~ Moreover Eq. 5 takes into account of the ~~energy and capacity needs of each equipment, based on the energy and mass balances carried out in the study~~depreciation of FCI.

~~The evaluation of the cost of operating labor (C_{OL})~~In particular, the C_{OL} is based on the number of workers needed for each work shift, obtained from the following equation:

$$N_{OL} = (6.29 + 31.7P^2 + 0.23N_{np})^{0.5} \quad \text{Eq. } 5\text{6}$$

where N_{OL} is the number of operators per shift, N_{np} is the number of non-particulate processing steps (compression, heating and cooling, mixing, and reaction) and P is the number of processing steps that require physical effort (transportation and distribution, particulate size control, and particulate removal).

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Once we estimated the TPC, by dividing it for the total production of standard cubic meters (smc) of methane per year with the proposed layout, we obtained a preliminary estimation for the production cost of one smc of methane.

C_{RM}, C_{WT} and C_{UT} represent the main contributors to the variable costs (VC), while C_{OL} to fixed costs (FC). The others FCs, i.e. Direct Supervisory, Maintenance, Tax & Insurance and Overhead have been calculated as 0.18 C_{OL}, 0.06FCI, 0.032FCI and 0.6(1.18 C_{OL} +0.06FCI), respectively, as suggested by [27].

~~4.0~~4. LIFE CYCLE ASSESSMENT

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The environmental performance and the main sources of environmental impacts (i.e., the "hot-spots") of the proposed plant layout were evaluated by means of the Life Cycle Assessment methodology (LCA~~).~~) [28,29]. Furthermore, its environmental performance was compared with ~~an equivalent~~similar reference ~~system~~systems that ~~provides~~provide the same function. The study was based on an attributional approach, and it was framed in the Italian context. The proposed process produces synthetic methane while we assumed that the plant does not produce excess of energy. The functional unit adopted was equal to 1kg of methane and the analysis ~~was "from~~ adopted a "cradle to gate" perspective, including all activities from the extraction of raw materials ~~up~~ to ~~methane~~the production of methane before its injection into the distribution infrastructure.

The reference ~~system, for comparative purposes, comprises~~systems compared with the ~~conventional pathway~~proposed one comprise the traditional pathways to produce fossil methane and bio-methane ~~production~~ from maize silage. We assume that ~~wasted~~hydrogen is produced from water using waste electricity from onshore wind farms ~~is used to produce hydrogen from water.~~. Fig.3 shows a simplified diagram of the comparison ~~performed~~. The life-cycle inventory ~~was~~is

based on the ~~results of the system modelling~~mass and energy balances developed in this study and on literature data.

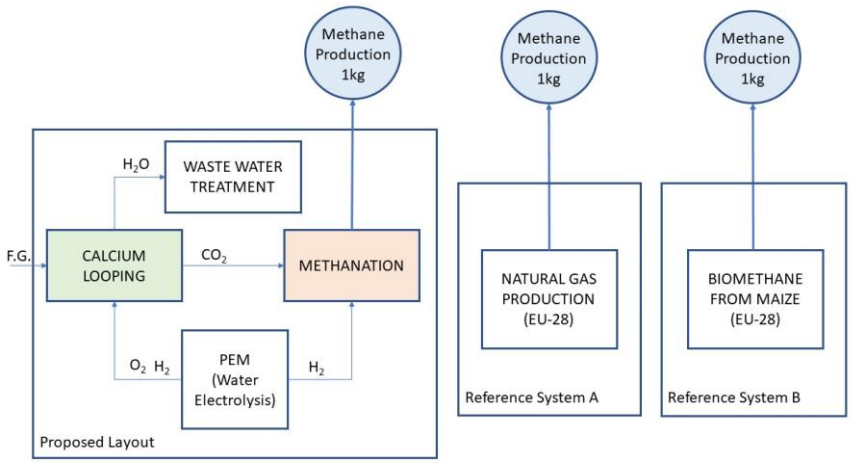

Figure 3. ~~Simplified diagram of the comparative analysis~~Comparison between the novel process proposed in this study (Proposed Layout) and the reference systems (A and B).

~~Results of the system model presented in this study (see following section) are used to describe the operation of the CaL and SEM units in terms of mass and energy inputs/outputs. Data for the PEM unit are based on this study and on the Ecoinvent database [32,33]. Life-cycle inventory data for the remaining activities such as Ni-based catalyst production (for Methanation), calcium carbonate supply, electricity production (Italian electricity mix), and comparative systems (i.e. methane from natural gas and bio-methane from maize silage) were obtained from the Ecoinvent~~

~~database. We did not consider the construction/decommissioning phase since it was found to be negligible in a previous study of a similar plant [23].~~

Life-cycle inventory data for the PEM unit and for the remaining activities such as Ni-based catalyst production (for Methanation), calcium carbonate supply, electricity production (Italian electricity mix), and comparative systems (i.e. methane from natural gas and bio-methane from maize silage) were obtained from the Ecoinvent database, version 3.5 cut-off model [32,33]. We did not consider the construction/decommissioning phase because it was found to be negligible in a previous study of a similar plant [24].

The Environmental Footprint (EF) 2.0 method developed by the Joint Research Centre (JRC) of the European Commission [32] was used for quantifying the environmental impacts. All impact categories were included. The environmental impacts were normalized to the reference impact per person of EU-28 using the EF 2.0 normalization factors [33]. We evaluated all the impact categories proposed in the EF2.0 method, which are reported in Table 1.

Table 1. Environmental impact categories analysed

IMPACT CATEGORY	METRIC
Acidification	Mole of H^+ eq.
Cancer human health effects	CTUh
Climate change	kg CO_2 eq.
Ecotoxicity freshwater	CTUe
Eutrophication freshwater	kg P eq.
Eutrophication terrestrial	Mole of N eq.
Ionizing radiations	kBq U235 eq.
Non-cancer human health effects	CTUh
Photochemical ozone formation - human health	kg NMVOC eq.
Resource use, energy carriers	MJ

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Resource use, mineral and metals	kg Sb eq.
Respiratory inorganics	Deaths

~~The Environmental Footprint (EF) 2.0 method developed by the Joint Research Centre (JRC) of the European Commission [34] was used for quantifying the environmental impacts. We included all impact categories, but report climate change impacts only in terms of the sum of the contributions from fossil and biogenic greenhouse gases and land-use change. For the comparative analysis, the environmental impacts were normalized to the reference impact per person of EU-28 using the EF 2.0 normalization factors [35]. This study evaluated all the impact categories comprised in the chosen methodology (Table 2).~~

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~~5.0~~5. RESULTS

Techno-Economic Analysis~~.~~

The main economic assumptions used in this study are reported in Table ~~3 reports the cost of the equipment involved in the process.~~ 2.

Table 2. Economic Assumptions

~~**Table 3.** Equipment Cost.~~

~~**Equipment cost**~~**Average Labour Cost**	~~**[€]**~~38000 €/y per person[†]	~~**%**~~
~~CaL Looping unit~~**Depreciation**	~~2.17E+06~~10% [27]	~~7.98%~~
~~SEM Unit~~**Stream Factor**	~~2.95E+05~~95% (working for 8300 h/y) [27]	~~1.09%~~
Electricity price	25 €/MWh [34]	
$CaCO_3$ price	20€/ton [35]	
Water price	0.01€/ton [35]	

The equipment costs (EC) are reported in Table 3. Data for conventional devices like heat exchangers, pumps, blowers, and cyclones were obtained from the Matches website (www.matche.com) and updated via the CEPCI 2020 index to account for inflation. ECs for the Calcium Looping unit and PEM were extrapolated from the literature ([36] and [37], respectively). Costs data for the SEM unit are not available in the scientific literature because this specific configuration envisaging two interconnected fluidized beds was only recently proposed by Coppola et al. [11]. However, since the reactor configuration of the SEM unit is similar to that of the CaL unit (which also comprises two interconnected fluidized beds), we estimated the EC of the SEM unit on the basis of that of the CaL unit, taking into account differences in size. Notably,

[†] From EuroStat: Average personnel costs by NACE Rev. 2 (online data code: TIN00154) (https://ec.europa.eu/eurostat/databrowser/view/tin00154/default/table?lang=en)

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we estimated the volume of each fluidized bed reactor considering the fluidizing gas and the fluidization regime. The cost of each reactor was estimated from its volume using the relation provided by [36].

Table 2. Equipment Cost.

Equipment cost	[€]	%
CaL unit	2.17E+06	7.98%
SEM unit	2.95E+05	1.09%
PEM	2.42E+07	89.01%
Combustor	2.34E+05	0.86%
Heat exchangers	1.19E+05	0.44%
Pumps & Blowers	4.50E+04	0.17%
Cyclones	1.25E+05	0.46%
Total	**2.72E+07**	**100%**

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~~As it can be noted, the highest cost is represented by the PEM electrolyzer, which accounts for about 90% of the whole equipment costs. It is known that PEM technology is more expensive and less mature than alkaline electrolyzers (AEC). Indeed, the AEC cost is about 1000-1200 €/kW$_{el}$ with respect to 1860-2320 €/kW$_{el}$ for PEMs [36]. However, PEM technology presents a higher purity of the produced gas, a faster system response and a lower cold-start time which make them more suitable for their combination with intermitted renewable energy systems. Moreover, technology projections estimate that PEM will reach similar costs to AEC in the next ten years, and that its lifetime will be significantly improved [36].~~

~~Table 4 reports the estimation of direct and indirect costs calculated according to the methodology of Turton et al. [26]. The TCI is around 6.4 M€ which means 8.4 k€ per MW$_{th}$ of methane[‡].~~As shown in Table 3, the highest cost is represented by the PEM electrolyzer, which accounts for about 90% of the whole equipment costs (EC). It must be noted that the PEM

~~‡ HHV$_{methane}$ =55MJ/kg~~

technology is more expensive and less mature than alkaline electrolyzers (AEC); the AEC cost is about 1000-1200 €/kW_{el} compared to 1860-2320 €/kW_{el} for PEMs [38]. However, PEMs yield a higher purity of the produced gas, a faster system response and a lower cold-start time which make them more suitable for their combination with intermitted renewable energy systems. Moreover, technology projections estimate that PEM will reach similar costs to AEC in the next ten years, and also that its lifetime will be significantly improved [38].

Table 4 reports estimations of direct and indirect costs of the plant configuration calculated according to the methodology of Turton et al. [27]. The TCI is around 6.4 M€ which corresponds to 8.4 k€ per MW_{th} of methane[§].

Table 3. Direct and Indirect Costs of the plant configuration.

Direct plant cost (DPC)			**[€]**
Equipment cost (EC)	100%	EC	2.72E+07
Piping	8%	EC	2.16E+06
Auxiliary system and services	12%	EC	3.23E+06
Electrical	10%	EC	2.69E+06
Instrumentation and control	10%	EC	2.69E+06
Civil work	20%	EC	5.39E+06
Total DPC	160%	EC	4.34E+07
Indirect plant cost (IPC)			
Engineering and supervision	12%	EC	3.23E+06
Total DPC & IPC	172%	EC	4.66E+07
Contingency	10%	DPC+IPC	4.66E+06
Contractor fee	10%	DPC+IPC	4.66E+06
Fixed Capital Investment (FCI)			5.59E+07
Working Capital (WC)	15%	FCI	8.39E+06
Total Capital Investment (TCI)		FCI+WC	**6.43E+07**

[§] $HHV_{methane}$ = 55MJ/kg

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Table 5 lists the fixed and variable costs of the whole plant. Among the variable costs (VC) the highest value comes from the cost of electricity for PEM operation which accounts for over 99% of the total operation costs. This means that ~~for~~ the ~~success~~economic competitiveness of ~~such technology, based~~our proposed plant layout is highly dependent on future reductions in the ~~utilization~~cost of ~~hydrogen production by electrolysis,~~electricity and/or the ~~abatement~~exploitation of ~~the~~waste energy ~~price becomes crucial.~~

The treatment of wastewater, which is mainly produced from the condensation of steam in the methanation section, has a low impact on VC~~. This~~: it accounts for ~~a~~only about 0.~~104~~1% of the operation costs. ~~Anyway~~However, it could be possible to re-utilize such wastewater as a ~~feeding for~~feed to the ~~electrolizer, obviously~~electrolyzer, after ~~suitable~~an appropriate purification step to eliminate any pollutant ~~able to~~that could jeopardize the correct functioning of the device. This option could represent a benefit not only from an economic ~~point of view,~~ but also from the environmental point of view, reducing the impact of freshwater consumption of the plant. Concerning the fixed costs~~,~~ (FC), it is worth noting that costs related to maintenance account for only about 0.~~123~~12% of the total~~.~~ operating costs. However, this value, which was estimated as 10% of the equipment costs, could be higher ~~taking into account~~due to the short lifetime of ~~electrolizers~~electrolyzers ~~[36]~~[38]; this aspect should be investigated in more detail in future studies.

Table 4. Fixed and variable costs.

Variable Costs (VC)	[€]/y	%
Utilities Costs (C_U)		
PEM	2.71E+09	99.~~669~~58%
Pumps & Blowers	2.85E+05	0.~~010~~01%
Waste treatment (C_{WT})	2.84E+06	0.~~104~~10%
Raw material cost (C_{RM})		

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$CaCO_3$	3.17E+05	0.~~012~~01%
Water	2.35E+04	0.~~001~~00%
Total VC	**2.~~72E~~71E+09**	**99.~~796~~71%**
Fixed Costs (FC)	[€]/y	
Cost operating labour (C_{OL})	5.70E+04	0.~~002~~00%
Direct supervisory	1.03E+05	0.~~004~~00%
Maintenance	3.34E+06	0.~~123~~12%
Tax & Insurance	1.78E+06	0.~~065~~07%
Overhead	2.69E+~~05~~06	0.~~010~~10%
Total FC	**~~5.55E~~7.97E+06**	**0.~~204~~29%**
Total VC & FC	**2.72E+09**	**100.~~000~~%**

~~The total product cost, considering the depreciation of the plant, is calculated as follows:~~

$$TPC_a = 0.180FCI + 2.73C_{OL} + 1.23(C_{UT} + C_{WT} + C_{KM}) = 3.35 \times 10^9 €/y \quad \text{Eq. 6}$$

~~resulting in a cost of methane production of about 0.66 €/Nm^3 (**).~~

~~In Europe the cost of natural gas exploration and production amounted to 0.17 €/Nm^3 in 2020 (ENI, financial report 2020 [37]), while that of methane produced with traditional methanation systems is about 0.51 €/Nm^3 not including the cost of electricity [27]. Finally, methane produced from anaerobic digestion has production cost of around 1 €/Nm^3 [38]. As recognized by other authors, the cost of electricity is the 'control knob' for the success of these technologies [27]. Indeed, to reach the parity grid for the configuration proposed in this work the electricity should have a price lower than 0.005 €/KWh$_{el}$.~~ The total product cost (TPC), considering the depreciation of the plant, is around 3.35x10^3 M€/y. The methane cost production was calculated as the ratio between TPC and the total amount of produced methane per year. The proposed system results in a cost of methane production of about 0.66 €/Nm^3 (††). In Europe the cost of natural gas exploration and

~~** 15.9 €/kmol; 0.99 €/kg; 0.018 €/MJ; 64.92 €/MWh~~
†† 15.9 €/kmol; 0.99 €/kg; 0.018 €/MJ; 64.92 €/MWh

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production corresponds to 0.17 €/Nm^3 in 2020 (ENI, financial report 2020 [39]), while that of methane produced with traditional methanation systems to about 0.51 €/Nm^3 not including the cost of electricity [34]. In addition, bio-methane produced from anaerobic digestion has a production cost of around 1 €/Nm^3 [40]. As recognized by other authors, the cost of electricity is the 'control knob' for the success of these technologies [34]. To reach the parity grid, in terms of methane production cost, for the configuration proposed in this work the electricity should have a price lower than 0.005 €/KWh_{el}. In particular, for the limiting case where the electricity cost becomes zero (i.e. when considered waste electricity) the cost of methane would be of about 0.02€/Nm^3, that is on order of magnitude lower than the cost of natural gas.

Life Cycle Assessment.

Table 6 reports the inventory data for the proposed plant layout. We assumed that the sorbent ($CaCO_3$) used in ~~this study. The~~the CaL unit can be reused in the SEM unit, thus reducing additional consumption. We also assumed a make-up of around 5% of the mass flow of the sorbent ($CaO+CaCO_3$) cycled between reactors. Literature data is used to describe the operation of the PEM unit in terms of efficiency and electricity consumption; in particular, the electric requirement for the PEM is 46.6 kWh/kgH_2 [30]. Note that we considered the environmental ~~performances of the proposed layout are reported in terms of normalized~~ impacts ~~in Figure 4.~~associated with the production of electricity from wind even if we assumed that this electricity would otherwise be wasted [13]. The inventory data for the remaining activities that supply energy and materials to the plant and for the reference systems (i.e. conventional and bio-based methane) are obtained from the Ecoinvent database.

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Table 6. Inventory used for this study.

Calcium Looping			
input			
	CO_2, flue gas	kg	2,10E+00
	H_2O, flue gas	kg	5,71E-01
	O_2, flue gas	kg	3,04E-01
	N_2, flue gas	kg	6,15E+00
	$CaCO_3$ bed	kg	2,74E-03
	$CaCO_3$ make-up	kg	7,71E-01
	electricity mix	kWh	4,10E-04
output			
	CO_2, emission to air	kg	1,05E-01
	H_2O, emission to air	kg	5,71E-01
	O_2, emission to air	kg	3,04E-01
	N_2, emission to air	kg	6,15E+00
Combustor			
output			
	H_2O, wastewater treatment	kg	1,05E-01
PEM			
input			
	H_2O	kg	4,90E+00
	electricity, wind	kWh	2,54E+01
	electricity mix	kWh	1,20E-08
Methanation			
input			
	H_2O	kg	4,90E+00
	electricity renewable	kWh	2,54E+01
	electricity mix	kWh	1,20E-08
output			
	CO_2, emission to air	kg	5,15E-02
	H_2O, emission to air	kg	1,81E+00
	O_2, emission to air	kg	1,16E+00
	N_2, emission to air	kg	7,62E+00
	CaO, solid waste	kg	4,31E-01
	~~H_2~~H_2, , emission to air	kg	9,39E-03

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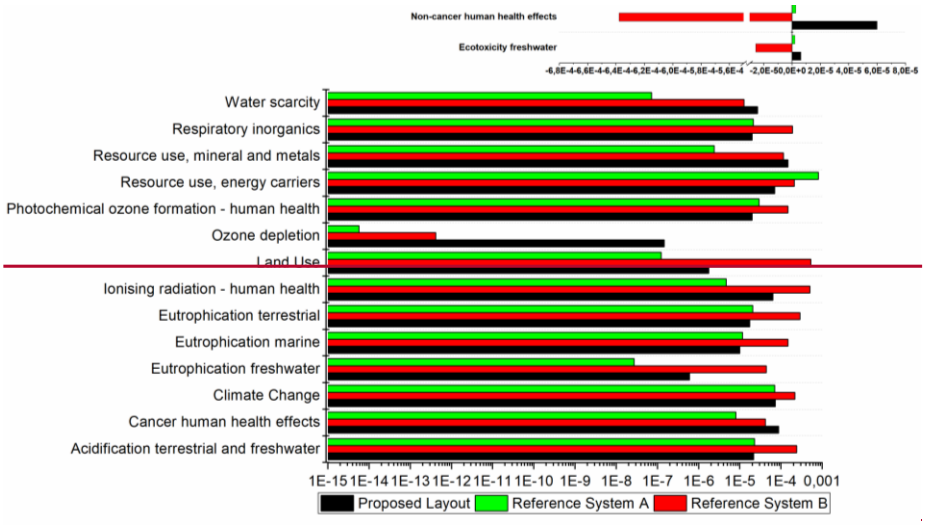
Figure 4 reports the normalised environmental impacts of the proposed plant layout and those of the reference systems. The comparative analysis ~~with the reference systems (natural gas production and~~ shows that methane production from ~~maize) shows that~~ the proposed ~~process outperforms~~layout yields lower environmental impacts than both reference systems ~~only with respect to~~in the categories terrestrial acidification ~~terrestrial~~, photochemical ozone formation, ~~eutrophication~~ marine and terrestrial eutrophication, resource use – energy carriers, and respiratory inorganics impact categories. In addition, ~~it delivers a reduction with respect to the~~ the proposed layout outperforms methane production from maize silage in the following categories: climate change, ecotoxicity freshwater, ionizing radiation, land use and non-cancer human health. ~~On the other hand, the~~The proposed ~~process yields significant increases~~layout is environmentally disadvantageous in the ~~other impact~~remaining environmental categories ~~compared to the reference systems~~.



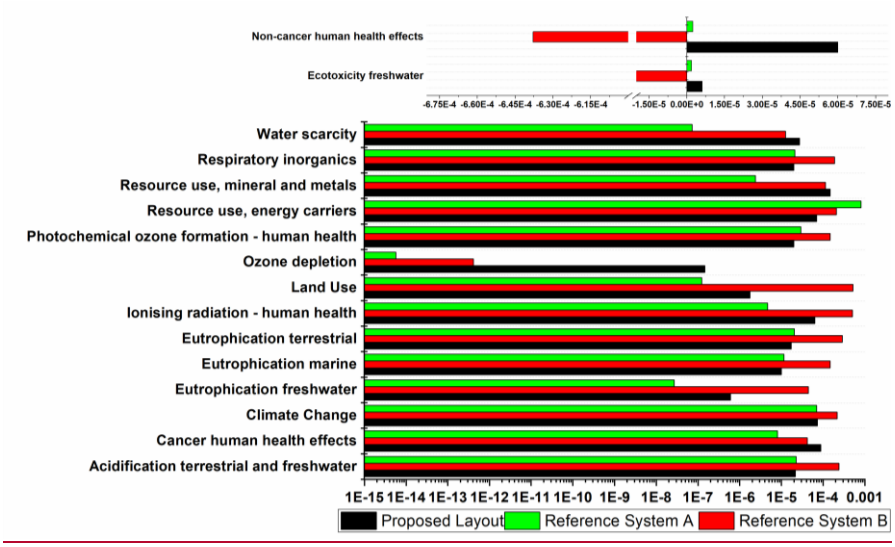


Figure 4. Normalized environmental impacts of the proposed process layout and the reference systems.

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Figure 5 reports ~~the~~a hot-spot analysis for the ~~process developed~~plant layout proposed in this work. The results show that the largest portion of the environmental impacts in ~~almost~~nearly all ~~the~~ impact categories originate from the PEM unit and, specifically, from the electricity wind production, with contributions ranging from 35% in the category ionizing radiation and up to ~100% in the category water scarcity, resource use-mineral and metal, land use and cancer human health. ~~Whilst the~~The CaL unit ~~mainly impacts~~has significant contributions in a limited number of categories including climate change (~30%), eutrophication terrestrial and marine (~40%), ionizing radiation (~62%) and ozone depletion (~100%). ~~Interestingly, the results from the LCA analysis reveal that the impacts of the CaL unit are primarily attributable to the production of the calcium oxide (to capture CO_2).~~The results from the analysis show that the impacts of the CaL unit are mostly attributable to the production of the calcium oxide (to capture CO_2). Similarly to what found in the techno-economic analysis, the LCA study indicates that the environmental impacts of

electricity consumption heavily affect the environmental performance of the proposed plant layout. As previously reported, these results include the environmental impacts associated with the production of electricity from wind even if this electricity would otherwise be wasted. Table A1 in the appendix reports the environmental performances for the proposed layout without including the wind electricity production. The comparison shows that the new proposed scenario outperforms conventional methane and bio-methane productions in almost all the impact categories except for eutrophication marine and terrestrial, ozone depletion and water scarcity.

A reduction in the electric consumption of the PEM unit will significantly reduce the environmental impacts of the proposed layout, which could make it environmentally advantageous across a larger number of environmental categories. The above also suggests that our results are heavily dependent on the assumed energy source; future studies should investigate the environmental performance when electricity is obtained from other sources such as solar, geothermal or nuclear.

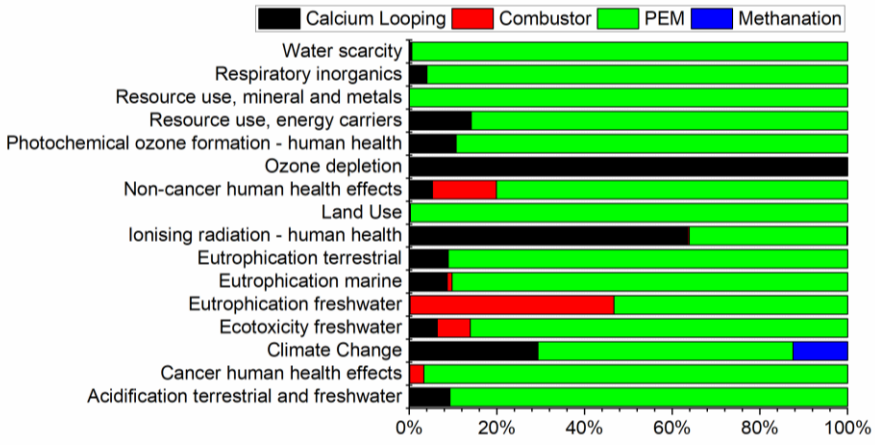

Figure 5. Hot-spot analysis of the proposed plant layout.

~~6.~~6. CONCLUSIONS

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In this work, we investigated the technical, economic and environmental performance of a novel ~~process~~plant layout for the production of synthetic methane using CO_2 captured from combustion flue gas. The ~~plant configuration~~layout integrates sorption-enhanced catalytic methanation with CO_2 capture ~~by~~via calcium looping, and renewable H_2 production ~~with a~~via PEM electrolyzer. The advantages of this configuration include good temperature control and low operating pressure of the methanation step, and the avoidance of a costly air separation unit for the calcium looping step.

The economic and environmental performances of ~~such system~~the proposed layout were ~~investigated and~~ compared with those of traditional natural gas production, and of biomethane production from maize~~. Results~~ silage. Our results show that the production cost of methane per unit Nm^3 is higher than that of natural gas, but lower than that of ~~biomethane~~bio-methane. The largest impact on these costs comes from the PEM electrolyzer~~; this~~, and in particular from the consumption of electricity. The PEM is currently ~~still~~ an expensive technology~~,~~ but its cost is forecasted to decrease significantly in the ~~next~~coming years. In addition, it is worth highlighting that the possible future introduction of significant carbon taxes would increase the economic attractiveness of synthetic methane production with respect to natural gas.

~~Results~~ The results of the LCA analysis ~~highlighted~~indicates the existence of several environmental trade-offs, with no systems outperforming the other across all environmental categories. ~~Like for economic costs, the PEM electrolyzer appears to account for most of the environmental impacts of the process~~Notably, from a climate change perspective the proposed layout is not advantageous when compared to the conventional pathway for methane production, yielding an increase of ~ 5%. Like for economic costs, the electricity consumption of the PEM electrolyzer accounts for most of the environmental impacts. Overall, our analysis indicates that the high electricity consumption of the PEM electrolyzer is the most critical aspect. Future

improvements in the PEM efficiency will significantly improve the economic and environmental performance of the proposed plant layout.

ACKNOWLEDGEMENTS

The help of Ms. Giulia Paone is gratefully acknowledged.

APPENDIX

Table A1. Mass balances of the whole plant in kg/h.

CALCIUM LOOPING							
CARBONATOR				**CALCINER**			
INPUT		**OUTPUT**		**INPUT**		**OUTPUT**	
$CaCO_3$	0.00E+00	$CaCO_3$	2.00E+06	$CaCO_3$	2.34E+06	$CaCO_3$	0.00E+00
CaO	3.82E+06	CaO	2.70E+06	CaO	2.70E+06	CaO	3.82E+06
Flue Gas	4.02E+06	Flue Gas	3.14E+06				
CO_2	9.24E+05	CO_2	4.62E+04	CO_2	0.00E+00	CO_2	1.39E+06
H_2O	2.52E+05	H_2O	2.52E+05	H_2O	0.00E+00	H_2O	2.99E+05
O_2	1.34E+05	O_2	1.34E+05	O_2	3.18E+05	O_2	5.30E+04
N_2	2.71E+06	N_2	2.71E+06	N_2	0.00E+00	N_2	0.00E+00
				CH_4	1.33E+05	CH_4	0.00E+00
COMBUSTOR				**PEM**			
INPUT		**OUTPUT**		**INPUT**		**OUTPUT**	
CO_2	1.39E+06	CO_2	1.39E+06	H_2O	2.42E+06	H_2O	0.00E+00
H_2O	2.99E+05	H_2O	4.18E+05	H_2	0.00E+00	H_2	2.69E+05
O_2	5.30E+04	O_2	0.00E+00	O_2	0.00E+00	O_2	1.08E+06
H_2	1.59E+04	H_2	2.65E+03				
SORPTION ENHANCED METHANATION							
METHANATOR				**REGENERATOR**			
INPUT		**OUTPUT**		**INPUT**		**OUTPUT**	
H_2	2.56E+05	H_2	4.72E+03	H_2		H_2	
CO_2	1.39E+06	CO_2	2.57E+04	CO_2		CO_2	
H_2O	0.00E+00	H_2O	5.71E+05	H_2O	0.00E+00	H_2O	3.50E+05
CaO	2.87E+06	CaO	1.09E+06	CaO	0.00E+00	CaO	2.87E+06
CH_4	0.00E+00	CH_4	4.98E+05	CH_4		CH_4	
O_2		O_2	0.00E+00	O_2	5.87E+05	O_2	5.87E+05
N_2		N_2	0.00E+00	N_2	3.87E+06	N_2	3.87E+06
$Ca(OH)_2$	0.00E+00	$Ca(OH)_2$	2.35E+06	$Ca(OH)_2$	2.35E+06	$Ca(OH)_2$	
CO	0.00E+00	CO	3.01E+01	CO		CO	
CaO_{mup}	1.91E+05					CaO_{sp}	1.91E+05

Table A2. Normalized environmental impacts of the proposed process layout without considering the wind electricity production and the reference systems.

	Proposed layout (no electricity)	Reference system A	Reference System B
Acidification terrestrial and freshwater	1,20E-04	1,33E-02	1,26E-03
Cancer human health effects	1,10E-10	1,61E-09	3,09E-10
Climate Change	2,38E-01	1,68E+00	5,39E-01
Ecotoxicity freshwater	1,25E-02	-3,03E-01	2,20E-02
Eutrophication freshwater	7,93E-07	1,12E-04	6,91E-08
Eutrophication marine	2,21E+00	4,17E-03	3,28E-04
Eutrophication terrestrial	2,49E+02	5,11E-02	3,60E-03
Ionising radiation - human health	1,73E-02	2,12E-01	1,97E-03
Land Use	-6,00E-02	6,95E+02	1,63E-01
Non-cancer human health effects	4,70E-09	-3,03E-07	1,15E-09
Ozone depletion	3,42E-09	9,64E-15	1,33E-16
Photochemical ozone formation - human health	9,10E-05	5,98E-03	1,18E-03
Resource use, energy carriers	6,90E-01	1,36E+01	5,25E+01
Resource use, mineral and metals	0,00E+00	6,56E-06	1,38E-07
Respiratory inorganics	5,00E-10	1,19E-07	1,34E-08
Water scarcity	2,38E-01	1,44E-01	8,30E-04

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Declaration of interests

☒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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Credit author statement

Roberto Chirone & Andrea Paulillo: LCA Conceptualization & Methodology, Writing. **Antonio Coppola**: TCA Conceptualization & Methodology, Writing, Original draft preparation. **Fabrizio Scala**: Supervision, Reviewing & Editing.