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

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Abstract

Solar energy is an intermittent resource and thus an energy storage system is required for practical applications of the collected solar irradiance. This work deals with the integration of a thermo-chemical energy storage (TCES) system based on the Calcium Looping (CaL) process with a concentrated solar tower power (CSP) plant. The objective of this work is the integration of a conventional 320 MWe Rankine cycle with a direct calcination for the energy harvesting. Particularly, this work addresses the use of CO_2 as the working fluid of a compressed–gas energy storage (CGES) system for hybrid energy storage with CaL process. The hybrid TC/CG–ES (Thermo–Chemical/Compressed–Gas Energy Storage) system can increase the competitiveness of the CSP with respect to conventional fossil-based power plants leading to a reduction in CO_2 emissions. The thermal integration with the Calcium Looping (CaL) system is optimized by means of the pinch analysis methodology. The obtained results show a reduction in the electrical efficiency of about four percentage points with respect to the conventional Rankine power cycle without CSP unit: the net electrical efficiency reduces from 43.7% to 39.5% while the global (thermal and electrical) efficiency of the plant reaches the peak value of 51.5% when low enthalpy energy is recovered (e.g. district heating network, district cooling network). The paper highlights the importance of the thermochemical CaO based material. With a conversion of CaO to $CaCO_3$ of 80% the storage efficiency defined as the ratio of the energy released during the carbonation and the CO_2 expansion to the energy collected by the solar field and required during the CO_2 compression is 87.3%.

Keywords

Energy Storage; Calcium Looping; Thermo–Chemical/Compressed–Gas Energy Storage; Use of compressed CO_2, Concentrated Solar Power (CSP); Rankine power cycle.

Highlights

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

1 Introduction

Climate change represents a critical issue for our planet and it is time to intensify the efforts of the researchers and scientists to mitigating the forthcoming impacts. For this purpose, on 12 December 2015, the nations that are members of UNFCCC reached an agreement with the aim to limit the global warming well below 2.0°C before pre-industrial level and try to reduce it down to 1.5°C [1]. In order to reach the ‘2°C target’, only 720 Gt of CO_2 can be emitted into the atmosphere from 2018 to 2100; according to [1] the current rate of CO_2 emission is 32.5 Gt/year.

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

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

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

Different technologies are used to store energy from CSP plants:

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

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

- Phase-change materials (PCM): The quantity of energy stored is highly dependent on the enthalpy of fusion (Δh_{fusion}) and the mass of material. The energy can be stored also in sensible form. Latent energy storage materials (inorganic salts, metallic) which can be coupled with system at very high temperature can have a phase change temperature between 579°C (Aluminium alloys) and 842°C (Fluorides salts) [7].

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

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

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

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

Thermochemical storage systems have several advantages :(i) The energy density is about two to five times higher than PCM and STES systems. A conventional STES, consisting of two tanks of molten salt based on nitrate (60% $NaNO_3$ - 40% KNO_3) with the approximate hot and cold temperatures between 565°C and 290°C has a storage capacity of 0.731 GJ/m^3 [9]. Latent energy storage have the advantages to provide heat at constant temperature, the carbonate salts (e.g. Li_2CO_3) have a high fusion temperature 726°C with a storage density of 1.34 GJ/m^3 [7]. Instead, this work proposes a thermochemical storage based on calcium looping process, with a reaction temperature of 895 °C and the energy storage density can reach 3.2 GJ/m^3 [10]; (ii) Since there is negligible thermal loss during storage via CaL, this technology can be considered as a seasonal storage unlike the others which are used more as daily or weekly storage; (iii) The heat of reaction is discharged at constant and high temperature.

The CaL process as energy storage have been proposed in the scientific literature mostly integrated in a tower solar. In [11] a calciner assisted by CSP to capture CO_2 from flue gas into carbonator reactor was proposed whereas in [12] [13] [14] the authors have conducted a comparison between closed and open CO2 based Brayton cycles with a conventional reheat Rankine cycle each of the three cycles equipped with a CaL energy storage system fitted with an indirect calcination reaction. Considering 10% of thermal dispersion in carbonator reactor, ΔT_{min}=10°C, 1% pressure drop in each heat exchange and X=0.5 (average CO_2 conversion) they have obtained: (i) 35.5% with reheat Rankine cycle; (ii) around 32% with sCO_2 Brayton cycle; (iii) 39% with a combined cycle that use the integration of CaL process with CO_2 Brayton and conventional Rankine cycles. However, direct expansion of CO_2 at the exit of the carbonator reactor is not recommended because it may contain solid particles that would damage the blades of the turbines placed downstream.

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

2 Calcium Looping as energy storage system

2.1 Fundamentals of Calcium Looping process

Calcium Looping (CaL) is a cyclic chemical process that comprises two key reactions: (i) calcination of $CaCO_3$ as reported in Eq. 4 and (ii) carbonation of CaO as reported in Eq. 5.

$$CaCO_3 \rightarrow CaO + CO_2 \; \Delta H^0_{298K} = +182.1 \frac{kJ}{mole} \qquad \text{(Eq.) 4}$$

$$CaO + CO_2 \rightarrow CaCO_3 \; \Delta H^0_{298K} = -182.1 \frac{kJ}{mole} \qquad \text{(Eq.) 5}$$

The main advantages of the CaL process is the low market price (9 €/ton [13]) of the CO_2 acceptor material and the absence of negative impacts for the environment and the health of human beings: CaO from naturally occurring materials (e.g. limestone or dolomite) are widely available and harmless towards the environment with several outlet market for spent materials (iron, steel and cement industries). For instance, commercial limestone rock generally contains more than 90% of calcium carbonate.

Shimitzu et al. [15] proposed for the first time the reaction of CaO with CO_2, i.e., the calcium looping process CaL, with the main goal of decarbonizing flue gas. Since the calcination reaction is endothermic, the heat of reaction is usually supplied by oxy-fuel combustion into the reactor. CaL process is gaining considerable interest as thermochemical energy storage process where calcination (Eq.4a) is the process for energy gathering and carbonation (Eq.4b) is the step for energy release. The carbonator reactor operates in a temperature range between 600 – 850°C with an operating pressure ranging from 1 bar to 3 bar when outgoing gas is not expanded in a gas turbine [13]. Since the carbonation reaction is an exothermic reaction, heat is released and steam can be produced to generate electricity by a submerged heat exchange in a fluidised bed carbonator. The produced $CaCO_3$ can be stored and successively transported to the calciner reactor to gather the excess of energy. Into the calciner reactor, the equilibrium temperature of the system CaO-$CaCO_3$-CO_2 is approximately 895 °C under atmospheric pressure. Therefore, the decomposition of $CaCO_3$ into CaO must take place at temperature above 895°C in case the molar fraction of CO_2 is 1 and the operating pressure of the calciner is 1 atm.

The process is illustrated in Figure 1.

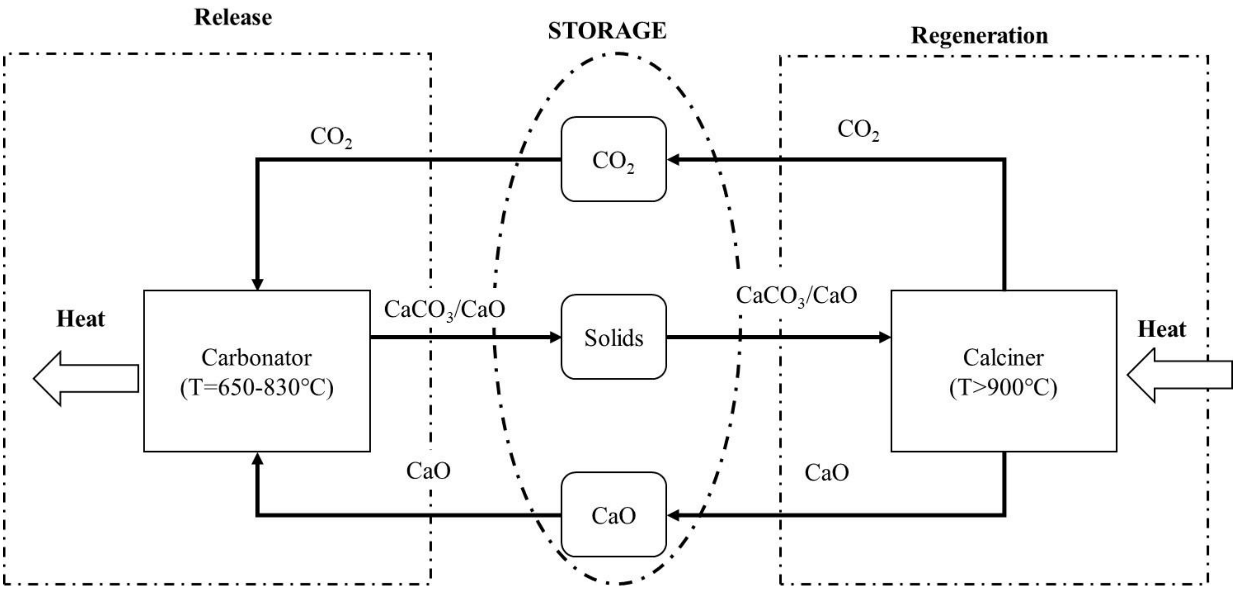


Figure 1: The Calcium Looping process used as thermochemical storage system. Calcium oxide and carbon dioxide react together into the carbonator reactor releasing heat of reaction at high temperature when energy is necessary. The spent material ($CaCO_3$) and unreacted CaO are, at the first time, stored into a silo. These materials are transported to the calciner to store excess of energy at high temperature with the inverse reaction.

It is possible to use the heat released during the carbonation at high temperature (650 – 830 °C) in order to produce steam to be expanded in a conventional turbine and generate electricity. Direct expansion of CO_2 at the exit of carbonator and calciner is not recommended because it may contain solid particles that would damage the blades of the turbines placed downstream.

It is demonstrated from several experimental works that calcite and dolomite can be used as sorbent for high temperature CO_2 capture [16]. However, it is also known that CaO-based solid sorbent are never fully utilized displaying the existence of maximum degree of carbonation conversion [16].

Stendardo and Foscolo [16] studied the multi-cycle carbonation/calcination reaction of the naturally-occuring dolomite. During different experiments they observed progressively decline of CaO conversion, which drops from 85% to 65% after only 4 cycles. A good strategy could be the replacement of natural dolomite with synthetic $CaCO_3$ or doped limestone that maintain a high degree of sorbent capture capacity. There are many papers in the literature focused on the research of synthetic Ca-based sorbents that enhance conversion in a multi cycling experiments

[17]. Chen et al. [18] showed that the CO_2 capture capacity of the new materials declines gradually and at a much slower rate than original limestone during multi-cycle experiments. The addition of alumina has slowed down the drop in CaO conversion allowing up to 70% percent of CO_2 capture capacity after 50 cycles.

The CO_2-rich stream leaving the regenerator is cooled, compressed and stored also for long period (seasonal storage). The produced CaO is cooled and stored in a conventional silo. The two stored materials are recombined into the carbonator reactor operating at high temperature (~800°C) to provide heat to a Rankine power cycle. We provide detailed mass and energy balances of the solar power plant and we calculate the performance of the same plant after energy integration of various heat sinks/sources of the overall process. This work paves the way for further demonstration of the concept.

2.2 Integration of CaL with Concentrated Solar Plants

The most common energy storage system for CSP applications is based on molten salts. The main used components are nitrates, chlorides, fluorides and carbonates. The fluoride salts have high heat storage capacity (2.3 GJ/m^3). However, they are very expensive and toxic [19]; chlorides have a high heat of fusion and are very cheap but highly corrosive [20]; carbonates have high temperature of phase change but high viscosity and they easy decay [21]; nitrate salts have low chemical reactivity, low corrosiveness and have low cost [7] and therefore suitable for thermal storage material in CSP. The issues of all the above-described materials are two: (i) the low melting point limits the efficiency of the system, in fact when the solar energy is not directly collected, the temperature of the storage has to be higher than melting temperature for each salt and therefore storage have to be heated; (ii) the low maximum temperature achievable that limits the (thermal) integration between the CSP field with the thermal storage system and the power cycle to temperature around 500-600 °C. This limitation is due to degradation of molten salts at high temperature. The coupling of CSP with CaL process avoids this problem enabling operating temperatures higher than 700°C in carbonator reactor reducing the size of heat exchanger due to higher temperature difference (maximum temperature of the Rankine heat transfer fluid equal to 538°C). According to thermodynamic equilibrium and kinetics, high temperature is necessary to drive the calcination reaction when operating under high CO_2 concentrations (~900°C at 1 atm) [22]. Nevertheless, the use of superheated steam or easily separable gas in calcination environment decrease the CO_2 partial pressure and therefore, the calcination temperature goes down to 700-750 °C as shown in **Figure 2** :

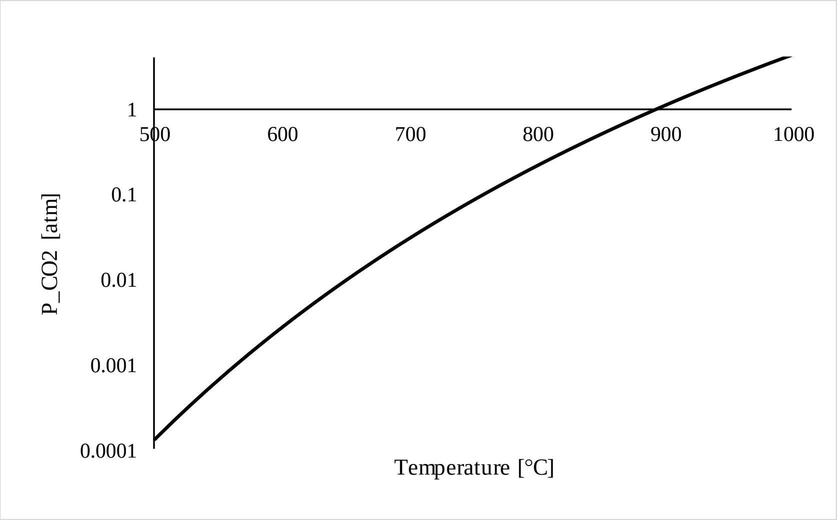


Figure 2: Decomposition pressure of Carbon dioxide over calcium carbonate at different operating temperature [22]

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

2.2.1 Indirect energy storage

In the indirect energy solution, the solar energy is gathered and transferred to a second medium (Ca-based materials) for its storage. Generally, the gathering medium is a fluid (heat transfer medium, HTF) whereas the storage medium consists of either liquid or solid materials. Several configurations have been proposed to harvest solar radiation. Therefore, several prototypes of solar receiver have been developed as rotary kilns, cyclone atmospheric reactor, falling particle receiver and fluidised bed reactor. As shown in Figure 3 , solar energy is collected into a central tower receiver and transferred to a calciner by HTF, which fluidises the $CaCO_3$/CaO particles. In order to not dilute the CO_2 leaving the calciner, the selected HTF is a pure CO_2 stream.

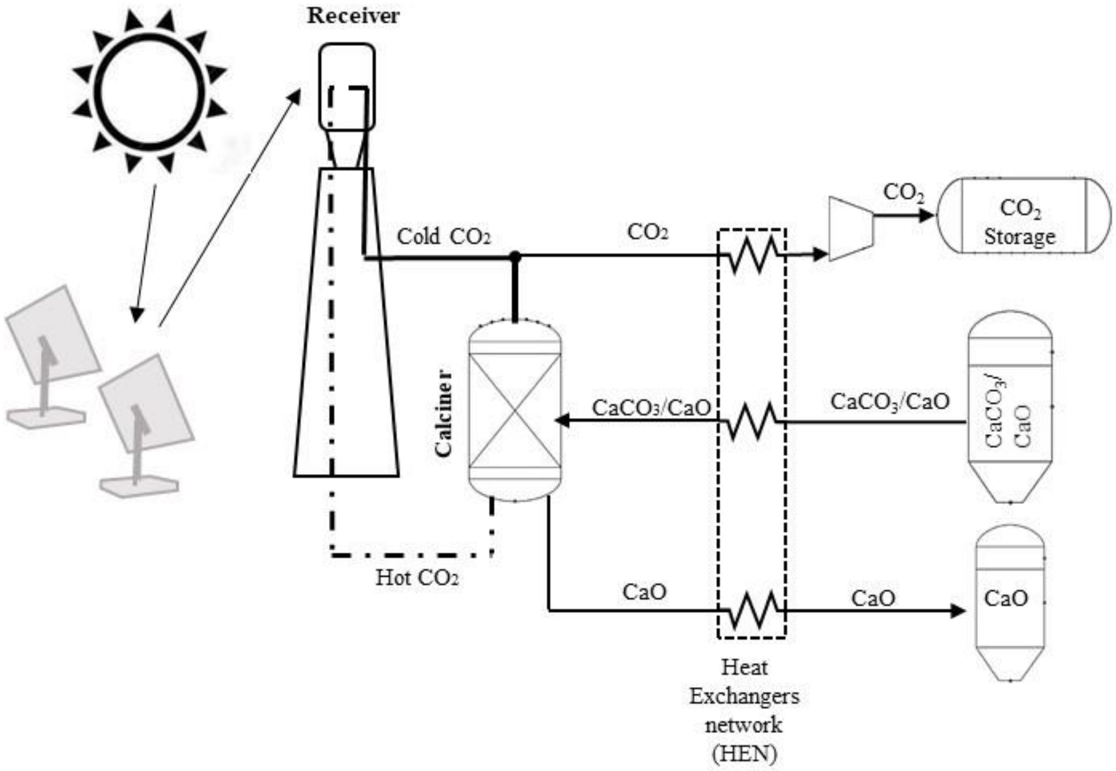


Figure 3: Integrated Solar Calcium Looping IS-CaL with indirect calcination reaction. Solar energy is concentrated into a solar receiver up to the tower. The HTF used into this system is the CO2 which has the task to provide the heat necessary for the regeneration of the spent sorbent and to fluidize the calciner.

2.2.2 Direct energy storage

In the direct energy storage solutions, the media (Ca-based material and CO_2) used for storing the energy are as the same as the materials to collect the solar energy into the innovative solar calciner reactor. An example of this solution is the gathering of the solar energy and its storage via a solid particles fluidised bed [23]. The solar energy reflected by the heliostats are concentrated in a single point of the reactor by means of a beam-down central reflector (see Figure 4). Therefore, it is possible to have a reactor at a lower height than the classic solar towers, reducing the problems of mechanical strength of the structure. Despite the optical losses due to another reflector, thermal losses are strongly reduced and therefore higher temperature can be reached [23] [24] [25] [26]. In order to not dilute the CO_2 to store, the fluidised bed will be fluidised with a recirculation of high-concentrated CO_2 stream.

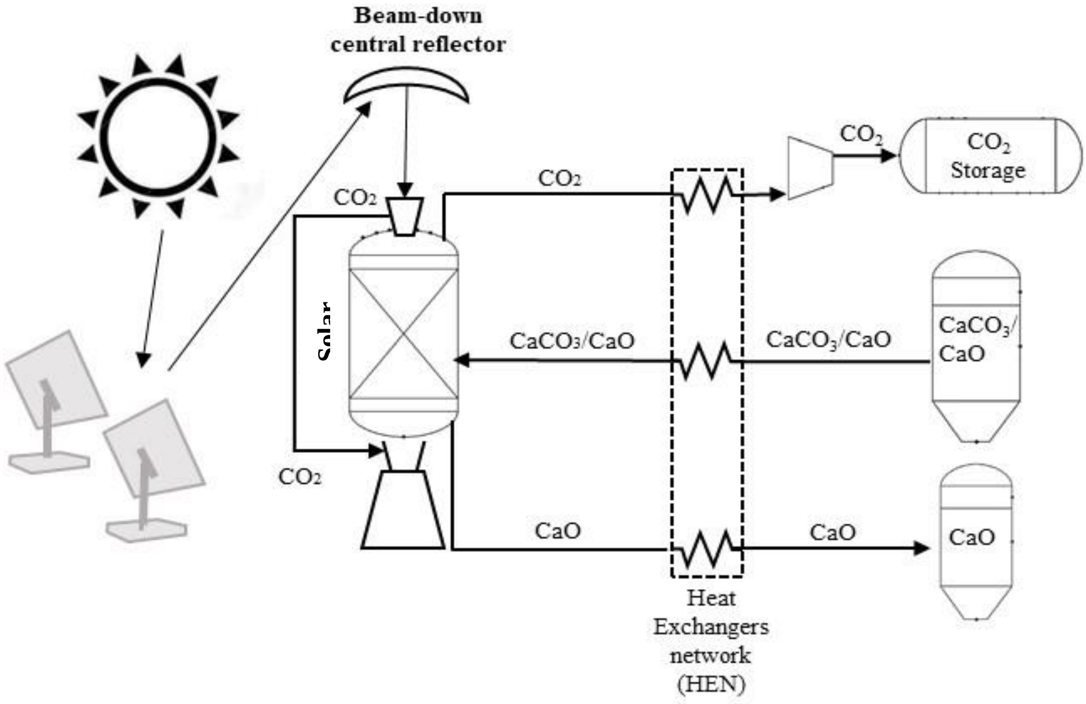


Figure 4: Integrated Solar Calcium Looping IS-CaL with direct calcination reaction into solar calciner. Solar calciner is a solid particles fluidised bed reactor with CO_2 to separate easily the product of calcination reaction. The compounds are stored at ambient temperature to avoid thermal losses.

In this work, a direct solution based on a solid particles fluidised bed solar calciner has been analysed and investigated Figure 4. The energy is stored in form of chemical compounds (CaO and CO_2) that, before reaching the storage tanks, are cooled down by passing through heat-recovery heat exchangers heating up the calcium carbonate.

Solids entering the solar calciner, that are CaCO3 and unreacted CaO, are pre-heated through a heat-exchanger network (HEN) by the hot products (i.e. CaO, CO_2) leaving the calciner. The solar calciner includes several cyclones and other components that are able to separate the fluidising $CO_2$and product CO_2 from the particles.

The excess of solar energy stored in the form of chemical products can be used to generate heat and electricity with zero CO_2 emissions, solving the problem of dispatchment and intermittency of renewable energy.

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

3 Rankine cycle assisted by CaL process

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

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

3.1.1 **Energy storage**

Energy storage takes place in the calciner in which decomposition of $CaCO_3$ into CaO and CO_2 occurs at high temperature (900 °C) by means of solar energy input. The solar calciner is a fluidised bed where the fluidising agent is a pure stream (i.e., $CO_{2,\text{fluid}}$) and the solid bed is mainly composed of $CaCO_3$ and CaO. The two products of calcination reaction (CO_2 and CaO) are cooled and stored at ambient temperature to avoid heat losses. Solids entering in the solar calciner, which consist of $CaCO_3$ and unreacted CaO, are pre-heated via a heat-exchanger network (HEN1) by the hot products (i.e. CaO, CO_2) leaving the reactor. CO_2 stream is cooled, compressed via the storing compressor (SC) at supercritical conditions and directed to a storage tank. The cooled CaO stream is transported to a conventional storage site (e.g. silos). Details of the SC component are provided in section 2.2. Part of the excess of solar heat can be used directly to produce steam via the stream $CO_{2, HTF\ calc}$. This option has not been taken into consideration in the remainder of the paper.

3.1.2 **Energy release**

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

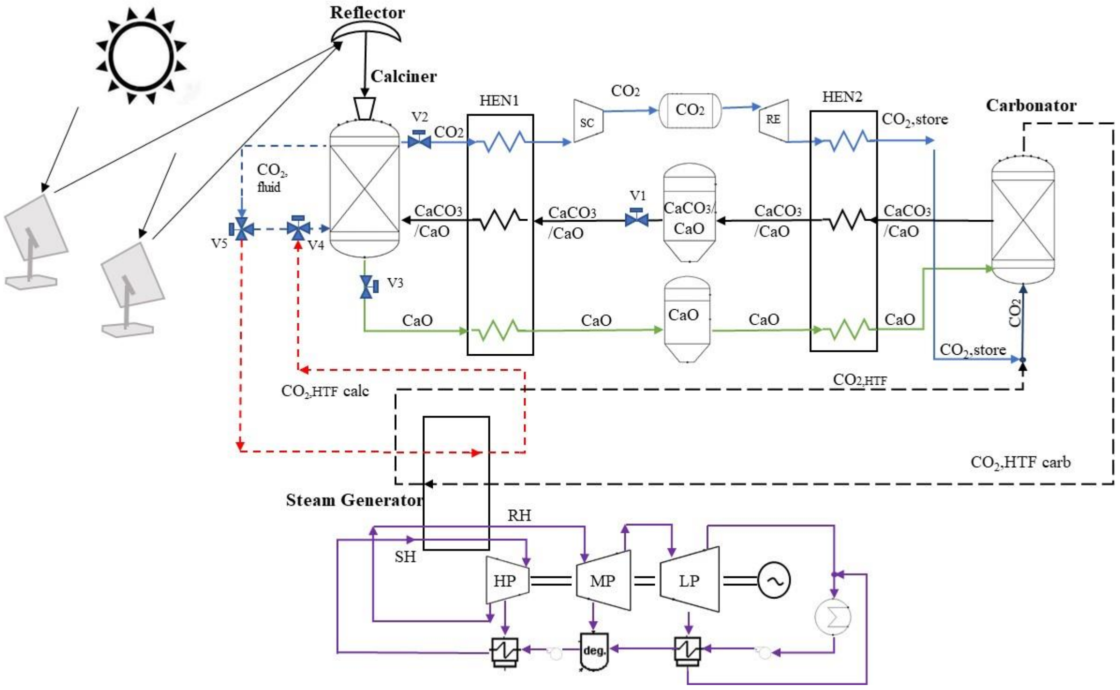


Figure 5: Thermo–Chemical/Compressed–Gas Energy Storage (TC/CG-ES) coupled with a conventional Rankine power cycle. During sunlight solar energy can be transformed directly in electricity or stored in chemical compound. There are three operational phase: (i) Only electricity is produced; (ii) only charging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

3.2 Heat recovery for the CO_2 storage site

The CO_2 is stored at 75 bar by a group of five compressors as shown in Figure 6. The CO_2 is stored at supercritical condition to reduce the storage volume [13]. Each compressor has a pressure ratio of 2.37 and an isentropic efficiency of 0.83. Each compressor is followed by an intercooler to minimize the compression work. The heat collected by the cooling system of the compression is used to feed a district heating network. Inside each individual intercooler water enters at 60°C and exits at 90°C at a pressure of 4 bar. Subsequently it is pumped up to 10.3 bar and sent to the district heating network as is common to do [27].

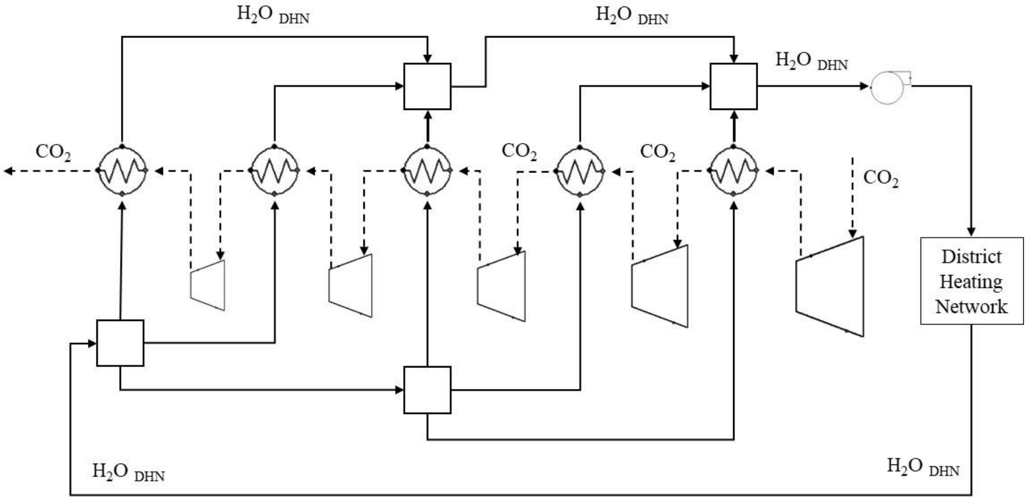


Figure 6: Train of five compressors with five inter-coolers. The heat at low temperature provided during compression, supply a district heating network.

From the storage unit (see Figure 5), the CO_2 stream feeds the carbonator reactor to react with calcium oxide. The expansion of previously stored CO_2 supplies useful work and provide efficiently cooling power. The expansion from 75 to 2 bar requires the use of inter-heating expansion to avoid the condensation of CO_2 and protect the turbine blades as showed in Figure 7. This Cooling system provides water at 6 °C and the same return into inter-heating at 12 °C.

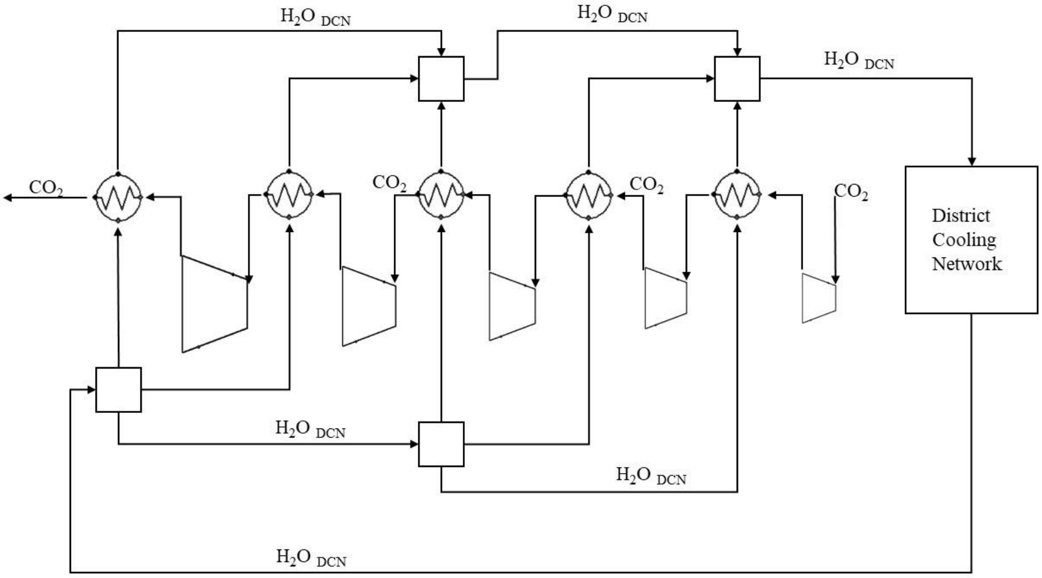


Figure 7: District cooling network used to avoid the condensation of the CO_2 and associate danger for the blade of turbine. The water used into the inter-heating at 12°C, is cooled until 6°C.

During heat release, CO_2 previously expanded, CaO from reservoir and the CO_2 used as heat transfer fluid are heated and then come into carbonator reactor where the release of energy occurs (see Figure 5). Under favourable conditions in the carbonator (P= 2bar; T= 850°C), CO_2 and part of CaO react in an exothermic reaction and the heat produced at higher temperature is transferred at power system throughout the $CO_{2,\ HTF}$. The solids stream composed of $CaCO_3$ and un-reacted CaO, is cooled and stored inside tank almost at ambient condition.

The carbonator reactor is connected to power cycles indirectly by CO_2 which acts both as fluidising agent and heat transfer fluid. The CO_2 at high temperature does not produce work directly in turbine. Therefore, the pressure of the carbonator reactor is set a 2 bar to overcome the pressure drops in the reactor and in the various heat exchangers however, it is not higher than 2 bar because increasing pressure, the storage efficiency goes down as it is showed in 4.3 section.

3.3 Energy and mass balance equations

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

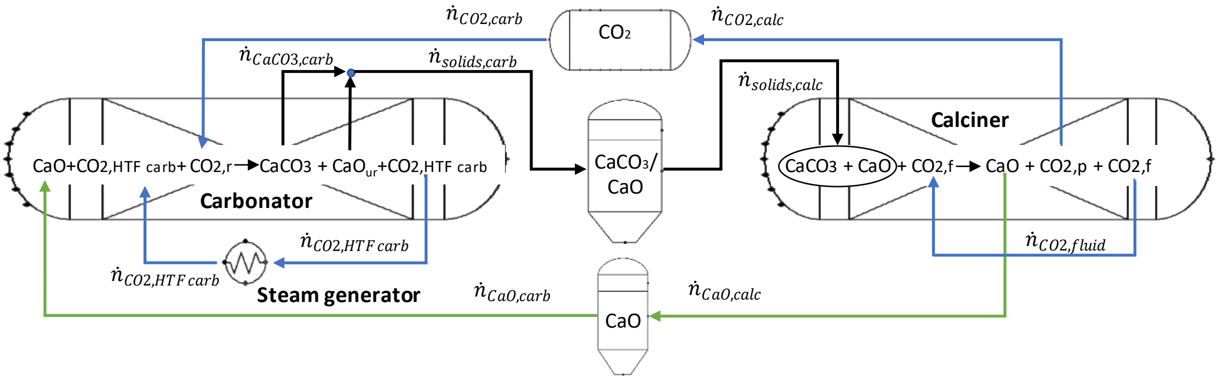


Figure 8: Molar balance schematic of the Calcium Looping process. In the right side calcination reaction and energy storage happen; In the other side CaO and CO_2 react into carbonator reactor and the heat of reaction is transported by the CO_2 used as HTF.

Into carbonator reactor, a carbonation reaction at 830°C and 2 bar occurs. Here the CO_2 that coming out from pressurize storage ($\dot{n}_{{CO_2}_{r,carb}}$) react with the CaO ($\dot{n}_{{CaO}_{carb}}$). Into the reactor the excess of CO_2 which acts as heat transfer fluid ($\dot{n}_{{CO_2}_{HTF\ carb}}$) flows. Calcium oxide does not react completely with the CO_2 due to loss of reactivity during different cycles and depending on the thermodynamic condition and residence time. The flow rate of the unreacted CaO is $\dot{n}_{CaO\ ur}$. Thus only part of the CaO reacts to produce $CaCO_3$ ($\dot{n}_{CaCO_3\ carb}$) and therefore solids ($\dot{n}_{solids_{carb}}$) at the carbonator outlet are composed of $CaCO_3$ and unreacted CaO. Indeed, CaO-based solid sorbent are never fully utilized displaying the existence of maximum degree of carbonation conversion, nevertheless it is fortunately possible regenerate all the calcium carbonate [16].

$$\dot{n}_{CaO_{carb}} + \dot{n}_{CO_2\ r,carb} + \dot{n}_{CO_2\ HTF\ carb} \rightarrow \dot{n}_{solids_{carb}} + \dot{n}_{CO_2\ HTF\ carb} \qquad \text{(Eq.)6}$$

$$\dot{n}_{solids_{carb}} = \dot{n}_{CaCO_3\ carb} + \dot{n}_{CaO\ ur} \qquad \text{(Eq.) 7}$$

The $CaCO_3$ phase contained in the solids stream ($\dot{n}_{solids_{calc}}$) entering the calciner will be completely regenerated to produce calcium oxide ($\dot{n}_{CaO_{calc}}$) and carbon dioxide ($\dot{n}_{CO_2\ calc}$) that will be compressed and stored.

$$\dot{n}_{solids_{calc}} + \dot{n}_{CO_2\ HTF\ calc} \rightarrow \dot{n}_{CaO_{calc}} + \dot{n}_{CO_2\ calc} + \dot{n}_{CO_2\ HTF\ calc} \qquad \text{(Eq.) 8}$$

$$\dot{n}_{solids_{calc}} = \dot{n}_{CaCO_3\ calc} + \dot{n}_{CaO\ calc} \qquad \text{(Eq.) 9}$$

One of the most important parameters for this technology is the average CaO conversion (X) useful to quantify the amount of CaO converted to $CaCO_3$ during carbonation reaction. This reaction extent is defined as follows:

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

In order to guarantee a steady state condition during the storage and release of energy, the solid material regenerated into calciner reactor has to be enough to produce the required heat during carbonation. The carbonator has to release the required energy for the whole operational time whereas the calciner is able to regenerate the solid material for a shorter time (eight hours approximately) when the solar energy is gathered. As a consequence, an adequate storage volume is required to store solids (i.e. CaO and $CaCO_3$) and CO_2 to continuously feed carbonator during the energy demand. In order to guarantee a steady state condition during power production, the sorbent regenerated into calciner reactor has to be enough to produce heat into carbonator side. Therefore, the following equation has to be satisfied:

$$\int_0^{24} \dot{n}_{CaCO_3\,carb}(t)\,dt = \int_0^{8} \dot{n}_{CaO_{calc}}(t)\,dt \qquad \text{(Eq.) 11}$$

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

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

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

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

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

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

$$\dot{n}_{CO_2\,HTF\,calc} \cdot \left[h_{CO_2 HTF}(T_{calc}) - h_{CO_2 HTF}(T_{in})\right] + \dot{n}_{solids_{calc}} \cdot \left[h_{solids_{calc}}(T_{calc}) - h_{solids_{calc}}(T_{in})\right] + \varepsilon_{calc}\,\Delta H_{react}(T_{calc}) = \;\; = \Phi_{CSP} \qquad \textit{(Eq.) 14}$$

$$\varepsilon_{calc} = \frac{\dot{n}_{CaCO_3\,calc}{}^{out} - \dot{n}_{CaCO_3\,calc}{}^{in}}{\nu_{CaCO_3}} \qquad \textit{(Eq.) 15}$$

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

$$\left(\dot{n}_{CO_2\,HTF\,carb} + \dot{n}_{CO_2\,r,carb}\right) \cdot \left[h_{CO_2}(T_{carb}) - h_{CO_2}\left(T_{CO_2\,in}\right)\right] + \dot{n}_{CaO_{carb}} \cdot \left[h_{CaO\,carb}(T_{carb}) - h_{CaO\,carb}(T_{CaO\,in})\right] + \varepsilon_{carb}\,\Delta H_{react}(T_{carb}) = \Phi_{waste} \quad \text{(Eq.) 16}$$

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

With the heat of reaction defined as:

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

Mass and energy balance are represented in Figure 9.

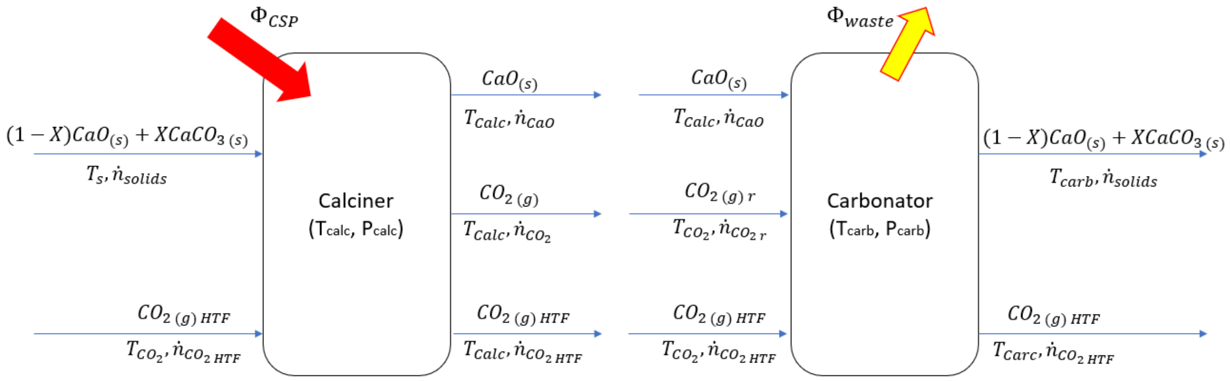


Figure 9: Energy balance of the storage system focused on the main critical reactors.

4 CaL process integrated with Rankine power cycle

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

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

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

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

The use of the CaL process in a CSP allows storing the excess of renewable energy by producing chemical compounds (i.e. CaO and CO_2). An indirect coupling of CaL to a Rankine cycle for generating power was analysed. Thermochemical storage must provide the necessary reagents so that the exothermic reaction supplies the heat requirement to the steam.

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

- Water evaporation occurs inside the water-tube walls (EVA) that absorb part of the heat of reaction;
- At the exit of fluidized bed, the CO_2 used as a heat transfer fluid (HTF) enters the superheater (SH) at 830°C, heating the steam at high pressure up to 538°C;

- then it enters the re-heater (RH), heating the medium pressure steam (about 37 bar) up to 538°C;
- Finally, the $CO_{2\ HTF}$ enters the economizer, heating the liquid water up to 267 °C and coming back to the carbonator at 287°C;

It was analysed the case in which Rankine power cycle was fed only with the carbonator. To optimize the heat exchangers network of (HEN), a pinch analysis of the storage system integrated with the Rankine cycle is performed.

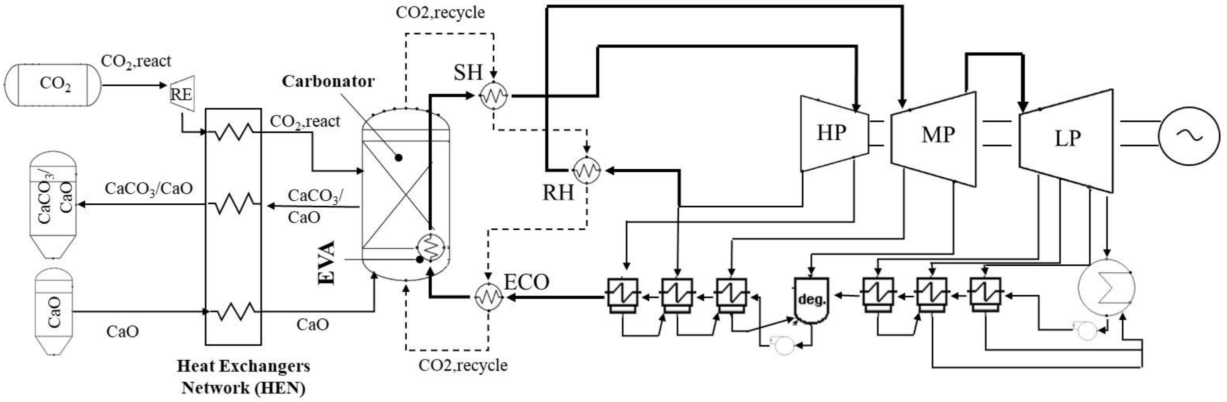


Figure 10: Release of energy via TC/CG–ES integrated with Rankine power cycle. The $CO_{2,recycle}$ fluidises the carbonator reactor and transfer heat to Rankine cycle.

4.1 Optimisation of the heat exchangers network

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

The analysis will be carried out separately for the two sides of the storage system (i.e. heat storage side and heat release side). The storage area composed of silos and pressurised tank of CO_2 is placed in the between of the calciner and carbonator in order to be able to separate not only temporally but also physically the storage (calciner) from the release (carbonator) of energy.

The first step of the analysis consists in identifying the components of the system and the related entering or exiting fluids. The energy storage system is composed of the reactor itself in which the calcination reaction occurs and the CO_2 compression system. The latter consists of five compressors with the relative inter-cooling system that exchanges heat with water acting as heat transfer fluid in the district heating network. The CO_2 compression system is reported as SC in Figure 5 and Figure 12.

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	CO2	HOT	900	20	594,13	0,66	582,4
3	CO2	HOT	70	20	594,13	2,67	133,4
4	CaO	HOT	900	20	946,3	0,88	770,6

Four fluid streams are identified (see **Table 2**), three of which are hot streams (i.e. (2) CO_2 leaving the calciner; (3) CO_2 leaving the compressor; (4) CaO leaving the calciner) and one cold stream (solids stream entering the calciner). The only cold fluid is made up of solids (i.e. X $CaCO_3$ and (1-X) CaO) that will be sent to the calciner in which a full regeneration of the sorbent takes place. A fixed value of CaO conversion to $CaCO_3$ (X=0.7) has been used.

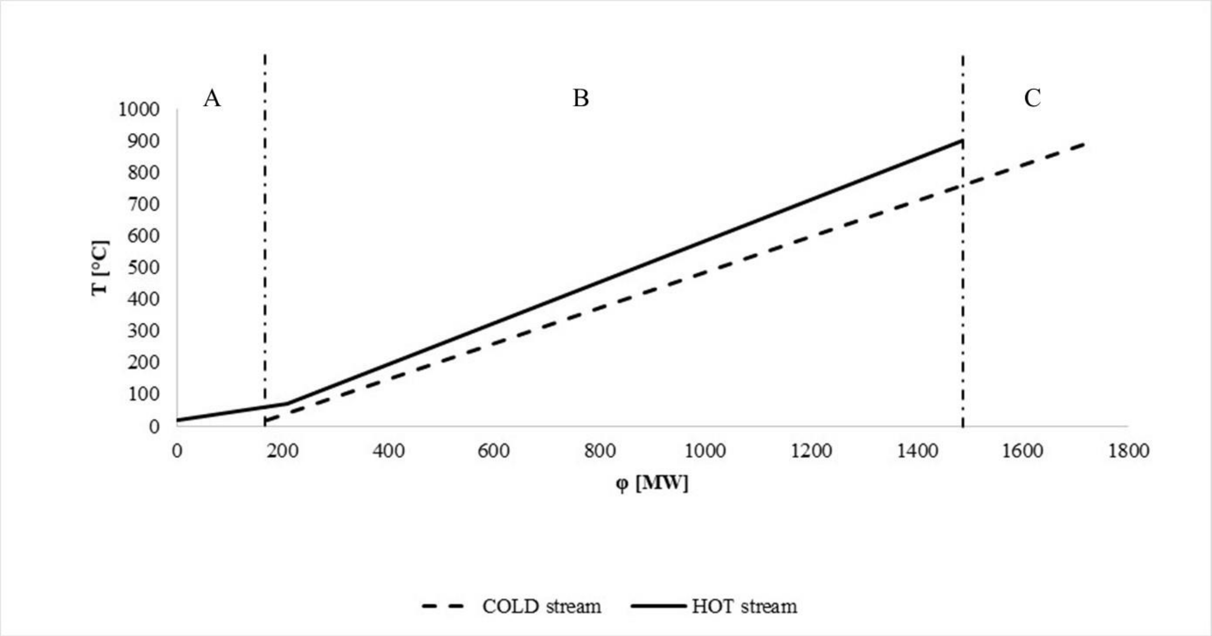


Figure 11: Composite curve of the solar calciner side. Section A represents the excess of heat at low temperature; in section B the hot streams provide heat to cold streams; in section C there aren't hot streams and the heat enough is provided by CSP to cold streams

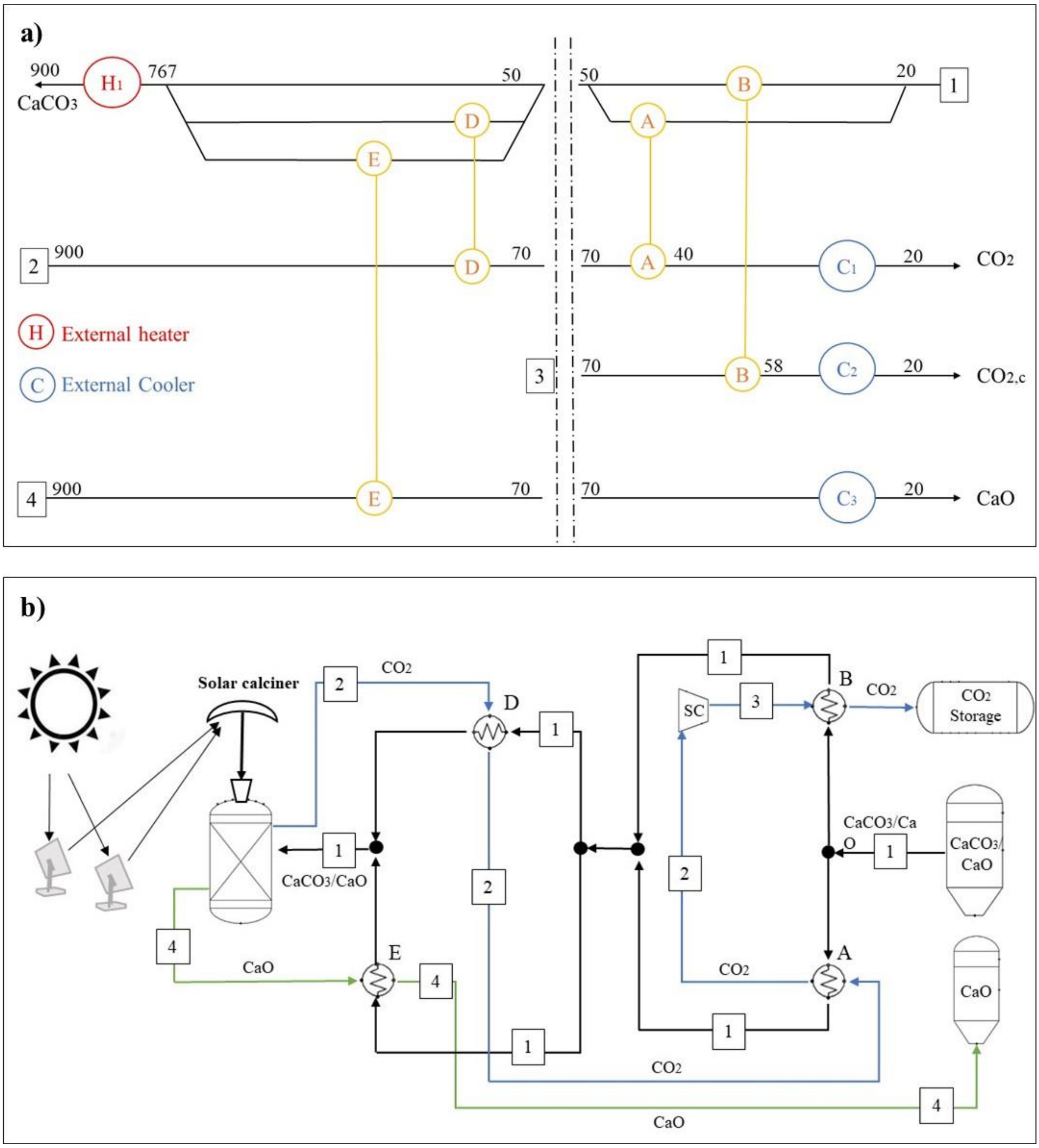


Figure 12: a) Minimum energy consumption network inferred from the pinch analysis in the calciner side. The values of temperature level are reported in degree Celsius. b) Plant configuration (calciner-side) resulting from the pinch analysis

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

CO_2 will be provided also by the CSP (2194 MW). The configuration of HEN, the phase change fluids and chemical reaction were treated following the methodology described in [29].

Following the analysis thoroughly performed for the energy storage, the pinch analysis for the carbonator section was also performed (energy release). The energy release section is mainly composed of two devices: (i) the carbonator in which the carbonation reaction occurs, and (ii) the turbine train in which compressed CO_2 is expanded from 75 to 2 bar. Through the expansion of CO_2 in the RE component (see Figure 5), it is possible to produce both power and cooling. After each expansion stage, the carbon dioxide is at the temperature of about -30 ° C and must be heated in order to avoid condensation and the consequent breakage of the blades. The heat released by the water in a refrigerant cycle (see Figure 7) is transferred to the CO_2 which is heated from -30 °C to 7 °C. The refrigerant fluid is sent to a second heat exchanger where it is heated up and an external environment is cooled (e.g. hospital). The size of the power chiller is approximately 29 MW. **Table 3** shows that the pinch analysis which accounts for ten fluids, two of which are hot streams leaving the carbonator at a temperature of 830 ° C and the remaining are cold streams to be heated as reported in Figure 14.

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

The cold fluids are (see ***Figure 14***): (7) the compressed CO_2, which is heated before entering the turbine in order to produce more power, (8) the CO_2 at the end of expansion, which temperature between 7 ° C to 287 ° C (minimum temperature of recirculation CO_2), (9) the CO_2 entering the reactor ranging from 287 ° C to the carbonation temperature, (10) CaO heated from ambient temperature to carbonation temperature, and finally (3-6) the working fluid of a conventional Rankine cycle, which is subjected to preheating, evaporation, overheating and re-heating.

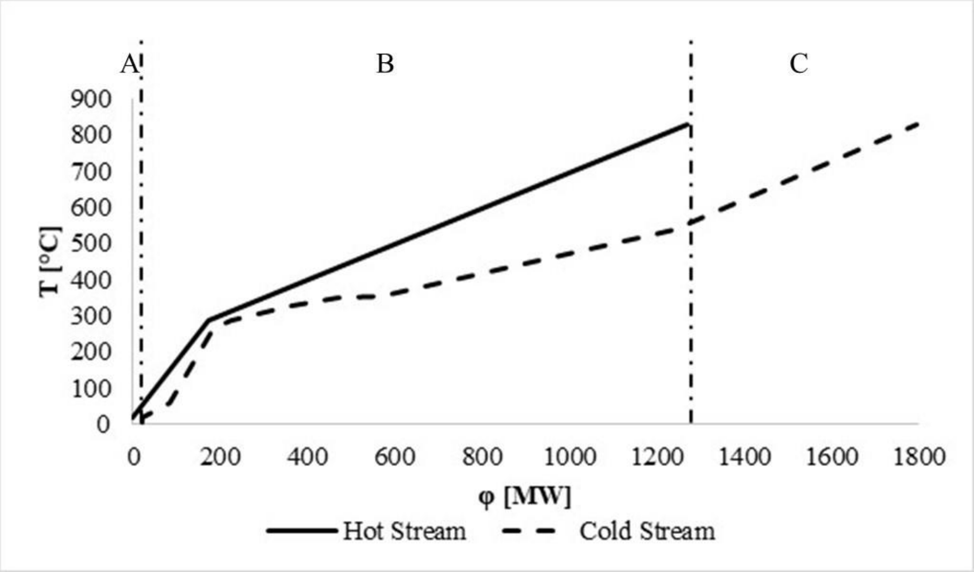
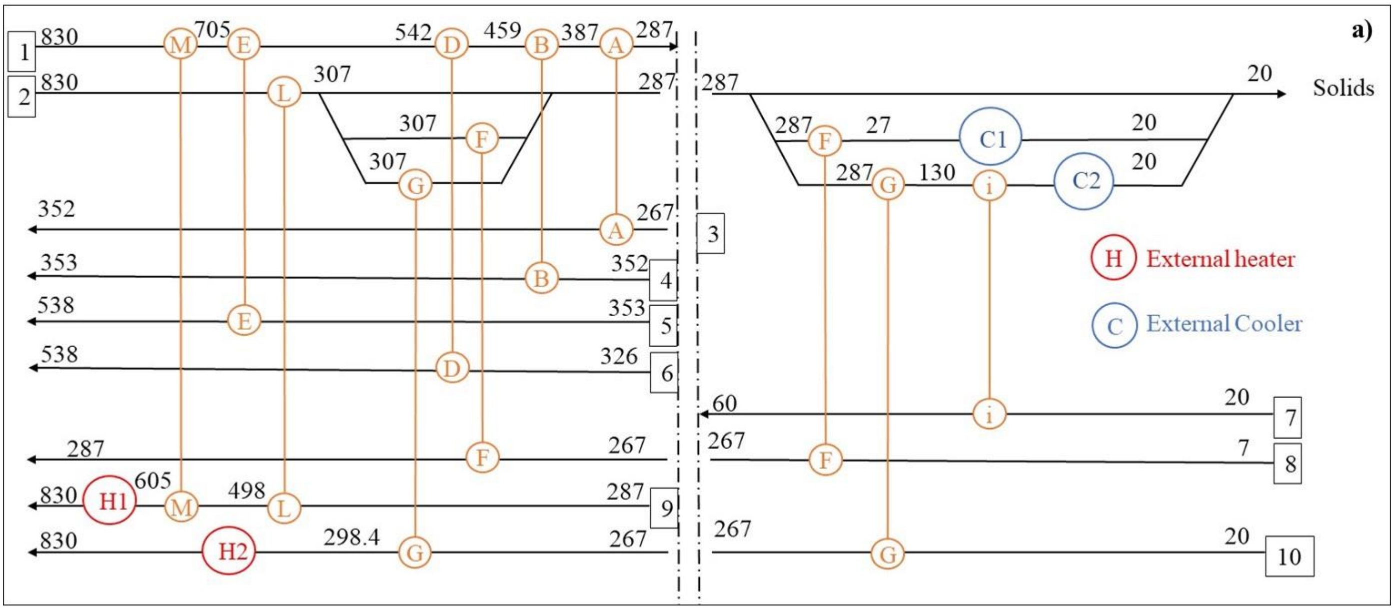


Figure 13: Composite curve of the carbonator side. Section A represents the excess of heat at low temperature; in section B the hot streams provide heat to cold streams; in section C there aren't hot streams and the heat enough is provided by carbonation reaction to cold streams



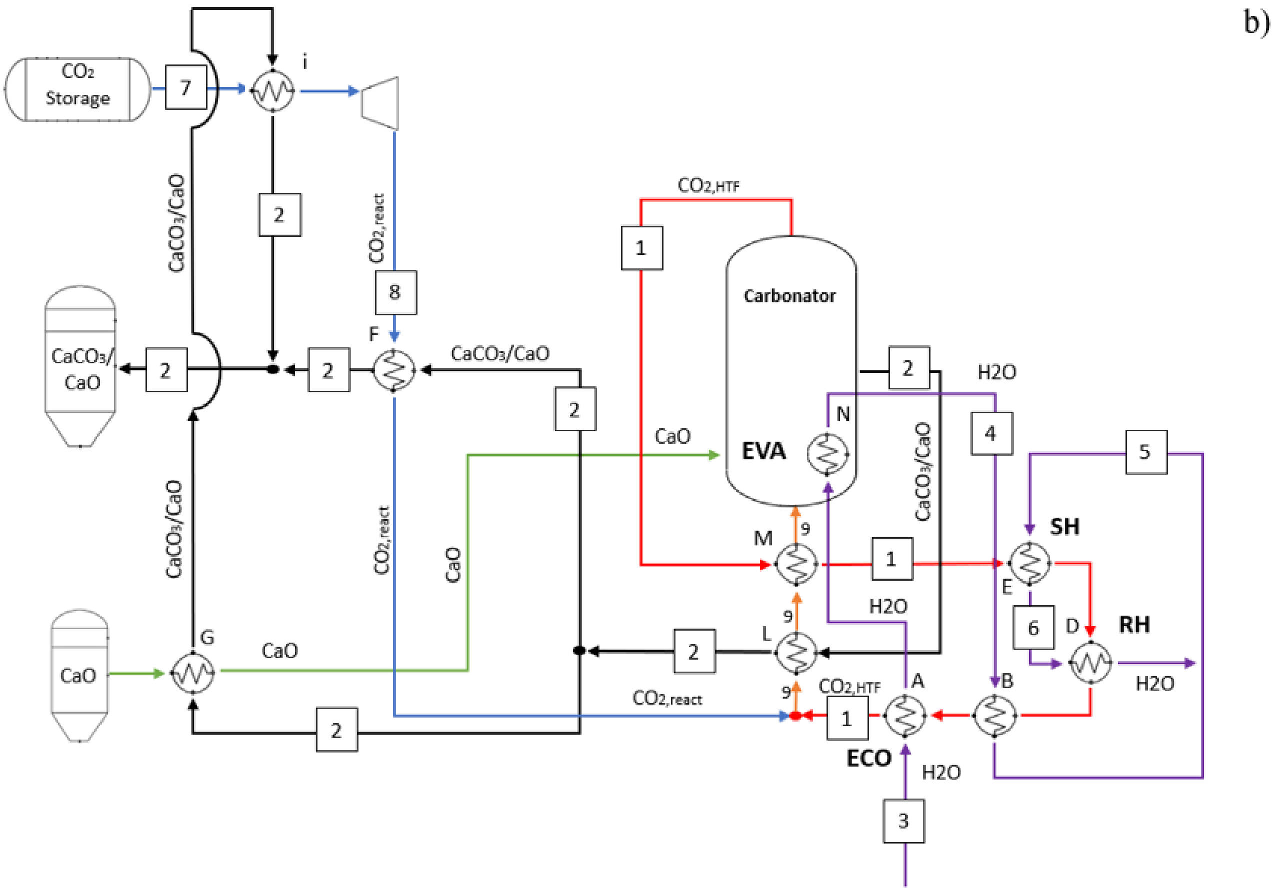


Figure 14: **a) Minimum energy consumption network inferred from the pinch analysis in the calciner side. The values of temperature level are reported in degree Celsius. b) Plant configuration (carbonator-side) resulting from the pinch analysis.**

The final goal of the analysis is to select a HEN which can be used in parametric analysis with regards to key operating parameters (e.g. X, operating temperature and pressure). In ***Figure 14***.b is showed the final HEN through pinch analysis to carbonator section. At the exit of economizer, saturate water flows into water-tube wall (exchanger N) and a partial evaporation (title of vapour: 0.635) occurs due to heat released by carbonation reaction (165MW). This fluid is not represented in pinch analysis because it cannot be coupled with other. The remaining heat of evaporation is provided by hot CO_2 (1). The heat of exothermic carbonation reaction heats fluids 9-10 (569MW) until temperature of reaction. The overall heat of carbonation reaction is 745 MW. 569 MW is used to pre heat the reactants and HTF. Almost the 4% of 172.2MW is lost to the environment. 165MW is used to partial evaporation of water in water-tube wall.

4.2 *Process model description*

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

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

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

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

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

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 [°C]	900
Calciner pressure [bar]	1
Ambient temperature [°C]	20
CaO average conversion [%]	70
Carbonator Temperature [°C]	830
Carbonator Pressure [bar]	2
CO_2 storage conditions [bar]	75
Daylight hours [h]	8
Isentropic efficiency [%]	83

The thermodynamic equilibrium is supposed to be reached in both carbonator and calciner reactors: the molar flow of calcium oxide feeding the carbonator was set to react with the CO_2 flowing through the RE providing the heat enough to run the Rankine cycle. According to experimental results [18] an average CaO conversion X of 0.7 was selected.

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

In addition, a complete conversion of $CaCO_3$ to CaO into the calciner operating at 900°C has been supposed. The performance of the calciner as well as the carbonator were analysed using the Gibbs free energy minimization model.

The CaL process requires a continuous make-up flow of fresh limestone to counteract the deactivation of lime with the number of carbonation/calcination cycles while a corresponding purge is also extracted from the calciner. The calcined purge is a potential material to be fed to the cement plant and other industrial process (e.g. iron and steel, glass and pulp). Due to the high resistance of the new sorbents at higher number of cycles and the negligible fine production, a continuous make-up flow is not simulated.

4.3 Parametric analysis and process simulation results

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

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

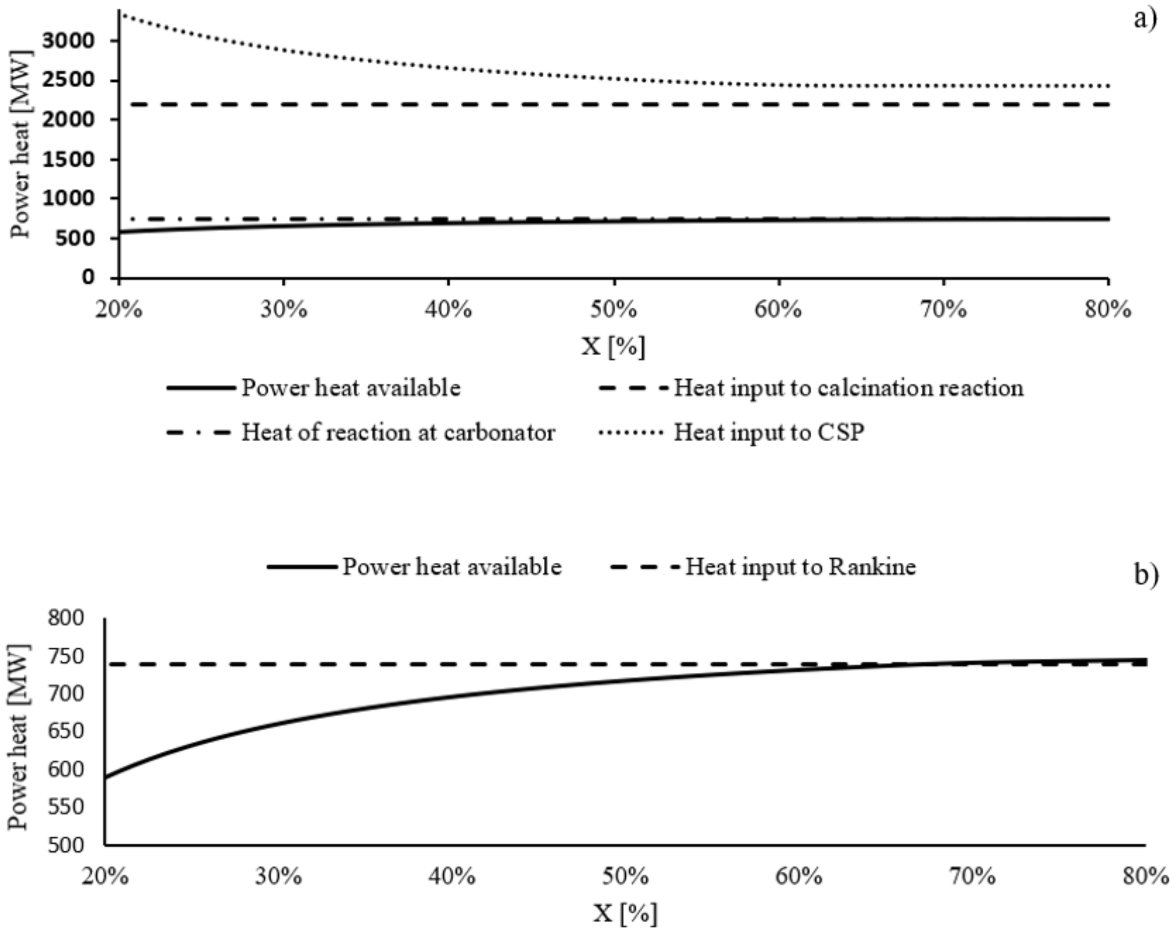


Figure 15: a) Thermal power fluxes of main reactors at varying CaO conversion. b) The heat enough from Rankine cycle is fixed, while change the heat provides by the storage system.

By fixing the quantities of the compounds that must react in the reactors (4.5 kmol/s both CO_2 and CaO), the necessary thermal power, produced respectively in the calciner (Φ_{calc} =-2194 MW) and carbonator (Φ_{carb} =745 MW) reactors due to reactions, remain constant. The sensible heat necessary to heat up the reactants to the temperature of the respective reactor, decreases significantly at high CaO conversion. This means that the lower the conversion of the CaO, the higher the molar flow rate of the solids and therefore the energy needed to heat up the entering solids increases.

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

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

- Use an external resource that provides the remaining power;
- Increase the flow rate of the reagents (CaO and CO_2), making the system operating at nominal power with less hours per day;

Figure 16 shows that increasing the CaO conversion, storage volume of the solid streams decreases while the CO_2 storage is not affected. This last observation is due to the fact that the CO_2 required for the carbonation reaction has not changed. The CO_2 storage volume is strongly depending on the thermodynamic storage conditions.

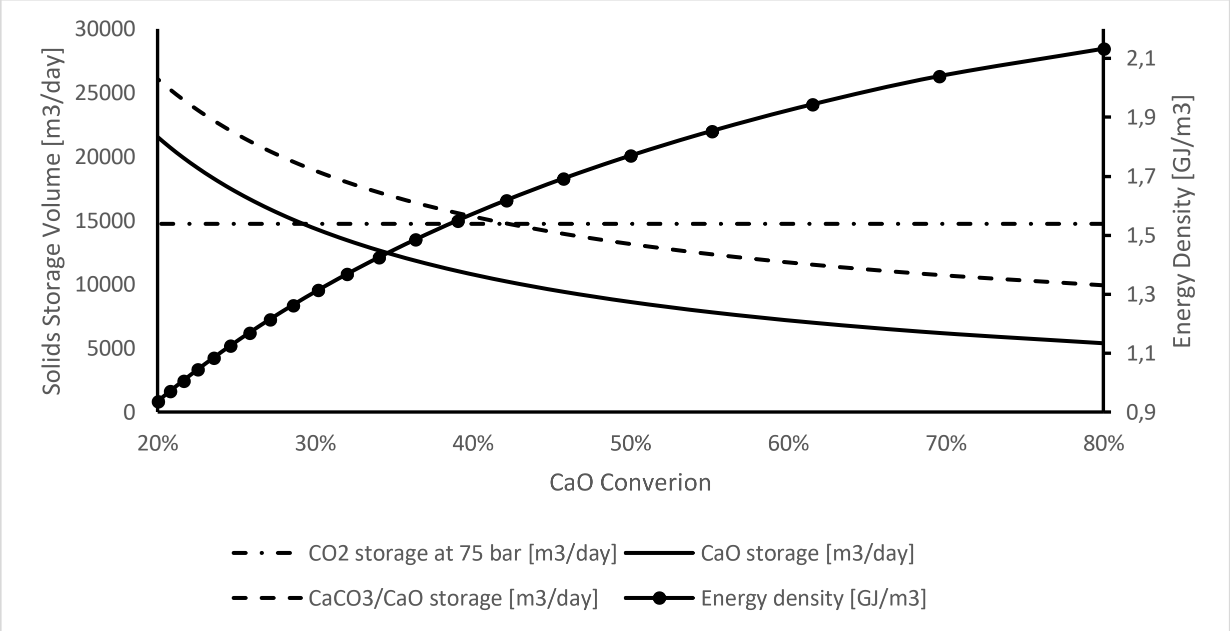


Figure 16: Parametric analysis: Daily storage volume with the change of CaO conversion

Another important parameter to evaluate and compare energy storage system is the energy density, represented in the same figure at different values of CaO conversion. It is illustrated that with small values of CaO conversion, the solids storage volume increase and therefore the energy density goes down starting from 2.1 MJ/m^3 to 0.95 MJ/m^3.

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

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

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

However, it is relevant also the storage condition and not only output/input thermal energy. The KPI to evaluate the effectiveness of the storage and release system is the *storage efficiency,* defined as the ratio of the heat released during carbonation reaction plus expansion work of CO_2 to the heat gathered by the CSP plus the compression work required during CO_2 storage.

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

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

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

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

At first time, a parametric analysis to assay the pressure condition of carbonator reactor was performed (**Figure 17**) and it was visible that increasing carbonator pressure, the heat of reaction goes down (η_{TSE}) while it is highlighted that electric power due to expansion work of CO_2 drop off (η_{SE}).

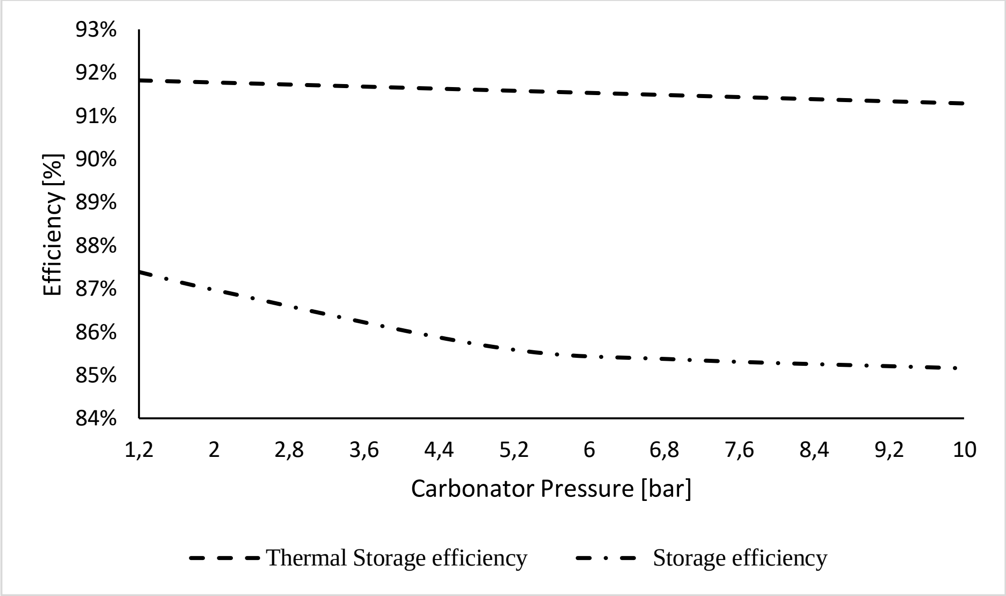


Figure 17: Trend of two KPI (Thermal Storage efficiency and Storage efficiency) function of carbonator pressure.

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

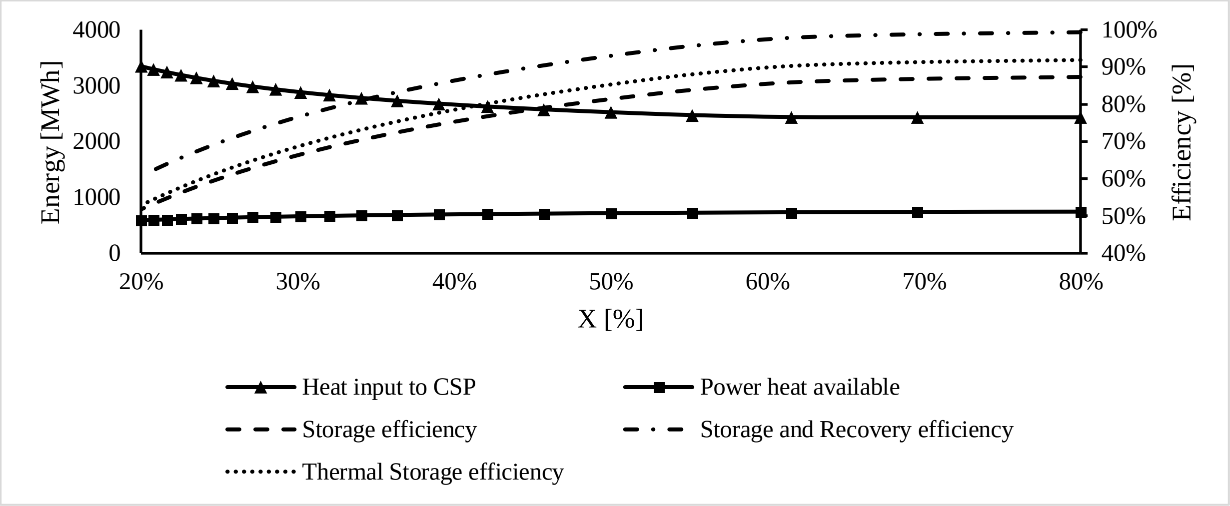


Figure 18: It is illustrated with whole line the thermal energy (left axis) of the heat provided by carbonator reactor (square indicator) and heat input to CSP power plant (triangle indicator). With the dash line is represented the three different efficiency of the storage system (right axis). These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

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

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

i. *Integrated efficiency*

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

ii. *Net efficiency*

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

iii. *Global efficiency*

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

Figure 19 reports: (i) The integrated efficiency (solid line) defined as energy produced by Rankine over input energy from CSP; (ii) the net efficiency (dot-dash line) defined as the ratio of energy produced by Rankine and CO_2 work expansion over the heat gathered by the CSP and work required during CO_2 compression; (ii) the global efficiency (dot line) defined as the ratio of energy produced by Rankine plus CO_2 work expansion and energy heat and cool of secondary systems over the heat gathered by the CSP and work required during CO_2 compression.

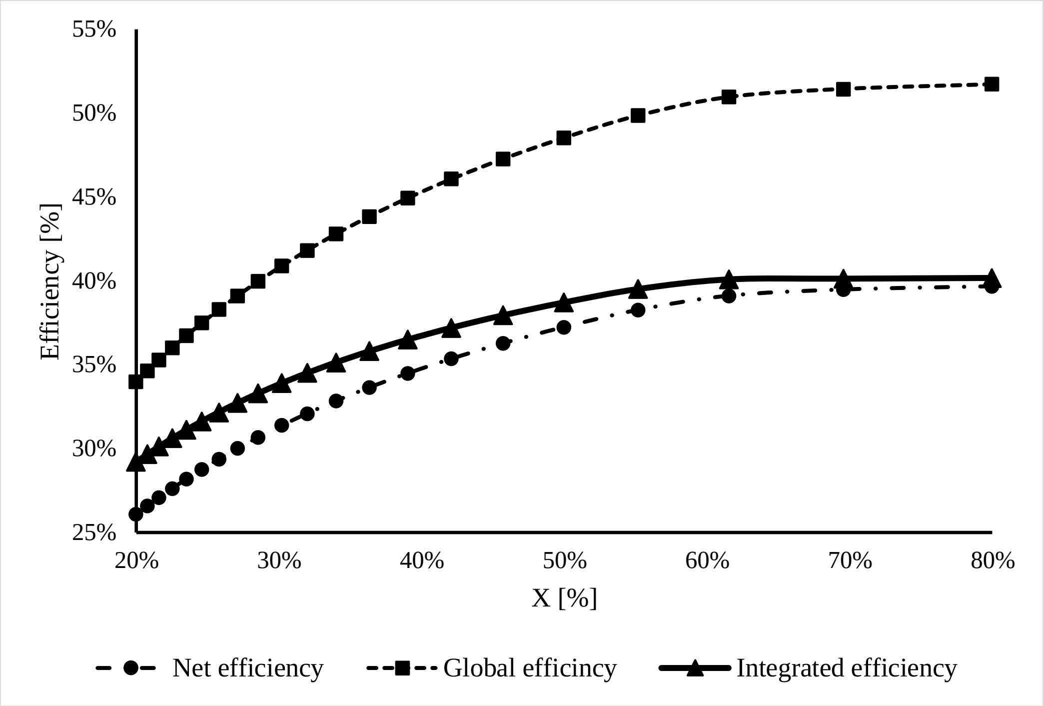


Figure 19: Efficiencies of the TC/CG–ES integrated with Rankine power cycle. Both efficiencies are strongly dependent of CaO conversion.

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

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

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 CO2 [MW]	24
	Electric energy from compressed CO2 [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]	58
	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 [%]	91.3
	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

4.4 Conclusions

A novel solution for solar energy storage by means of a hybrid thermo-chemical/compressed-gas energy storage (TC/CG–ES) is presented in this manuscript. The solar energy is used to decompose $CaCO_3$ into CaO and CO_2 at high temperature. The produced streams are stored at ambient temperature. Solar energy is harvested directly into an innovative solar receiver (solid particles fluidised bed) in which solar radiation collection and energy storage (calcination reaction) occur simultaneously. The solar energy is stored in chemical form which can be used in a different place and in a different time without heat loss overcoming the fluctuation of power generation from solar energy. During energy release, CO_2 is expanded into a turbine and sent into a carbonator where it reacts with CaO coming from silos, and releasing reaction heat at high temperature, used for power production.

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

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

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

NOMENCLATURE

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
cp [(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
η [-]	Efficiency
Φ [MW_{th}]	Thermal power
$\boldsymbol{\nu}$ [mol/s]	Stochiometric 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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