

THE UNIVERSITY of EDINBURGH

Edinburgh Research Explorer

Hybrid solar power plant with thermochemical energy storage: a multi-objective operational optimisation

Citation for published version:

Bravo, R, Ortiz, C, Chacartegui, R & Friedrich, D 2020, 'Hybrid solar power plant with thermochemical energy storage: a multi-objective operational optimisation', *Energy Conversion and Management*, vol. 205, 112421. https://doi.org/10.1016/j.enconman.2019.112421

Digital Object Identifier (DOI):

10.1016/j.enconman.2019.112421

Link:

Link to publication record in Edinburgh Research Explorer

Document Version: Peer reviewed version

Published In: Energy Conversion and Management

General rights

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The University of Édinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.



Hybrid solar power plant with thermochemical energy storage: a multi-objective operational optimisation

R.Bravo^{a,1}, C.Ortiz^{b,c}, R.Chacartegui^d, D.Friedrich^{a,*}

^aSchool of Engineering, Institute for Energy Systems, The University of Edinburgh, UK

^b Facultad de Física, Universidad de Sevilla, Avenida Reina Mercedes s/n, 41012, Sevilla, Spain

^cDepartamento de Ingeniería, Universidad Loyola Andalucía, Av. de las Universidades s/n, Dos Hermanas, 41704, Sevilla, Spain

^dDepartamento de Ingeniería Energética, Universidad de Sevilla, Camino de los Descubrimientos s/n, 41092, Sevilla, Spain

Abstract

Energy storage is key to decarbonising the energy sector by reducing intermittency and increasing the integration of renewable energy. Thermochemical energy storage (TCES) integrated with concentrated solar and photovoltaic power plants, has the potential to provide dispatchable and competitive energy. Here we develop a multi-objective optimisation framework to find the best operational strategy of a hybrid solar power plant with a TCES system. The model uses a typical meteorological year to optimise one-year hourly operation. The results demonstrate that the integration of a calcium-looping process as TCES in a concentrated solar power plant provides dispatchability and, when hybridised with photovoltaic, enhances its competitiveness with current electricity prices. The low mismatch between supply and demand, even when a fixed commitment is required throughout the year, together with a high overall efficiency, indicates that the integration of calcium-looping in hybrid solar power plants is an opportunity to increase the penetration of solar energy in the power sector. Through the optimisation framework presented, a seasonal energy storage analysis can be developed, although a second optimisation stage is required to improve the sizing of the main components of the system in order to further reduce the energy costs.

Keywords: Calcium-looping, Thermochemical energy storage, Hybrid energy systems, Concentrated solar power, Photovoltaic systems, Multi-objective optimisation

40

41

42

1. Introduction

Renewable energies are key to enhance the sustainable 22 2 development and decarbonisation of the power sector, and its agile implementation is required to reduce the nega- $_{24}$ 4 tive effects of global warming [1]. Renewable power plants $_{25}$ 5 (other than hydropower) have low maintenance and oper- $_{\rm 26}$ 6 ational costs [2], their carbon emissions are substantially 27 lower compared to fossil fuel power stations [3] and their $_{28}$ 8 development is key to energy independence. However, 29 9 these are not dispatchable (i.e. renewable power plants $_{30}$ 10 can dispatch energy just when the resource is available). 31 11 Some renewable power plants are very competitive, where 32 12 in some locations, bids for recent auctions have reached $_{33}$ 13 prices even below 20 USD MWh^{-1} (mainly based on wind 14 and solar technologies) [4]. 15

The continuous growth in the penetration of renewable energy technologies in the power sector and the natural variability of the resource (e.g. solar, wind) adds large fluctuations in generation and large mismatches with power

demand [5]. To reduce variability and increase dispatchability of renewable power plants, the integration of energy storage allows to have control in the power dispatch [6]. Therefore, to increase the penetration of solar technologies in the power sector, the integration of energy storage is essential. On the one hand, in the case of photovoltaic systems (PV), despite the fact that the rate of projects under development is very high, the integration of electric batteries as energy storage is not economically feasible [7], but it could be competitive in the long term if the current high price of large scale electric batteries is reduced considerably [8]. On the other hand, concentrated solar power technologies (CSP) integrated with energy storage are key systems that could provide clean and dispatchable energy [9]. Furthermore, the development of CSP plants integrated with energy storage and hybridised with PV systems give solar technologies dispatchability at competitive costs [10] [11], [12]. In addition, in order to improve the dispatchability and capacity factor of solar hybrid power plants, by integrating a small fossil back-up unit, flexibility is given by allowing some carbon emissions [13], [14]. Different energy storage technologies have been proposed in concentrated solar power plants, based on three different concepts: sensible, latent and thermochemical en-

ergy storage. Sensible thermal energy storage is a mature

^{*}Corresponding author

Email address: d.friedrich@ed.ac.uk (D.Friedrich)

¹The author is supported by a PhD student scholarship from BE- ⁴³ CAS CHILE, CONICYT. ⁴⁴

technology used in concentrated solar power plants, which 97 45 works with a temperature difference of a substance, for ex- 98 46 ample, water or molten salts [15]. Latent thermal energy 99 47 storage uses the heat stored or released during the phase₁₀₀ 48 change of a material [16]. Finally, thermochemical energy¹⁰¹ 49 storage uses the heat of reaction of a reversible chemical¹⁰² 50 reaction that absorbs and rejects energy depending on the103 51 operation [17]. Promising thermochemical energy storage¹⁰⁴ 52 technologies that can be integrated into concentrated so-105 53 lar power plants are the calcination-carbonation process¹⁰⁶ 54 of calcium carbonate [18], [19], or magnesium oxide [20].107 55 Whilst TCES systems based on magnesium oxide work at 108 56 lower temperatures (350-400 $^{\circ}C$) and are considered in-109 57 teresting processes to use the waste heat from industrial110 58 processes [20], TCES based on calcium carbonate works¹¹¹ 59 at higher temperatures and is an attractive and more ef-112 60 ficient technology to integrate into CSP plants [21]. This113 61 process is based on the following reaction that involves cal-114 62 cium carbonate $(CaCO_3)$, calcium oxide (CaO) and car-115 63 bon dioxide (CO_2) : 64 116

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$
 (1)¹¹⁸₁₁₉
with $\Delta \hat{H}_r^{\circ} = 178 \ kJ \ mol^{-1}[22]$ ¹²⁰

The integration of this process, also known as calcium-122 65 looping (CaL), as a energy storage system, has several ben-123 66 efits. For instance, because its high energy density, a rel-124 67 atively small storage volume has the potential to operate¹²⁵ 68 as long-term energy storage, and the precursor materials₁₂₆ 69 used in the process, such as limestone or dolomite, are127 70 an abundant, non-corrosive, non-toxic and cheap material₁₂₈ 71 [18]. In order to decrease the deactivation of the material¹²⁹ 72 due to a multi-cyclic operation, modified materials can be130 73 used in the process [23]. In this context, [21] compares dif-131 74 ferent materials and conditions to enhance the multicycle₁₃₂ 75 CaO conversion. Hence, the integration of a CaL process133 76 as thermochemical energy storage (TCES) technology in₁₃₄ 77 concentrated solar power plants is a suitable sustainable 78 alternative to provide dispatchable power. 79

In order to evaluate the dispatchability of solar power 80 plants integrated with CaL as a TCES, current studies136 81 focus on the simulation of the operation using a typical₁₃₇ 82 period to estimate the operation of a whole year [24], [7], 138 83 for instance, one or two representative days with hourly₁₃₉ 84 time steps. Nevertheless, these studies suggest that a one₁₄₀ 85 year with hourly time steps simulation is crucial to evalu-141 86 ate the operation of the solar power plant under variable142 87 solar irradiation, to consider daily and seasonal variability143 88 of the solar resource [24]. According to [25], to define the144 89 best operational strategy for a renewable energy system₁₄₅ 90 integrated with energy storage, an optimisation study is146 91 required, however, the storage system increase the com-92 plexity of the problem. Several studies exploit synergies 93 between expensive but dispatchable power plants, such as 94 CSP with thermal energy storage, integrated with afford-148 95 able but intermittent renewable technologies, e.g. PV [13],149 96

[12]. These studies, based on the application of optimisation techniques, focus on the development of operational strategies that minimises and/or maximises different key performance indicators as objective functions. In this context, [13] optimises the operation of a hybrid solar power plant integrated with thermal energy storage in the Atacama Desert, concluding that a multi-objective optimisation routine is crucial to estimate and analyse the trade-off between technical and financial performance. The focus of this research is to find the best operational strategy of a renewable power plant by maximising both the energy supplied and the dispatchability under a specific commitement, two goals that during some periods of the year are conflicting objectives.

Consequently, a multi-objective optimisation framework to model a one-year hourly operation strategy of a hybrid solar power plant with thermochemical energy storage is the main focus of the present study. Here we exploit the capacity of linear programming to optimise the annual performance of the power plant, taking into account the daily and seasonal variability of the solar resource. To reach this goal, the CaL process is modelled as mass and energy balances, where the energy balance of each subsystem depends on the temperature and the mass flow rate of the fluid. In addition, the thermodynamic properties also depend on the temperature. To simplify this non-linear model, the temperature of each process will be fixed and defined according to [24]. To handle both objectives, a linear scalarisation method is applied, as discussed in [11]. The results of this multi-objective optimisation method is a Pareto frontier that represents the trade-off between the net energy dispatched $(GWh \ year^{-1})$ (that influences the levelised cost of the electricity), and the mismatch between supply and demand, estimated here through the loss of power supply capacity $(GWh \ year^{-1})$, that represents the dispatchability of the power plant under a given commitment.

Abbreviations

DNI: Direct normal irradiation GTI: Global tilted irradiation TMY: Typical meteorological year CSP: Concentrated solar power CaL: Calcium-looping process TCES: Thermochemical energy storage PV: Photovoltaic LCOE: Levelised cost of electricity LPS: Loss of power supply SoC: State of Charge

Nomenclature

i: subscript, period (hours) *k*: subscript, material

 DNI_i : direct normal irradiation period i 150 GTI_i : global tilted irradiation period i 151 A^{CSP} : solar tower heliostats field area 152 $P^{\rm ST}$: steam turbine capacity 153 P^{MC} : main CO_2 compressor capacity 154 P^{MT} : main CO_2 turbine capacity 155 P^{HPSC} : high pressure CO_2 compressor capacity 156 P^{HPST} : high pressure CO_2 turbine capacity 157 STO^{CO_2} : CO_2 storage vessel capacity 158 STO^{CaO} : CaO storage tank capacity 159 STO^{Solids} : Solids storage tank capacity 160 $A^{\rm PV}$: photovoltaic field area 161 η^{opt} : optical efficiency solar field (DNI to receiver) 162 $\eta^{receiver}$: thermal efficiency receiver 163 P_i^{net} : net power period i 164 E^{net} : net energy generated 165 P_i^{demand} : power demand period i 166 LPS_i : loss of power supply period i 167 \hat{m}_i : molar flow rate (kmol/s)168 \dot{m}_i : mass flow rate (kg/s)169 \hat{h} : molar enthalpy (kJ/mol)170 h: enthalpy $\binom{kJ}{kg}$ 171 MW_i : molecular weight, component i 172 $\Delta \hat{h}_{f,i}^0$: molar enthalpy of formation 173 X: CaO conversion 174 175

¹⁷⁶ 2. Methodology and Framework description

In this section, the modelling of a CaL thermochem-²³¹ ical energy storage process, integrated in a hybrid solar power plant, is presented. Then, a multi-objective opti-²³³ misation method to define the best one-year hourly oper-²³⁵ ational strategy is described.²³⁶

182 2.1. **Description**

202

238 Figure 1 represents the process involved in the gener- $_{_{239}}$ 183 ation of electricity through the use of a CaL process inte- $_{240}$ 184 grated in a CSP and hybridised with a PV system. The₂₄₁ 185 CSP-CaL scheme (and nomenclature) is taken from the $_{242}$ 186 base case proposed in [24]. Each stream is represented by $_{243}$ 187 a letter and a number, where the letter defines the $\mathrm{type}_{_{244}}$ 188 of substance (g: CO_2 ; c: CaO; s: solids $CaO + CaCO_3$),₂₄₅ 189 and the number indicates the position of the stream in_{246} 190 the diagram. For the present study, a Python model has 191 been developed to optimise the operation of a hybrid $\text{solar}_{_{248}}$ 192 plant with CaL energy storage by mass and energy bal-249 193 ances. This model uses real solar irradiation as input, and 194 by linear programming, optimises the annual hourly oper- $_{251}$ 195 ation of a defined power plant (CSP with CaL plus PV).₂₅₂ 196 Note that the current algorithm optimises the plant oper-253 197 ation and not the components sizing; hence, the capacity $_{254}$ 198 of each component in this study is an input to the model. $_{\scriptscriptstyle 255}$ 199 The following list summarises the capacities of the $main_{256}$ 200 components of the power plant: 201 257

3

258

• Steam Turbine capacity: P^{ST} , MW

203

204

205

206

207

208

209

210

211

212

213

214

215

216

217

218

219

220

221

222

223

224

225

226

227

228

229

230

237

- Main CO_2 Compressor capacity: P^{MC} , MW
- Main CO_2 Turbine capacity: $P^{\rm MT}$, MW
- High Pressure CO_2 Compressor capacity: P^{HPSC} , MW
- High Pressure CO_2 Turbine capacity: P^{HPST} , MW
- CO_2 Storage Vessel: STO^{CO_2} , m^3
- CaO Storage Tank: STO^{CaO} , m^3
- Solids Storage Tank: STO^{Solids}, m³
- Photovoltaic field area: $A^{\rm PV}$, m^2

In the model, the CSP is a solar tower technology that provides heat to carry out the endothermic reaction that splits $CaCO_3$ into CaO and CO_2 at 900°C, according to equation 1. The location where this reaction takes place is known as calciner and coincides with the solar receiver. Full calcination is assumed in the model [26]. CaO exiting the calciner is stored at atmospheric pressure and high temperature in an insulated tank. The atmosphere inside the CaO tank is regulated by injecting an inert gas such as N_2 or He, in order to reduce the presence of CO_2 and avoid partial carbonation [21]. Nevertheless, it must be highlighted that the CaO tank for this integration with hot storage of the solids, is maintained at $900^{\circ}C$ and the kinetics of carbonation near to the equilibrium, although possible, is notably slow [27], [28]. The second stream that exits the calciner, consisting of pure CO_2 at $900^{\circ}C$, first exchanges heat in a Heat Recovery Steam Generator (HRSG) to produce electricity. Next, the CO_2 leaves the heat exchanger and cools to approximately $40^{\circ}C$ to improve the efficiency of the compression process that is occurring afterwards. After the compressor, this stream (now with a pressure of approximately $3 \ bar$) has two possibilities: (i) it can be used in the carbonator to produce the reversible exothermic reaction (carbonation) where it reacts with CaO from the CaO storage tank forming $CaCO_3$ and releasing heat according to the previous reaction; (ii) or can be stored at high pressure in a 75 bar vessel, by using a multi-stage compressor. Then, when power needs to be dispatched, this high-pressure stream first drives a turbine to generate electricity and then mixes with the stream flowing from the power loop. This flow is heated in a regenerative system, which reaches around $654^{\circ}C$ and is then sent to the carbonator to drive the exothermic reaction described above. The storage of solids is carried out under atmospheric pressure. A mechanical conveyor system is considered here to transport the material, hence, in order to decouple the pressure between solids storage tanks (1 bar) and carbonator (3 bar), lock hoppers are used in the conveyor system [24].

The CaO conversion (X) in the carbonator is highly dependent on the reactor conditions (pressure, temperature, $\% v/v CO_2$) and the CaO precursor used [21]. In this work, a conservative value of X=0.15 is assumed. The heat released from the reaction is taken by the CO_2 that is present in excess in the carbonator. After that, this pure CO_2 stream runs a gas turbine (main turbine) to produce

electricity that is used to drive the main compressor and 259 the surplus is dispatched to the network. The CO_2 leaves 260 the turbine at 1 bar and approximately $700^{\circ}C$ and then it 261 exchanges heat in the regenerative system to increase the 262 temperature of the CO_2 stream before entering the car-263 bonator. Then, the CO_2 flow described above is cooled 264 to $40^{\circ}C$ to be compressed in the main compressor, closing 265 the cycle (see figure 1). 266 304

267

268 2.2. Energy systems analysis

The following section describes the mass and energy₃₀₈ 269 balances used in the model for the operation of the main 270 processes of the power plant. The main components are:309 271 solar field (heliostats and receiver), reactors (carbonator 272 and calciner), heat exchangers, coolers, compressors and 273 turbines. Main properties for $CaCO_3$, CaO and CO_2 are 274 summarised in table 1. All the variables described below 275 are non-negative real numbers unless otherwise stated. 276

277 2.2.1. Solar field:

In the solar field, each heliostat focuses the solar irradiation on the calciner that is located in the top of the solar ³¹⁰ tower (receiver). The total thermal power transferred and used in the receiver at each time step ($Q_i^{calciner}$) is calculated according equation 2.

$$Q_i^{Calciner} = DNI_i \cdot \eta_i^{opt} \cdot \eta^{receiver} \cdot A^{CSP} - Q_i^{Curtailment \ ^{315}} \tag{2}$$

Where DNI_i is the direct normal irradiation, A^{CSP} is the³¹⁸ 278 total area covered by the heliostats, η_i^{opt} is the optical³¹⁹ 279 efficiency of the solar field that varies every hour in the³²⁰ 280 model and depends on the relative position between the³²¹ 281 sun, the heliostats and the tower (including losses related³²² 282 to blocking, soiling, reflectance, attenuation, interception³²³ 283 and cosine effect [29]) and $\eta^{receiver}$ is the efficiency of the³²⁴ 284 receiver, which is assumed in this work as 0.85 [29]. A sen-³²⁵ 285 sitivity analysis on this value is carried out in section 4.1.³²⁶ 286 The curtailment $(Q_i^{curtailment})$ is the power that has to be 287 curtailed when the power cycle is running at full capacity 288 and the storage system is fully charged. 289 327 290

291 2.2.2. Calciner:

The endothermic calcination reaction occurs within the 292 calciner, which in this case coincides with the receiver $^{\scriptscriptstyle 330}$ 293 chamber located in the top of the tower. In this reactor, 294 the stream s2, which contains calcium carbonate and cal-295 cium oxide, is heated to drive the calcination. According 296 to [24], to achieve full calcination at amospheric pressure 297 and short residence times, a temperature around $900^{\circ}C$ 298 is required. In the present model, fully calcination is as-200 sumed [23]. Hence, because there is no accumulation of₃₃₁ 300 energy in the system, nor shaft work, all the heat from the₃₃₂ 301 solar field is used to heat the stream s2 and complete the₃₃₃ 302 reaction, according to: 334 303

$$Q_i^{Calciner} = \Delta(\hat{m}_{k,i} \cdot \hat{h}_{k,i}) + \Delta \hat{h}_{r,i}$$
(3)
with,

$$\Delta(\hat{m}_{k,i} \cdot \hat{h}_{k,i}) = \hat{m}_{g1,i} \cdot \hat{h}_{g1,i} + \hat{m}_{c1,i} \cdot \hat{h}_{c1,i} - \hat{m}_{s2,i} \cdot \hat{h}_{s2,i}$$
$$\Delta\hat{h}_{r,i} = \hat{m}_{s2,i} \cdot \Delta\hat{H}_r^{\circ}$$

The molar flow rate of CO_2 (stream g1) is equal to the molar flow rate of CO_2 produced in the reaction. Finally, the CaO molar flow rate (stream c1) is equal to the molar flow rate of CaO in stream s2 plus the molar flow rate of CaO produced in the reaction.

2.2.3. Heat exchangers, heaters and coolers:

In a heat exchanger, there is no energy accumulation, and if considered as adiabatic, the amount of heat transferred from the hot fluid (h) to the cold fluid (c) can be modelled by [31]:

$$\dot{m}_{h_{in},i} \cdot h_{h_{in},i} - \dot{m}_{h_{out},i} \cdot h_{h_{out},i} =$$

$$\dot{m}_{c_{out},i} \cdot h_{c_{out},i} - \dot{m}_{c_{in},i} \cdot h_{c_{in},i}$$

$$(4)$$

However, the model considers thermal efficiencies in heat exchangers. As presented in previous studies [7], electric heaters can be used as heaters to use the excess electricity when supply exceed commitment. In the case of cooler 4, the CO_2 stream exiting the recuperator HXG (g12) is cooled from $150^{\circ}C$ down to $40^{\circ}C$ and part of this heat is used to heat up the CO_2 coming from the storage (Heater 1). Heater 2 was included in the process in order to avoid a non-linear relation in the carbonator, and its electrical consumption is included in the operational electrical consumption of the power plant.

Coolers are modelled similarly to heat exchangers (no energy accumulation, no shaft work, adiabatic), the difference here is that the working fluid cools while a refrigerant is heating (air in this case). The energy balance for coolers is described as:

$$\dot{n}_{r,i} \cdot c_{p_r} \cdot \Delta T_{r,i} = \dot{m}_{h_{in},i} \cdot (h_{h_{out},i} - h_{h_{in},i}) \tag{5}$$

Where c_{p_r} is the specific heat capacity of the refrigerant $(c_{p,air} (23^{\circ}C, 41\% \text{ rel. humidity}) = 1.012 \text{ kJ/kg} \cdot K [22])$

2.2.4. Superheated steam Rankine cycle:

1

In order to simplify the model, the turbine power output (ST) of the Rankine cycle is simulated as a linear relation with the heat absorbed in the heat recovery steam generator (HRSG) according to:

$$P_i^{ST} = Q_i^{HRSG} \cdot \eta^{SSRC} \tag{6}$$

where η^{SSRC} is the global efficiency from thermal to electrical power. Based on models and results analysed by using the commercial software ASPEN PLUS, an efficiency $\eta^{SSRC} = 0.268$ will be considered in this study.

328

329

305

306



Figure 1: Mass and energy flow model of the calcium-looping system

Table 1: Properties of main components

	$\Delta \hat{h}_{f}^{0} (^{kJ}/_{mol}) [22]$	$Cp \; (^{cal}/_{mol} \cdot _{K})[30]$	$MW \ (^{kg/_{kmol}}) \ [30]$
$CaCO_3$	-1207	$19.68 + 0.01189 \cdot T - 307600 \cdot T^{-2}$	100.09
CaO	-635	$10.00 + 0.00484 \cdot T - 108000 \cdot T^{-2}$	56.08
CO_2	-394	$10.34 + 0.00274 \cdot T - 195500 \cdot T^{-2}$	44.01

347

335 2.2.5. Compressors and turbines:

The following relations are used to estimate the total³⁴⁸ work in turbines and compressors according to [32]: 349

 $\Delta(\dot{m_i}h_{turb,i}) = \dot{m_i}\frac{\gamma_i}{\gamma_i - 1}\frac{P_{in,i}}{\rho_{in,i}} \left\{ 1 - \left(\frac{P_{out,i}}{P_{in,i}}\right)^{\frac{\gamma_i - 1}{\gamma_i}} \right\} \eta_s^{351}$ $(7)^{353}$ $\Delta(\dot{m_i}h_{comp}) = \dot{m_i}\frac{\gamma_i}{\gamma_i - 1}\frac{P_{in,i}}{\rho_{in,i}} \left\{ \left(\frac{P_{out,i}}{P_{in,i}}\right)^{\frac{\gamma_i - 1}{\gamma_i}} - 1 \right\} \eta_s$ (8)

where γ is the heat capacity ratio, used here as the isentropic expansion factor, and η_s is the isentropic efficiency of the turbine or compressor.

341 2.2.6. Carbonator:

In the carbonator, the reverse reaction of the calciner occurs. In this reactor, pure CaO from the CaO storage tank is combined with CO_2 from the CO_2 storage cycle to produce $CaCO_3$ and heat (with a conversion of 15%). After the carbonator, while the resulting solid stream (CaO+ $CaCO_3$) is stored in the solid storage tank, the CO_2 stream (presented here in excess to absorb the heat released in the reaction) is first conducted to a turbine to produce electricity, then to a heat exchanger to use part of the heat available in the regenerative system, finally to a cooler and compressor to close the cycle.

2.2.7. Storage tanks:

The three storage components (*CaO* and solids storage tanks, and the CO_2 storage vessel) are modelled by mass balances. Where the density under storage conditions considers internal porosity and particle packing density of the material, as described in [24]. Here the state of charge (*SoC_i* in m^3) is defined as the volume of material that is present in the tank in period i, which is equal to the state of charge of the previous period plus the input minus the output flows during the current period (in m^3), according to the following expressions:

$$SoC_{i}(m^{3}) = \begin{cases} SoC_{i=0}(\%) \cdot STO^{capacity}(m^{3}), & \text{if } i = 0\\ SoC_{i-1} + (\dot{m}_{in} - \dot{m}_{out}) \cdot \Delta t \cdot \frac{1}{\rho_{i}}, & i \ge 1 \end{cases}$$
(9)

In our model, the state of charge (in percentage) for each $_{380}$ tank at the start of the operation (i=0) is defined as: $_{381}$

$$\begin{cases} 100\% \quad CaO \text{ tank} \end{cases}$$

$$SoC_{i=0} = \begin{cases} 0\% & \text{Solids} (CaO + CaCO_3) \text{ tank } (10)_{384} \\ 100\% & CO_2 \text{ vessel} \end{cases}$$

This means that during the operation of the first hours, the³⁸⁷ storage tanks of the thermochemical energy storage system³⁸⁸ are fully charge, which allows the plant to dispatch energy³⁸⁹ even without solar irradiation. This is just a criterion for³⁹⁰ the simulations, which has insignificant influence in the³⁹¹ yearly results. In the operational optimisation routine, to³⁹² calculate the actual net energy dispatched, it is necessary to estimate the difference between the available energy in the initial and final periods of the annual operation. To calculate this difference, an average energy density factor (ξ) is calculated as the rate between net power dispatched, ³⁹³ and *CaO* mass flow rate that feeds the carbonator:

$$\xi_i \left(\frac{MWh}{ton_{CaO}}\right) = \frac{P_i^{net}(MW)}{\dot{m}_{c2}(\frac{kg_{CaO}}{s}) \cdot 3600(\frac{s}{h}) \cdot \frac{1}{1000}(\frac{ton}{kg})} \quad (11)_{_{396}}^{^{395}}$$

The results of the model were analysed along the year to³⁹⁸ estimate this rate and a specific power production value of³⁹⁹ $\xi_i \approx 0.053 \ MWh \ ton_{CaO}^{-1}$ was calculated.

357 2.2.8. Photovoltaic power plant:

Finally, the photovoltaic power plant converts the solar 358 irradiation (in this case, the total irradiance received on a_{400} 359 plane with fixed tilt) that reaches each solar module into 360 electric power by the photovoltaic effect. In the simplified⁴⁰¹ 361 model shown in figure 1, the power flows to the inverter⁴⁰² 362 and then is dispatched to the grid. According the model⁴⁰³ 363 described in [11], the total efficiency of the PV plant, from 364 the solar irradiation to the electric power, considers the ef-365 ficiency of panels and inverters, in addition with the losses 366 related with module mismatch, connections and wiring. 367

368 2.3. Key performance indicators

373

374

In order to compare the operational strategy of dif-406 ferent configurations based on measurable results, the following are key indicators for technical and financial performance used in this study:

- E^{net} is the total net electric energy dispatched by the power plant in one year of operation.
- LPSC is the total loss of power supply capacity dur-⁴⁰⁸ ing one year of operation, and LPSP is the loss of⁴⁰⁹ power supply probability according to: ⁴¹⁰ 411

$$LPSC = \sum LPS_i \tag{12}$$

$$LPSP = \frac{LPSC}{P_i^{Commitment} \cdot 8760}$$
(13)

• $E^{Commitment}$ is the electricity dispatched to fulfil the commitment .

- E^{Excess} is the electricity dispatched when the net energy exceeds the commitment (in this model there is no restriction for the maximum power dispatched).
- $E^{Curtailed}$ is the amount of energy available in the heliostat solar field that has to be curtailed when the power plant is running at full capacity and the storage tanks are fully charged.
- ΔE_{f-i} is the energy difference between the last hour and the first hour of operation. This difference is used to calculate the net electricity dispatched during one year of operation.
- \bar{P}^{Net} is the average power dispatched in one year, according to:

$$\bar{P}^{Net} = \frac{E^{Net}}{8760} \tag{14}$$

- *P^{Max}* is the maximum power dispatched during at least one hour, over one year of operation.
- CF^{CSP} is the capacity factor referred to the CO_2 Brayton cycle [33], where $E^{net,Brayton \ Cycle}$ is the total energy dispatched by the Brayton cycle during one year of operation, and $P^{max,Brayton \ Cycle}$ is the maximum power dispatched.

$$CF^{CSP} = \frac{E^{net, Brayton \ Cycle}}{P^{max, Brayton \ Cycle} \cdot 8760}$$
(15)

Two estimations for efficiencies will be calculated:

• $\eta^{CSP,Rec}$ is the efficiency of the solar tower power plant considering the energy available and used in the calciner:

$$\eta^{CSP,Rec} = \frac{\sum E_i^{Net,CSP}}{\sum Q_i^{Calciner}}$$
(16)

• $\eta^{CSP,DNI}$ is the overall efficiency of the solar power plant considering the solar energy available in the solar field:

$$\eta^{CSP,DNI} = \frac{\sum E_i^{Net,CSP}}{\sum DNI_i \cdot A^{CSP}}$$
(17)

• Levelised cost of the energy: representing the present value (considering an annual interest rate of r = 7%) of the total life cycle costs (TLCC) involved in the generation of each unit of energy during the lifetime of the power plant (N = 25 years) [34].

$$LCOE = \frac{TLCC}{E^{Net}} \cdot \frac{r}{1 - (1+r)^{-N}}$$
 (18)

404

412 2.4. Operational optimisation by linear program-441 413 ming 442 442

The main objective of this research is to model one443 year of operation (8760 timesteps), considering the hourly

solar resource of a typical meteorological year. In order to⁴⁴⁴ 416 linearise the equations presented above, the temperatures $^{\rm 445}$ 417 of the processes are fixed, according to the parameters and⁴⁴⁶ 418 results presented in [24], were non-linear models are used⁴⁴⁷ 419 to simulate the operation of the CSP plant with CaL. In $^{\rm 448}$ 420 a power plant, this may be possible by the instrumenta-449 421 tion engineering, through the definition and control of the 422 temperatures of each process. Hence, the operational op_{450} 423 timisation routine optimises the mass flow rate of some 424 streams and calculate those that are dependent (because⁴⁵¹ 425 there are direct relationships between some streams) in or-452 426 der to optimise the hourly operation. 453 427

428 Optimisation objectives can be defined according to user454
429 preferences, and these can be easily changed in the model.455
430 In this study, for a fixed power plant, the objectives of the456
431 operational optimisation are defined by: 457

• Maximisation of the net energy supplied during one₄₅₈ year of operation (typical year), where the hourly₄₅₉ net power dispatched is defined by:

$$P_i^{Net} = P_i^{Generated} - P_i^{Own \ consumption} \qquad (19)_{_{462}}^{_{461}}$$

Minimisation of the loss of power supply (LPS), which⁶³
 estimates the mismatch between the energy supplied⁴⁶⁴
 and the commitment, i.e. the net power to be dispatched by the power plant, according to the follow-⁴⁶⁵
 ing equation:

$$LPS_{i} = \begin{cases} P_{i}^{\text{Commitment}} - P_{i}^{Net} &, P_{i}^{\text{Commitment}} > P_{i}^{Net} & _{469} \\ 0 &, \text{otherwise.} & ^{470} \end{cases}$$

$$(20)^{471}$$

440 2.5. Scalarisation method

In order to handle both objectives, and according to the ⁴⁷⁴/₄₇₅ results presented in [11], here a linear scalarisation method ⁴⁷⁶/₄₇₆ is implemented. The model developed in [11], which opti-⁴⁷⁷/₄₇₇ mises the annual operation of a hybrid solar power plant ⁴⁷⁸/₄₇₈ with energy storage, found that the linear scalarisation ⁴⁷⁹ method works faster than the epsilon (ϵ) constrain method, ⁴⁸⁰ obtaining the same Pareto frontier. The only precaution is ⁴⁸¹ to choose a suitable scaling factor (ω) to scale the second ⁴⁸² objective (section 3.3 presents the analysis to define the ⁴⁸³ value of ω for the case study described below). Therefore, ⁴⁸⁴ the function that describes the multi-objective optimisa-⁴⁸⁵ tion problem in the present study is:

maximize
$$\sum_{i=1}^{I} \{ P_i^{Net} \cdot \Delta t_i - w \cdot LPS_i \cdot \Delta t_i \}$$
(21)

2.6. Computer system and tools

All optimisations presented in this study were performed using the following resources:

- PC: Intel Core i7-6700 CPU @ 3.4 *GHz*, 16 *GB* RAM.
- Operating system: 64-bits Windows 10 Education.
- Programming language: Python 3.5.3 [35]
- Optimisation package: Pyomo 5.6.1 [36], [37]
- Solver: Gurobi 8.1.1 [38]

3. Case Study

To evaluate the model and compare the results with published data, the power plant under analysis will be located in Seville, Spain. Here public data available for Seville is used ($\approx N \, 37.4^{\circ} W \, 6.2^{\circ}$, elevation 72 m), in the "Photovoltaic Geographical information system" (PVGIS project) of the European Commission Joint Research Centre [39].

3.1. Input data

460

467

472

473

3.1.1. Technical parameters

To run the model, the following hourly annual input data is required:

- Direct normal irradiation (DNI)
- Optical efficiency solar field (η^{opt})
- Global tilted irradiation (GTI)

In the present study, the typical meteorological year (TMY) is used as a representative year. Then, the direct normal irradiation is used to model a solar tower plant in SAM 2019 [29] to estimate the hourly optical efficiency of the heliostat field of the solar tower system. While values of hourly optical efficiency during summer days are from 0.42 to 0.6, winter day values are between 0.3 to 0.55, and the annual average value $(\bar{\eta}^{opt})$ is around 0.53. According to the previous equations and relations, the model also needs a series of technical and financial parameters. Among the technical parameters necessary to run the model are: efficiencies of each component (from [29]), thermodynamic properties of the elements (from table 1), and operational temperatures and pressures of each subsystem from [40]. In addition, the model considers thermal efficiencies and heat losses in the carbonator and heat exchangers. Storage tanks are modelled by mass balances, and heat losses are considered according to the design of the tanks, i.e. the insulation of the storage tanks is designed to achieve a heat transfer coefficient in the order of 100 $W m^{-2}$, and its losses are included as electrical consumption of the power plant.

487 3.1.2. Financial parameters

Financial parameters used in the model are invest-522 ment costs (IC) and operational and maintenance costs⁵²³ (O&MC) of the solar tower, the CaL system and the photovoltaic system. The capital cost of the heliostat field,⁵²⁴ the solar tower and the photovoltaic system were obtained by modelling both a solar tower power plant and a photovoltaic system in SAM [29]. Then, the estimate of the total land area and cost (using a value of 25000 USD/ha) was used from these simulations. Capital costs for the calciner (here the investment cost was increased by 10%to include the connections necessaries to install it in the solar tower receiver), carbonator, compressors, turbines, and other major components for the CaL system are summarised in table 2 where the average exchange rate considered was $r_{exch} = 1.18$ (EUR USD, 2018) [41]. For the calciner and carbonator, equations 2 and 22 are used to estimate the thermal power in order to calculate the scaling parameter applied in the equation for investment cost:

$$Q^{Carbonator} = Q^{Calciner} \cdot \eta^{overall,th} \tag{22}$$

where $\eta^{opt} \approx 0.53$, $\eta^{receiver} = 0.85$, $DNI_{design} = 0.95 \ kW/m^2$, $Q^{curtailment} = 0$, and $\eta^{overall,th} = 0.9$.

Finally, a contingency of 7% and an EPC (engineering, 490 procurement and construction) cost of 13% were consid-491 ered [29]. In addition, to include all other components and 492 auxiliary systems, a balance of plant of 10% was used. 493 The last necessary input data is the hourly power that 494 the power plant have to dispatch: P_i^{demand} . This is used 495 to calculate the loss of power supply (LPS_i) as a metric 496 to estimate the reliability or dispatchability of the power 497 plant under that commitment. 498

499 3.2. Validation Aspen $Plus^{TM}$

In order to validate the model, different configurations 500 (based on [24]) were evaluated using Aspen PlusTM and 501 optimised by our model written in Python. Table 3 com-502 pares three different cases, which shows the mass flow rate 503 of different streams $(kg \ s^{-1})$ and the energy conversion in 504 turbines, compressors, and heat exchangers (MW). In the 505 table, the three sections in the first row indicate: the ther-506 mal power available in the calciner (MW_{th}) , solar multiple 507 (SM) as described in [45] and CaO conversion in the car-508 bonator (X). As can be seen in the table, in most of the 509 values, the difference between the values obtained through⁵²⁵ 510 the Python and Aspen models is less than 1%. 526 511

512 3.3. Linear scalarisation method, definition of ω 528

In the present study, as shown in table 4, different opti-513 misation routines with different ω were evaluated (accord-514 ing section 2.5). Table 4 shows that an $\omega = 1$ is a suitable 515 scaling factor. This can be explained because the units 516 of both objectives are the same and both have the same 517 order of magnitude in each operation time step. In addi-518 tion, in the present model there are no penalties or cost 519 for energy not served. In other cases, for instance, when 520

the cost associated with unserved energy is greater than the cost of energy generation, a large scaling factor may be more appropriate.

3.4. Solar Power Plant Design

According figure 1, to optimise the annual operation of the power plant, the equipment sizes have to be known. This section presents a process to estimate the capacities of each main component using the equations and relationships described above. In a future study, this method will be improved by defining a second optimisation stage (similar to the design optimisation routine by genetic algorithms developed in [13]).

To establish a case study, it is necessary to define the capacities of the main components of the solar power plant. The process starts with the definition of the expected average power dispatched by the CSP+CaL system. In this case, a capacity of 15 MW is defined. Then, according to the estimated global efficiency value reported in [24] $(\eta_{CSP,Rec} = 0.321)$, it is possible to estimate the average power needed in the calciner: $\bar{Q}^{calc} \approx 47MW_{th}$. Next, using the equation 2 modified to take into account the average thermal power available in the calciner (\bar{q}^{calc}) per square meter of heliostat field, it is possible to have an estimate value for the heliostat aperture area (A^{CSP}) :

$$\bar{Q}^{Calc} = A^{CSP} \cdot \bar{q}^{Calc} = 47,000 \ kW \tag{23}$$
where

where

$$\bar{q}^{Calc} = \frac{\sum_{1}^{8760} \eta_i^{opt} \cdot \eta^{receiver} \cdot DNI_i}{8760} \approx 0.1089 \ \frac{kW}{m^2} \tag{24}$$

By using SAM [29] for the simulation of solar tower plant located in Seville, the average thermal power in the receiver per square meter of heliostat reflective area is approximately $0.1032 \ ^{kW}/m^2$. Hence,

$$A^{CSP} \approx 430,000 \ m^2$$

Then, with this solar field aperture area, the design capacity of the calciner is calculated considering the equation given above (with $\bar{\eta}^{opt} \approx 0.53$, $\eta^{receiver} = 0.85$, $DNI_{design} = 0.95$):

$$Q^{calc,design} \approx 180 \ MW_{th}$$

After that, in order to find the capacities of each component mentioned in section 3.4, this thermal power is used as input in the Aspen model ($Q^{calc} = 180 \ MW_{th}$), and the following capacities for each components were obtained:

$$P^{\rm ST} \approx 10 \ MW$$

 $P^{\rm MC} \approx 23 \ MW$
 $P^{\rm MT} \approx 43 \ MW$
 $P^{\rm HPSC} \approx 10 \ MW$
 $P^{\rm HPST} \approx 2 \ MW$

Table 2: References for estimating CaL components

Component	Scaling parameter	Investment cost (IC) in MUSD	Ref.
		TO (10110 0067 10 6)	[(0]
Calciner	Thermal Power (MW_{th})	$IC = (13140 \cdot Q_{calc}^{0.07} \cdot 10^{-6}) \cdot r_{exch}$	[42]
Carbonator	Thermal Power (MW_{th})	IC= $(16591 \cdot Q_{carb}^{0.67} \cdot 10^{-6}) \cdot r_{exch}$	[42]
Steam power cycle	Cycle gross capacity (MW_e)	$IC = (290 + 1040) \cdot P_{max}^{ST} \cdot 10^{-6}$	[29]
Heat exchangers	area (m^2) and pressure (bar)	$\text{IC} = (2546.9 \cdot A_{HE}^{0.67} \cdot P_{HE}^{0.28} \cdot 10^{-6}) \cdot r_{exch}$	[42]
Cooling towers	Thermal Power (MW_{th})	$IC = (32.3 \cdot Q_{cool} \cdot 10^{-3}) \cdot r_{exch}$	[42]
CO_2 compressors and turbines	-	See reference for calculation procedure	[42]
CO_2 storage vessel	-	See reference for calculation procedure	[43]
Solids storage tanks	-	See references for calculation procedure	[44], [43]

Table 3: Validation Aspen $Plus^{TM}$

		100 MW	$f_{th}, SM=3$	$ 33MW_t$	$_h$, SM=1	$100MW_{th}, x=0.3$		
item	unit	Aspen	Python	Aspen	Python	Aspen	Python	
s2	kg/s	216.6	215.8	72.2	71.6	125.6	125.2	
c2	kg/s	64.6	64.3	64.6	64	33.9	33.8	
g9	kg/s	133.9	134	133.8	134.4	132.6	132.7	
g13	kg/s	126.2	126.5	126.2	126.8	124.6	124.7	
ST	MW	5.8	5.8	1.9	1.9	6.1	6.1	
MC	MW	12.9	12.8	12.9	11.5	12.8	12.7	
MT	MW	23.9	24	23.9	24	23.6	23.6	
HPSC	MW	5.3	5.3	0	0	5.6	5.6	
HPST	MW	0	0	0	0	0	0	
HXG	MW	75.9	75.8	75.9	76	75	74.8	
P^{Net}	MW	8.2	8.2	11.3	12.5	9.3	9.3	

Table 4: Scalarisation method

Objective	unit	$\omega = 0$	$\omega = 1$	$\omega ightarrow \infty$
E^{net*} LPSC	$ m GWhyear^{-1}$ $ m GWhyear^{-1}$	$118.2 \\ 24.6$	$\begin{array}{c} 117.6\\ 21.0\end{array}$	$115.6 \\ 18.9$

Then, a number of storage hours can be defined to combine with the specific power production defined above, to estimate the capacity of the *CaO* storage tank (with $\rho_{CaO} \approx 3370 \ kg/m^3$ [46], and values of porosity and packing density of solids equals to 0.5 and 0.6 respectively). For instance, with 20 hours of storage:

$$\xi_{i,P} = 0.053 \ \frac{MWh}{ton_{CaO}} = \frac{15 \ MW \cdot 20 \ h}{STO^{CaO} \cdot \rho_{CaO}}$$

$$\rightarrow STO^{CaO} \approx 5650 \ m^3$$

Now, considering the following properties in the stor-535 age tanks: $\rho_{CaCO_3} \approx 2700 \ ^{kg}/m^3$ [46] (porosity = 0.5) and₅₅₁ 536 $\rho_{CO_2} \approx 762 \ kg/m^3$, a CaO conversion X=0.15, an estimate 537 of the capacity in m^3 of the two other tanks can be cal-552 culated as a ratio of STO^{CaO} , where $V_{m,i}$ is the molar553 538 539 volume of substance i, defined as the volume occupied by 554 540 one mole of component i in the storage tank or vessel, by 555 541 the following relationships: 542 556

$$V_{m,i} = \frac{MW_i}{\rho_i} \tag{25}$$

$$STO^{Solids} = STO^{CaO} \cdot \left(x \cdot \frac{V_{m,CaCO_3}}{V_{m,CaO}} + (1-x) \right)$$
(26)
\$\approx 5735 m^3\$

$$STO^{CO_2} = STO^{CaO} \cdot \left(x \cdot \frac{V_{m,CO_2}}{V_{m,CaO}}\right) \approx 875 \ m^3$$
 (27)

Finally, according to section 2.5, the model was evaluated with $\omega = 0$ to maximise the energy dispatched and the capacities of all components indicated above. By the operational optimisation routine, it was calculated that the total net energy delivered in one year is 118.4 *GWh*, and the average power dispatched is 13.5 *MW*. Therefore, for the following calculations, the power commitment will be defined as $P_i^{commit} = 13.5 MW$, $\forall i$.

4. Results and Analysis

To compare the results of different designs, nine configurations were analysed, which are summarised in table 5. The estimated capacities above are shown as "Base Case" configuration. The columns of table 5 show the name given to the configuration (Base Case, A to H), then the aperture

546

547

area of the heliostat field, the power capacity of the steam⁶¹⁴ 557 turbine, the main compressor and turbine capacities, next,615 558 the capacities of the high pressure compressor and turbine,616 559 columns 8 to 10 show the capacities of the storage tanks,617 560 and finally, the photovoltaic solar field area. In each row, 618 561 different designs are presented, which are related to the619 562 Base Case, and all the configurations have the same aper-620 563 ture area of the heliostat field. For example, in configura-621 564 tion A the capacity of each component was increased by 622 565 20%, while in configuration B by 50%. Compressors and 623 566 turbines of configuration C increased by 50% and storage624 567 remains the same. Capacities of the storage systems in₆₂₅ 568 configuration D were multiplied by 3. Configuration E, F,626 569 G and H are similar to B (50% increase in the capacity of $_{627}$ 570 each component), but now integrated with 10, 20, 30 and 628 571 40 hectare (1 hectare = 10,000 m^2) of photovoltaic solar₆₂₉ 572 field area. 573 630

The results of the operational optimisation for all configu-631 574 rations described in table 5 are presented in table 6. This632 575 table shows all configurations and all key performance in-633 576 dicators mentioned in section 2.3. 577 634 First, the Base Case: according to table 6, for this configu-635 578 ration and considering the typical meteorological year, the636 579 total net energy delivered to the network reaches 118 GWh₆₃₇ 580 (97 GWh dispatched to the commitment and 21 GWh sur-638 581 plus sent to the grid), and 18% of the commitment is not639 582 supplied. 52 GWh_{th} have to be curtailed in the solar field, 640 583 and the difference between the initial and the final hour of_{641} 584 operation was 220 MWh (equivalent to approximately 16642 585 hours fulfilling the 13.5 MW commitment). The average₆₄₃ 586 net power was 13.4 MW, while the maximum power dis-644 587 patched by the system was 22 MW. The capacity factor is645 588 65%, and it is highly dependent on the capacity of the main 646 589 components. As a comparison, a capacity factor of 58%647 590 was estimated by [33] for a CSP with 16 hours of TCES.648 591 In a future work, the capacity factor of this hybrid solar649 592 power plant would be improved by the optimisation of the650 593 size of the units. The efficiency based on the energy used₆₅₁ 594 in the receiver is 32.8% (compared with 32.1 estimated by $_{552}$ 595 [24]), and the efficiency based on direct normal irradiation₆₅₃ 596 falls to 12.2%. Finally, the estimated investment is 323654 597 MUSD and the operational and maintenance costs are 1.9655 598 MUSD per year, resulting in a levelised cost of energy of 656 599 252 USD MWh^{-1} . 600

Comparing the Base Case with configuration A, the re-658 601 sults indicate that by increasing the capacities of all com-659 602 ponents by 20%, the net energy increases by 11% and the 660 603 curtailment is reduced by 76%, improving the global ef-661 604 ficiency based on the DNI. The LPSP still exceeds 15%,662 605 and although the investment increase by 2%, the LCOE₆₆₃ 606 is reduced by 7%. Then, configuration B (which increases₆₆₄ 607 all capacities by 50%), resulted in zero curtailment, which₆₆₅ 608 means that in this configuration, the design of the CSP-666 609 CaL is oversized. The previous results show the key im-667 610 portance of selecting a certain equipment size for the plant₆₆₈ 611 efficiency, which is out of the scope of the present paper,669 612 but will be addressed in a future optimisation study. 613 670

When comparing configurations B, C and D, it is possible to note that, starting with the Base Case, an increase in the capacity of compressors and turbines results in more energy dispatched but a lower dispatchability and capacity factor compared with increasing the storage tank capacities, nevertheless, a better approximation to an optimal design would be by an appropriate and independent sizing of all units. Therefore, this enhances the importance of including a second optimisation stage in order to find the best design based on technical and financial performances. Finally, configurations E, F, G and H show that the integration of a photovoltaic system is important to reduce the levelised cost of the energy, by including intermittent (non-dispatchable) but less expensive power generation. In these cases, the LCOE becomes less than 200 USD MWh^{-1} . However, the integration of PV without a reduction in the capacities of the CSP-CaL system means a large energy generation and a large surplus that have to be dispatched to the network. For instance, in configuration G, which includes 30 hectare of PV modules, the energy dispatched to fulfil the commitment is 111 GWh (47% of total) while the excess of energy that have to be sent to the grid reaches 124 GWh (53% of total). In this case, it is possible that the dispatch of the surplus has negative effects on the local market, and that, depending on the mechanisms of the market, the energy may not be sold at a competitive price.

In order to know the power flow profiles of a hybrid solar power plant with thermochemical energy storage, figures 2a and 2b show two weeks of operation of configuration G, one week in summer and another in winter along with the solar resource. The continuous purple line and the dashed black line show the solar irradiation (direct normal and global tilted respectively), for the location under study. The green and orange bars of the diagrams represent the power dispatched by the PV system and the CSP-CaL respectively. These results highlight that in the case of a hybrid solar power plant composed of CSP-CaL and PV, the strategy suggested by the optimisation routine is that the photovoltaic system delivers energy during the day, while the CSP-CaL stores energy to be dispatched during the night, unless there is a large solar irradiation available that allows the CSP-CaL to dispatch energy during day and night (in the case of summer). In addition, these results demonstrate the importance of the multi-objective optimisation technique presented. The diagram confirms that during winter and cloudy summer days, the CSP-CaL dispatch energy following both objectives, maximising the energy delivered, and fulfilling the commitment. Another crucial finding, shown in the diagram as a dashed red line, is the state of charge of the CaO storage tank. Because the state of charge of the storage never reaches 0% during the week presented for the summer, and despite that there is no restriction in the maximum capacity that can be dispatched, it could be inferred that the storage system is oversized compared with the capacities of compressor and turbines. Besides, the operation profile during winter suggests that there are some capacities that could be712
increased in the CSP-CaL system in order to increase the713
dispatchability of the hybrid plant.

674 4.1. Sensitivity Analysis

In this last section, a sensitivity analysis will be carried⁷¹⁷ out by varying different financial and technical parameters,⁷¹⁸ as well as the design of some of the components of config-⁷¹⁹ uration G presented in table 6. The parameters selected⁷²⁰ for the sensitivity analysis and its original values are:

 $\eta^{receiver} = 0.85$, efficiency reveiver-calciner r = 7%, annual interest rate $A^{PV} = 30,000 \ m^2$, area photovoltaic field $\kappa^{Sto} = 1$, multiplier capacities storage tanks

 $\kappa^{T\&C} = 1$, multiplier capacities turbines and compressors ζ^{726}_{727} $\zeta^{Reactors} = 1$, multiplier investment carbonator and calcinger

729 In this case, because the analysis covers financial and tech- $_{730}$ 675 nical parameters, appropriate key performance indicators $_{731}$ 676 are the levelised cost of the energy (LCOE) and the loss of $_{732}$ 677 power supply probability (LPSP) (see section 2.3). Figures₇₃₃ 678 3a and 3b show the sensitivity analysis for the LCOE and $_{734}$ 679 LPSP by varying the parameters described above between $_{735}$ 680 minus 10% and plus 10% from the original value reported. $_{736}$ 681 Figure 3a indicates that the parameters that have the $_{737}$ 682 largest influence on the LCOE are the efficiency of the $_{738}$ 683 calciner, the interest rate, and the investment cost of re-684 actors. The efficiency of the calciner increases the thermal $_{740}$ 685 energy available in the endothermic reaction and the total₇₄₁ 686 energy dispatched, for instance, if $\eta^{receiver}$ is increased by 687 5% ($\eta^{receiver} \approx 0.89$), the LCOE decreases by 3%. More-688 over, the configuration of the cycle could integrate differ- $_{744}$ 689 ent components to increase the cycle efficiency as shown₇₄₅ 690 in [47], in order to improve the affordability and dispatch- $_{746}$ 691 ability of the system. Next, the interest rate also has an $_{\rm _{747}}$ 692 important influence in the estimation of the LCOE, for $_{748}$ 693 example, if the project can be financed with a $r \approx 6.3\%_{_{749}}$ 694 (instead of 7%), the LCOE falls by 6%. Finally, a reduc- $_{750}$ 695 tion in 10% in the capital cost of the reactors (calciner₇₅₁ 696 and carbonator) decreases the LCOE in 4%. This reduc-697 tion is very likely to be achieved because this technology $_{753}$ 698 is at an early stage of maturity. Furthermore, the $\mathrm{LCOE}_{_{754}}$ 699 is highly dependent on the location of the power plant. $_{755}$ 700 In a future study, different regions will be analysed in or- $_{756}$ 701 der to compare key performance indicators under different 702 solar resource and market features. For instance, if con-703 figuration G (with modifications in the solar field to $\operatorname{keep}_{759}$ 704 fixed the total energy available) is analysed under the solar $_{760}$ 705 irradiation data corresponding to Atacama-1, a hybrid so-761 706 lar power plant located in Northern Chile [11], the $\mathrm{LCOE}_{_{762}}$ 707 drops to 138 USD MWh^{-1} and the LPSP reaches 0.1%. 708 For the LPSP, by increasing any of the parameters shown $\frac{1}{764}$ 709 in figure 3b, the energy dispatched to fulfil the commit- $\frac{1}{765}$ 710 ment increases (and the LPSP decreases). Figure 3b shows $_{766}$ 711

that increasing the efficiency of the calciner or the capacity of the storage is key to increase the dispatchability. Finally, the results and diagrams suggest that by increasing the storage capacities it is possible to dispatch a similar amount of energy, and when a large storage capacity is available, it is possible to manage the time when energy is dispatched, increasing the dispatchability of the power plant, allowing a long-term energy storage capacity.

5. Conclusions

715

716

721

722

723

724

725

This paper presents a multi-objective optimisation framework and a linearised scalarisation technique for the operation of a concentrated solar power plant with calciumlooping (CaL) as thermochemical energy storage. The model is developed with a linear programming model of the operation of the power plant validated against the software Aspen Plus. Different designs and the hybridisation with a photovoltaic system were evaluated. This contribution provides relevant information to make renewable energy systems affordable and reliable. The optimisation framework focuses on finding the best strategy of a hybrid power plant to dispatch energy during the year, and is able to report the hourly power flow profiles by each main component of the power plant, as well as the mass flow rates of each stream. In addition, this framework enables long-term studies for the optimisation of the operation of solar power plants with thermochemical energy storage and their integration into energy systems.

The results summarise key performance indicators obtained by optimising the operation of a power plant located in Seville, Spain, using the solar irradiation data of the typical meteorological year as input. Among these indicators it is possible to find the total energy dispatched during the year, the mismatch between supply and demand for a given commitment, the overall efficiency of the power plant, the investment and the levelised cost of the energy. In addition, by changing the input data it is possible to optimise a similar solar power plant in any location.

The findings of this study indicate that the use of a thermochemical energy storage system in concentrated solar power plants increases the dispatchability, and by hybridising with a photovoltaic system, it can become cost competitive. However, the high differences in the solar irradiation in Seville between summer and winter could have a negative effect on the power system during summer by dispatching a large amount of power during the day. Therefore, a detailed analysis of the local electrical system and its flexibility have to be analysed together with the correct design of the power plant.

Our research has highlighted the importance of the multiobjective optimisation of the operation of a renewable power plant to reduce the fluctuations and maximise the energy delivered, which also influences the levelised cost of the energy. When the design of the main components of the CaL is oversized (keeping the solar field fixed), less energy



Figure 2: Optimised Operation of the hybrid solar power plant, configuration G, plus solar resource and commitment

Configuration name	$\begin{array}{c} A^{CSP} \\ m^2 \end{array}$	$\begin{array}{c} P^{\rm ST} \\ \rm MW \end{array}$	$\begin{vmatrix} P^{\rm MC} \\ MW \end{vmatrix}$	P^{MT} MW	P^{HPSC} MW	P^{HPST} MW	$\frac{STO^{CaO}}{m^3}$	$\frac{STO^{Solids}}{m^3}$	$\frac{STO^{CO_2}}{m^3}$	$\begin{array}{c} A^{\rm PV} \\ m^2 \end{array}$
Base Case	430,000	10	23	43	10	2	5650	5735	875	0
А	430,000	12	28	52	12	2.5	6780	6880	1050	0
В	430,000	15	35	65	15	3	8475	8600	1310	0
С	430,000	15	35	65	15	3	5650	5735	875	0
D	430,000	10	23	43	10	2	16950	17200	2625	0
Ε	430,000	15	35	65	15	3	8475	8600	1310	100,000
F	430,000	15	35	65	15	3	8475	8600	1310	200,000
G	430,000	15	35	65	15	3	8475	8600	1310	300,000
Н	430,000	15	35	65	15	3	8475	8600	1310	400,000

Table 5: Different configurations analysed

Table 6: Operational optimisation all previous designs (table 5)

KPI	unit	Base Case	A	В	\mathbf{C}	D	Ε	F	G	H
E^{net*}	$\rm GWhyear^{-1}$	118	131	137	134	124	169	202	235	268
LPSP	%	18	16	14	17	13	9	7	6	5
E^{commit}	$\rm GWhyear^{-1}$	97	100	101	98	103	107	110	111	112
E^{excess}	$\rm GWhyear^{-1}$	20	32	35	37	21	62	92	124	156
$E^{curtailed}$	$GWh_{th} \ year^{-1}$	52	13	0	9	33	0	0	0	0
ΔE_{f-i}	MWh	220	330	420	270	820	420	420	420	420
\bar{P}^{net}	MW	13.4	15.0	15.6	15.3	14.1	19.3	23.1	26.8	30.6
P_{CSP}^{max}	MW	22.0	26.6	33.2	33.2	22.0	33.2	33.2	33.2	33.2
CF_{CSP}	%	65	60	50	48	69	50	50	50	50
$\eta_{CSP,Rec}$	%	33.8	33.0	33.3	33.4	32.7	33.1	33.1	33.2	33.2
$\eta_{CSP,DNI}$	%	12.2	13.6	14.2	13.9	12.8	14.1	14.1	14.1	14.1
P_{hybrid}^{max}	MW	22.0	26.6	33.2	33.2	22.0	44.8	58.9	74.9	91.3
Investment	MUSD	323	331	341	336	341	384	427	470	513
O&M	$MUSD \ year^{-1}$	1.9	2.2	2.7	2.7	1.9	2.8	3.0	3.1	3.3
LCOE	$\rm USDMWh^{-1}$	252	233	233	235	252	212	196	185	176

have to be curtailed, and more energy can be dispatched.789 767 However, this requires larger investments and results in⁷⁹⁰ 768 lower capacity factors, therefore a proper balance between₇₉₁ 769 capacities and curtailed energy should be pursued. In ad-792 770 dition, it was found that the integration of a large CaL793 771 system, which has the capacity to store a larger amount⁷⁹⁴ 772 of energy, results in an significant reduction in the loss of₇₉₅ 773 power supply and an increase in the capacity factor. This₇₉₆ 774 means that a system with a large capacity to store energy₇₉₇ 775 can work as a medium (or even long) term energy storage. 776

Similar to the previous point, greater energy storage ca pacity requires larger investment.

The hybridisation with a photovoltaic system has impor-779 tant effects. Because a larger solar field area is available, 780 there is an improvement in both the energy dispatched₈₀₁ 781 and the loss of power supply. In addition, the operational $_{802}$ 782 strategy allows that, during the day the PV dispatches 783 power while the CSP stores energy, and during the night $_{804}$ 784 the CSP could dispatch, reducing the mismatch between $_{\scriptscriptstyle 805}$ 785 supply and demand when no solar irradiation is available. $_{806}$ 786 Because PV is cheaper compared with CSP, the hybrid is- $_{\scriptscriptstyle 807}$ 787 ation results in a global reduction in the levelised cost $\mathrm{of}_{\scriptscriptstyle 808}$ 788

energy.

This study is the first step to improve the modelling and optimisation of the integration of CaL as thermochemical energy storage system in hybrid solar power plants. Currently a second stage optimisation is under development, in order to define the best capacities of the main components of the power plant by exploiting synergies related with the dispatchability of CSP-CaL and affordability of PV systems.

Acknowledgements

Ruben Bravo is supported by a PhD Scholarship from Becas Chile, National Commission for Scientific and Technological Research (CONICYT-Chile), Folio 72160177, 2015. The present research was supported by the Energy Technology Partnership (ETP), International Exchange Grants for Postgraduate and Early Career Researcher Exchanges (PECRE) 2018. Part of this project was developed within the Horizon 2020 Project Socratces, Grant Agreement 727348. Part of this work has been supported by the Spanish Government Agency Ministerio de Economia y Competitivi-



 809 dad (MINECO- FEDER funds) under contract CTQ2017-876 870 83602-C2 (-1-R and -2-R).

811 References

- [1] IEA, Energy Technology Perspectives 2017, International En ergy Agency, Organisation for Economic Co-operation and De
 velopment (2017). doi:10.1787/energy_tech-2017-en.
 - [2] NREL, System Advisor Model (SAM) (2018).
- [2] NREL, System Advisor Model (S
 URL https://sam.nrel.gov/
- [3] M. Pehl, A. Arvesen, F. Humpenöder, A. Popp, E. G. Hertwich,
 [3] M. Pehl, A. Arvesen, F. Humpenöder, A. Popp, E. G. Hertwich,
 [3] G. Luderer, Understanding future emissions from low-carbon
 power systems by integration of life-cycle assessment and inte grated energy modelling, Nature Energy 2 (12) (2017) 939–945.
 [30] doi:10.1038/s41560-017-0032-9.
- [4] M. Keay, D. Robinson, The limits of auctions: reflections on the
 role of central purchaser auctions for long-term commitments
 in electricity systems, Tech. rep., Oxford Institute for Energy
 Studies (2019). doi:10.26889/9781784671341.
- [5] P. Denholm, M. Hand, Grid flexibility and storage required to achieve very high penetration of variable renewable electricity, Energy Policy 39 (3) (2011) 1817–1830. doi:10.1016/j.enpol.
 2011.01.019.
- [6] P. Denholm, J. Jorgenson, M. Miller, E. Zhou, C. Wang, Meth-⁹⁰⁰ ods for Analyzing the Economic Value of Concentrating Solar⁹⁰¹ Power with Thermal Energy Storage Methods for Analyzing the⁹⁰³ Economic Value of Concentrating Solar Power with Thermal⁹⁰⁴ Energy Storage, Tech. Rep. July, National Renewable Energy⁹⁰⁵ Laboratory (2015).
- [7] R. Fernández, C. Ortiz, R. Chacartegui, J. M. Valverde, J. A.
 Becerra, Dispatchability of solar photovoltaics from thermo-908

chemical energy storage, Energy Conversion and Management 191 (2019) 237-246. doi:10.1016/j.enconman.2019.03.074.

- [8] R. Bravo, D. Friedrich, Integration of energy storage with hybrid solar power plants, Energy Procedia 151 (2018) 182–186. doi: 10.1016/j.egypro.2018.09.045.
- [9] C. Ortiz, R. Chacartegui, J. M. Valverde, A. Alovisio, J. A. Becerra, Power cycles integration in concentrated solar power plants with energy storage based on calcium looping, Energy Conversion and Management 149 (2017) 815–829. doi:10.1016/ j.enconman.2017.03.029.
- [10] A. Zurita, C. Mata-Torres, C. Valenzuela, C. Felbol, J. M. Cardemil, A. M. Guzmán, R. A. Escobar, Techno-economic evaluation of a hybrid CSP + PV plant integrated with thermal energy storage and a large-scale battery energy storage system for base generation, Solar Energy 173 (2018) 1262-1277. doi:10.1016/j.solener.2018.08.061.
- R. Bravo, D. Friedrich, Two-stage optimisation of hybrid solar power plants, Solar Energy 164 (2018) 187–199. doi:10.1016/ j.solener.2018.01.078.
- [12] M. Petrollese, D. Cocco, Optimal design of a hybrid CSP-PV plant for achieving the full dispatchability of solar energy power plants, Solar Energy 137 (2016) 477-489. doi: 10.1016/j.solener.2016.08.027.
- [13] R. Bravo, D. Friedrich, Two-Stage, Multi-objective Optimisation Framework for an Efficient Pathway to Decarbonise the Power Sector, in: EngOpt 2018 Proceedings of the 6th International Conference on Engineering Optimization, Springer International Publishing, Cham, 2018, pp. 1420–1433. doi: 10.1007/978-3-319-97773-7_122.
- [14] M. Gambini, M. Vellini, Hybrid thermal power plants: Solarelectricity and fuel-electricity productions, Energy Conversion and Management (2019) 682–689doi:10.1016/j.enconman. 2019.04.073.
- [15] M. Medrano, A. Gil, I. Martorell, X. Potau, L. F. Cabeza, State of the art on high-temperature thermal energy storage for power generation. Part 2-Case studies, Renewable and Sustainable Energy Reviews 14 (1) (2010) 56-72. doi:10.1016/j.rser.2009. 07.036.
- [16] B. Zalba, J. M. Marín, L. F. Cabeza, H. Mehling, Review on thermal energy storage with phase change: Materials, heat transfer analysis and applications, Applied Thermal Engineering 23 (3) (2003) 251–283. doi:10.1016/S1359-4311(02) 00192-8.
- [17] P. Pardo, A. Deydier, Z. Anxionnaz-Minvielle, S. Rougé, M. Cabassud, P. Cognet, A review on high temperature thermochemical heat energy storage, Renewable and Sustainable Energy Reviews 32 (2014) 591-610. doi:10.1016/j.rser.2013. 12.014.
- [18] R. Chacartegui, A. Alovisio, C. Ortiz, J. M. Valverde, V. Verda, J. A. Becerra, Thermochemical energy storage of concentrated solar power by integration of the calcium looping process and a CO 2 power cycle, Applied Energy 173 (2016) 589-605. doi: 10.1016/j.apenergy.2016.04.053.
- [19] P. E. Sánchez Jiménez, A. Perejón, M. Benítez Guerrero, J. M. Valverde, C. Ortiz, L. A. Pérez Maqueda, High-performance and low-cost macroporous calcium oxide based materials for thermochemical energy storage in concentrated solar power plants, Applied Energy (2019) 543–552doi:10.1016/j.apenergy.2018. 10.131.
- [20] C. Knoll, D. Müller, W. Artner, J. M. Welch, E. Eitenberger, G. Friedbacher, A. Werner, P. Weinberger, M. Harasek, Magnesium oxide from natural magnesite samples as thermochemical energy storage material, in: Energy Procedia, Vol. 158, Elsevier Ltd, 2019, pp. 4861–4869. doi:10.1016/j.egypro.2019. 01.707.
- [21] C. Ortiz, J. Valverde, R. Chacartegui, L. Perez-Maqueda, P. Giménez, The Calcium-Looping (CaCO3/CaO) process for thermochemical energy storage in Concentrating Solar Power plants, Renewable and Sustainable Energy Reviews 113 (2019) 109252. doi:10.1016/j.rser.2019.109252.
- [22] R. L. Jaffe, T. Washington, The physics of energy, Cambridge

875

879

880

881

University Press, Cambridge, United Kingdom; New York, NY,980 2018. doi:10.1017/9781139061292. 981

909

910

940 941

942

943

944

946 947

948 949

950

951

952

953

956 957

- J. Obermeier, K. G. Sakellariou, N. I. Tsongidis, D. Baciu,982 [23]911 G. Charalambopoulou, T. Steriotis, K. Müller, G. Karagian-983 912 nakis, A. G. Konstandopoulos, A. Stubos, W. Arlt, Material984 913 development and assessment of an energy storage concept based985 914 on the CaO-looping process, Solar Energy 150 (2017) 298-309.986 915 doi:10.1016/j.solener.2017.04.058. 916 987
- [24]C. Ortiz, M. C. Romano, J. M. Valverde, M. Binotti,988 917 R. Chacartegui, Process integration of Calcium-Looping ther-989 918 mochemical energy storage system in concentrating solar power990 919 plants, Energy 155 (2018) 535-551. doi:10.1016/j.energy.991 920 2018.04.180. 921 992
- [25]R. Renaldi, D. Friedrich, Multiple time grids in operational op-993 922 timisation of energy systems with short- and long-term thermal994 923 energy storage, Energy 133 (2017) 784-795. doi:10.1016/j.995 924 energy.2017.05.120. 925
- A. Meier, N. Gremaud, A. Steinfeld, Economic evaluation of997 926 [26]the industrial solar production of lime. Energy Conversion and 998 927 928 Management 46 (6) (2005) 905-926. doi:10.1016/j.enconman.999 2004.06.005 929 1000
- [27]C. Ortiz, J. M. Valverde, R. Chacartegui, L. A. Perez-Maqueda³⁰⁰¹ 930 Carbonation of Limestone Derived CaO for Thermochemicalou2 931 Energy Storage: From Kinetics to Process Integration in Con₁₀₀₃ 932 centrating Solar Plants, ACS Sustainable Chemistry and Engi+004 933 934 neering 6 (5) (2018) 6404-6417. doi:10.1021/acssuschemeng1005 8Ъ00199. 935 1006
- [28]K. Kyaw, M. Kubota, F. Vvatanabe, H. Matsuda, M. Hasatanii,007 936 Study of carbonation of CaO for high temperature thermal en-937 ergy storage, Journal of Chemical Engineering of Japan 31 (2) 938 (1998) 281-284. doi:10.1252/jcej.31.281. 939
 - [29]NREL, Concentrating Solar Power Projects (2017).
 - URL https://www.nrel.gov/csp/solarpaces/
 - R. H. Perry, D. W. Green, J. O. Maloney, Perry's Chemical [30]engineers' handbook., seventh ed Edition, McGraw-Hill, New York ; London, 1997.
- [31] I. Dincer, M. A. Rosen, P. Ahmadi, Optimization of energy 945 systems, Wiley, 2017. doi:10.1002/9781118894484.
 - [32] E. Dick, Fundamentals of Turbomachines, Vol. 109, Springer, Dordrecht, 2015. doi:10.1007/978-94-017-9627-9.
 - [33] C. Ortiz, M. Binotti, M. C. Romano, J. M. Valverde, R. Chacartegui, Off-design model of concentrating solar power plant with thermochemical energy storage based on calciumlooping, in: AIP Conference Proceedings, Vol. 2126, AIP Publishing LLC, 2019, p. 210006. doi:10.1063/1.5117755.
- [34]D. Y. Goswami, Principles of solar engineering, third edit Edi-954 tion, Boca Raton, FL : CRC Press, 2015. 955
 - [35]Python Software Foundation, Python 3.5.3 (2017).
 - URL https://www.python.org/
- [36]W. E. Hart, C. D. Laird, J.-P. Watson, D. L. Woodruff, G. A. 958 Hackebeil, B. L. Nicholson, J. D. Siirola, Pyomo — Optimiza-959 960 tion Modeling in Python, Vol. 67 of Springer Optimization and Its Applications, Springer International Publishing, Cham, 961 2017. doi:10.1007/978-3-319-58821-6. 962
- [37]W. E. Hart, J. P. Watson, D. L. Woodruff, Pyomo: Modeling 963 and solving mathematical programs in Python, Mathematical 964 Programming Computation 3 (3) (2011) 219-260. doi:10.1007/ 965 s12532-011-0026-8. 966
- L. Gurobi Optimization, Gurobi Optimizer Reference Manual [38]967 (2019)968 969
 - URL http://www.gurobi.com
- [39]J. R. C. European Commission, JRC Photovoltaic Geographical 970 Information System (PVGIS) - European Commission (2017). 971 URL https://re.jrc.ec.europa.eu 972
- C. Ortiz, J. M. Valverde, R. Chacartegui, L. A. Perez-Maqueda, [40]973 974 Carbonation of Limestone Derived CaO for Thermochemical Energy Storage: From Kinetics to Process Integration in Con-975 centrating Solar Plants, ACS Sustainable Chemistry and Engi-976 neering 6 (5) (2018) 6404-6417. doi:10.1021/acssuschemeng. 977 8b00199 978
- [41] J. Cherowbrier, Euro to U.S. dollar exchange rate 1999-2018 979

– Statista (2019).

URL https://www.statista.com

- S. Michalski, D. P. Hanak, V. Manovic, Techno-economic feasi-[42]bility assessment of calcium looping combustion using commercial technology appraisal tools, Journal of Cleaner Production $219\ (2019)\ 540-551.\ {\tt doi:10.1016/j.jclepro.2019.02.049}.$
- [43]A. Bayon, R. Bader, M. Jafarian, L. Fedunik-Hofman, Y. Sun, J. Hinkley, S. Miller, W. Lipiński, Techno-economic assessment of solid-gas thermochemical energy storage systems for solar thermal power applications, Energy 149 (2018) 473-484. doi: 10.1016/j.energy.2017.11.084.
- [44]M. Jonemann, Advanced Thermal Storage System with Novel Molten Salt: December 8, 2011 - April 30, 2013, Tech. rep., National Renewable Energy Laboratory (2013). doi:10.2172/ 1080117.
- C. Ortiz, J. M. Valverde, R. Chacartegui, Energy Consump-[45]tion for CO2 Capture by means of the Calcium Looping Process: A Comparative Analysis using Limestone, Dolomite, and Steel Slag, Energy Technology 4 (10) (2016) 1317-1327. doi: 10.1002/ente.201600390.
- [46]J. M. Valverde, P. E. Sanchez-Jimenez, L. A. Perez-Maqueda, Limestone Calcination Nearby Equilibrium: Kinetics, CaO Crystal Structure, Sintering and Reactivity, The Journal of Physical Chemistry (2015). doi:10.1021/jp508745u.
- [47]A. Alovisio, R. Chacartegui, C. Ortiz, J. M. Valverde, V. Verda, Optimizing the CSP-Calcium Looping integration for Thermochemical Energy Storage, Energy Conversion and Management 136 (2017) 85-98. doi:10.1016/j.enconman.2016.12.093.