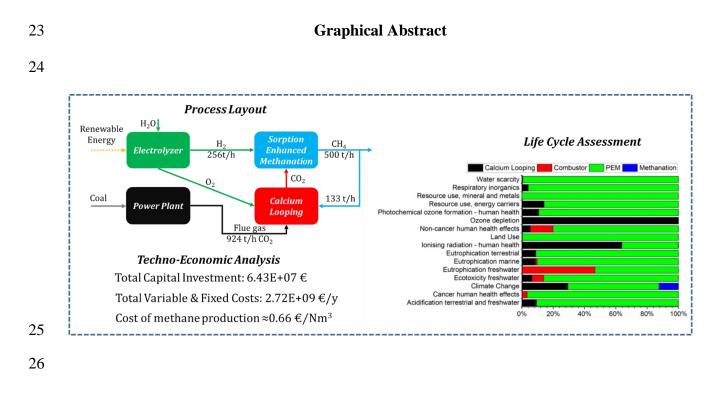
1	CARBON CAPTURE AND UTILIZATION VIA CALCIUM LOOPING, SORPTION
2	ENHANCED METHANATION AND GREEN HYDROGEN: A TECHNO-ECONOMIC
3	ANALYSIS AND LIFE CYCLE ASSESSMENT STUDY
4	
5	
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#### 29 ABSTRACT

30 The production of synthetic methane using  $CO_2$  from flue gases and green hydrogen appears to be 31 a promising way to combine the concepts of renewable energy, chemical storage, and utilization 32 of CO<sub>2</sub>. Recently, a new reactor configuration for catalytic methanation has been proposed, 33 integrating sorption-enhanced methanation and chemical looping in interconnected fluidized bed 34 systems. This configuration would ensure high methane yields while keeping good temperature 35 control and low operating pressure. In this work, such novel system layout for the catalytic 36 production of methane was combined with a calcium looping unit for CO<sub>2</sub> capture from flue gases of a coal-fired power plant, and with a water electrolyzer sustained by renewable energy. The 37 38 integrated layout offers a series of advantages deriving from the integration of different mass and 39 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 40 41 cycle assessment was carried out to quantify the environmental impact of all process units. Results 42 of the techno-economic analysis indicated that the production cost of methane is higher than that 43 of natural gas (0.66 vs 0.17  $\notin$ /Nm<sup>3</sup>), but lower than that of biomethane (1  $\notin$ /Nm<sup>3</sup>). The largest impact on such costs comes from the PEM electrolyzer. The LCA analysis showed that the 44 45 environmental performance is better in some categories and worse in others with respect to 46 traditional scenarios. Again, the PEM electrolyzer appears to account for most of the 47 environmental impacts of the process.

48

Keywords: Techno-Economic Analysis; Life Cycle Assessment; CO<sub>2</sub> Capture; Carbon Capture
and Utilization; Calcium Looping; Sorption Enhanced Methanation.

#### 51 Nomenclature

Cyclone 1	LCA	Life Cycle Assessment
Cyclone 2	N <sub>np</sub>	Number of non-particulate processing
		steps
Cyclone 3	N <sub>OL</sub>	Number of operators per shift
Cyclone 4	Р	Number of processing steps
Calcium Looping	PEM	Polymer Electrolyte Membrane
		electrolyzer
Cost of operating labor	S1	Blower 1
Cost of raw materials	S2	Blower 2
Cost of utilities	S3	Blower 3
Cost of waste treatment	S4	Blower 4
Direct Plant Cost	SEM	Sorption Enhanced Methanation
Equipment Cost	TCI	Total Capital Investment
Fixed Costs	TEA	Techno-Economic Analysis
Fixed Capital Investment	TPC	Total Product Cost
Heat exchanger 1	VC	Variable Costs
Heat exchanger 2	WC	Working Capital
Indirect Plant Cost		
	Cyclone 2 Cyclone 3 Cyclone 4 Calcium Looping Cost of operating labor Cost of raw materials Cost of utilities Cost of utilities Cost of waste treatment Direct Plant Cost Equipment Cost Equipment Cost Fixed Costs Fixed Capital Investment Heat exchanger 1 Heat exchanger 2	Cyclone 2NnpCyclone 3NoLCyclone 4PCalcium LoopingPEMCost of operating laborS1Cost of raw materialsS2Cost of utilitiesS3Cost of waste treatmentS4Direct Plant CostSEMEquipment CostTCIFixed CostsTEAFixed Capital InvestmentTPCHeat exchanger 1VCHeat exchanger 2WC

52

## 53 1. INTRODUCTION

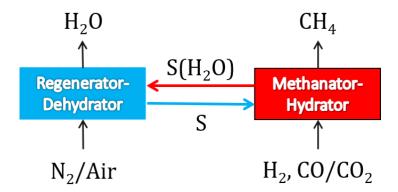
54 The most attractive solution to rapidly reduce CO<sub>2</sub> emissions and the consumption of fossil 55 fuels, responsible for 85% of the greenhouse gas emissions, is the implementation of renewable 56 energy systems, mostly based on solar and wind energy. However, these technologies will not be 57 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<sub>2</sub> 58 59 emissions generated by fossil fuel consumption may be represented by Carbon Capture and 60 Utilization (CCU) technologies. Among all the possible final products obtainable with these 61 technologies [3,4], synthetic methane is one of the most attractive, due to the existence of a welldeveloped infrastructure for distribution, and to the wide demand and acceptance of this fuel for 62 63 industrial and domestic usage. In addition, methane represents a smart energy carrier that can store 64 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 67 68 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 69 70 and hence preventing the deactivation of the catalyst [5,6]. A sufficiently high methane purity is 71 needed for injecting synthetic methane into the natural gas grid. The concept of Sorption-Enhanced 72 Methanation (SEM), first formulated by Borgschulte et al. [7] and Walspurger et al. [8], on the 73 basis of the Le Chatelier principle, would allow the process to achieve high degrees of methane 74 conversion at lower pressures, leading to savings in compression energy up to 40%. Specifically, 75 the steam generated by the methanation reaction can be removed from the catalytic bed by adding 76 a suitable sorbent material, in order to push the equilibrium reaction towards methane formation 77 [7,8].

78 Recently, Coppola et al. [9–11] proposed a novel reactor configuration which combines the 79 concepts of SEM and of chemical looping in dual interconnected fluidized bed systems. Such 80 configuration would ensure good temperature control and lower operating pressure, and most 81 importantly the possibility to carry out a steady process, contrary to fixed bed arrangements. One 82 reactor, the methanator, is used for the catalytic methanation and simultaneous steam capture by 83 means of a suitable sorbent. While the regeneration of the sorbent takes place in another reactor 84 (dehydrator) where H<sub>2</sub>O is released from the sorbent by increasing the temperature (or by decreasing the H<sub>2</sub>O partial pressure). The two reactors are connected to each other in a dual-85 86 interconnected fluidized bed configuration as shown in Fig.1, allowing for the continuous 87 circulation of the solid sorbent between the two reactors.

88





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



94 In this work, we propose a new system layout for catalytic methane production that integrates 95 the above SEM concept with a Calcium Looping unit (CaL) for CO<sub>2</sub> capture from flue gas of a 96 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 97 98 referring to the Italian scenario, where large amounts of renewable electricity are wasted (i.e. they 99 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<sup>3</sup> of methane produced via a techno-100 101 economic analysis (TEA). The environmental performance was assessed using the Life Cycle 102 Assessment (LCA) methodology. While many articles in the literature report techno-economic 103 [1,2,13–20] or environmental [22–24] analysis of traditional power-to-methane (PtM) 104 configurations, we could not find any work in the literature assessing a similar configuration which 105 integrates Calcium Looping and Sorption-Enhanced Methanation.

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#### 108 **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<sub>2</sub> emissions:
- 111

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

- 113 ii. Proton Exchange Membrane (PEM) unit in light blue.
- 114 iii. Sorption-Enhanced Methanation (SEM) unit in green.
- 115

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:

$$CaO + CO_2 \rightarrow CaCO_3$$
 Eq. 1

119

120 According to [25] the CO<sub>2</sub> capture efficiency was chosen to be equal to 95% (molar). Two 121 streams leave the carbonator reactor: the solid carbonated sorbent and the cleaned flue gas. The 122 carbonated sorbent is transferred to the calciner reactor where the reverse reaction (namely 123 calcination) takes place at around 940°C for regenerating the CaO. To thermally sustain the 124 calcination reaction, which is an endothermic reaction, part of the produced methane is burnt in 125 the calciner. The methane is burnt with an excess of oxygen of 50%, which is provided by the 126 PEM. From mass and energy balances, about 35% in volume of the produced synthetic methane 127 is necessary to maintain the temperature of the calciner. We chose this plant layout to avoid 128 utilization of an energy-intensive air separation unit [26]. Furthermore, to account for sorbent 129 deactivation and attrition, a fresh sorbent make-up stream and an exhausted sorbent purge stream 130 were considered at the inlet and at the outlet of the calciner, respectively. The gas leaving the 131 calciner, mainly composed of CO<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O, is partially recycled to the reactor both to support 132 its fluidization and to act as a thermal buffer for the methane combustion reaction.

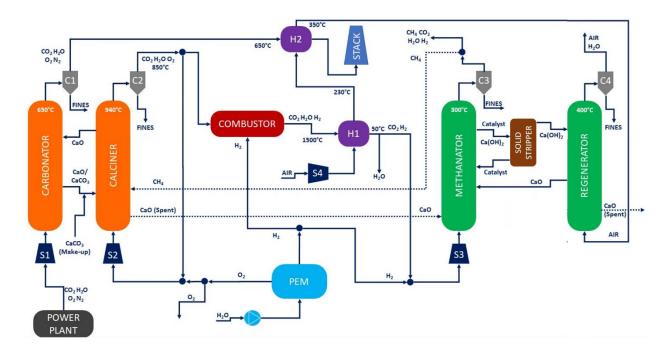




Figure 2. Layout of the Calcium Looping, PEM and Sorption Enhanced Methanation integrated
 system.

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<sub>2</sub> coming from the PEM to obtain the appropriate stoichiometric H<sub>2</sub>/CO<sub>2</sub> 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

149 In the methanation reactor the produced steam is captured by the spent CaO coming from the 150 calciner purge stream: the spent sorbent in terms of CO<sub>2</sub> capture still has a good reactivity towards 151 water vapor, as demonstrated in previous studies [10], therefore it is suitable for the SEM process. 152 The hydration reaction is:

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

153 In addition to the methanator, the SEM unit includes a regenerator reactor operated at 400°C 154 for sorbent regeneration. The hydrated sorbent stream exiting the methanator passes through a 155 solid-solid stripper (based on density/size difference) to separate the Ni-based catalyst from the 156 sorbent. The catalyst, which is recirculated back to the methanator, in fact should not enter the 157 regenerator since it would be deactivated by oxygen.

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## **3. TECHNO-ECONOMIC ANALYSIS**

161 We considered CO<sub>2</sub> 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 162 163 by Endesa Generation Spain: designed for a maximum power of 1400 MW<sub>e</sub> with a sub-critical 164 steam cycle, it uses as primary fuel lignite and sub-bituminous coal, and as secondary fuel natural 165 gas. The plant comprises four boilers and four turbines connected to the national electric grid, with about 5.5 Mt CO<sub>2</sub> emissions in 2019<sup>\*</sup>. The electrolyzer considered in this study was a proton 166 167 exchange membrane (PEM) system powered by renewable energy. The whole system can generate about 500 t/h of methane (about 7000 MWth). Complete mass balances are reported in Table A1 168 169 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.

$$TCI = DPC + IPC + StC$$
 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.

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

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

181 where,  $C_{OL}$  is the cost of operating labor,  $C_{UT}$  is the cost of utilities (i.e. the electricity needed 182 for the PEM, pumps and blowers),  $C_{WT}$  is the cost of waste treatment and  $C_{RM}$  is the cost of raw 183 materials. Moreover Eq. 5 takes into account of the depreciation of FCI.

184 In particular, the  $C_{OL}$  is based on the number of workers needed for each work shift, obtained 185 from the following equation:

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

186 where  $N_{OL}$  is the number of operators per shift,  $N_{np}$  is the number of non-particulate processing 187 steps (compression, heating and cooling, mixing, and reaction) and P is the number of processing 188 steps that require physical effort (transportation and distribution, particulate size control, and 189 particulate removal). 190 Once we estimated the TPC, by dividing it for the total production of standard cubic meters 191 (smc) of methane per year with the proposed layout, we obtained a preliminary estimation for the 192 production cost of one smc of methane.

193  $C_{RM} C_{WT}$  and  $C_{UT}$  represent the main contributors to the variable costs (VC), while  $C_{OL}$  to 194 fixed costs (FC). The others FCs, i.e. Direct Supervisory, Maintenance, Tax & Insurance and 195 Overhead have been calculated as  $0.18C_{OL}$ , 0.06FCI, 0.032FCI and  $0.6(1.18C_{OL}+0.06FCI)$ , 196 respectively, as suggested by [27].

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#### 199 **4. LIFE CYCLE ASSESSMENT**

200 The environmental performance and the main sources of environmental impacts (i.e., the "hot-201 spots") of the proposed plant layout were evaluated by means of the Life Cycle Assessment 202 methodology (LCA) [28,29]. Furthermore, its environmental performance was compared with 203 similar reference systems that provide the same function. The study was based on an attributional 204 approach, and it was framed in the Italian context. The proposed process produces synthetic 205 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, 206 207 including all activities from the extraction of raw materials to the production of methane before its 208 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.

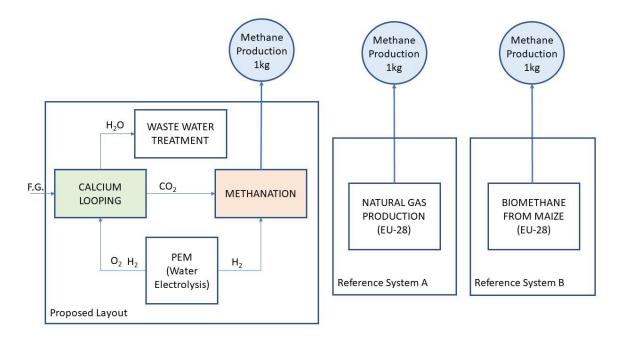




Figure 3. Comparison between the novel process proposed in this study (Proposed Layout) and the reference systems (A and B).

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.

Table 1. Environmental	impact categories analysed
CT CATEGORY	METRIC

IMPACT CATEGORY	METRIC
Acidification	Mole of H <sup>+</sup> 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

#### **5. RESULTS**

- 235 Techno-Economic Analysis
- The main economic assumptions used in this study are reported in Table 2.
- 237
- 238

 Table 2. Economic Assumptions

Average Labour Cost	38000 €/y per person <sup>†</sup>
Depreciation	10% [27]
Stream Factor	95% (working for 8300 h/y) [27]
Electricity price	25 €/MWh [34]
CaCO <sub>3</sub> price	20€/ton [35]
Water price	0.01€/ton [35]

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241 The equipment costs (EC) are reported in Table 3. Data for conventional devices like heat 242 exchangers, pumps, blowers, and cyclones were obtained from the Matches website 243 (www.matche.com) and updated via the CEPCI 2020 index to account for inflation. ECs for the 244 Calcium Looping unit and PEM were extrapolated from the literature ([36] and [37], respectively). 245 Costs data for the SEM unit are not available in the scientific literature because this specific 246 configuration envisaging two interconnected fluidized beds was only recently proposed by 247 Coppola et al. [11]. However, since the reactor configuration of the SEM unit is similar to that of 248 the CaL unit (which also comprises two interconnected fluidized beds), we estimated the EC of 249 the SEM unit on the basis of that of the CaL unit, taking into account differences in size. Notably, 250 we estimated the volume of each fluidized bed reactor considering the fluidizing gas and the 251 fluidization regime. The cost of each reactor was estimated from its volume using the relation 252 provided by [36].

<sup>&</sup>lt;sup>†</sup> 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)

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%

Table 2. Equipment Cost.

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257 As shown in Table 3, the highest cost is represented by the PEM electrolyzer, which accounts 258 for about 90% of the whole equipment costs (EC). It must be noted that the PEM technology is 259 more expensive and less mature than alkaline electrolyzers (AEC); the AEC cost is about 1000-260 1200 €/kWel compared to 1860-2320 €/kWel for PEMs [38]. However, PEMs yield a higher purity 261 of the produced gas, a faster system response and a lower cold-start time which make them more 262 suitable for their combination with intermitted renewable energy systems. Moreover, technology 263 projections estimate that PEM will reach similar costs to AEC in the next ten years, and also that 264 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<sub>th</sub> of methane<sup>‡</sup>.

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 $HHV_{methane} = 55MJ/kg$ 

Table 3. Direct and Indirect Cost	ts of the plant configuration.
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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) 5.59			5.59E+07
Working Capital (WC)	15%	FCI	8.39E+06
Total Capital Investment (TCI)FCI+WC6.43E+07			

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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 the economic competitiveness of our proposed plant layout is highly dependent on future reductions in the cost of electricity and/or the exploitation of 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

- 288 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.
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- 291

Table 4.	Fixed	and	variable	costs.

Variable Costs (VC)	[€]/y	%
Utilities Costs (C <sub>U</sub> )		
PEM	2.71E+09	99.58%
Pumps & Blowers	2.85E+05	0.01%
Waste treatment (C <sub>wr</sub> )	2.84E+06	0.10%
Raw material cost (C <sub>RM</sub> )		
CaCO <sub>3</sub>	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 (Col)	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%

#### 293

The total product cost (TPC), considering the depreciation of the plant, is around  $3.35 \times 10^3 \text{ M} \text{e/y}$ . 294 295 The methane cost production was calculated as the ratio between TPC and the total amount of 296 produced methane per year. The proposed system results in a cost of methane production of about 0.66 €/Nm<sup>3 (§)</sup>. In Europe the cost of natural gas exploration and production corresponds to 0.17 297 €/Nm<sup>3</sup> in 2020 (ENI, financial report 2020 [39]), while that of methane produced with traditional 298 299 methanation systems to about 0.51 €/Nm<sup>3</sup> not including the cost of electricity [34]. In addition, bio-methane produced from anaerobic digestion has a production cost of around 1 €/Nm<sup>3</sup> [40]. As 300 301 recognized by other authors, the cost of electricity is the 'control knob' for the success of these 302 technologies [34]. To reach the parity grid, in terms of methane production cost, for the

<sup>&</sup>lt;sup>§</sup> 15.9 €/kmol; 0.99 €/kg; 0.018 €/MJ; 64.92 €/MWh

303	configuration proposed in this work the electricity should have a price lower than 0.005 $\ensuremath{\in}/\ensuremath{KWh_{el}}$ .
304	In particular, for the limiting case where the electricity cost becomes zero (i.e. when considered
305	waste electricity) the cost of methane would be of about 0.02€/Nm <sup>3</sup> , that is on order of magnitude
306	lower than the cost of natural gas.
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309	Life Cycle Assessment.
310	Table 6 reports the inventory data for the proposed plant layout. We assumed that the sorbent
311	(CaCO <sub>3</sub> ) used in the CaL unit can be reused in the SEM unit, thus reducing additional
312	consumption. We also assumed a make-up of around 5% of the mass flow of the sorbent
313	(CaO+CaCO <sub>3</sub> ) cycled between reactors. Literature data is used to describe the operation of the
314	PEM unit in terms of efficiency and electricity consumption; in particular, the electric requirement
315	for the PEM is 46.6 kWh/kgH <sub>2</sub> [30]. Note that we considered the environmental impacts associated
316	with the production of electricity from wind even if we assumed that this electricity would
317	otherwise be wasted [13]. The inventory data for the remaining activities that supply energy and
318	materials to the plant and for the reference systems (i.e. conventional and bio-based methane) are
319	obtained from the Ecoinvent database.
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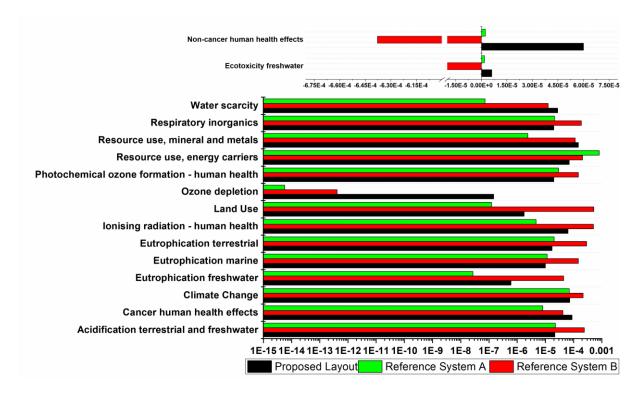
<b>Calcium Loop</b>	ing		
input			
	CO <sub>2</sub> , flue gas	kg	2,10E+00
	$H_2O$ , flue gas	kg	5,71E-01
	$O_2$ , flue gas	kg	3,04E-01
	N <sub>2</sub> , flue gas	kg	6,15E+00
	$CaCO_3$ bed	kg	2,74E-03
	CaCO <sub>3</sub> make-up	kg	7,71E-01
	electricity mix	kWh	4,10E-04
output	-		
	$CO_2$ , emission to air	kg	1,05E-01
	$H_2O$ , emission to air	kg	5,71E-01
	$O_2$ , emission to air	kg	3,04E-01
	N <sub>2</sub> , emission to air	kg	6,15E+00
Combustor		-	
output			
-	H <sub>2</sub> O, 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 <sub>2</sub> O	kg	4,90E+00
	electricity renewable	kWh	2,54E+01
	electricity mix	kWh	1,20E-08
output			
	CO <sub>2</sub> , emission to air	kg	5,15E-02
	H <sub>2</sub> O, emission to air	kg	1,81E+00
	O <sub>2</sub> , emission to air	kg	1,16E+00
	N <sub>2</sub> , 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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Figure 4 reports the normalised environmental impacts of the proposed plant layout and those of the reference systems. The comparative analysis shows that methane production from the proposed layout yields lower environmental impacts than both reference systems in the categories terrestrial acidification, photochemical ozone formation, marine and terrestrial eutrophication, 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.

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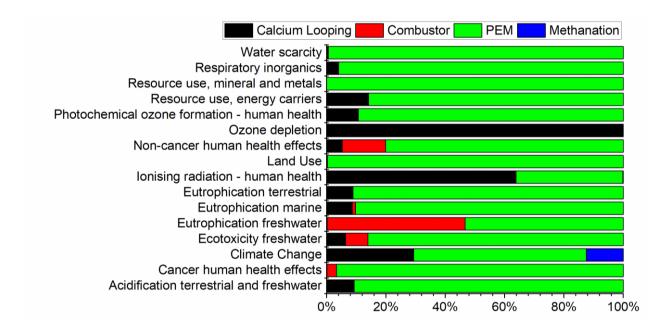


## 341

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

344 Figure 5 reports a hot-spot analysis for the plant layout proposed in this work. The results show 345 that the largest portion of the environmental impacts in nearly all impact categories originate from 346 the PEM unit and, specifically, from the electricity wind production, with contributions ranging 347 from 35% in the category ionizing radiation and up to ~100% in the category water scarcity, 348 resource use-mineral and metal, land use and cancer human health. The CaL unit has significant 349 contributions in a limited number of categories including climate change (~30%), eutrophication 350 terrestrial and marine (~40%), ionizing radiation (~62%) and ozone depletion (~100%). The results 351 from the analysis show that the impacts of the CaL unit are mostly attributable to the production 352 of the calcium oxide (to capture CO<sub>2</sub>). Similarly to what found in the techno-economic analysis, 353 the LCA study indicates that the environmental impacts of electricity consumption heavily affect 354 the environmental performance of the proposed plant layout. As previously reported, these results 355 include the environmental impacts associated with the production of electricity from wind even if 356 this electricity would otherwise be wasted. Table A1 in the appendix reports the environmental 357 performances for the proposed layout without including the wind electricity production. The 358 comparison shows that the new proposed scenario outperforms conventional methane and bio-359 methane productions in almost all the impact categories except for eutrophication marine and 360 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.



370

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

## 371 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<sub>2</sub> 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.

378 The economic and environmental performances of the proposed layout were compared with 379 those of traditional natural gas production, and of biomethane production from maize silage. Our 380 results show that the production cost of methane per unit Nm<sup>3</sup> is higher than that of natural gas, 381 but lower than that of bio-methane. The largest impact on these costs comes from the PEM 382 electrolyzer, and in particular from the consumption of electricity. The PEM is currently an 383 expensive technology but its cost is forecasted to decrease significantly in the coming years. In 384 addition, it is worth highlighting that the possible future introduction of significant carbon taxes 385 would increase the economic attractiveness of synthetic methane production with respect to natural 386 gas. The results of the LCA analysis indicates the existence of several environmental trade-offs, 387 with no systems outperforming the other across all environmental categories. Notably, from a 388 climate change perspective the proposed layout is not advantageous when compared to the 389 conventional pathway for methane production, yielding an increase of ~ 5%. Like for economic 390 costs, the electricity consumption of the PEM electrolyzer accounts for most of the environmental 391 impacts. Overall, our analysis indicates that the high electricity consumption of the PEM 392 electrolyzer is the most critical aspect. Future improvements in the PEM efficiency will 393 significantly improve the economic and environmental performance of the proposed plant layout.

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395	
396	ACKNOWLEDGEMENTS
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# 398 The help of Ms. Giulia Paone is gratefully acknowledged.

## **APPENDIX**

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

CALCIUM	LOOPING						
CARBONA	TOR			CALCINER			
INPUT OUTPUT			INPUT		OUTPUT		
CaCO <sub>3</sub>	0.00E+00	CaCO <sub>3</sub>	2.00E+06	CaCO <sub>3</sub>	2.34E+06	CaCO <sub>3</sub>	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 <sub>2</sub>	9.24E+05	CO <sub>2</sub>	4.62E+04	CO <sub>2</sub>	0.00E+00	CO <sub>2</sub>	1.39E+06
H <sub>2</sub> O	2.52E+05	H <sub>2</sub> O	2.52E+05	H <sub>2</sub> O	0.00E+00	H <sub>2</sub> O	2.99E+05
O <sub>2</sub>	1.34E+05	O <sub>2</sub>	1.34E+05	O <sub>2</sub>	3.18E+05	O <sub>2</sub>	5.30E+04
N <sub>2</sub>	2.71E+06	N <sub>2</sub>	2.71E+06	N <sub>2</sub>	0.00E+00	N <sub>2</sub>	0.00E+00
				CH <sub>4</sub>	1.33E+05	CH <sub>4</sub>	0.00E+00
COMBUST	FOR	-		PEM			
INPUT	-	OUTPUT		INPUT		OUTPUT	
CO <sub>2</sub>	1.39E+06	CO <sub>2</sub>	1.39E+06	H <sub>2</sub> O	2.42E+06	H <sub>2</sub> O	0.00E+00
H <sub>2</sub> O	2.99E+05	H <sub>2</sub> O	4.18E+05	H <sub>2</sub>	0.00E+00	H <sub>2</sub>	2.69E+05
O <sub>2</sub>	5.30E+04	O <sub>2</sub>	0.00E+00	O <sub>2</sub>	0.00E+00	O <sub>2</sub>	1.08E+06
H <sub>2</sub>	1.59E+04	H <sub>2</sub>	2.65E+03				
SORPTION	N ENHANCED	METHANA	TION				
METHANA	ATOR			REGENER	ATOR		
INPUT OUTPUT			INPUT OUTPUT				
$H_2$	2.56E+05	H <sub>2</sub>	4.72E+03	H <sub>2</sub>		H <sub>2</sub>	
CO <sub>2</sub>	1.39E+06	CO <sub>2</sub>	2.57E+04	CO <sub>2</sub>		CO <sub>2</sub>	
$H_2O$	0.00E+00	H <sub>2</sub> O	5.71E+05	H <sub>2</sub> O	0.00E+00	H <sub>2</sub> O	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 <sub>4</sub>	4.98E+05	CH <sub>4</sub>		$CH_4$	
02		O <sub>2</sub>	0.00E+00	02	5.87E+05	O <sub>2</sub>	5.87E+05
$N_2$		N <sub>2</sub>	0.00E+00	N <sub>2</sub>	3.87E+06	N <sub>2</sub>	3.87E+06
Ca(OH) <sub>2</sub>	0.00E+00	Ca(OH) <sub>2</sub>	2.35E+06	Ca(OH) <sub>2</sub>	2.35E+06	Ca(OH) <sub>2</sub>	
CO	0.00E+00	CO	3.01E+01	CO		CO	
CaO <sub>mup</sub>	1.91E+05					CaO <sub>sp</sub>	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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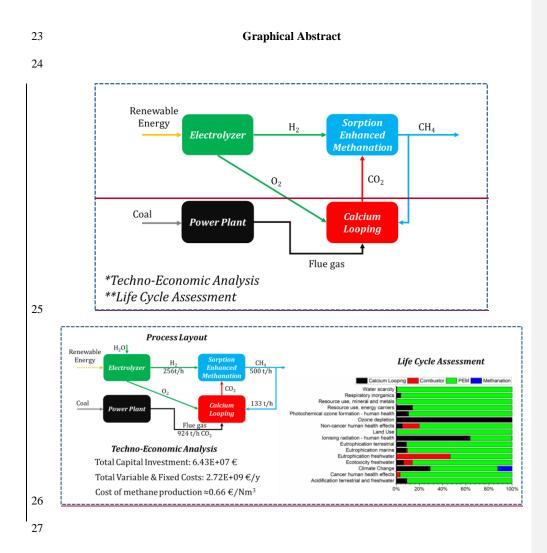
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1	CARBON CAPTURE AND UTILIZATION VIA CALCIUM LOOPING, SORPTION
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3	ANALYSIS AND LIFE CYCLE ASSESSMENT STUDY
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#### 30 ABSTRACT

31 The production of synthetic methane using  $CO_2$  from flue gases and green hydrogen appears to be 32 a promising way to combine the concepts of renewable energy, chemical storage, and utilization 33 of CO<sub>2</sub>. Recently, a new reactor configuration for catalytic methanation has been proposed, integrating sorption-enhanced methanation and chemical looping in interconnected fluidized bed 34 35 systems. This configuration would ensure high methane yields while keeping good temperature 36 control and low operating pressure. In this work, such novel system layout for the catalytic 37 production of methane was combined with a calcium looping unit for CO<sub>2</sub> capture from flue gases 38 of a coal-fired power plant, and with a water electrolyzer sustained by renewable energy. The 39 integrated layout offers a series of advantages deriving from the integration of different mass and 40 energy flows of the different sections of the plant. The performance of this latter was assessed in 41 terms of construction and production costs, as well as from an environmental point of view: a life 42 cycle assessment was carried out to quantify the environmental impact of all process units. Results 43 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<sup>3</sup>), but lower than that of biomethane. (1 €/Nm<sup>3</sup>). The largest 44 45 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 46 47 traditional scenarios. Again, the PEM electrolyzer appears to account for most of the environmental impacts of the process. 48

- 49
- Keywords: Techno-Economic Analysis; Life Cycle Assessment; CO<sub>2</sub> Capture; Carbon Capture
  and Utilization; Calcium Looping; Sorption Enhanced Methanation.

#### 52 <u>Nomenclature</u>

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

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#### **<u>1.01.</u>** INTRODUCTION

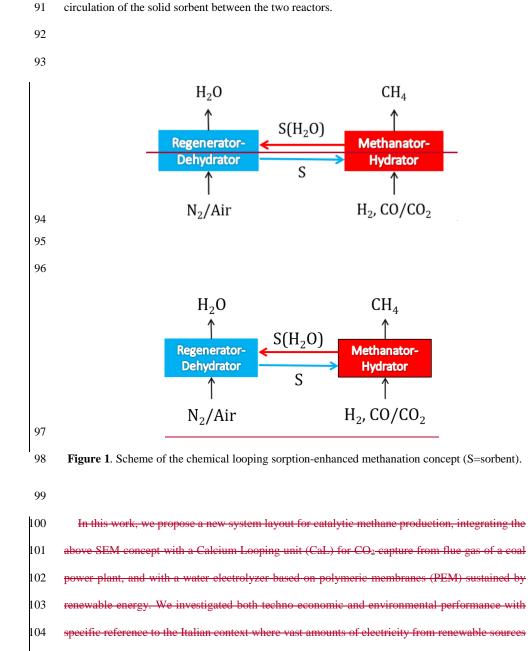
55 The most attractive solution to rapidly reduce CO2 emissions and the consumption of fossil 56 fuels, responsible for 85% of the greenhouse gas emissions, is the implementation of renewable 57 energy systems, mostly based on solar and wind energy. However, these technologies will not be 58 ready to totally replace the fossil energy systems in the short/medium term, especially because of 59 their intermittent energy production mode [1,2]. Thus, a short-term solution to contain-the CO<sub>2</sub> 60 emissions generated by fossil fuel consumption may be represented by Carbon Capture and 61 Utilization (CCU) technologies. Among all the possible final products obtainable with these 62 technologies [3,4], synthetic methane is one of the most attractive, due to the existence of a well-63 developed infrastructure for distribution, and to the wide demand and acceptance of this fuel for 64 industrial and domestic usage. In addition, methane represents a smart energy carrier able tothat can store largesignificant amounts of energy from renewable sourcesenergy in the natural gas grid. 65

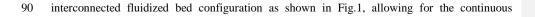
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Global methane market is expected to reach \$151.27 billion by 2026 growing at a Compound
Annual Growth Rate (CAGR) of 6.1% during the period from 2017 to 2026.

68 From thean industrial point of view, the exothermic catalytic methanation of CO<sub>2</sub> is typically 69 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 70 71 temperature of the system and, hence, to prevent preventing the deactivation of the catalyst [5,6]. 72 A sufficiently high methane purity is needed to allow the injection of for injecting synthetic 73 methane into the natural gas grid. The concept of Sorption-Enhanced Methanation (SEM), first 74 formulated by Borgschulte et al. [7] and Walspurger et al. [7] and Walspurger et al. [8], on the basis 75 of the Le Chatelier principle, would allow the process to achieve high degrees of methane 76 conversion at lower pressures, implyingleading to savings in compression energy saving up to 77 40%. Specifically, the steam generated by the methanation reaction can be removed from the 78 catalytic bed by adding a suitable sorbent material, in order to push the equilibrium reaction 79 towards methane formation  $\frac{[7,8]}{[7,8]}$ .

80 Recently, Coppola et al. [9-11] proposed a novel reactor configuration, which combines the 81 eoncepts of SEM and of chemical looping in dual interconnected fluidized bed systems. Such 82 configuration would ensure both[9-11] proposed a novel reactor configuration which combines 83 the concepts of SEM and of chemical looping in dual interconnected fluidized bed systems. Such 84 configuration would ensure good temperature control and lower operating pressure, and most 85 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 86 87 means of a suitable sorbent. While the regeneration of the sorbent takes place in another reactor (dehydrator) where H<sub>2</sub>O is released from the sorbent by increasing the temperature (or by 88 89 decreasing the H<sub>2</sub>O partial pressure). The two reactors are connected to each other in a dual-





105	are wasted as direct consequence of the Italian transmission grid (i.e. not dispatched nor stored
106	[12]). The economic performance was assessed in terms of the €/Nm <sup>3</sup> of methane produced thought
107	a techno-economic analysis (TEA). The environmental performance was evaluated using the Life
108	Cycle Assessment (LCA) methodology. While many papers are available in the literature reporting
109	techno economic [1,2,13-20] or environmental [21-23] analysis of traditional power to methane
110	(PtM) configurations, to the best of the authors' knowledge, there is no previous work in the
111	literature proposing a similar configuration integrating Calcium Looping and Sorption Enhanced
112	Methanation.
113	In this work, we propose a new system layout for catalytic methane production that integrates
114	the above SEM concept with a Calcium Looping unit (CaL) for CO <sub>2</sub> capture from flue gas of a
115	coal power plant, and with a water electrolyzer based on polymeric membranes (PEM) sustained
116	by renewable energy. We investigated both techno-economic and environmental performance
117	referring to the Italian scenario, where large amounts of renewable electricity are wasted (i.e. they
118	are not dispatched, nor stored), as a direct consequence of the Italian transmission grid [12,13].
119	The economic performance was assessed in terms of the €/Nm <sup>3</sup> of methane produced via a techno-
120	economic analysis (TEA). The environmental performance was assessed using the Life Cycle
121	Assessment (LCA) methodology. While many articles in the literature report techno-economic
122	[1,2,13-20] or environmental [22-24] analysis of traditional power-to-methane (PtM)
123	configurations, we could not find any work in the literature assessing a similar configuration which
124	integrates Calcium Looping and Sorption-Enhanced Methanation.
125	
126	
127	2.02. METHODOLOGY

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Figure 2 shows a flowsheet of the <u>proposed</u> plant <u>analyzed in this worklayout</u> consisting of

129 three main units able to retrofit a typical power plant with high CO<sub>2</sub> 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<sub>7\_</sub> mainly composed of CO<sub>2</sub>, H<sub>2</sub>O, O<sub>2</sub>, and N<sub>2</sub> -leaves the power plant and is sent
bythrough a blower toenters the carbonator reactor, operated at 650°C, where the CO<sub>2</sub> capture step
takes place according to the following gas-solid reaction:

 $CaO + CO_2 \rightarrow CaCO_{3_4}$ 

138

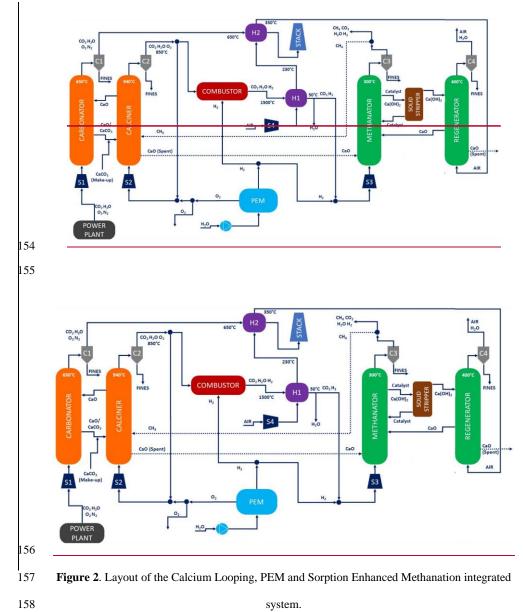
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139 According to [24] the CO2 capture efficiency was chosen equal to 95% (molar).[25] the CO2 140 capture efficiency was chosen to be equal to 95% (molar). Two streams leave the carbonator 141 reactor: the solid carbonated sorbent and the cleaned flue gas. The carbonated sorbent is transferred 142 to the calciner reactor where the reverse reaction (namely calcination) takes place at around 940°C 143 for regenerating the CaO. To thermally sustain the calcination reaction, which is an endothermic 144 reaction, part of the produced methane is burnt in the calciner. The methane is burnt with an excess 145 of oxygen of 50%-%, which is provided by the PEM. From mass and energy balances, about 35% 146 in volume of the produced synthetic methane is necessary to maintain the temperature of the 147 calciner. This We chose this plant solution was chosen in order layout to avoid the utilization of a 148 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<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O, is partially recycled to the reactor both to support its fluidization and to act as a thermal buffer for the methane combustion reaction.

Eq. 1 Formatted Table

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160 The remaining gas flow leaving the calciner requires an additional purification step to remove 161 residual oxygen, before entering the methanator. To avoid the use of somewhat expensive 162 solutions for the stream purification, we proposed propose a post-combustor burning hydrogen 163 coming from the PEM. The excess of hydrogen adopted is around 20% with respect to the 164 stoichiometric combustion conditions. At the exit of the combustor, the hot gas - mainly composed 165 byof CO<sub>2</sub>, H<sub>2</sub>O and H<sub>2</sub> - is cooled in a heat exchanger (H1) both to permit theenable condensation 166 of water, before entering the methanator, and to recover the heat-duty, which is used to heat up the 167 air used for the regeneration reactor of the SEM unit.

The purified stream of  $CO_2$  reaches<u>enters</u> the methanator<u>, through a blower, which is</u> operated at 300°C and 1 atm, together with an additional stream of H<sub>2</sub> coming from the PEM<sub>7</sub> to obtain the right<u>appropriate</u> stoichiometric H<sub>2</sub>/CO<sub>2</sub> 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:

	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O_4$ Eq. 2	Formatted Table
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17	74	Formatted: Right
17	75 In the methanation reactor the produced steam is captured by the spent CaO coming from the	
17	76 calciner purge stream: the spent sorbent in terms of CO <sub>2</sub> -capture still has a good reactivity towards	
17	77 water vapor, as demonstrated in previous studies [10], therefore it is suitable for the SEM process.	
17	78 The hydration reaction is:	
17	79	
18	80 In the methanation reactor the produced steam is captured by the spent CaO coming from the	
18	$calciner purge stream: the spent sorbent in terms of CO_2 capture still has a good reactivity towards$	
18	82 water vapor, as demonstrated in previous studies [10], therefore it is suitable for the SEM process.	
18	83 <u>The hydration reaction is:</u>	

	$CaO + H_2O \rightarrow Ca(OH)_2$ Eq. 3	_	Formatted: Right
			Formatted Table
184			Formatted: Font: Times New Roman
185	The SEM unit includes, in In addition to the methanator, the SEM unit includes a regenerator		
186	reactor operated at 400°C for sorbent regeneration. The hydrated sorbent stream exiting the		
187	methanator passes through a solid-solid stripper (based on density/size difference) to separate the		
188	Ni-based catalyst from the sorbent. The catalyst, which is recirculated back to the methanator, in		
189	fact should not enter the regenerator since it would be deactivated by oxygen.		
190			
191			
192	3.03TECHNO-ECONOMIC ANALYSIS ←		Formatted: Bullets and Numbering
193	We considered CO <sub>2</sub> emissions from a real power plant for the <u>our</u> analysis. The reference plant		
194	was the "As Pontes Coal Power Plant", located in As Pontes de Garcia Rodriguez in Spain and		
195	managed by Endesa Generation Spain: designed for a maximum power of 1400 $MW_e$ with a sub-		
196	critical steam cycle, it uses as primary fuel lignite and sub-bituminous coal, and as secondary fuel		
197	natural gas. It is composed of The plant comprises four boilers and four turbines connected to the		
198	national electric grid, with about 5.5 Mt CO <sub>2</sub> emissions in 2019*. The electrolyzer considered in		
199	this study was a proton exchange membrane (PEM) system powered by renewable energy. The		
200	whole system can generate about 500 t/h of methane (about 7000 $MW_{\text{th}}$ ). Complete mass balances		
201	are reported in Table A1 in the appendix section.		
202	The main economic assumptions used in this study are collected in Table 1. The methodology		
203	proposed by Turton et al. [26] was used for the evaluation of the Total Capital Investment (TCI)		
204	and the Total Product Cost (TPC).		
205			

<sup>\*</sup> http://globalenergyobservatory.org/geoid/43758

206			
207	Table 1. The methodology proposed by Turton et al. [2]	7] was used for the evaluation of the	
208	Total Capital Investment (TCI) and the Total Product Co	ost (TPC). The former is calculated	
209	according to equation 4.		
210	Economic Assumptions	•	
	Average Labor Cost	<del>38000 €/y per person<u>Eq</u>. 4</del> .•	Formatted: No Spacing, Left
	Depreciacion	<del>10%</del>	Formatted: No Spacing, Right Formatted Table
			Formatted: Font: Times New Roman
	Start up period	<del>3 years</del>	Formatted: Font: Times New Roman
	Plant Lifetime	<del>20 years</del>	
		95% (working for 8300-	
	Stream Factor	<del>h/y)</del>	
	Electricity price	<del>25 €/MWh [27]</del>	
211			
212			
213	The costs of conventional devices, such as heat exchan	gers, pumps, blowers, and cyclones,	
214	were collected on the Matches website (www.matche.com)	and updated by CEPCI 2020 index to	
215	account for inflation.		
216	The cost of the PEM was estimated from the literature	e [28,29]. Conversely, reactors were	
217	designed basing mainly on the fluidizing gas, the fluidiza	tion regime and TDH estimation, to	
218	evaluate the volume of each reactor. Finally, the volume of	each unit was related to its cost [30].	
219	The relation between the reactor volume and cost was extrap	polated from literature [31].	
220	Total Capital Cost, including equipment cost and startup	cost, and Total Product Costs were	
221	evaluated. Where DPC, IPC and StC are the direct plant cos	t, indirect plant cost and start-up cost	
222	respectively. In particular, DPC includes equipment costs	(EC), piping, auxiliary system and	
223	services, electrical instrumentation and control, and civil wo	rk. Remarkably, except for EC all the	

224	other DPC items were calculated as a percentage of the equipment cost ([27]). IPC which includes	
225	engineering and supervision activities, contingency and contractor fee were calculated as a	
226	percentage of direct costs and equipment cost. StC were estimated as a percentage of the fixed	
227	capital investment (FCI). The latter was calculated as the sum of DPC and IPC.	
228	Furthermore, the Total Product Cost (TPC) was obtained from the following is calculated	
229	according to equation: 5.	
230		
	$TPC = 0.245FCI + 1.21C_{OL} + 1.03 (C_{UT} + C_{WT} + C_{RM}) $ Eq. 45 •	Formatted: Font: Times New Roman
231		Formatted Table
232	where FCI is the fixed capital investment, $C_{OL}$ is the cost of operating labor, $C_{UT}$ is the cost of	
233	utilities, (i.e. the electricity needed for the PEM, pumps and blowers), $C_{WT}$ is the cost of waste	
234	treatment and $C_{RM}$ is the cost of raw materials.	
235	All these costs were evaluated according to the assumptions outlined before and toMoreover	Formatted: Indent: First line: 0"
236	Eq. 5 takes into account of the energy and capacity needs of each equipment, based on the energy	Formatted: English (United Kingdom)
237	and mass balances carried out in the studydepreciation of FCI.	
238	The evaluation of the cost of operating labor $(C_{OE})$ In particular, the $C_{OL}$ is based on the number	
239	of workers needed for each work shift, obtained from the following equation:	
240		
	$N_{OL} = (6.29 + 31.7P^2 + 0.23N_{np})^{0.5}$ Eq. 56 •	Formatted Table
241		Formatted: Font: Times New Roman
242	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.  $C_{PM}$   $C_{WT}$  and  $C_{UT}$  represent the main contributors to the variable costs (VC), while  $C_{ol}$  to

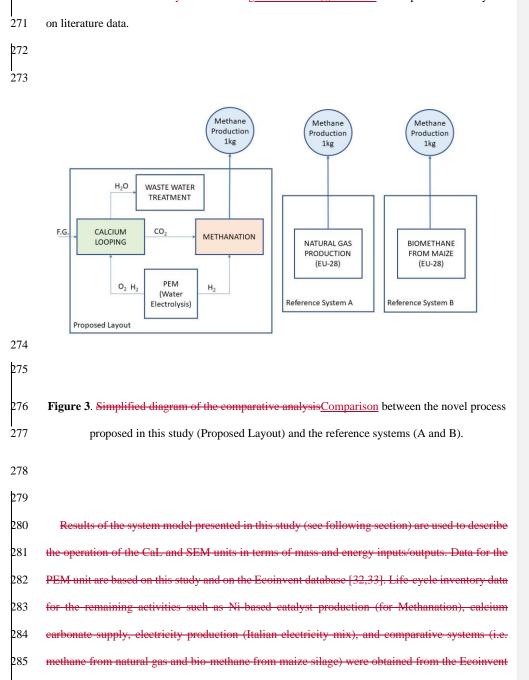
 $C_{RM} C_{WT} \text{ and } C_{UT} \text{ represent the main contributors to the variable costs (VC), while } C_{OL} \text{ to}$  fixed costs (FC). The others FCs, i.e. Direct Supervisory, Maintenance, Tax & Insurance and  $Overhead have been calculated as 0.18C_{OL}, 0.06FCI, 0.032FCI and 0.6(1.18C_{OL}+0.06FCI),$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

#### 255 4.04. LIFE CYCLE ASSESSMENT

253 254

#### 256 The environmental performance and the main sources of environmental impacts (i.e., the "hot-257 spots") of the proposed plant layout were evaluated by means of the Life Cycle Assessment 258 methodology (LCA): [28,29]. Furthermore, its environmental performance was compared with 259 an equivalentsimilar reference systemsystems that provides provide the same function. The study 260 was based on an attributional approach, and it was framed in the Italian context. The proposed 261 process produces synthetic methane while we assumed that the plant does not produce excess of 262 energy. The functional unit adopted was equal to 1kg of methane and the analysis was "from 263 adopted a "cradle to gate" perspective, including all activities from the extraction of raw materials 264 up-to methane the production of methane before its injection into the distribution infrastructure.

The reference system, for comparative purposes, comprisessystems compared with the conventional pathwayproposed one comprise the traditional pathways to produce fossil methane and bio-methane production from maize silage. We assume that wastedhydrogen 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 wasis Formatted: Bullets and Numbering



270 based on the results of the system modelling mass and energy balances developed in this study and

286	database. We did not consider the construction/decommissioning phase since it was found to be
287	negligible in a previous study of a similar plant [23].
288	
289	
290	Life-cycle inventory data for the PEM unit and for the remaining activities such as Ni-based
291	catalyst production (for Methanation), calcium carbonate supply, electricity production (Italian
292	electricity mix), and comparative systems (i.e. methane from natural gas and bio-methane from
293	maize silage) were obtained from the Ecoinvent database, version 3.5 cut-off model [32,33]. We
294	did not consider the construction/decommissioning phase because it was found to be negligible in
295	a previous study of a similar plant [24].
296	The Environmental Footprint (EF) 2.0 method developed by the Joint Research Centre (JRC)
297	of the European Commission [32] was used for quantifying the environmental impacts. All impact
298	categories were included. The environmental impacts were normalized to the reference impact per
299	person of EU-28 using the EF 2.0 normalization factors [33]. We evaluated all the impact
300	categories proposed in the EF2.0 method, which are reported in Table 1.
301	

Table 1. Environmental impact categories analysed

IMPACT CATEGORY METRIC	
Acidification	Mole of H <sup>+</sup> 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

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	Resource use, mineral and metals	kg Sb eq.	•	Formatted: Font color: Black
	Respiratory inorganics	Deaths	•	Formatted: Line spacing: single
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				Formatted: Centered, Line spacing: single
804				Formatted: Font color: Black
504			//	Formatted: Line spacing: single
				Formatted: Font color: Black
305	The Environmental Footprint (EF) 2.0 method develo	pped by the Joint Research Centre	<del>(JRC)</del>	Formatted: Centered, Line spacing: single
306	of the European Commission [34] was used for quant	tifying the environmental impact	<del>s. We</del>	
307	included all impact categories, but report climate change	impacts only in terms of the sum	of the	
308	contributions from fossil and biogenic greenhouse gases a	nd land-use change. For the compa	trative	
309	analysis, the environmental impacts were normalized to the	he reference impact per person of l	<del>EU-28</del>	
310	using the EF 2.0 normalization factors [35]. This stud	dy evaluated all the impact cate	<del>gories</del>	
311	comprised in the chosen methodology (Table 2).			

313	5.05. RESULTS			Formatted: Bullets and Numbering
314	Techno-Economic Analysis			
514	Techno-Leonomic Analysis:			
315	The main economic assumptions	s used in this study are reported in Table 3 reports the cost of		
316	the equipment involved in the proce	<u>****2.</u>		
317				
318	Tal	ble 2. Economic Assumptions		
319		Table 3. Equipment Cost.		
	Equipment cost	<del>%</del>		Formatted: Normal, Left, Line spacing: single,
	<u>Equipment cost</u> Labour Cost	<b>f€]</b> 38000 €/y per person <sup>†</sup>		Widow/Orphan control, Adjust space between Latin
	Cal Looping	7.98%	$\mathcal{J}$	and Asian text, Adjust space between Asian text and numbers, Tab stops: Not at 0.15" + 0.5"
	unit Depreciation	<del>2.17E+06</del> 10% [27]	M/	Formatted Table
		2.95E+0595% (working for 8300 1.09%	1////	Deleted Cells
	SEM UnitStream Factor	<u>h/y) [27]</u>	1///	Formatted: Font: Times New Roman, Font color: Auto
	Electricity price	<u>25 €/MWh [34]</u>	$\ \  \rangle$	Formatted: Font: Times New Roman, Font color: Auto
320	<u>CaCO₃ price</u> Water price	<u>20€/ton [35]</u> 0.01€/ton [35]		Formatted: Normal, Left, Line spacing: single, Widow/Orphan control, Adjust space between Latin and Asian text, Adjust space between Asian text and numbers, Tab stops: Not at 0.15" + 0.5"
321				Formatted: Font: Times New Roman, Font color: Auto
521				Formatted: Font: Times New Roman, Font color: Auto
322 323		reported in Table 3. Data for conventional devices like heat nd cyclones were obtained from the Matches website		Formatted: Normal, Left, Line spacing: single, Widow/Orphan control, Adjust space between Latin and Asian text, Adjust space between Asian text and numbers, Tab stops: Not at 0.15" + 0.5"
324	(www.mataba.com) and undated wi	a the CEPCI 2020 index to account for inflation. ECs for the	1	Formatted: Font: Times New Roman, Font color: Auto
524	(www.matche.com) and updated vi	a the CEPCI 2020 index to account for initiation. ECS for the		Formatted: Font: Times New Roman, Font color: Auto
325	Calcium Looping unit and PEM wer	re extrapolated from the literature ([36] and [37], respectively).		
326	Costs data for the SEM unit are n	not available in the scientific literature because this specific		
327	configuration envisaging two inte	erconnected fluidized beds was only recently proposed by		
328	Coppola et al. [11]. However, since	the reactor configuration of the SEM unit is similar to that of		
329	the CaL unit (which also comprises	s two interconnected fluidized beds), we estimated the EC of		
330	the SEM unit on the basis of that of	the CaL unit, taking into account differences in size. Notably,		

<u>\*</u> 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) 331 we estimated the volume of each fluidized bed reactor considering the fluidizing gas and the

332 fluidization regime. The cost of each reactor was estimated from its volume using the relation

- provided by [36]. 333
- 334
- 335

## Table 2. Equipment Cost.

Equipment cost	<u>[€]</u>	<u>%</u>
CaL unit	2.17E+06	<u>7.98%</u>
SEM unit	2.95E+05	<u>1.09%</u>
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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<sup>336</sup> 837

557	•
338	As it can be noted, the highest cost is represented by the PEM electrolyzer, which accounts for
339	about 90% of the whole equipment costs. It is known that PEM technology is more expensive and
340	less mature than alkaline electrolyzers (AEC). Indeed, the AEC cost is about 1000-1200 €/kWet
341	with respect to 1860 2320 €/kWel for PEMs [36]. However, PEM technology presents a higher
342	purity of the produced gas, a faster system response and a lower cold-start time which make them
343	more suitable for their combination with intermitted renewable energy systems. Moreover,
344	technology projections estimate that PEM will reach similar costs to AEC in the next ten years,
345	and that its lifetime will be significantly improved [36].
346	Table 4 reports the estimation of direct and indirect costs calculated according to the
347	methodology of Turton et al. [26]. The TCI is around 6.4 M€ which means 8.4 k€ per MW <sub>th</sub> of
348	methane <sup>‡</sup> -As shown in Table 3, the highest cost is represented by the PEM electrolyzer, which
1	

349 accounts for about 90% of the whole equipment costs (EC). It must be noted that the PEM

\*\_HHV<sub>methane</sub> =55MJ/kg

technology is more expensive and less mature than alkaline electrolyzers (AEC); the AEC cost is
about 1000-1200 €/kWel compared to 1860-2320 €/kWel 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 <sub>th</sub> of methane <sup>§</sup> .

 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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<u>**§** HHV<sub>methane</sub> = 55MJ/kg</u>

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 successeconomic competitiveness of such technology, basedour proposed plant layout is highly dependent on future reductions in the utilizationcost of hydrogen production by electrolysis, electricity and/or the abatement exploitation of the waste energy price becomes crucial.

372 The treatment of wastewater, which is mainly produced from the condensation of steam in the 373 methanation section, has a low impact on VC. This: it accounts for aonly about 0.1041% of the 374 operation costs. AnywayHowever, it could be possible to re-utilize such wastewater as a feeding 375 forfeed to the electrolizer, obviously electrolyzer, after suitable an appropriate purification step to 376 eliminate any pollutant able tothat could jeopardize the correct functioning of the device. This 377 option could represent a benefit not only from an economic point of view, but also from the 378 environmental point of view, reducing the impact of freshwater consumption of the plant. 879 Concerning the fixed costs, (FC), it is worth noting that costs related to maintenance account for 380 only about 0.12312% of the total- operating costs. However, this value, which was estimated as 381 10% of the equipment costs, could be higher taking into accountdue to the short lifetime of 382 electrolizerselectrolyzers [36][38]; this aspect should be investigated in more detail in future 383 studies.

384

365

385 386

#### Table 4. Fixed and variable costs.

Variable Costs (VC)	[€]/y	%
Utilities Costs (C <sub>U</sub> )		
PEM	2.71E+09	99. <del>669<u>58</u>%</del>
Pumps & Blowers	2.85E+05	0. <del>010<u>01</u>%</del>
Waste treatment (C <sub>WT</sub> )	2.84E+06	0. <del>104<u>10</u>%</del>
Raw material cost (C <sub>RM</sub> )		

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Total VC & FC	2.72E+09	100 <del>.000</del> %
Total FC	<del>5.55E<u>7.97E</u>+06</del>	0. <del>204<u>29</u>%</del>
Overhead	2.69E+ <mark>05<u>06</u></mark>	0. <del>010<u>10</u>%</del>
Tax & Insurance	1.78E+06	0. <del>065<u>07</u>%</del>
Maintenance	3.34E+06	0. <del>123</del> 12%
Direct supervisory	1.03E+05	0. <del>004<u>00</u>%</del>
Cost operating labour (C <sub>OL</sub> )	5.70E+04	0. <del>002</del> 00%
Fixed Costs (FC)	[€]/y	<b>A</b>
Total VC	2. <del>72E<u>71E</u>+09</del>	99. <del>796</del> 71%
Water	2.35E+04	0. <del>001<u>00</u>%</del>
CaCO <sub>3</sub>	3.17E+05	0. <del>012</del> 01%

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

 $TPC_{d} = 0.180FCI + 2.73C_{OL} + 1.23(C_{OT} + C_{WT} + C_{RM}) = 3.35 \times 10^{9} \text{e/y}$ <del>Eq. 6</del> 391 392 resulting in a cost of methane production of about 0.66 €/Nm<sup>3 (\*\*)</sup>. 393 In Europe the cost of natural gas exploration and production amounted to 0.17 €Nm<sup>3</sup> in 2020 (ENI, 394 financial report 2020 [37]), while that of methane produced with traditional methanation systems 395 is about 0.51 6Nm<sup>3</sup> not including the cost of electricity [27]. Finally, methane produced from 396 anaerobic digestion has production cost of around 1 €/Nm<sup>3</sup>[38]. As recognized by other authors, 397 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 398 399 lower than 0.005 €/KWhet-The total product cost (TPC), considering the depreciation of the plant, 400 is around 3.35x10<sup>3</sup> M€/y. The methane cost production was calculated as the ratio between TPC 401 and the total amount of produced methane per year. The proposed system results in a cost of 402 methane production of about 0.66 €/Nm3 (††). In Europe the cost of natural gas exploration and

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<sup>&</sup>lt;sup>aa</sup> 15.9 €/kmol; 0.99 €/kg; 0.018 €/MJ; 64.92 €/MWh <sup>††</sup> 15.9 €/kmol; 0.99 €/kg; 0.018 €/MJ; 64.92 €/MWh

403	production corresponds to 0.17 €/Nm <sup>3</sup> in 2020 (ENI, financial report 2020 [39]), while that of
404	methane produced with traditional methanation systems to about 0.51 €/Nm <sup>3</sup> not including the cost
405	of electricity [34]. In addition, bio-methane produced from anaerobic digestion has a production
406	cost of around 1 €/Nm <sup>3</sup> [40]. As recognized by other authors, the cost of electricity is the 'control
407	knob' for the success of these technologies [34]. To reach the parity grid, in terms of methane
408	production cost, for the configuration proposed in this work the electricity should have a price
409	lower than 0.005 €/KWh <sub>el</sub> . In particular, for the limiting case where the electricity cost becomes
410	zero (i.e. when considered waste electricity) the cost of methane would be of about 0.02€/Nm <sup>3</sup> ,
411	that is on order of magnitude lower than the cost of natural gas.
412	
413	
414	Life Cycle Assessment.
415	Table 6 reports the inventory data for the proposed plant layout. We assumed that the sorbent
416	(CaCO <sub>3</sub> ) used in this study. Thethe CaL unit can be reused in the SEM unit, thus reducing
417	additional consumption. We also assumed a make-up of around 5% of the mass flow of the sorbent
418	(CaO+CaCO <sub>3</sub> ) cycled between reactors. Literature data is used to describe the operation of the
419	PEM unit in terms of efficiency and electricity consumption; in particular, the electric requirement
420	for the PEM is 46.6 kWh/kgH <sub>2</sub> [30]. Note that we considered the environmental performances of
421	the proposed layout are reported in terms of normalized impacts in Figure 4.associated with the
422	production of electricity from wind even if we assumed that this electricity would otherwise be
423	wasted [13]. The inventory data for the remaining activities that supply energy and materials to
424	the plant and for the reference systems (i.e. conventional and bio-based methane) are obtained
425	from the Ecoinvent database.
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Table 6.	Inventory	used for	this	study.
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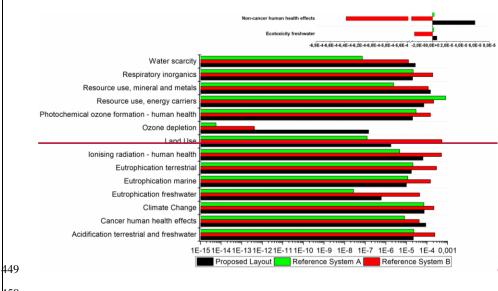
Calcium Lo	oping		
nput	CO. flue ges	ka	2,10E+00
	$CO_2$ , flue gas	kg ka	,
	$H_2O_{, flue gas}$	kg	5,71E-01 3,04E-01
	O <sub>2</sub> , flue gas	kg	6,15E+00
	N <sub>2</sub> , flue gas CaCO <sub>3</sub> bed	kg	,
		kg	2,74E-03 7,71E-01
	CaCO <sub>3</sub> make-up	kg	,
	electricity mix	kWh	4,10E-04
output		1	1.055.01
	$CO_2$ , emission to air	kg	1,05E-01
	$H_2O$ , emission to air	kg	5,71E-01
	O <sub>2</sub> , emission to air	kg	3,04E-01
	N <sub>2</sub> , emission to air	kg	6,15E+00
Combustor			
output			
	H <sub>2</sub> O, wastewater treatment	kg	1,05E-01
PEM			
input			
	H <sub>2</sub> O	kg	4,90E+00
	electricity, wind	kWh	2,54E+01
	electricity mix	kWh	1,20E-08
Methanatio	1		
input			
	$H_2O$	kg	4,90E+00
	electricity renewable	kWh	2,54E+01
	electricity mix	kWh	1,20E-08
output	-		
1	CO <sub>2</sub> , 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
	$H_2H_2$ , emission to air	kg	9,39E-03

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437 Figure 4 reports the normalised environmental impacts of the proposed plant layout and those 438 of the reference systems. The comparative analysis with the reference systems (natural gas 439 production and shows that methane production from maize) shows that the proposed process 440 outperformslayout yields lower environmental impacts than both reference systems only with 441 respect to in the categories terrestrial acidification-terrestrial, photochemical ozone formation, 442 eutrophication marine and terrestrial eutrophication, resource use - energy carriers, and respiratory 443 inorganics impact categories. In addition, it delivers a reduction with respect to the the proposed 444 layout outperforms methane production from maize silage in the following categories: climate 445 change, ecotoxicity freshwater, ionizing radiation, land use and non-cancer human health. On the 446 other hand, the The proposed process yields significant increases layout is environmentally 447 disadvantageous in the other impactremaining environmental categories compared to the reference 448 systems.



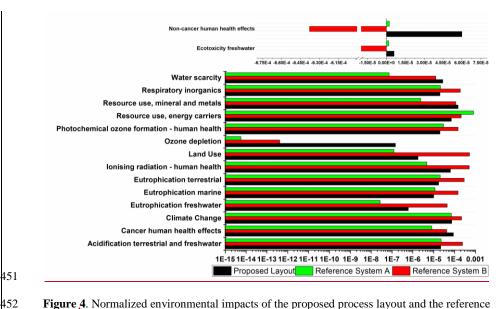


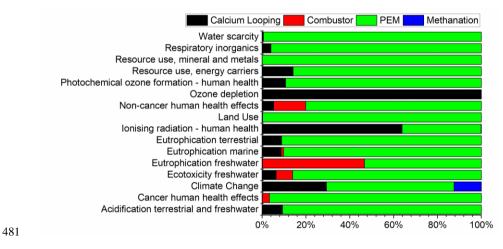
Figure 4. Normalized environmental impacts of the proposed process layout and the reference Formatted: Font: 9 pt, Italic systems.

455 Figure 5 reports thea hot-spot analysis for the process developed plant layout proposed in this work. 456 The results show that the largest portion of the environmental impacts in almostnearly all-the 457 impact categories originate from the PEM unit and, specifically, from the electricity wind 458 production, with contributions ranging from 35% in the category ionizing radiation and up to 459 ~100% in the category water scarcity, resource use-mineral and metal, land use and cancer human 460 health. Whilst the The CaL unit mainly impacts has significant contributions in a limited number of 461 categories including climate change (~30%), eutrophication terrestrial and marine (~40%), 462 ionizing radiation (~62%) and ozone depletion (~100%). Interestingly, the results from the LCA 463 analysis reveal that the impacts of the CaL unit are primarily attributable to the production of the 464 calcium oxide (to capture CO<sub>2</sub>). The results from the analysis show that the impacts of the CaL unit 465 are mostly attributable to the production of the calcium oxide (to capture CO<sub>2</sub>). Similarly to what 466 found in the techno-economic analysis, the LCA study indicates that the environmental impacts of

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467	electricity consumption heavily affect the environmental performance of the proposed plant layout.
468	As previously reported, these results include the environmental impacts associated with the
469	production of electricity from wind even if this electricity would otherwise be wasted. Table A1
470	in the appendix reports the environmental performances for the proposed layout without including
471	the wind electricity production. The comparison shows that the new proposed scenario
472	outperforms conventional methane and bio-methane productions in almost all the impact
473	categories except for eutrophication marine and terrestrial, ozone depletion and water scarcity.
474	A reduction in the electric consumption of the PEM unit will significantly reduce the
475	environmental impacts of the proposed layout, which could make it environmentally advantageous
476	across a larger number of environmental categories. The above also suggests that our results are
477	heavily dependent on the assumed energy source; future studies should investigate the
478	environmental performance when electricity is obtained from other sources such as solar,
479	geothermal or nuclear.

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Figure 5. Hot-spot analysis of the proposed <u>plant</u> layout.

#### 484 6.06. CONCLUSIONS

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485 In this work, we investigated the technical, economic and environmental performance of a novel 486 processplant layout for the production of synthetic methane using  $CO_2$  captured from combustion 487 flue gas. The plant configuration layout integrates sorption-enhanced catalytic methanation with 488 CO2 capture byvia calcium looping, and renewable H2 production with avia PEM electrolyzer. The 489 advantages of this configuration include good temperature control and low operating pressure of 490 the methanation step, and the avoidance of a costly air separation unit for the calcium looping step. 491 The economic and environmental performances of such systemthe proposed layout were 492 investigated and compared with those of traditional natural gas production, and of biomethane 493 production from maize. Results silage. Our results show that the production cost of methane per 494 unit Nm<sup>3</sup> is higher than that of natural gas, but lower than that of biomethanebio-methane. The 495 largest impact on these costs comes from the PEM electrolyzer; this, and in particular from the 496 consumption of electricity. The PEM is currently still-an expensive technology, but its cost is 497 forecasted to decrease significantly in the next coming years. In addition, it is worth highlighting 498 that the possible future introduction of significant carbon taxes would increase the economic 499 attractiveness of synthetic methane production with respect to natural gas.

500 Results The results of the LCA analysis highlighted indicates the existence of several 501 environmental trade-offs, with no systems outperforming the other across all environmental 502 categories. Like for economic costs, the PEM electrolyzer appears to account for most of the 503 environmental impacts of the processNotably, from a climate change perspective the proposed 504 layout is not advantageous when compared to the conventional pathway for methane production, 505 yielding an increase of  $\sim$  5%. Like for economic costs, the electricity consumption of the PEM 506 electrolyzer accounts for most of the environmental impacts. Overall, our analysis indicates that 507 the high electricity consumption of the PEM electrolyzer is the most critical aspect. Future

508	improvements in the PEM efficiency will significantly improve the economic and environmental
509	performance of the proposed plant layout.
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512	ACKNOWLEDGEMENTS
513	
514	The help of Ms. Giulia Paone is gratefully acknowledged.
515	
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## 518 APPENDIX

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

CARBONA	TOR			CALCINER	ł		
INPUT		OUTPUT		INPUT		OUTPUT	
CaCO <sub>3</sub>	0.00E+00	CaCO <sub>3</sub>	2.00E+06	CaCO <sub>3</sub>	2.34E+06	CaCO₃	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 <sub>2</sub>	9.24E+05	CO <sub>2</sub>	4.62E+04	CO <sub>2</sub>	0.00E+00	CO <sub>2</sub>	1.39E+06
H <sub>2</sub> O	2.52E+05	H <sub>2</sub> O	2.52E+05	H <sub>2</sub> O	0.00E+00	H <sub>2</sub> O	2.99E+05
02	1.34E+05	O <sub>2</sub>	1.34E+05	O <sub>2</sub>	3.18E+05	O <sub>2</sub>	5.30E+04
N <sub>2</sub>	2.71E+06	N <sub>2</sub>	2.71E+06	N <sub>2</sub>	0.00E+00	N <sub>2</sub>	0.00E+00
				CH <sub>4</sub>	1.33E+05	CH <sub>4</sub>	0.00E+00
COMBUST	FOR			PEM			
INPUT		OUTPUT		INPUT		OUTPUT	
CO <sub>2</sub>	1.39E+06	CO <sub>2</sub>	1.39E+06	H <sub>2</sub> O	2.42E+06	H <sub>2</sub> O	0.00E+00
H <sub>2</sub> O	2.99E+05	H <sub>2</sub> O	4.18E+05	H <sub>2</sub>	0.00E+00	H <sub>2</sub>	2.69E+05
02	5.30E+04	O <sub>2</sub>	0.00E+00	O <sub>2</sub>	0.00E+00	O <sub>2</sub>	1.08E+06
H <sub>2</sub>	1.59E+04	H <sub>2</sub>	2.65E+03				
SORPTION	N ENHANCED	METHANA	TION				
METHAN	ATOR	1		REGENER	ATOR		
INPUT	<b>T</b>	OUTPUT	<b>T</b>	INPUT	1	OUTPUT	
H <sub>2</sub>	2.56E+05	H <sub>2</sub>	4.72E+03	H <sub>2</sub>		H <sub>2</sub>	
CO <sub>2</sub>	1.39E+06	CO <sub>2</sub>	2.57E+04	CO <sub>2</sub>		CO <sub>2</sub>	
H₂O	0.00E+00	H <sub>2</sub> O	5.71E+05	H <sub>2</sub> O	0.00E+00	H <sub>2</sub> O	3.50E+05
CaO	2.87E+06	CaO	1.09E+06	CaO	0.00E+00	CaO	2.87E+06
CH <sub>4</sub>	0.00E+00	CH <sub>4</sub>	4.98E+05	CH <sub>4</sub>		CH <sub>4</sub>	
02		O <sub>2</sub>	0.00E+00	O <sub>2</sub>	5.87E+05	O <sub>2</sub>	5.87E+05
N <sub>2</sub>		N <sub>2</sub>	0.00E+00	N <sub>2</sub>	3.87E+06	N <sub>2</sub>	3.87E+06
Ca(OH) <sub>2</sub>	0.00E+00	Ca(OH) <sub>2</sub>	2.35E+06	Ca(OH) <sub>2</sub>	2.35E+06	Ca(OH)₂	
СО	0.00E+00	CO	3.01E+01	CO		CO	
CaO <sub>mup</sub>	1.91E+05					CaO <sub>sp</sub>	1.91E+05

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

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

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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.