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1 **Solar-powered Rankine cycle assisted by an innovative** 2 **calcium looping process as energy storage system**

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8 **Abstract**

9 Solar energy is an intermittent resource and thus an energy storage system is required for practical
10 applications of the collected solar irradiance. This work deals with the integration of a thermo-
11 chemical energy storage (TCES) system based on the Calcium Looping (CaL) process with a
12 concentrated solar tower power (CSP) plant. The objective of this work is the integration of a
13 conventional 320 MWe Rankine cycle with a direct calcination for the energy harvesting.
14 Particularly, this work addresses the use of CO₂ as the working fluid of a compressed-gas energy
15 storage (CGES) system for hybrid energy storage with CaL process. The hybrid TC/CG-ES
16 (Thermo-Chemical/Compressed-Gas Energy Storage) system can increase the competitiveness
17 of the CSP with respect to conventional fossil-based power plants leading to a reduction in CO₂
18 emissions. The thermal integration with the Calcium Looping (CaL) system is optimized by
19 means of the pinch analysis methodology. The obtained results show a reduction in the electrical
20 efficiency of about four percentage points with respect to the conventional Rankine power cycle
21 without CSP unit: the net electrical efficiency reduces from 43.7% to 39.5% while the global
22 (thermal and electrical) efficiency of the plant reaches the peak value of 51.5% when low

23 enthalpy energy is recovered (e.g. district heating network, district cooling network). The paper
24 highlights the importance of the thermochemical CaO based material. With a conversion of CaO
25 to CaCO₃ of 80% the storage efficiency defined as the ratio of the energy released during the
26 carbonation and the CO₂ expansion to the energy collected by the solar field and required during
27 the CO₂ compression is 87.3%.

28 **Keywords**

29 Energy Storage; Calcium Looping; Thermo–Chemical/Compressed–Gas Energy Storage; Use
30 of compressed CO₂, Concentrated Solar Power (CSP); Rankine power cycle.

31 **Highlights**

- 32 • A novel solar power Rankine cycle with integrated energy storage by calcium looping
33 process is proposed.
- 34 • Calculated net and global system efficiencies are 39.5% and 51.5% respectively;
- 35 • The electrical efficiency penalty is about 4 percentage points from the conventional
36 Rankine plant to the solar plant.

37 **1 Introduction**

38 Climate change represents a critical issue for our planet and it is time to intensify the efforts of
39 the researchers and scientists to mitigating the forthcoming impacts. For this purpose, on 12
40 December 2015, the nations that are members of UNFCCC reached an agreement with the aim
41 to limit the global warming well below 2.0°C before pre-industrial level and try to reduce it down
42 to 1.5°C [1]. In order to reach the ‘2°C target’, only 720 Gt of CO₂ can be emitted into the
43 atmosphere from 2018 to 2100; according to [1] the current rate of CO₂ emission is 32.5 Gt/year.

44 The production of gross electricity has been increasing since 1974, except during economic crisis
45 that caused a drop in global production. Currently, the largest part of electricity (67.3% of total
46 electricity production [2] in 2016) is produced with conventional combustion of energy sources
47 as fossil fuels, biofuel and wastes.

48 At the end of 2023, almost 30% of power demand in the electricity sector will be provided by
49 renewables reaching also 12.4% of global energy demand [3]. Concentrated solar power will
50 have the highest growth with respect to the trend of the past five years [3]. New plants will be
51 constructed in Chile, Morocco and South Africa. However, technology risk, long construction
52 times and still inefficient energy storage solutions continue to curb the development of this
53 technology. Generally increasing the variable renewable energy plants there will be same period
54 during the day in which the energy produced exceeds power demand [4].

55 Concentrated solar power depends on the availability of direct sunlight. Hence, energy storage
56 systems and more wide flexibility are highly needed [5] to increase the capacity factors of solar-
57 powered plants and to correct the mismatch between the discontinuous renewable energy supply
58 and demand. Thus, cheap and efficient energy storage can help to boost the applicability of CSP
59 and thus contribute to mitigating global warming during the energy transition.

60 Different technologies are used to store energy from CSP plants:

61 - Sensible thermal energy storage systems (STES): The quantity of stored energy $Q_{sensible}$ is a
62 function of temperature difference ($T_h - T_c$), specific heat capacity (c_p) and mass of stored material.
63 High specific heat capacity materials are used such as molten salts [6] (nitrates, carbonates,
64 chlorides) and solids (ceramic materials or graphite).

65
$$Q_{sensible} = m \int_{T_c}^{T_h} c_p(T) dT \quad (\text{Eq.}) 1$$

66 - Phase-change materials (PCM): The quantity of energy stored is highly dependent on the
67 enthalpy of fusion (Δh_{fusion}) and the mass of material. The energy can be stored also in sensible

68 form. Latent energy storage materials (inorganic salts, metallic) which can be coupled with
69 system at very high temperature can have a phase change temperature between 579°C
70 (Aluminium alloys) and 842°C (Fluorides salts) [7].

$$71 \quad Q_{latent} = m \int_{T_c}^{T_h} c_p(T) dT + m \Delta h_{fusion} |_{T=T_{melting}} \quad (\text{Eq.}) 2$$

72 - Thermochemical energy storage (TCES): solar energy is converted into separately chemical
73 materials through an endothermic reaction [8]. The stored energy $Q_{thermochemical}$ is a function
74 of the enthalpy of reaction $\Delta h_{reaction}$, the mass of stored material and sensible heat.

$$75 \quad Q_{thermochemical} = m \int_{T_c}^{T_R} c_p(T) dT + m \Delta h_{reaction} |_{T=T_R} + m \int_{T_R}^{T_h} c_p(T) dT \quad (\text{Eq.}) 3$$

76 Both sensible and latent heat storage systems have a low efficiency due to energy losses in the
77 short-medium term, instead TCES storage avoids the loss of heat producing stable chemical
78 compounds that can be stored at ambient temperature. During cloudy days or, generally,
79 whenever energy is needed, the produced chemical materials are brought together under
80 favourable thermodynamic conditions in order to promote an exothermic reaction. The released
81 heat during the reaction can be used to produce electricity and to power a district heating network.

82 Thermochemical storage systems have several advantages :(i) The energy density is about two
83 to five times higher than PCM and STES systems. A conventional STES, consisting of two tanks
84 of molten salt based on nitrate (60% NaNO_3 - 40% KNO_3) with the approximate hot and cold
85 temperatures between 565°C and 290°C has a storage capacity of 0.731 GJ/m³ [9]. Latent energy
86 storage have the advantages to provide heat at constant temperature, the carbonate salts (e.g.
87 Li_2CO_3) have a high fusion temperature 726°C with a storage density of 1.34 GJ/m³ [7]. Instead,
88 this work proposes a thermochemical storage based on calcium looping process, with a reaction
89 temperature of 895 °C and the energy storage density can reach 3.2 GJ/m³ [10]; (ii) Since there
90 is negligible thermal loss during storage via CaL, this technology can be considered as a seasonal

91 storage unlike the others which are used more as daily or weekly storage; (iii) The heat of reaction
92 is discharged at constant and high temperature.

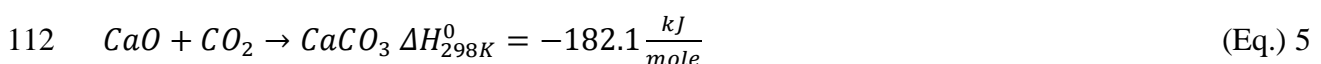
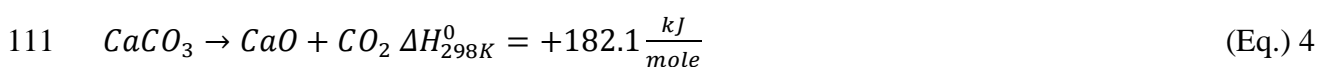
93 The CaL process as energy storage have been proposed in the scientific literature mostly
94 integrated in a tower solar. In [11] a calciner assisted by CSP to capture CO₂ from flue gas into
95 carbonator reactor was proposed whereas in [12] [13] [14] the authors have conducted a
96 comparison between closed and open CO₂ based Brayton cycles with a conventional reheat
97 Rankine cycle each of the three cycles equipped with a CaL energy storage system fitted with an
98 indirect calcination reaction. Considering 10% of thermal dispersion in carbonator reactor,
99 $\Delta T_{\min}=10^{\circ}\text{C}$, 1% pressure drop in each heat exchange and $X=0.5$ (average CO₂ conversion) they
100 have obtained: (i) 35.5% with reheat Rankine cycle; (ii) around 32% with sCO₂ Brayton cycle;
101 (iii) 39% with a combined cycle that use the integration of CaL process with CO₂ Brayton and
102 conventional Rankine cycles. However, direct expansion of CO₂ at the exit of the carbonator
103 reactor is not recommended because it may contain solid particles that would damage the blades
104 of the turbines placed downstream.

105 The novelty of this paper is the integration of a conventional reheat Rankine cycle assisted by a
106 CaL system with a direct calcination reaction.

107 **2 Calcium Looping as energy storage system**

108 **2.1 Fundamentals of Calcium Looping process**

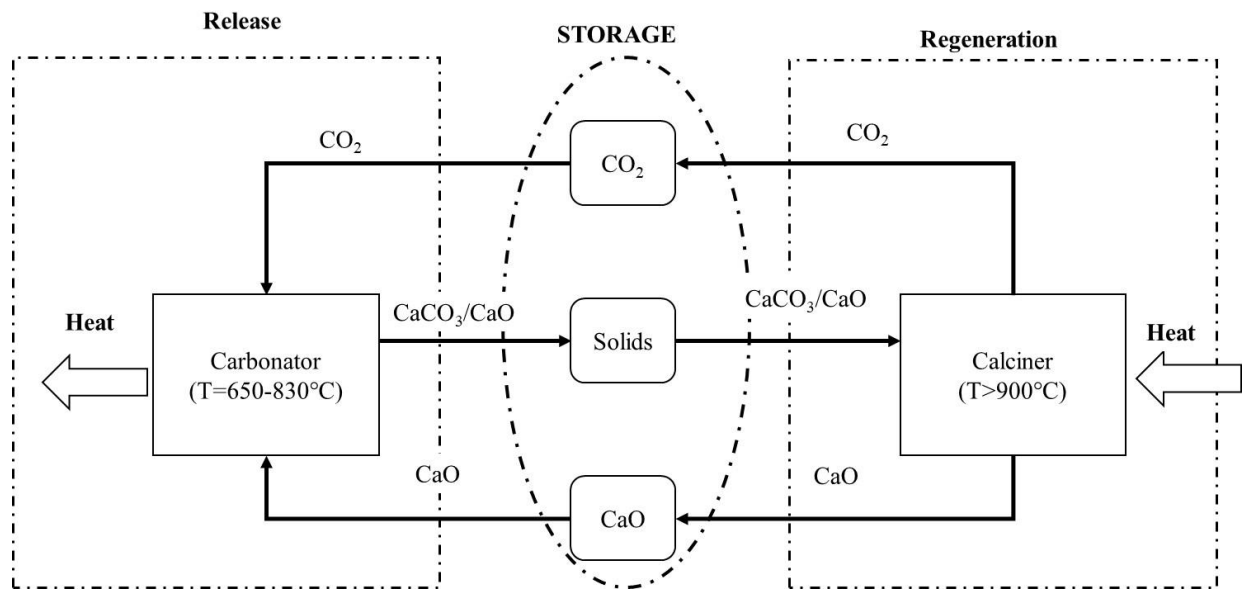
109 Calcium Looping (CaL) is a cyclic chemical process that comprises two key reactions: (i)
110 calcination of CaCO₃ as reported in Eq. 4 and (ii) carbonation of CaO as reported in Eq. 5.



113 The main advantages of the CaL process is the low market price (9 €/ton [13]) of the CO₂ acceptor
114 material and the absence of negative impacts for the environment and the health of human beings:
115 CaO from naturally occurring materials (e.g. limestone or dolomite) are widely available and
116 harmless towards the environment with several outlet market for spent materials (iron, steel and
117 cement industries). For instance, commercial limestone rock generally contains more than 90%
118 of calcium carbonate.

119 Shimitzu et al. [15] proposed for the first time the reaction of CaO with CO₂, i.e., the calcium
120 looping process CaL, with the main goal of decarbonizing flue gas. Since the calcination reaction
121 is endothermic, the heat of reaction is usually supplied by oxy-fuel combustion into the reactor.
122 CaL process is gaining considerable interest as thermochemical energy storage process where
123 calcination (Eq.4a) is the process for energy gathering and carbonation (Eq.4b) is the step for
124 energy release. The carbonator reactor operates in a temperature range between 600 – 850°C with
125 an operating pressure ranging from 1 bar to 3 bar when outgoing gas is not expanded in a gas
126 turbine [13]. Since the carbonation reaction is an exothermic reaction, heat is released and steam
127 can be produced to generate electricity by a submerged heat exchange in a fluidised bed
128 carbonator. The produced CaCO₃ can be stored and successively transported to the calciner
129 reactor to gather the excess of energy. Into the calciner reactor, the equilibrium temperature of
130 the system CaO-CaCO₃-CO₂ is approximately 895 °C under atmospheric pressure. Therefore,
131 the decomposition of CaCO₃ into CaO must take place at temperature above 895°C in case the
132 molar fraction of CO₂ is 1 and the operating pressure of the calciner is 1 atm.

133 The process is illustrated in Figure 1.



134

135 **Figure 1: The Calcium Looping process used as thermochemical storage system. Calcium oxide and carbon**
 136 **dioxide react together into the carbonator reactor releasing heat of reaction at high temperature when energy**
 137 **is necessary. The spent material (CaCO₃) and unreacted CaO are, at the first time, stored into a silo. These**
 138 **materials are transported to the calciner to store excess of energy at high temperature with the inverse**
 139 **reaction.**

140 It is possible to use the heat released during the carbonation at high temperature (650 – 830 °C)
 141 in order to produce steam to be expanded in a conventional turbine and generate electricity. Direct
 142 expansion of CO₂ at the exit of carbonator and calciner is not recommended because it may
 143 contain solid particles that would damage the blades of the turbines placed downstream.

144 It is demonstrated from several experimental works that calcite and dolomite can be used as
 145 sorbent for high temperature CO₂ capture [16]. However, it is also known that CaO-based solid
 146 sorbent are never fully utilized displaying the existence of maximum degree of carbonation
 147 conversion [16].

148 Stendardo and Foscolo [16] studied the multi-cycle carbonation/calcination reaction of the
 149 naturally-occurring dolomite. During different experiments they observed progressively decline
 150 of CaO conversion, which drops from 85% to 65% after only 4 cycles. A good strategy could be
 151 the replacement of natural dolomite with synthetic CaCO₃ or doped limestone that maintain a
 152 high degree of sorbent capture capacity. There are many papers in the literature focused on the
 153 research of synthetic Ca-based sorbents that enhance conversion in a multi cycling experiments

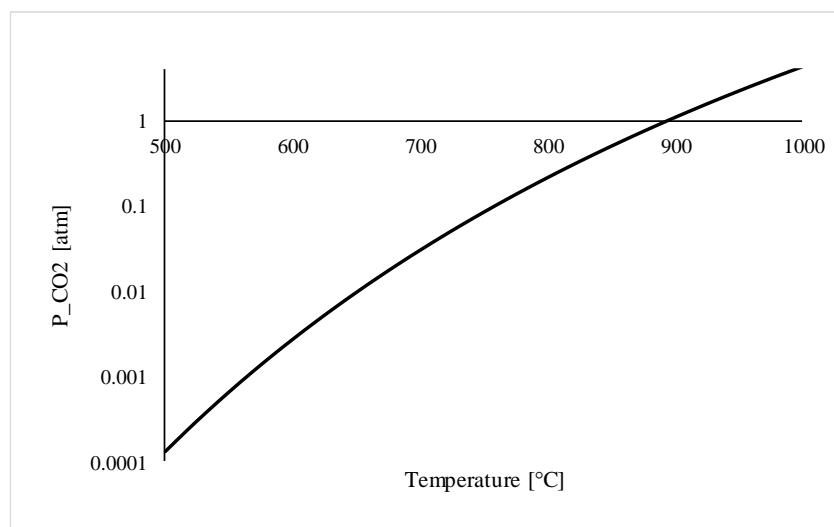
154 [17]. Chen et al. [18] showed that the CO₂ capture capacity of the new materials declines
155 gradually and at a much slower rate than original limestone during multi-cycle experiments. The
156 addition of alumina has slowed down the drop in CaO conversion allowing up to 70% percent of
157 CO₂ capture capacity after 50 cycles.

158 The CO₂-rich stream leaving the regenerator is cooled, compressed and stored also for long
159 period (seasonal storage). The produced CaO is cooled and stored in a conventional silo. The two
160 stored materials are recombined into the carbonator reactor operating at high temperature
161 (~800°C) to provide heat to a Rankine power cycle. We provide detailed mass and energy
162 balances of the solar power plant and we calculate the performance of the same plant after energy
163 integration of various heat sinks/sources of the overall process. This work paves the way for
164 further demonstration of the concept.

165 **2.2 *Integration of CaL with Concentrated Solar Plants***

166 The most common energy storage system for CSP applications is based on molten salts. The
167 main used components are nitrates, chlorides, fluorides and carbonates. The fluoride salts have
168 high heat storage capacity (2.3 GJ/m³). However, they are very expensive and toxic [19];
169 chlorides have a high heat of fusion and are very cheap but highly corrosive [20]; carbonates
170 have high temperature of phase change but high viscosity and they easy decay [21]; nitrate salts
171 have low chemical reactivity, low corrosiveness and have low cost [7] and therefore suitable for
172 thermal storage material in CSP. The issues of all the above-described materials are two: (i) the
173 low melting point limits the efficiency of the system, in fact when the solar energy is not directly
174 collected, the temperature of the storage has to be higher than melting temperature for each salt
175 and therefore storage have to be heated; (ii) the low maximum temperature achievable that limits
176 the (thermal) integration between the CSP field with the thermal storage system and the power
177 cycle to temperature around 500-600 °C. This limitation is due to degradation of molten salts at
178 high temperature. The coupling of CSP with CaL process avoids this problem enabling operating

179 temperatures higher than 700°C in carbonator reactor reducing the size of heat exchanger due to
180 higher temperature difference (maximum temperature of the Rankine heat transfer fluid equal to
181 538°C). According to thermodynamic equilibrium and kinetics, high temperature is necessary to
182 drive the calcination reaction when operating under high CO₂ concentrations (~900°C at 1 atm)
183 [22]. Nevertheless, the use of superheated steam or easily separable gas in calcination
184 environment decrease the CO₂ partial pressure and therefore, the calcination temperature goes
185 down to 700-750 °C as shown in **Figure 2** :



186

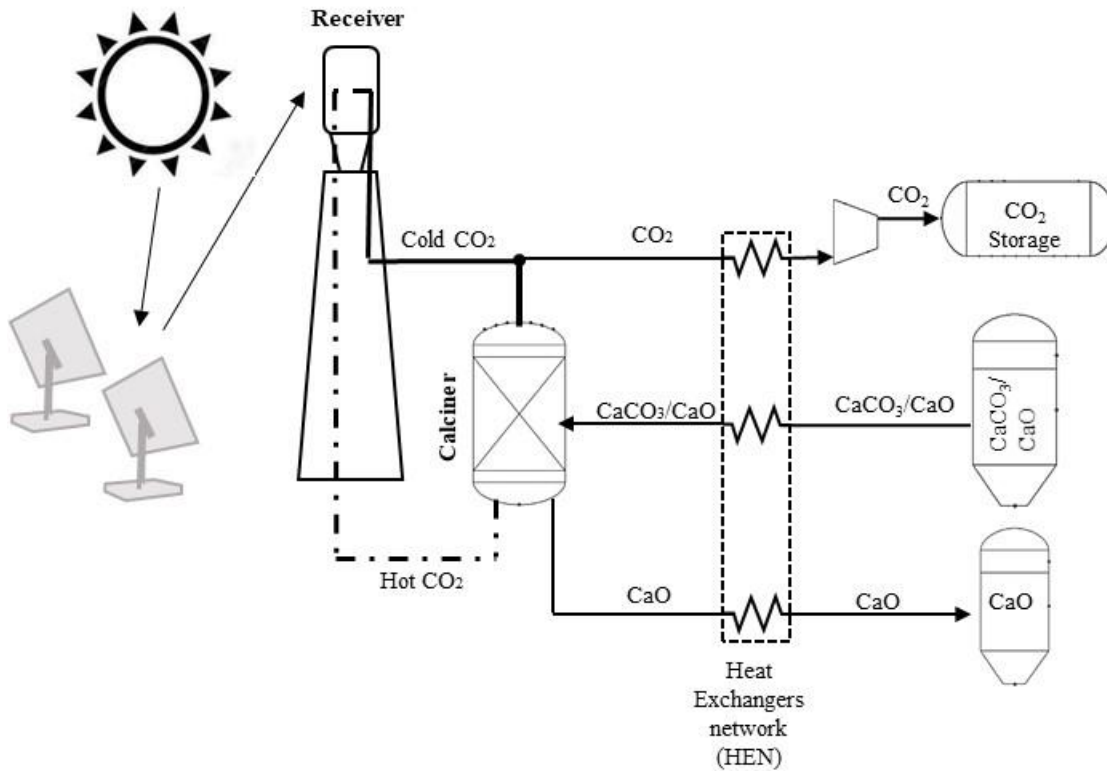
187 **Figure 2: Decomposition pressure of Carbon dioxide over calcium carbonate at different operating**
188 **temperature [22]**

189 The solutions for solar energy storage via CaL technology can be classified according to the
190 media used to gather and store the energy. These options are currently classified into (i) indirect
191 (or mediated) and (ii) direct storage solutions.

192 2.2.1 Indirect energy storage

193 In the indirect energy solution, the solar energy is gathered and transferred to a second medium
194 (Ca-based materials) for its storage. Generally, the gathering medium is a fluid (heat transfer
195 medium, HTF) whereas the storage medium consists of either liquid or solid materials. Several
196 configurations have been proposed to harvest solar radiation. Therefore, several prototypes of
197 solar receiver have been developed as rotary kilns, cyclone atmospheric reactor, falling particle

198 receiver and fluidised bed reactor. As shown in Figure 3 , solar energy is collected into a central
 199 tower receiver and transferred to a calciner by HTF, which fluidises the CaCO_3/CaO particles. In
 200 order to not dilute the CO_2 leaving the calciner, the selected HTF is a pure CO_2 stream.

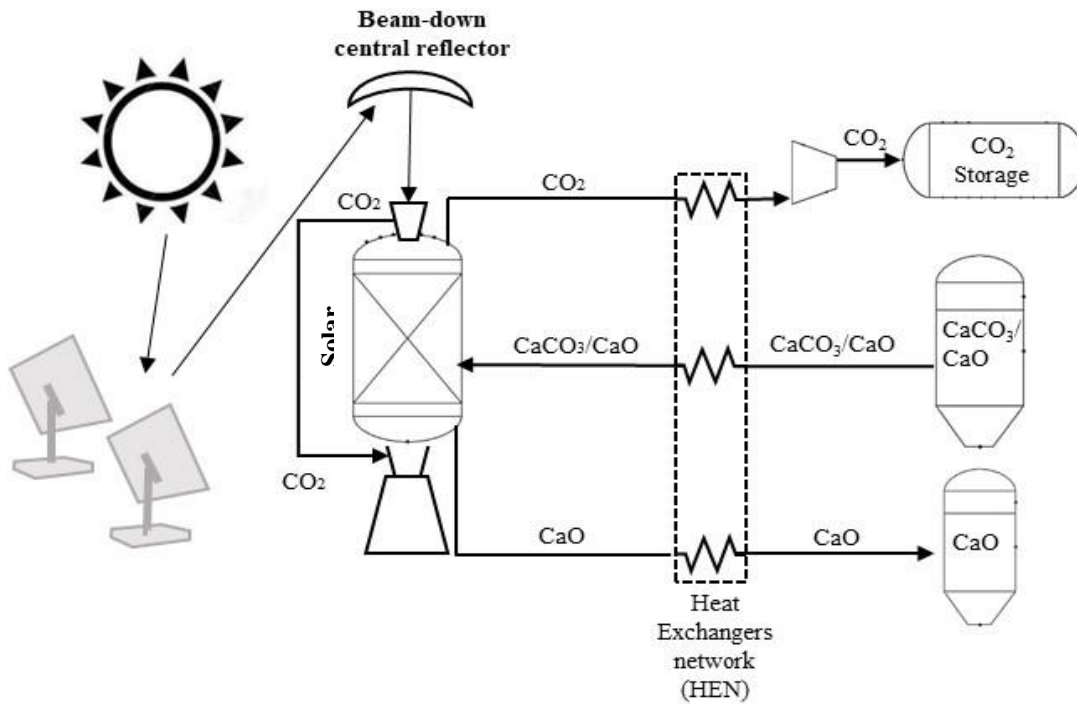


201
 202 **Figure 3: Integrated Solar Calcium Looping IS-CaL with indirect calcination reaction. Solar energy is**
 203 **concentrated into a solar receiver up to the tower. The HTF used into this system is the CO_2 which has the**
 204 **task to provide the heat necessary for the regeneration of the spent sorbent and to fluidize the calciner.**

205 2.2.2 Direct energy storage

206 In the direct energy storage solutions, the media (Ca-based material and CO_2) used for storing
 207 the energy are as the same as the materials to collect the solar energy into the innovative solar
 208 calciner reactor. An example of this solution is the gathering of the solar energy and its storage
 209 via a solid particles fluidised bed [23]. The solar energy reflected by the heliostats are
 210 concentrated in a single point of the reactor by means of a beam-down central reflector (see
 211 Figure 4). Therefore, it is possible to have a reactor at a lower height than the classic solar towers,
 212 reducing the problems of mechanical strength of the structure. Despite the optical losses due to
 213 another reflector, thermal losses are strongly reduced and therefore higher temperature can be

214 reached [23] [24] [25] [26]. In order to not dilute the CO₂ to store, the fluidised bed will be
 215 fluidised with a recirculation of high-concentrated CO₂ stream.



216

217 **Figure 4: Integrated Solar Calcium Looping IS-CaL with direct calcination reaction into solar calciner. Solar**
 218 **calciner is a solid particles fluidised bed reactor with CO₂ to separate easily the product of calcination**
 219 **reaction. The compounds are stored at ambient temperature to avoid thermal losses.**

220 In this work, a direct solution based on a solid particles fluidised bed solar calciner has been
 221 analysed and investigated Figure 4. The energy is stored in form of chemical compounds (CaO
 222 and CO₂) that, before reaching the storage tanks, are cooled down by passing through heat-
 223 recovery heat exchangers heating up the calcium carbonate.

224 Solids entering the solar calciner, that are CaCO₃ and unreacted CaO, are pre-heated through a
 225 heat-exchanger network (HEN) by the hot products (i.e. CaO, CO₂) leaving the calciner. The
 226 solar calciner includes several cyclones and other components that are able to separate the
 227 fluidising CO₂ and product CO₂ from the particles.

228 The excess of solar energy stored in the form of chemical products can be used to generate heat
229 and electricity with zero CO₂ emissions, solving the problem of dispatchment and intermittency
230 of renewable energy.

231 The remainder of the work is focused on the analysis of a Rankine cycle assisted by a CaL unit
232 and powered by a direct solar calcination.

233 **3 Rankine cycle assisted by CaL process**

234 **3.1 Description of the Thermo–Chemical/Compressed–Gas Energy Storage**

235 This work analyses a solar powered Rankine cycle assisted by a CaL process as a direct energy
236 storage solution capable of generating electricity and providing energy to a district heating and
237 cooling network. The proposed system layout as formulated in Figure 5 can operate in three
238 different main configurations. The solar energy is collected from the field of heliostats and is
239 reflected by the beam down central reflector to the solar calciner. The collected energy can be (i)
240 used directly to generate electricity and/or (ii) stored through direct CaL process.

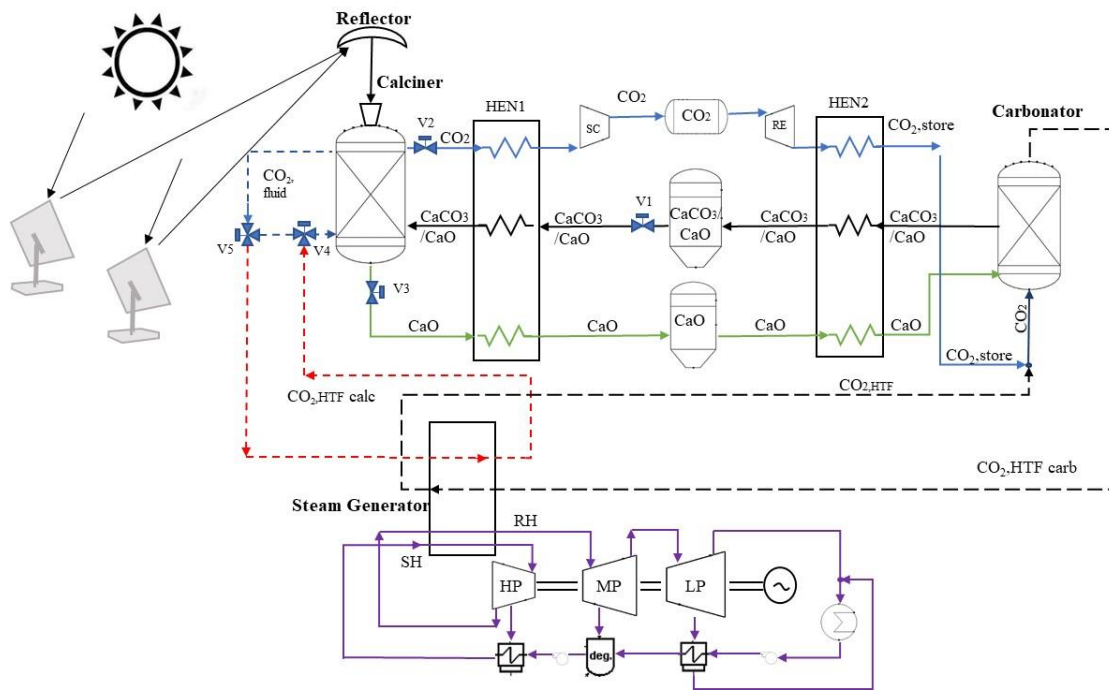
241 **3.1.1 Energy storage**

242 Energy storage takes place in the calciner in which decomposition of CaCO₃ into CaO and CO₂
243 occurs at high temperature (900 °C) by means of solar energy input. The solar calciner is a
244 fluidised bed where the fluidising agent is a pure stream (i.e., CO_{2, fluid}) and the solid bed is mainly
245 composed of CaCO₃ and CaO. The two products of calcination reaction (CO₂ and CaO) are
246 cooled and stored at ambient temperature to avoid heat losses. Solids entering in the solar
247 calciner, which consist of CaCO₃ and unreacted CaO, are pre-heated via a heat-exchanger
248 network (HEN1) by the hot products (i.e. CaO, CO₂) leaving the reactor. CO₂ stream is cooled,
249 compressed via the storing compressor (SC) at supercritical conditions and directed to a storage
250 tank. The cooled CaO stream is transported to a conventional storage site (e.g. silos). Details of
251 the SC component are provided in section 2.2. Part of the excess of solar heat can be used directly

252 to produce steam via the stream $\text{CO}_{2, \text{HTF calc}}$. This option has not been taken into consideration in
253 the remainder of the paper.

254 3.1.2 Energy release

255 During steady state operation, a hot stream (i.e. $\text{CO}_{2, \text{HTF, carb}}$) leaves the carbonator, as shown in
256 Figure 5, to generate steam in boiler to be used as a working fluid in a Rankine cycle. The heat
257 required to produce the hot stream $\text{CO}_{2, \text{HTF, carb}}$ is released by the reaction between CaO and CO_2
258 inside the carbonator. Indeed, this reactor is fed by a CaO stream leaving the silos and a CO_2
259 stream composed of: (i) a stream leaving the steam generator (i.e. $\text{CO}_{2, \text{HTF, carb}}$) and (ii) a stream
260 leaving the storage site (i.e. $\text{CO}_{2, \text{store}}$) via a recovery expander (RE). These two components will
261 be mixed and react releasing the heat and producing the aforementioned hot stream (i.e. $\text{CO}_{2, \text{HTF, carb}}$)
262 leaving the carbonator and making continuous the generation of steam. The storage sites (i.e.
263 CaO silo and CO_2 tank) have been sized in order to keep power production continuous (see later
264 for the details). CaO and CO_2 entering carbonator are pre-heated via a heat-exchanger network
265 (HEN2) by the hot product (CaCO_3) leaving the reactor. CaCO_3 is cooled and stored in
266 conventional silos. Details of RE component will be given in section 3.2. Figure 5 shows the
267 Thermo-Chemical/Compressed-Gas Energy Storage (TC/CG-ES) that comprises of: (i) calciner,
268 storing compressor (SC), (ii) turbo expander (RE) for recovery of energy and (iii) carbonator. In
269 this mechanical and chemical system, the CO_2 is used both as working and reacting fluid: it is
270 compressed in SC and expanded in RE for storing and releasing the energy.

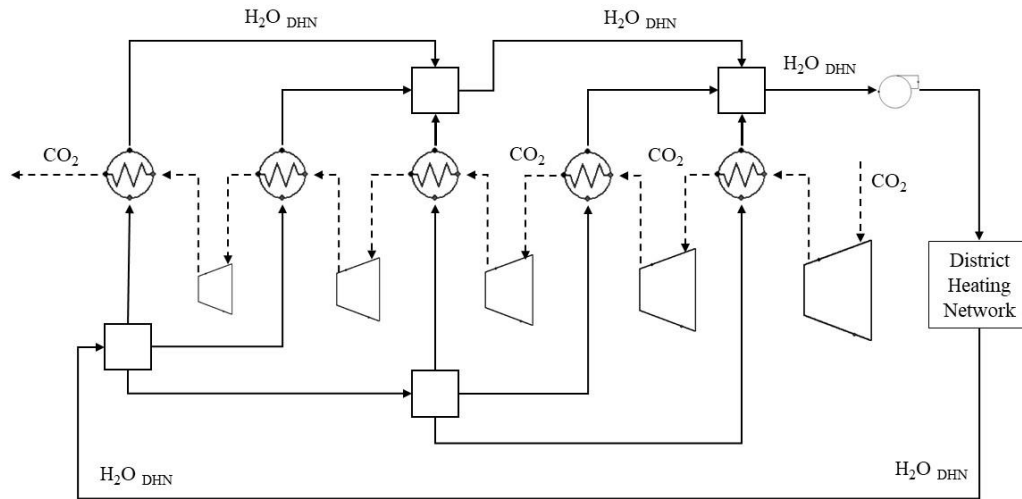


271

272 **Figure 5: Thermo-Chemical/Compressed-Gas Energy Storage (TC/CG-ES) coupled with a conventional**
 273 **Rankine power cycle. During sunlight solar energy can be transformed directly in electricity or stored in**
 274 **chemical compound. There are three operational phase: (i) Only electricity is produced; (ii) only charging of**
 275 **storage system; (iii) Both electricity and chemical compounds are produced.**

276 3.2 Heat recovery for the CO₂ storage site

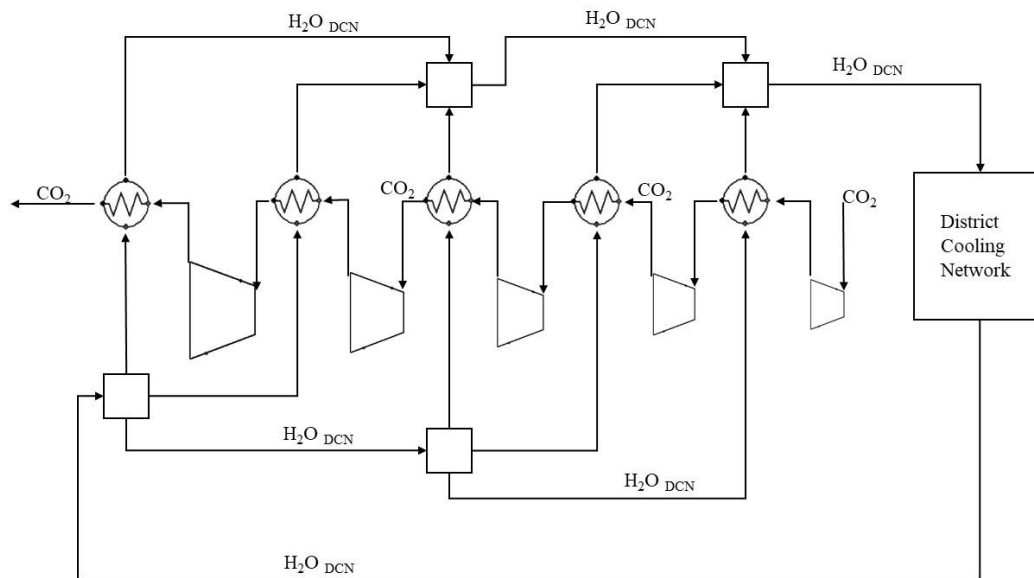
277 The CO₂ is stored at 75 bar by a group of five compressors as shown in Figure 6. The CO₂ is
 278 stored at supercritical condition to reduce the storage volume [13]. Each compressor has a
 279 pressure ratio of 2.37 and an isentropic efficiency of 0.83. Each compressor is followed by an
 280 intercooler to minimize the compression work. The heat collected by the cooling system of the
 281 compression is used to feed a district heating network. Inside each individual intercooler water
 282 enters at 60°C and exits at 90°C at a pressure of 4 bar. Subsequently it is pumped up to 10.3 bar
 283 and sent to the district heating network as is common to do [27].



284

285 **Figure 6: Train of five compressors with five inter-coolers. The heat at low temperature provided during**
 286 **compression, supply a district heating network.**

287 From the storage unit (see Figure 5), the CO₂ stream feeds the carbonator reactor to react with
 288 calcium oxide. The expansion of previously stored CO₂ supplies useful work and provide
 289 efficiently cooling power. The expansion from 75 to 2 bar requires the use of inter-heating
 290 expansion to avoid the condensation of CO₂ and protect the turbine blades as showed in Figure
 291 7. This Cooling system provides water at 6 °C and the same return into inter-heating at 12 °C.



292

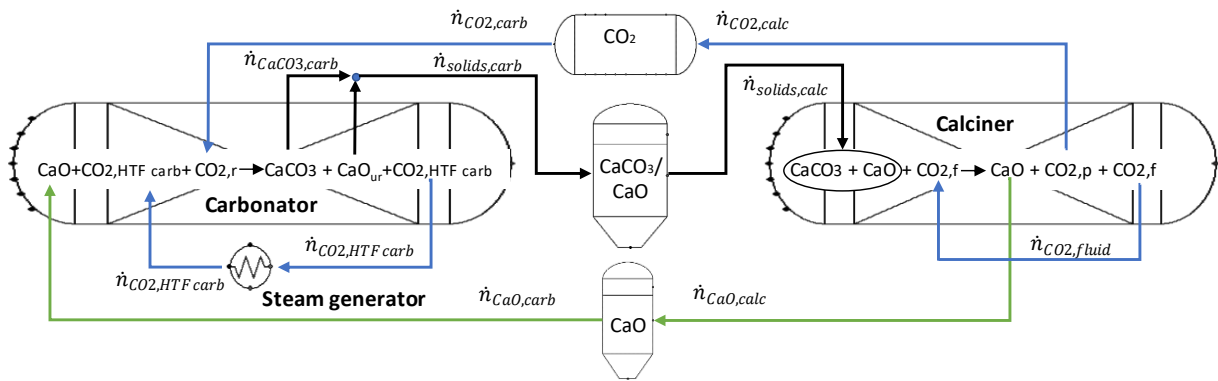
293 **Figure 7: District cooling network used to avoid the condensation of the CO₂ and associate danger for the blade of turbine.**
 294 **The water used into the inter-heating at 12°C, is cooled until 6°C.**

295 During heat release, CO₂ previously expanded, CaO from reservoir and the CO₂ used as heat
 296 transfer fluid are heated and then come into carbonator reactor where the release of energy occurs
 297 (see Figure 5). Under favourable conditions in the carbonator (P= 2bar; T= 850°C), CO₂ and part
 298 of CaO react in an exothermic reaction and the heat produced at higher temperature is transferred
 299 at power system throughout the CO_{2, HTF}. The solids stream composed of CaCO₃ and un-reacted
 300 CaO, is cooled and stored inside tank almost at ambient condition.

301 The carbonator reactor is connected to power cycles indirectly by CO₂ which acts both as
 302 fluidising agent and heat transfer fluid. The CO₂ at high temperature does not produce work
 303 directly in turbine. Therefore, the pressure of the carbonator reactor is set a 2 bar to overcome
 304 the pressure drops in the reactor and in the various heat exchangers however, it is not higher than
 305 2 bar because increasing pressure, the storage efficiency goes down as it is showed in 4.3 section.

306 3.3 Energy and mass balance equations

307 The Figure 8 illustrates the molar streams of CaL system equipped with storage.



308
 309 **Figure 8: Molar balance schematic of the Calcium Looping process. In the right side calcination reaction and energy**
 310 **storage happen; In the other side CaO and CO₂ react into carbonator reactor and the heat of reaction is transported by**
 311 **the CO₂ used as HTF.**

312 Into carbonator reactor, a carbonation reaction at 830°C and 2 bar occurs. Here the CO₂ that
 313 coming out from pressurize storage ($\dot{n}_{CO_2,r,carb}$) react with the CaO ($\dot{n}_{CaO,carb}$). Into the reactor
 314 the excess of CO₂ which acts as heat transfer fluid ($\dot{n}_{CO_2,HTF,carb}$) flows. Calcium oxide does not
 315 react completely with the CO₂ due to loss of reactivity during different cycles and depending on

316 the thermodynamic condition and residence time. The flow rate of the unreacted CaO is $\dot{n}_{CaO\ ur}$.
 317 Thus only part of the CaO reacts to produce CaCO₃ ($\dot{n}_{CaCO_3\ carb}$) and therefore solids ($\dot{n}_{solids\ carb}$)
 318 at the carbonator outlet are composed of CaCO₃ and unreacted CaO. Indeed, CaO-based solid
 319 sorbent are never fully utilized displaying the existence of maximum degree of carbonation
 320 conversion, nevertheless it is fortunately possible regenerate all the calcium carbonate [16].

$$321 \quad \dot{n}_{CaO\ carb} + \dot{n}_{CO_2\ r,carb} + \dot{n}_{CO_2\ HTF\ carb} \rightarrow \dot{n}_{solids\ carb} + \dot{n}_{CO_2\ HTF\ carb} \quad (\text{Eq.})6$$

$$322 \quad \dot{n}_{solids\ carb} = \dot{n}_{CaCO_3\ carb} + \dot{n}_{CaO\ ur} \quad (\text{Eq.}) 7$$

323 The CaCO₃ phase contained in the solids stream ($\dot{n}_{solids\ calc}$) entering the calciner will be
 324 completely regenerated to produce calcium oxide ($\dot{n}_{CaO\ calc}$) and carbon dioxide ($\dot{n}_{CO_2\ calc}$) that
 325 will be compressed and stored.

$$326 \quad \dot{n}_{solids\ calc} + \dot{n}_{CO_2\ HTF\ calc} \rightarrow \dot{n}_{CaO\ calc} + \dot{n}_{CO_2\ calc} + \dot{n}_{CO_2\ HTF\ calc} \quad (\text{Eq.}) 8$$

$$327 \quad \dot{n}_{solids\ calc} = \dot{n}_{CaCO_3\ calc} + \dot{n}_{CaO\ calc} \quad (\text{Eq.}) 9$$

328 One of the most important parameters for this technology is the average CaO conversion (X)
 329 useful to quantify the amount of CaO converted to CaCO₃ during carbonation reaction. This
 330 reaction extent is defined as follows:

$$331 \quad X = \frac{\dot{n}_{CaCO_3\ carb}}{\dot{n}_{CaO\ carb}} \quad (\text{Eq.}) 10$$

332 In order to guarantee a steady state condition during the storage and release of energy, the solid
 333 material regenerated into calciner reactor has to be enough to produce the required heat during
 334 carbonation. The carbonator has to release the required energy for the whole operational time
 335 whereas the calciner is able to regenerate the solid material for a shorter time (eight hours
 336 approximately) when the solar energy is gathered. As a consequence, an adequate storage volume
 337 is required to store solids (i.e. CaO and CaCO₃) and CO₂ to continuously feed carbonator during

338 the energy demand. In order to guarantee a steady state condition during power production, the
 339 sorbent regenerated into calciner reactor has to be enough to produce heat into carbonator side.
 340 Therefore, the following equation has to be satisfied:

$$341 \int_0^{24} \dot{n}_{CaCO_3 carb}(t) dt = \int_0^8 \dot{n}_{CaO calc}(t) dt \quad (\text{Eq.}) 11$$

342 The left-hand side represent the mole of $CaCO_3$ producing into the carbonator reactor during the
 343 24-h time span. This term has to be equal to the mole of CaO regenerated into the calciner. It is
 344 possible to write $\dot{n}_{i,in}$ and $\dot{n}_{i,out}$ the molar rate of the i-th component that comes in and comes out
 345 respectively from one of two calciner and carbonator reactors.

346 The extent of reaction that represents the degree of reaction (e.g. $\varepsilon = 1$ the reactants react
 347 completely) can be defined as:

$$348 \varepsilon = \frac{\dot{n}_{i,out} - \dot{n}_{i,in}}{\nu_i} \quad (\text{Eq.}) 12$$

349 where ν_i is the stoichiometric coefficient the molar rate reacted is written as:

$$350 \dot{n}_{i,out} - \dot{n}_{i,in} = \varepsilon \nu_i \quad (\text{Eq.}) 13$$

351 Arranging the first law of thermodynamic and considering that the out flow is at the same
 352 condition of the reactor, the power heat provided by CSP plant to regenerate completely the
 353 sorbent is:

$$354 \dot{n}_{CO_2 HTF calc} \cdot [h_{CO_2 HTF}(T_{calc}) - h_{CO_2 HTF}(T_{in})] + \dot{n}_{solids calc} \cdot [h_{solids calc}(T_{calc}) -$$

$$355 h_{solids calc}(T_{in})] + \varepsilon_{calc} \Delta H_{react}(T_{calc}) = \Phi_{CSP} \quad (\text{Eq.}) 14$$

$$356 \varepsilon_{calc} = \frac{\dot{n}_{CaCO_3 calc out} - \dot{n}_{CaCO_3 calc in}}{\nu_{CaCO_3}} \quad (\text{Eq.}) 15$$

357 The energy balance of the carbonator reactor can be written to compute the molar flow rate of
 358 the CO_2 needed to remove part of the heat of carbonation reaction:

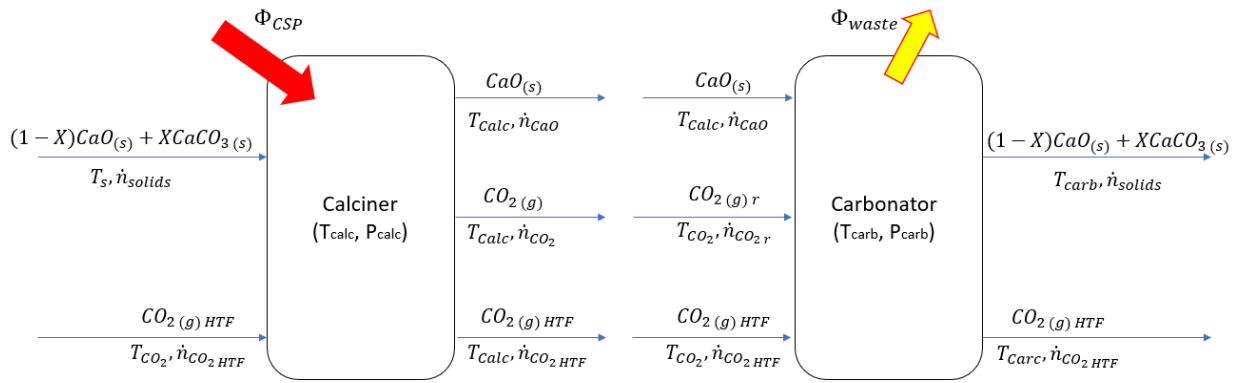
$$\begin{aligned}
359 \quad & (\dot{n}_{CO_2 HTF carb} + \dot{n}_{CO_2 r,carb}) \cdot [h_{CO_2}(T_{carb}) - h_{CO_2}(T_{CO_2 in})] + \dot{n}_{CaO carb} \cdot [h_{CaO carb}(T_{carb}) - \\
360 \quad & h_{CaO carb}(T_{CaO in})] + \varepsilon_{carb} \Delta H_{react}(T_{carb}) = \Phi_{waste} \quad (Eq.) 16
\end{aligned}$$

$$361 \quad \varepsilon_{carb} = \frac{\dot{n}_{CaO carb out} - \dot{n}_{CaO carb in}}{\nu_{CaO}} \quad (Eq.) 17$$

362 With the heat of reaction defined as:

$$363 \quad \Delta H_{react}(T_{react}) = \Delta H^{\circ}_{react} + \sum_i \nu_i \cdot \int_{T_{ref}}^{T_{react}} c_{p i}(T) dT \quad (Eq.) 18$$

364 Mass and energy balance are represented in Figure 9.



365

366 **Figure 9: Energy balance of the storage system focused on the main critical reactors.**

367 **4 CaL process integrated with Rankine power cycle**

368 A reheat power Rankine cycle with eight extraction streams with 320 MW groups with 43.7%
369 efficiency is used to produce electricity [28]. Within the power plant, 1023.3 tonne per hour of
370 water circulates, which must be heated by the heat transfer fluid (HTF) leaving the carbonator.
371 Turbine and pump efficiencies values of 83% have been considered as well as a heat exchangers
372 minimum temperature difference of 20°C. On the other hand, non-pressure drops are assumed.
373 All the main operating parameters of the Rankine power cycle are summarised in the following
374 **Table 1.**

375

Table 1: Main process parameters of the Rankine power cycle [28]

$T_{in,HP}$ [°C]	538
$P_{in,HP}$ [bar]	170
$G_{in,HP}$ [t/h]	1023
$T_{in,MP}$ [°C]	538
$P_{in,MP}$ [bar]	37.7
$G_{in,MP}$ [kg/h]	835430
$T_{in,LP}$ [°C]	322
$P_{in,LP}$ [bar]	7.2
$G_{in,LP}$ [kg/h]	738100
$\eta_{is,turbine}$ [-]	0.83
$\eta_{is,pump}$ [-]	0.83
$T_{out,reg}$ [°C]	267
ΔT_{min} [°C]	20
$W_{Rankine}$ [MW]	320
$\eta_{Rankine}$ [-]	0.437

376 The high pressure (HP) turbine of the investigated Rankine cycle plant operates at a pressure of
 377 170 bar and super-heated and re-super-heated temperature of 538°C.

378 In Italy, these plants represent the baseload for power production). The plants located in the
 379 internal areas are generally built for operation with oil fuel that with natural gas. Oil is supplied
 380 by pipelines or by tankers or rail tankers. Natural gas is supplied through methane pipelines.

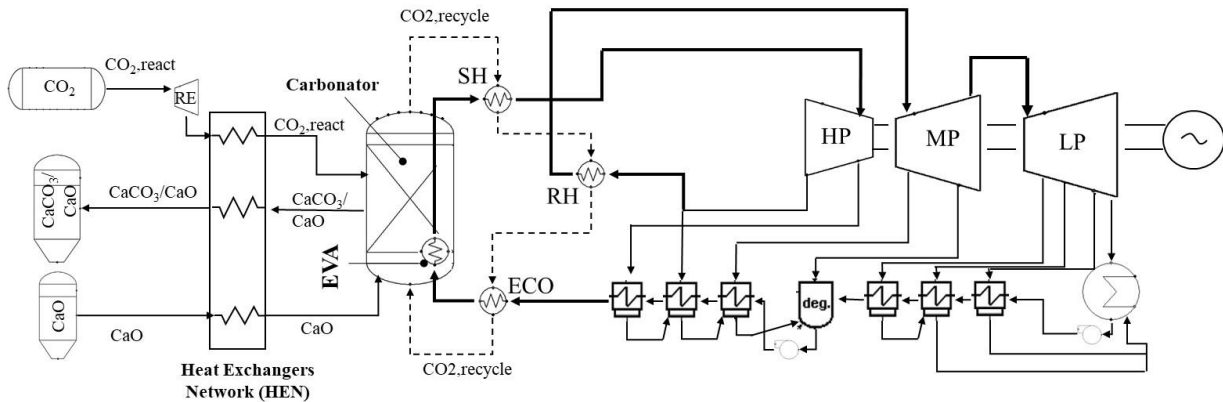
381 The use of the CaL process in a CSP allows storing the excess of renewable energy by producing
 382 chemical compounds (i.e. CaO and CO₂). An indirect coupling of CaL to a Rankine cycle for
 383 generating power was analysed. Thermochemical storage must provide the necessary reagents so
 384 that the exothermic reaction supplies the heat requirement to the steam.

385 The heat is mainly supplied in four components (see Figure 10)

386 - Water evaporation occurs inside the water-tube walls (EVA) that absorb part of the heat
 387 of reaction;

388 - At the exit of fluidized bed, the CO₂ used as a heat transfer fluid (HTF) enters the
 389 superheater (SH) at 830°C, heating the steam at high pressure up to 538°C;

390 - then it enters the re-heater (RH), heating the medium pressure steam (about 37 bar) up to
 391 538°C;
 392 - Finally, the CO₂ HTF enters the economizer, heating the liquid water up to 267 °C and
 393 coming back to the carbonator at 287°C;
 394 It was analysed the case in which Rankine power cycle was fed only with the carbonator. To
 395 optimize the heat exchangers network of (HEN), a pinch analysis of the storage system integrated
 396 with the Rankine cycle is performed.



397
 398 **Figure 10: Release of energy via TC/CG–ES integrated with Rankine power cycle. The CO_{2,recycle} fluidises the**
 399 **carbonator reactor and transfer heat to Rankine cycle.**

400 **4.1 Optimisation of the heat exchangers network**

401 Pinch analysis is a useful technique to optimise the heat exchanged in energy systems minimising
 402 external supply of heat and cold. The easiest and often most expensive way is to use external hot
 403 or cold resources. The most efficient way is to couple the different fluids through heat exchangers
 404 where simultaneous heating and cooling among the streams happens. To achieve this purpose, it
 405 is necessary to provide a heat recovery system thus building a network of heat exchangers.
 406 However, this analysis must always take into account the constraint of the second law of
 407 thermodynamics, while the difference in temperature between the cold and hot fluids must be
 408 sufficiently high to not result in excessive heat exchange surfaces.

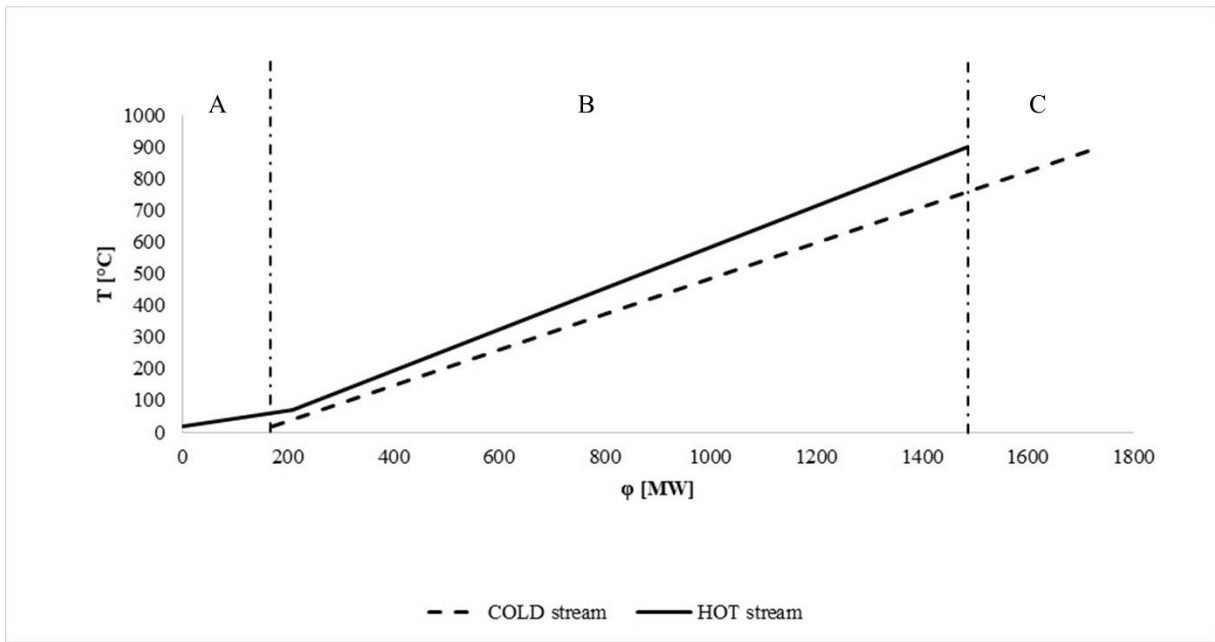
409 The analysis will be carried out separately for the two sides of the storage system (i.e. heat storage
 410 side and heat release side). The storage area composed of silos and pressurised tank of CO₂ is
 411 placed in the between of the calciner and carbonator in order to be able to separate not only
 412 temporally but also physically the storage (calciner) from the release (carbonator) of energy.

413 The first step of the analysis consists in identifying the components of the system and the related
 414 entering or exiting fluids. The energy storage system is composed of the reactor itself in which
 415 the calcination reaction occurs and the CO₂ compression system. The latter consists of five
 416 compressors with the relative inter-cooling system that exchanges heat with water acting as heat
 417 transfer fluid in the district heating network. The CO₂ compression system is reported as SC in
 418 Figure 5 and Figure 12.

419 **Table 2: Streams identified during the pinch analysis of the calciner side**

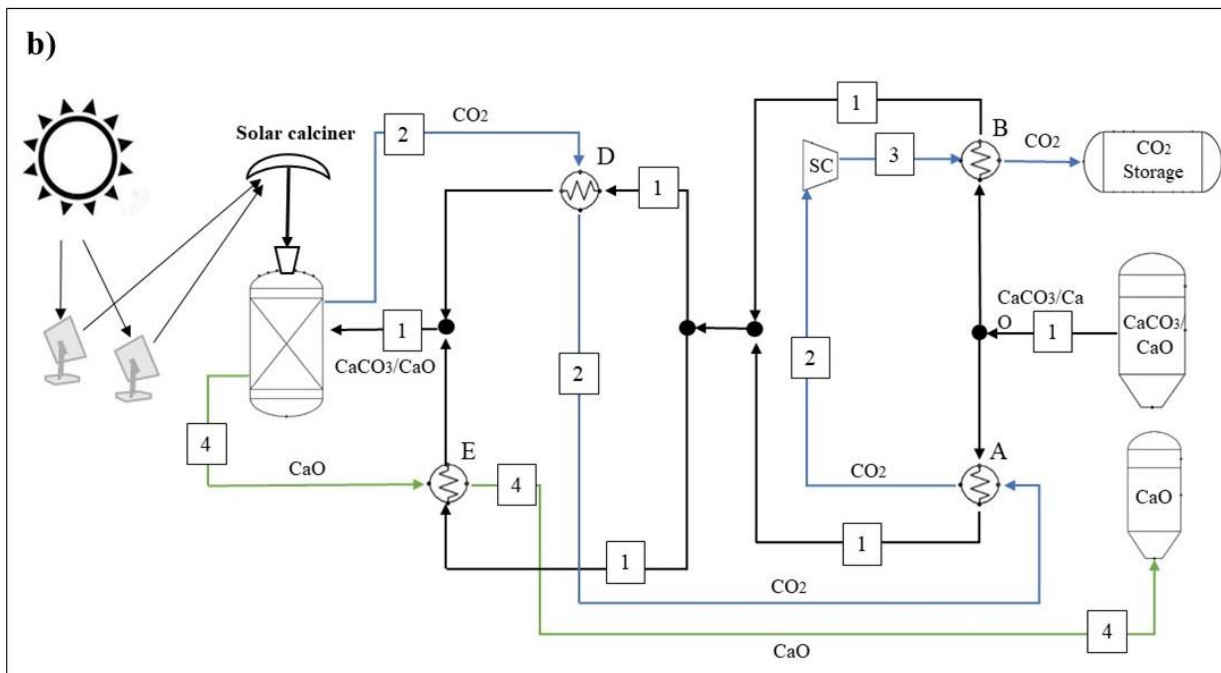
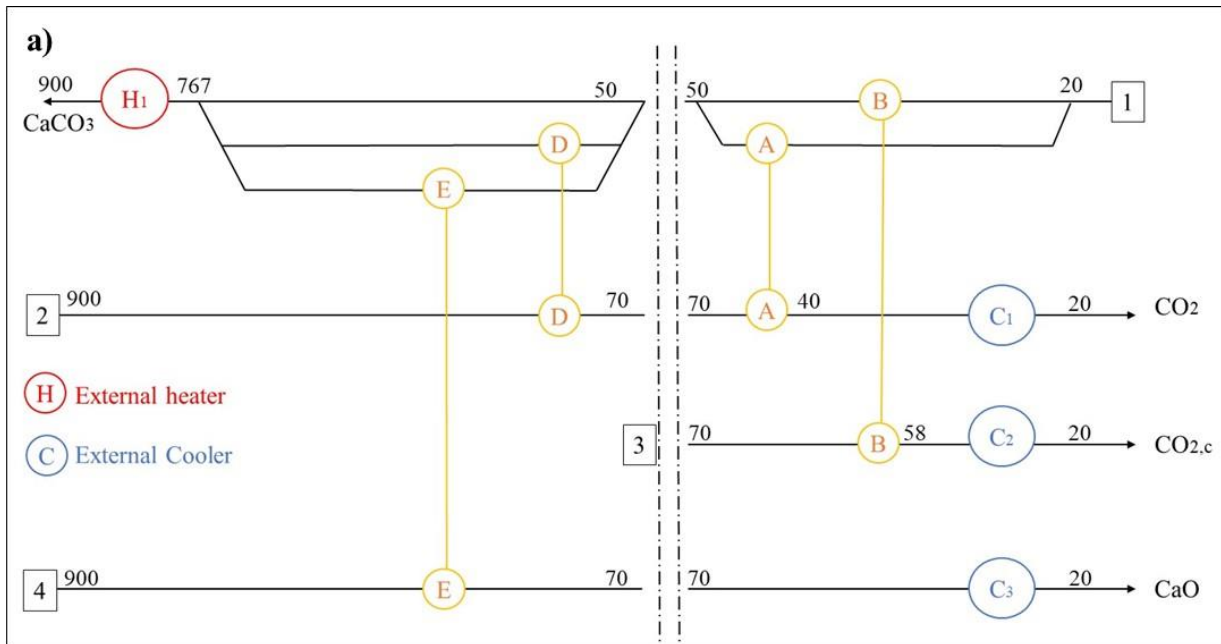
# of stream pynch	Component	Type of stream	T _{in} [°C]	T _{out} [°C]	Mass rate [kg/s]	G x cp [MW/K]	Power Heat [MW]
1	Solids	COLD	20	900	1540,4	1,78	-1566,5
2	CO ₂	HOT	900	20	594,13	0,66	582,4
3	CO ₂	HOT	70	20	594,13	2,67	133,4
4	CaO	HOT	900	20	946,3	0,88	770,6

420
 421 Four fluid streams are identified (see **Table 2**), three of which are hot streams (i.e. (2) CO₂ leaving
 422 the calciner; (3) CO₂ leaving the compressor; (4) CaO leaving the calciner) and one cold stream
 423 (solids stream entering the calciner). The only cold fluid is made up of solids (i.e. X CaCO₃ and
 424 (1-X) CaO) that will be sent to the calciner in which a full regeneration of the sorbent takes place.
 425 A fixed value of CaO conversion to CaCO₃ (X=0.7) has been used.



426

427 **Figure 11: Composite curve of the solar calciner side. Section A represents the excess of heat at low**
 428 **temperature; in section B the hot streams provide heat to cold streams; in section C there aren't hot streams**
 429 **and the heat enough is provided by CSP to cold streams**



430

431 **Figure 12: a) Minimum energy consumption network inferred from the pinch analysis in the calciner side.**
 432 **The values of temperature level are reported in degree Celsius. b) Plant configuration (calciner-side) resulting**
 433 **from the pinch analysis**

434 The result of the pinch analysis is the HEN showed in Figure 12. As you can see, in this case
 435 incoming stream (CaCO_3) into calciner reached a temperature of 767 °C due to the HEN. The
 436 remaining sensible energy to heat the spent solids up to 900 °C is provided by the heat exchanger
 437 H1 (238 MW) which represents part of the energy gathered by CSP (2432 MW). The remaining
 438 energy necessary to drive the calcination and decompose CaCO_3 into the respective CaO and

439 CO₂ will be provided also by the CSP (2194 MW). The configuration of HEN, the phase change
 440 fluids and chemical reaction were treated following the methodology described in [29].

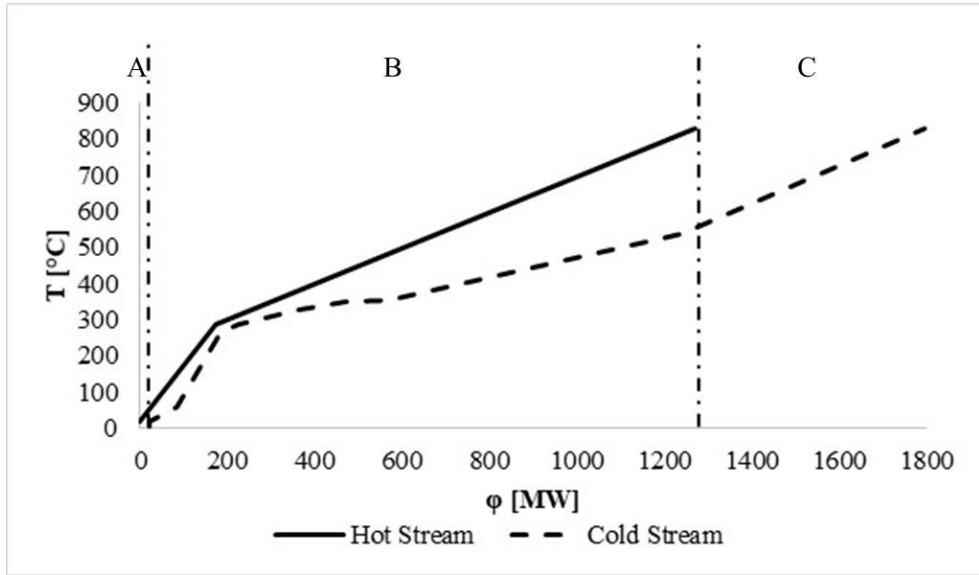
441 Following the analysis thoroughly performed for the energy storage, the pinch analysis for the
 442 carbonator section was also performed (energy release). The energy release section is mainly
 443 composed of two devices: (i) the carbonator in which the carbonation reaction occurs, and (ii)
 444 the turbine train in which compressed CO₂ is expanded from 75 to 2 bar. Through the expansion
 445 of CO₂ in the RE component (see Figure 5), it is possible to produce both power and cooling.
 446 After each expansion stage, the carbon dioxide is at the temperature of about -30 ° C and must
 447 be heated in order to avoid condensation and the consequent breakage of the blades. The heat
 448 released by the water in a refrigerant cycle (see Figure 7) is transferred to the CO₂ which is heated
 449 from -30 °C to 7 °C. The refrigerant fluid is sent to a second heat exchanger where it is heated
 450 up and an external environment is cooled (e.g. hospital). The size of the power chiller is
 451 approximately 29 MW. Table 3 shows that the pinch analysis which accounts for ten fluids, two
 452 of which are hot streams leaving the carbonator at a temperature of 830 ° C and the remaining
 453 are cold streams to be heated as reported in Figure 14.

454 **Table 3: Streams identified during the pinch analysis of the carbonator side**

# of stream pynch	Component	Type of stream	T_in [°C]	T_out [°C]	Mass rate [kg/s]	G x cp [MW/K]	Power Heat [MW]
1	CO2	HOT	830	287	1173,6	1,3721	745,1
2	Solids	HOT	830	20	513,48	0,6489	525,6
3	H2O(l)	COLD	267	352	284,25	1,6263	-138,24
4	H2O	COLD	352	353	284,25	97,7600	-97,76
5	H2O(v)	COLD	353	538	284,25	1,2078	-223,45
6	H2O(v)	COLD	325,9	538	232,064	0,5402	-114,57
7	CO2	COLD	20	60	198,045	1,0353	-41,41
8	CO2	COLD	7	287	198,045	0,1900	-53,20
9	CO2	COLD	287	830	1371,645	1,6035	-870,68
10	CaO	COLD	20	830	315,43	0,2908	-235,55

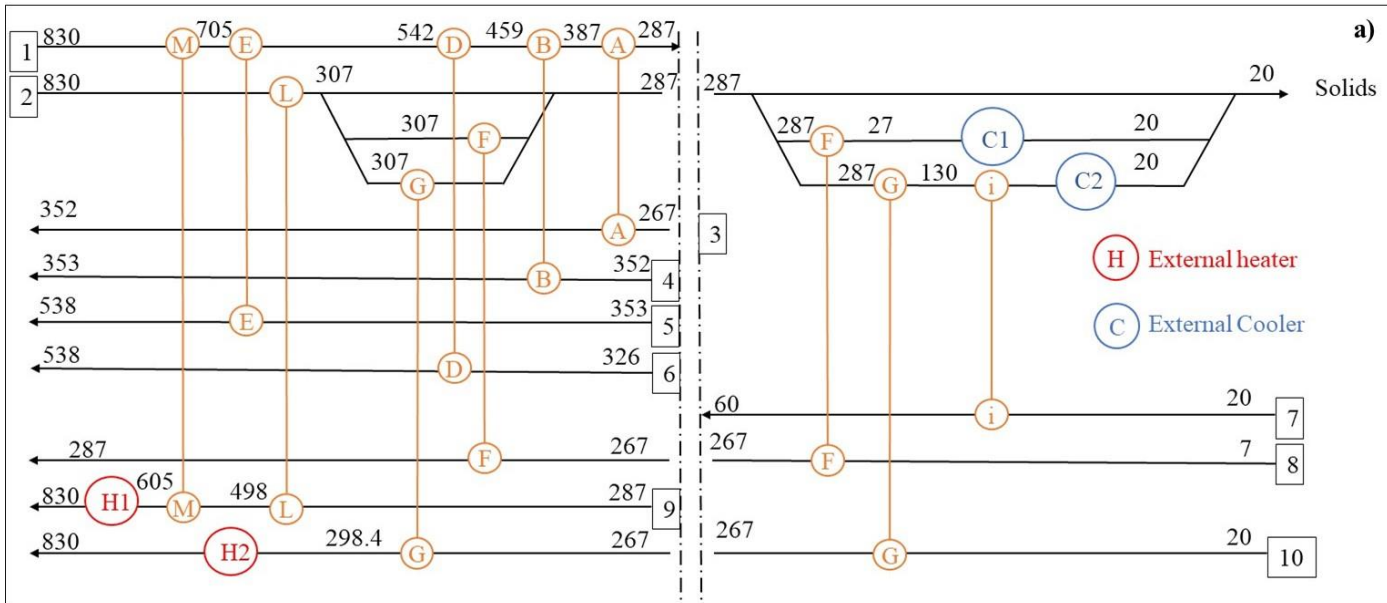
455 The cold fluids are (see *Figure 14*): (7) the compressed CO₂, which is heated before entering the
 456 turbine in order to produce more power, (8) the CO₂ at the end of expansion, which temperature

457 between 7 ° C to 287 ° C (minimum temperature of recirculation CO₂), (9) the CO₂ entering the
 458 reactor ranging from 287 ° C to the carbonation temperature, (10) CaO heated from ambient
 459 temperature to carbonation temperature, and finally (3-6) the working fluid of a conventional
 460 Rankine cycle, which is subjected to preheating, evaporation, overheating and re-heating.



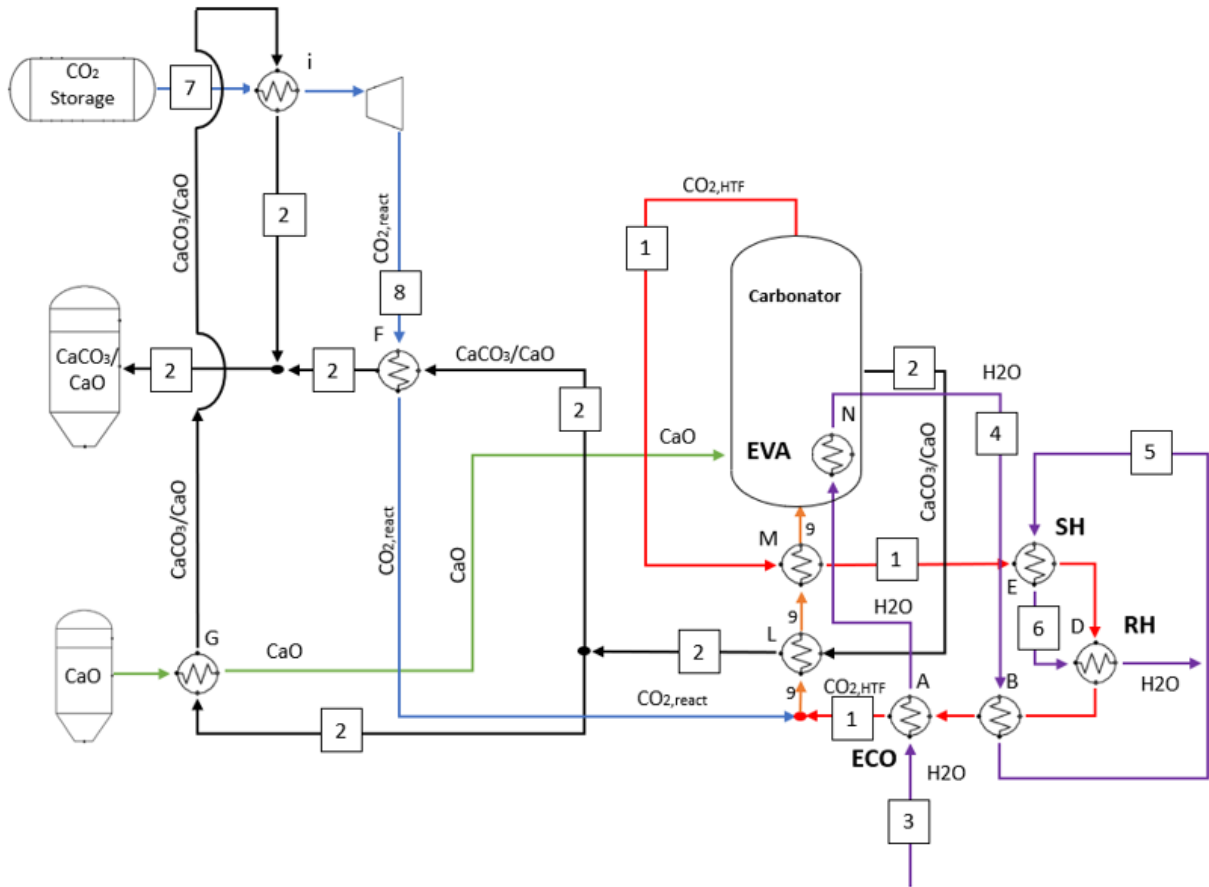
461

462 **Figure 13: Composite curve of the carbonator side. Section A represents the excess of heat at low temperature;**
 463 **in section B the hot streams provide heat to cold streams; in section C there aren't hot streams and the heat**
 464 **enough is provided by carbonation reaction to cold streams**



465

b)



466

467 **Figure 14: a) Minimum energy consumption network inferred from the pinch analysis in the calciner side.**
 468 **The values of temperature level are reported in degree Celsius. b) Plant configuration (carbonator-side)**
 469 **resulting from the pinch analysis.**

470 The final goal of the analysis is to select a HEN which can be used in parametric analysis with
 471 regards to key operating parameters (e.g. X, operating temperature and pressure). In *Figure 14.b*
 472 is showed the final HEN through pinch analysis to carbonator section. At the exit of economizer,
 473 saturate water flows into water-tube wall (exchanger N) and a partial evaporation (title of vapour:
 474 0.635) occurs due to heat released by carbonation reaction (165MW). This fluid is not represented
 475 in pinch analysis because it cannot be coupled with other. The remaining heat of evaporation is
 476 provided by hot CO₂ (1). The heat of exothermic carbonation reaction heats fluids 9-10 (569MW)
 477 until temperature of reaction. The overall heat of carbonation reaction is 745 MW. 569 MW is
 478 used to pre heat the reactants and HTF. Almost the 4% of 172.2MW is lost to the environment.
 479 165MW is used to partial evaporation of water in water-tube wall.

480 **4.2 Process model description**

481 The commercial software ChemcadTM was used for the modelling and simulation of the Rankine
482 cycle power plant integrated with calcium looping technology. This is used to solve material and
483 energy balances of complex systems providing a large database of chemical components. It is
484 designed to simulate chemical reactions with regards to the power production.

485 Both the Rankine cycle plant and the CaL unit were simulated through several components such
486 as reactors, flow mergers/splitter, heat exchangers. Due to the large amount of sub-processes
487 taking place and to their complexity, some simplifying assumptions had to be made:

- 488 - Operation of all components is at steady state;
- 489 - Only thermodynamic equilibrium has been considered;
- 490 - The ambient temperature and pressure are constant and equal to 20°C and 1 bar,
491 respectively;
- 492 - The pressure losses were neglected;
- 493 - The heat losses in the piping and in the rest of the system were neglected with the
494 exception of the carbonator reactor in which about 4% of heat produced is lost.
- 495 - The performance of the main reactors e.g. carbonator and calciner were represented using
496 the chemical and phase equilibrium through the free energy minimization at the operating
497 temperature;
- 498 - A complete calcination of calcium carbonate takes place into solar calciner;
- 499 - Minimum temperature difference (pinch temperature) is 20°C for all main heat
500 exchangers and 10°C for intercooler;

501 - The plant is equipped with a solid-solid heat exchanger, gas-solid heat exchanger and
502 with gas-gas regenerator.

503 Several of this assumption are summarized in the **Table 4**.

504 **Table 4: Main operating data of the Calcium Looping storage system**

Solar heat provided to calciner [MW_{th}]	2431.58
Thermal dispersion in carbonator [%]	3.85
Calciner temperature [$^{\circ}C$]	900
Calciner pressure [bar]	1
Ambient temperature [$^{\circ}C$]	20
CaO average conversion [%]	70
Carbonator Temperature [$^{\circ}C$]	830
Carbonator Pressure [bar]	2
CO ₂ storage conditions [bar]	75
Daylight hours [h]	8
Isentropic efficiency [%]	83

505
506 The thermodynamic equilibrium is supposed to be reached in both carbonator and calciner
507 reactors: the molar flow of calcium oxide feeding the carbonator was set to react with the CO₂
508 flowing through the RE providing the heat enough to run the Rankine cycle. According to
509 experimental results [18] an average CaO conversion X of 0.7 was selected.

510 The thermal energy input required by the calciner is mainly due to the decomposition of calcium
511 carbonate to calcium oxide and carbon dioxide. Consequently, the calciner energy consumption
512 is estimated based on the average amount of solids sent into the regeneration/storage step.

513 In addition, a complete conversion of CaCO₃ to CaO into the calciner operating at 900 $^{\circ}C$ has
514 been supposed. The performance of the calciner as well as the carbonator were analysed using
515 the Gibbs free energy minimization model.

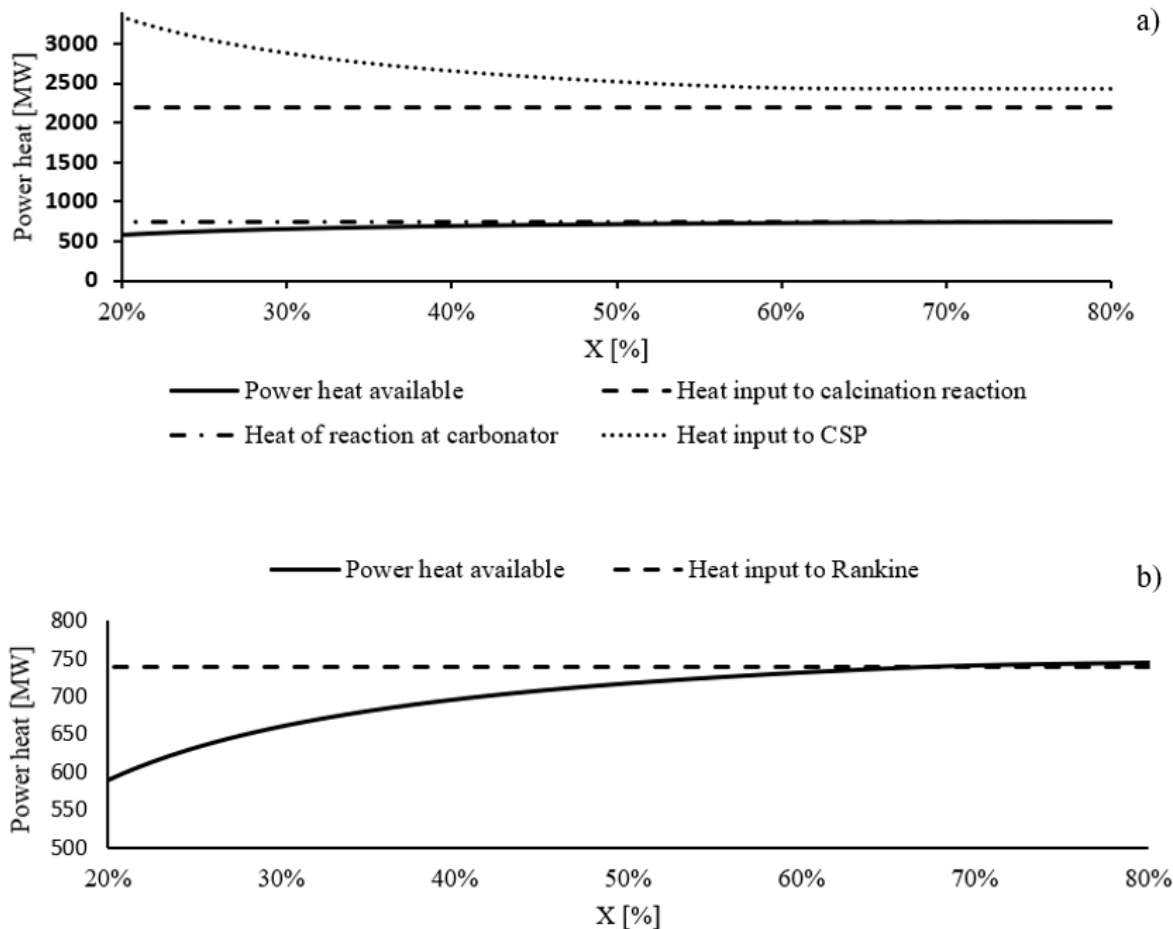
516 The CaL process requires a continuous make-up flow of fresh limestone to counteract the
517 deactivation of lime with the number of carbonation/calcination cycles while a corresponding

518 purge is also extracted from the calciner. The calcined purge is a potential material to be fed to
519 the cement plant and other industrial process (e.g. iron and steel, glass and pulp). Due to the high
520 resistance of the new sorbents at higher number of cycles and the negligible fine production, a
521 continuous make-up flow is not simulated.

522 ***4.3 Parametric analysis and process simulation results***

523 In order to evaluate how the performance of the sorbent affects the previously selected HEN, a
524 parametric analysis was carried out by varying the CaO conversion X . This parameter has an
525 important influence on the system as whole: in particular, for the selection of (i) size of storage
526 vessels, (ii) solids flow rates and (iii) heat requirements.

527 As mentioned above, we are considering the case in which: (i) the electric power is produced
528 through the heat transferred only by the carbonator to the Rankine cycle and (ii) the CSP is used
529 only to regenerate the spent sorbent. The heat transferred from CSP to the Rankine cycle is
530 negligible compared to the heat transferred by the carbonator to the Rankine cycle. The thermal
531 energy produced by carbonator reactor has to meet the Rankine cycle and heat the inert materials
532 entering with the active CaO. During this analysis, the power production of the Rankine cycle is
533 fixed. **Figure 15** shows the effect of the CaO conversion on the thermal power in both main
534 reactors in which the carbonation and calcination reaction occur.



535

536 **Figure 15: a) Thermal power fluxes of main reactors at varying CaO conversion. b) The heat enough from**
 537 **Rankine cycle is fixed, while change the heat provides by the storage system.**

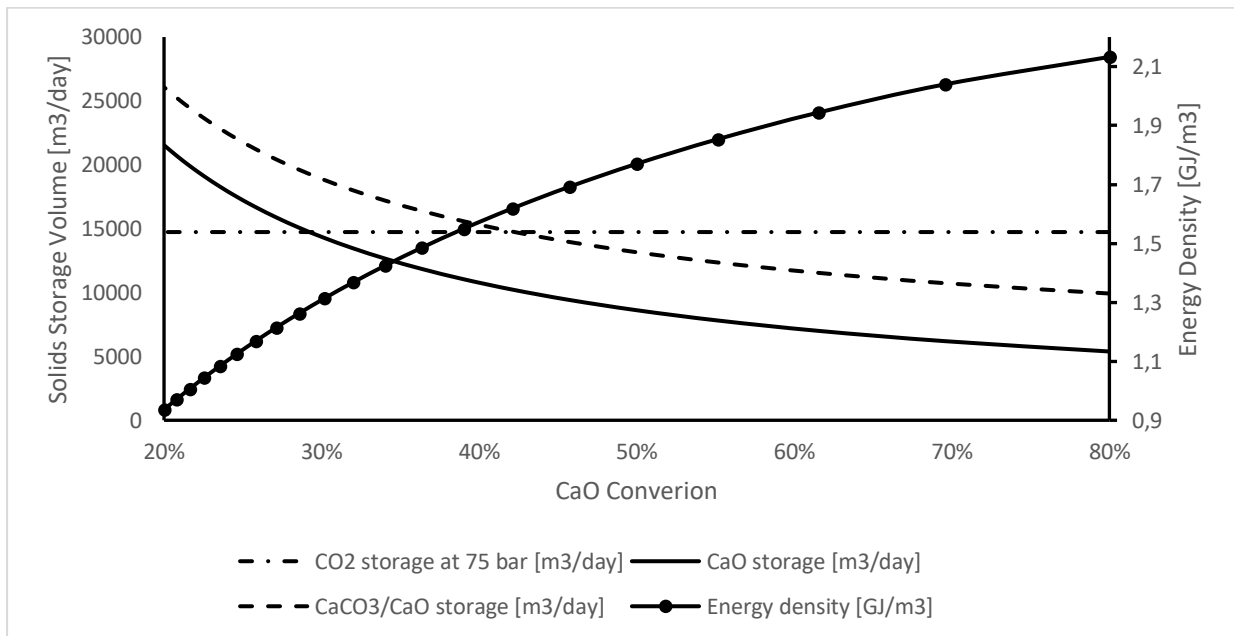
538 By fixing the quantities of the compounds that must react in the reactors (4.5 kmol/s both CO₂
 539 and CaO), the necessary thermal power, produced respectively in the calciner ($\Phi_{\text{calc}} = -2194$ MW)
 540 and carbonator ($\Phi_{\text{carb}} = 745$ MW) reactors due to reactions, remain constant. The sensible heat
 541 necessary to heat up the reactants to the temperature of the respective reactor, decreases
 542 significantly at high CaO conversion. This means that the lower the conversion of the CaO, the
 543 higher the molar flow rate of the solids and therefore the energy needed to heat up the entering
 544 solids increases.

545 Therefore, in case of loss of performance of the sorbent (low X), it may be necessary:

- 546 • Reduce the power produced, thus producing less energy in the carbonator;

- 547 • Use an external resource that provides the remaining power;
- 548 • Increase the flow rate of the reagents (CaO and CO₂), making the system operating at
- 549 nominal power with less hours per day;

550 **Figure 16** shows that increasing the CaO conversion, storage volume of the solid streams decreases
 551 while the CO₂ storage is not affected. This last observation is due to the fact that the CO₂ required
 552 for the carbonation reaction has not changed. The CO₂ storage volume is strongly depending on
 553 the thermodynamic storage conditions.



554
 555 **Figure 16: Parametric analysis: Daily storage volume with the change of CaO conversion**

556 Another important parameter to evaluate and compare energy storage system is the energy
 557 density, represented in the same figure at different values of CaO conversion. It is illustrated that
 558 with small values of CaO conversion, the solids storage volume increase and therefore the energy
 559 density goes down starting from 2.1 MJ/m³ to 0.95 MJ/m³.

560 A key performance indicator (KPI) to evaluate thermal efficiency during one cycle of
 561 carbonation/calcination is the *Thermal Storage efficiency*. It is calculated considering only the
 562 thermal energy released to carbonation reaction and the energy input to calciner reactor over 24h.

$$563 \quad \eta_{TSE} = \frac{Q_{carbonator}}{Q_{CSP}} \quad (Eq.) 19$$

564 Thermal storage efficiency takes into account the only thermal energy of the storage avoiding
 565 the summing of thermal power and mechanical power used in the next KPI and it is useful to
 566 compare other energy storage.

567 However, it is relevant also the storage condition and not only output/input thermal energy. The
 568 KPI to evaluate the effectiveness of the storage and release system is the *storage efficiency*,
 569 defined as the ratio of the heat released during carbonation reaction plus expansion work of CO₂
 570 to the heat gathered by the CSP plus the compression work required during CO₂ storage.

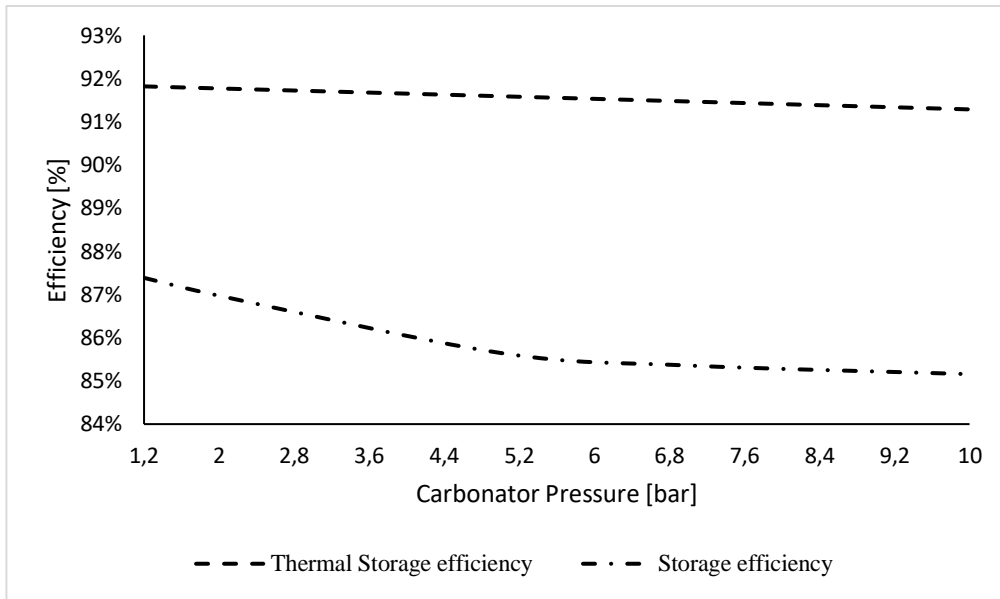
$$571 \quad \eta_{SE} = \frac{Q_{carbonator} + L_{CO_2, expansion}}{Q_{CSP} + L_{CO_2, compression}} \quad (Eq.) 20$$

572 In order to take in consideration other benign effects of the system the following *storage and*
 573 *recovery efficiency* has been formulated: This parameter takes into account the low enthalpy heats
 574 exchanged by the storage system through the system boundary to the district heating and cooling
 575 network.

$$576 \quad \eta_{SRE} = \frac{Q_{carbonator} + L_{CO_2 expansion} + Q_{district cooling} + Q_{district heating}}{Q_{CSP} + L_{CO_2 compression} + L_{pump}} \quad (Eq.) 21$$

577 Each term of the KPI represents an energy and it is calculated by multiplying the thermal or
 578 mechanical power by the respective operating time.

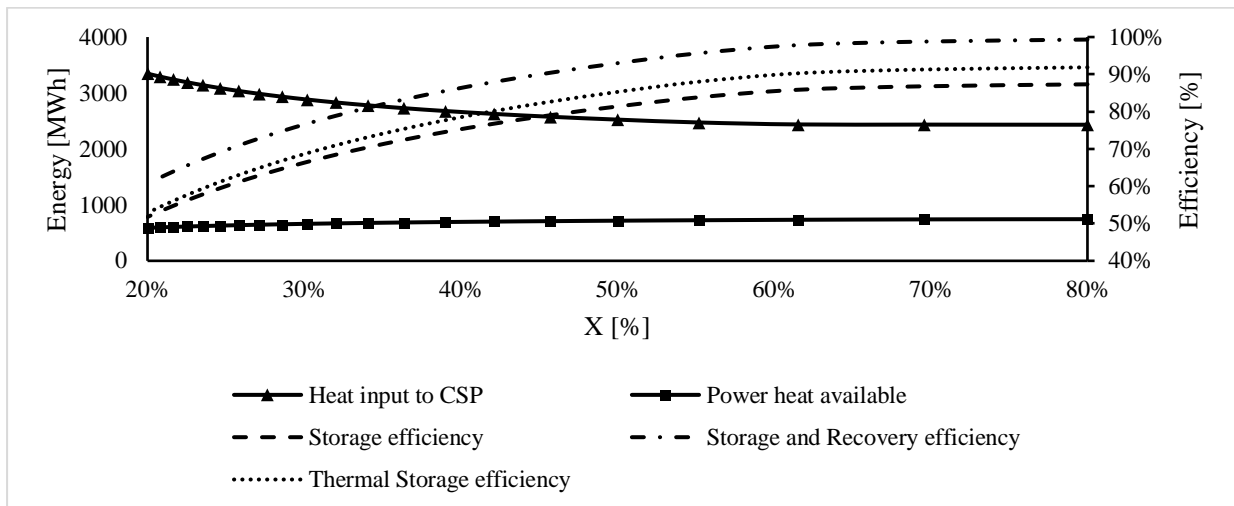
579 At first time, a parametric analysis to assay the pressure condition of carbonator reactor was
 580 performed (**Figure 17**) and it was visible that increasing carbonator pressure, the heat of reaction
 581 goes down (η_{TSE}) while it is highlighted that electric power due to expansion work of CO₂ drop
 582 off (η_{SE}).



583

584 **Figure 17: Trend of two KPI (Thermal Storage efficiency and Storage efficiency) function of carbonator**
 585 **pressure.**

586 The maximum differences in Thermal Storage efficiency (η_{TSE}) and Storage efficiency (η_{SE})
 587 increasing carbonator pressure are 0.6% and 2.6% respectively. As mentioned in previous
 588 section, carbonator pressure is set at 2 bar to ensure the circulation of gas in all storage system
 589 leading a reduction in the efficiencies mentioned above by 0.1% and 0.5% respectively.



590 **Figure 18: It is illustrated with whole line the thermal energy (left axis) of the heat provided by carbonator**
 591 **reactor (square indicator) and heat input to CSP power plant (triangle indicator). With the dash line is**
 592 **represented the three different efficiency of the storage system (right axis). These parameters are function of**
 593 **CaO conversion.**

595 **Figure 18** shows the comparison of the storage efficiency (right axis) with the energy stored and
 596 released with the change of the CaO conversion X. The efficiency of the storage system increases

597 with high values of released energy and low values of solar energy required. Storage and recovery
 598 efficiency is always higher than storage efficiency and thermal storage efficiency because it takes
 599 into account the heat at low enthalpy exchanged with the district heating and cooling network.
 600 The three KPIs (thermal storage efficiency, storage efficiency, storage and recovery efficiency)
 601 represented in **Figure 18** increase significantly with the increasing of X and they reach a value of
 602 91.9%, 87.3% and 99.3% respectively when CaO conversion is higher (X=80%). Therefore, it is
 603 better to work with a material having excellent conversion performance and recover the energy
 604 at low temperature to achieve very high levels of efficiency for a storage system.

605 Three other fundamental key performance indicators for the integrated system consider the power
 606 generated by the Rankine cycle turbines. In this case, the optical and thermodynamic efficiencies
 607 of the CSP were not considered in this analysis. The three KPIs are below defined:

608 *i. Integrated efficiency*

$$609 \quad \eta_{IE} = \frac{L_{Rankine}}{Q_{CSP}} \quad (\text{Eq.}) \quad 22$$

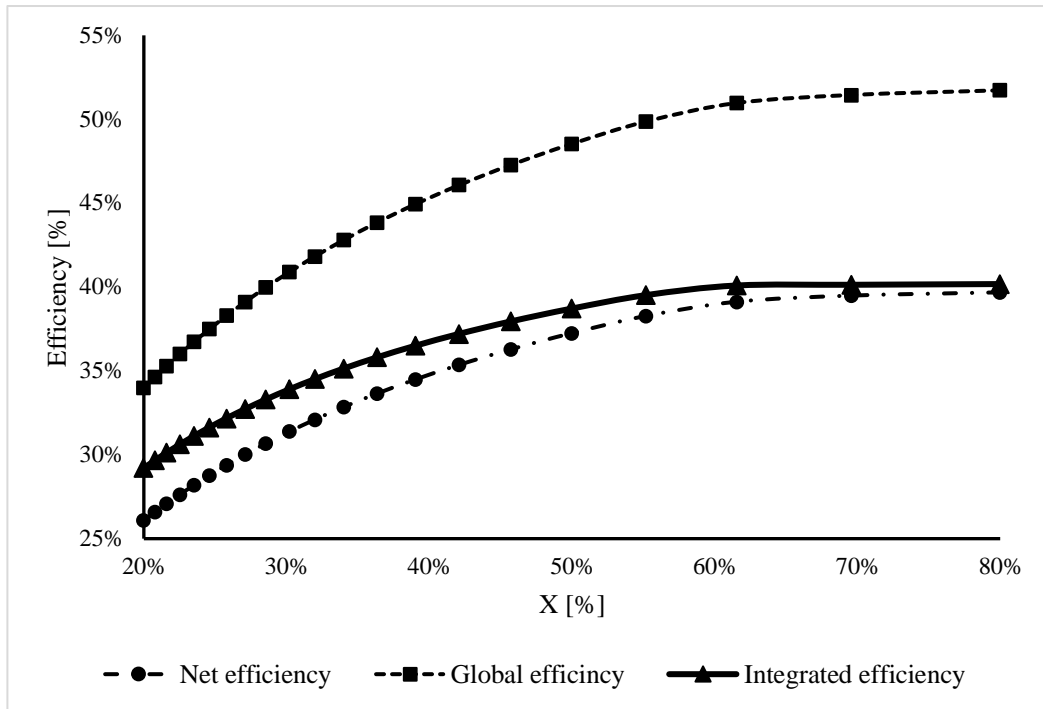
610 *ii. Net efficiency*

$$611 \quad \eta_{NE} = \frac{L_{Rankine} + L_{CO_2, expansion}}{Q_{CSP} + L_{CO_2, compression}} \quad (\text{Eq.}) \quad 23$$

612 *iii. Global efficiency*

$$613 \quad \eta_{GE} = \frac{L_{Rankine} + L_{CO_2, expansion} + Q_{district cooling} + Q_{district heating}}{Q_{CSP} + L_{CO_2, compression} + L_{pump}} \quad (\text{Eq.}) \quad 24$$

614 Figure 19 reports: (i) The integrated efficiency (solid line) defined as energy produced by
 615 Rankine over input energy from CSP; (ii) the net efficiency (dot-dash line) defined as the ratio
 616 of energy produced by Rankine and CO₂ work expansion over the heat gathered by the CSP and
 617 work required during CO₂ compression; (iii) the global efficiency (dot line) defined as the ratio
 618 of energy produced by Rankine plus CO₂ work expansion and energy heat and cool of secondary
 619 systems over the heat gathered by the CSP and work required during CO₂ compression.



620

621 **Figure 19: Efficiencies of the TC/CG–ES integrated with Rankine power cycle. Both efficiencies are strongly**
 622 **dependent of CaO conversion.**

623 Therefore, when the conversion degree X of the sorbent decreases, the material should be
 624 changed with fresh material in order to increase the efficiency of the system. At high conversion
 625 levels, the system efficiency increases, reaching almost 40% of integrated and net efficiency,
 626 exceeding 50% if we supply a district heating and cooling networks consider into global
 627 efficiency.

628 All the electrical and thermal power streams produced and consumed by the various components,
 629 and the values of the plant efficiencies at a fixed CaO conversion value set at 0.7 are summarized
 630 in **Table 5**.

631

Table 5: Main results obtained at a fixed CaO conversion value set at 0.7

Calciner side	Power Heat from CSP to calciner [MW]	-2432
	Daylight hours [h]	8
	Energy heat from CSP [MWh]	-19459
	Electric power to compress CO2 [MW]	-208
	Electric energy to compress CO2 [MWh]	-1665
	Power pump to water networking [MW]	-1,3
	Energy to pump water networking [MWh]	-10

	Power to district heating [MW]	232
	Energy to district heating [MWh]	1856
Carbonator side	Electric power from compressed CO ₂ [MW]	24
	Electric energy from compressed CO ₂ [MWh]	569
	Cool power [MW]	29
	Cool energy [MWh]	689
	Power to Rankine cycle [MW]	745
	Energy to Rankine cycle [MWh]	17877
	Rankine cycle	HP T1 [MW]
HP T2 [MW]		39
MP T1 [MW]		54
MP T2 [MW]		43
LP T1 [MW]		43
LP T2 [MW]		38
LP T3 [MW]		23
LP T4 [MW]		35
P1 [MW]		-0,1
P2 [MW]		-6
Power output from Rankine [MW]		326
Daily work [h]		24
Energy output from Rankine [MWh]		7818
Efficiency		Thermal Storage efficiency [%]
	Storage efficiency [%]	86.8
	Storage and Recovery efficiency [%]	98.8
	Rankine efficiency [%]	43.7
	Integrated efficiency [%]	40.1
	Net efficiency [%]	39.5
	Global efficiency [%]	51.5

632

633 **4.4 Conclusions**

634 A novel solution for solar energy storage by means of a hybrid thermo-chemical/compressed-gas
635 energy storage (TC/CG-ES) is presented in this manuscript. The solar energy is used to
636 decompose CaCO₃ into CaO and CO₂ at high temperature. The produced streams are stored at
637 ambient temperature. Solar energy is harvested directly into an innovative solar receiver (solid
638 particles fluidised bed) in which solar radiation collection and energy storage (calcination
639 reaction) occur simultaneously. The solar energy is stored in chemical form which can be used
640 in a different place and in a different time without heat loss overcoming the fluctuation of power

641 generation from solar energy. During energy release, CO₂ is expanded into a turbine and sent
642 into a carbonator where it reacts with CaO coming from silos, and releasing reaction heat at high
643 temperature, used for power production.

644 An integration with a conventional Rankine cycle rated 320 MWe is proposed. A pinch analysis
645 is performed to optimize these energy systems. A parametric analysis was carried out to evaluate
646 the reduction of plant efficiency when varying the main CaL process parameters (such as
647 carbonation extent, temperature and pressure of carbonation reactor).

648 With respect to molten salt based energy storage the CaL technology has these advantages: (i)
649 no heat loss (can be used as seasonal storage) while molten salts are sensible storage and therefore
650 there are thermal loss; (ii) storage temperature equal to environmental temperature (no issue of
651 solidification) while storage temperature of molten salts have to be higher than solidification
652 temperature; (iii) maximum temperature achievable very high ($T_{\text{Carb}}=830^{\circ}\text{C}$) while maximum
653 temperature of molten salts frequently used is 550°C ; (iv) high energy density (3.2 GJ/m^3) while
654 energy density of molten salt is 0.9 GJ/m^3 .

655 The use of CaL process with a conventional Rankine cycle makes this solution a good candidate
656 for the decarbonisation of the power sector reaching the higher values of Integrated efficiency,
657 Net efficiency (electric) and Gross efficiency (electric and thermal) equal to 40.1%, 39.5% and
658 51.5% respectively reaching the higher value of gross efficiency equal to 51.5% providing energy
659 to district heating and cooling network. The design of the heat exchanger network by means of a
660 pinch analysis and a parametric study focused on the efficiency of the system when changing the
661 main KPI (i.e. conversion CaO) were also performed.

662

Acronyms

CaL	Calcium Looping
CSP	Concentrated Solar Plant
ECO	Economizer
EVA	Evaporator
GHG	Green House Gas
HEN	Heat Exchange Network
HTF	Heat Transfer Fluid
KPI	Key Performance Indicator
PCM	Phase Change Material
RE	Recovery expander
RH	Re-heater
SC	Storing Compressor
SH	Superheater
TCES	Thermochemical energy storage
STES	Sensible thermal Energy Storage
UNFCCC	United Nations Framework Convention on Climate Change

Parameters

\dot{n} [mol/s]	Molar flow rate
c_p [(J kg)/K]	Specific heat capacity
G [kg/s]	Mass flow rate
h [kJ/mol]	Enthalpy
L [MJ]	Work
m [kg]	mass
P [bar]	Pressure
Q [MJ]	Heat
T [°C]	Temperature
t [s]	Time
W [MW]	Power
X [-]	CaO Conversion
ΔH [kJ/mol]	Enthalpy difference
ΔT [°C]	Temperature difference

ε [-]	Extent of reaction	664
η [-]	Efficiency	
Φ [MW _{th}]	Thermal power	
ν [mol/s]	Stoichiometric coefficient	

Subscripts

c	cold
calc	calciner
carb	carbonator
GE	Global efficiency
h	hot
HP	High pressure turbine
in	inlet
is	isentropic
LP	Low pressure
min	minimum
MP	Average pressure
NE	Net efficiency
out	outlet
R	reaction
react	reaction
ref	reference
reg	Regeneration system
SE	Storage efficiency
SRE	Storage and recovery efficiency

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