

Dry Carbonate Process for CO₂ capture and storage:

Integration with solar thermal power

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Abstract

Capture and sequestration of CO₂ released by conventional fossil fuel combustion is an urgent need to mitigate global warming. In this work, main CO₂ capture and sequestration (CCS) systems are reviewed, with the focus on their integration with renewables in order to achieve power plants with nearly zero CO₂ emissions. As a case study, the manuscript analyses the integration of a CO₂ sorption-desorption cycle based on Na₂CO₃/NaHCO₃ into a coal fired power plant (CFPP) for CO₂ capture with solar support for sorbent regeneration. The Dry Carbonate Process relies on the use of a dry regenerable sorbent such as sodium carbonate (Na₂CO₃) to remove CO₂ from flue gases. Na₂CO₃ is converted to sodium bicarbonate (NaHCO₃) through reaction with CO₂ and water steam. Na₂CO₃ is regenerated when NaHCO₃ is heated, which yields a gas stream mostly containing CO₂ and H₂O. Condensation of H₂O produces a pure CO₂ stream suitable for its subsequent use or compression and sequestration. In this paper, the application of the Dry Carbonate CO₂ capture process in a coal-based power plant is studied with the goal of optimizing CO₂ capture efficiency, heat and power requirements. Integration of this CO₂ capture process requires an additional heat supply which would reduce the global power plant efficiency by around 9-10%. Dry Carbonate Process has the advantage compared with other CCS technologies that requires a relatively low temperature for sorbent regeneration (<200°C). It allows an effective integration of medium temperature solar thermal power to assist NaHCO₃ decarbonation. This integration reduces efficiency losses to the associated with mechanical parasitic consumption, resulting in a fossil fuel energy penalty of 3-4% (including CO₂ compression). The paper shows the viability of the concept through economic analyses under different scenarios. The results suggest the interest of advancing in this Solar-CCS integrated concept, which shows favourable outputs compared to other CCS technologies.

Keywords

Carbon capture, Post-combustion carbon capture, Coal fired power plant, Dry Carbonate Process, CCS Economy, Solar thermal power.

1

2 **Nomenclature**

<p>ASU: Air separation unit BAC: Biomass annual cost BFB: Bubbling fluidized bed CaL: Calcium-Looping process CCS: Carbon capture and storage CFB: Circulating fluidized bed CFPP: Coal-fired power plant COE: Cost of electricity c_{CO_2}: Carbon tax COP21: 2015 Paris Climate Conference CPU: CO₂ purification unit CSP: Concentrated solar power ECCS: Emission ratio with dry carbonate process integrated ECO₂ AVOIDED: Avoided cost due to the avoided emission of CO₂, EDRYCARBONATE: Carbon capture system installation cost ENET, GAIN, year: Annual benefit due to avoided emissions. EO&M: Operation and maintenance cost EINCR: Revenues due to electricity incremented cost Eref: Reference plant emission ratio ESOLAR: Solar plant installation cost ETOT, REV: Total annual revenues ETOT: Total investment cost FB: Fluidized Bed FC: Fuel cost FCF: Fixed charge factor FGD: Flue gas desulfurization GHG: Greenhouse gases IPCC: Intergovernmental Panel on Climate Change IRR: Internal rate of return (%)</p>	<p>$m_{CO_2, FGPLANT}$: CO₂ mass flows of flue gas exits the CFPP $m_{CO_2, CARB.OUT}$: CO₂ mass flows of flue gas exits the carbonator MEA: Monoethanolamine solvent NGCC: Natural gas combined cycles NPV: Net Present Value O&M: Operation and maintenance PCC: Post-combustion capture $P_{NET, year}$: Total electric energy per year produced by the plant. Q_{CFPP}: CFPP thermal power consumptions Q_{DC}: Dry carbonate thermal power consumption SE-SMR: Sorption-enhanced steam methane reforming SMR: Steam methane reforming SPB: Simple payback SPECCA: Specific energy consumption for CO₂ avoided TCR: Capital cost $ton_{CO_2, ref}$: Reference plant CO₂ emissions $ton_{CO_2, CCS}$: CO₂ emissions with the dry carbonate process integrated VOM: Variable cost W_{CFPP}: CFPP net power production W_{COMP}: Electric consumption for CO₂ compression $W_{cons, DC}$: Dry carbonate electric power consumption W_{solid}: Electric consumption for solids conveying WGS: Water gas shift YR: Yearly Revenues ϵ_{ABS}: Absorption efficiency η_{plant}: Plant efficiency η_{CCS}: Plant efficiency with the dry carbonate process integrated</p>
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1. Introduction

There is a worldwide interest in finding competitive solutions for capturing and sequestering the carbon dioxide (CO₂) released from fossil fuel combustion processes to mitigate global warming. In the 2015 Paris Climate Conference (COP21), a universal agreement signed by the consensus of 195 countries was reached, which has been ratified in 2016, to drastically reduce CO₂ emissions in order to keep global warming below 2°C from preindustrial levels [1]. To this end future coal-fired power plants (CFPPs) must be near to CO₂ emissions free. Currently, 76.5% of the electricity generation in the world is produced by non-renewable sources [2]. The main R&D challenge for the viability of CFPPs and other fossil fuel based facilities is to capture CO₂ by means of feasible and affordable technologies while, at the same time, penalties on power production and efficiency are minimized.

Carbon capture and storage (CCS) technologies can be classified into three main groups: pre-combustion, post-combustion and oxy-fuel combustion processes [3]. Despite post-combustion capture (PCC) processes are being widely investigated in the last years, Boundary Dam (100MWe) in Canada is currently the only commercial CFPP that applies CCS by using a chemical absorption process based on monoethanolamine (MEA). In amine-based systems the CO₂ loaded solvent is separated from the rest of the exhaust gas and heated, which yields relatively pure CO₂ ready for compression and sequestration. After regeneration, the solvent is cooled to be reused [4]. A main issue of systems based on amine absorption is the large amount of heat required to regenerate the solvent. This heat, which is usually obtained from the steam cycle, penalizes significantly the power plant efficiency. Moreover, amine-based systems have serious problems related to toxicity and corrosion [5]. In addition, additional power is required to compress the captured CO₂ for transporting it through the pipeline network to the storage site.

Among the new generation of CCS technologies under R&D the Dry Carbonate Process stands as one of the most interesting options. This process uses Na₂CO₃ solid particles as dry sorbent to separate CO₂ from other flue gases through the gas-solid carbonation reaction. An important advantage of this approach is that sorption can occur at relatively low temperature (below 100°C) to achieve a high capture capacity whereas regeneration is also carried out at relatively low temperatures (around 200°C). Such temperatures do not cause significant degradation of the sorbent besides of not requiring high amounts of energy supply [6]. Other advantages of the Dry Carbonate Process are the low cost of the sorbent as well as the high CO₂ sorption capacity [7]. Due to the high interest attracted by this technology, CO₂ capture pilot plants have been integrated in CFPP in USA and Korea [8]. Recent studies have analysed also its potential integration with the production of chemical products [9].

In this paper, a novel integration of the Dry Carbonate Process for CO₂ capture with solar thermal power is analysed. The relative low temperature in the regeneration reactor allows for an effective integration with solar thermal power, which supplies medium temperature heat at relatively reduced cost. This combination yields a significantly reduced penalty in the global efficiency compared with other technologies. Therefore, the Dry Carbonate Process has the potential for a real breakthrough as CO₂ capture system integrated in CFPP with a reduced penalty on the global process and a high CO₂ capture efficiency, which would help achieving a near to zero CO₂ emissions power plant. The deployment of the Dry Carbonate process could represent an enormous step forward to efficiently

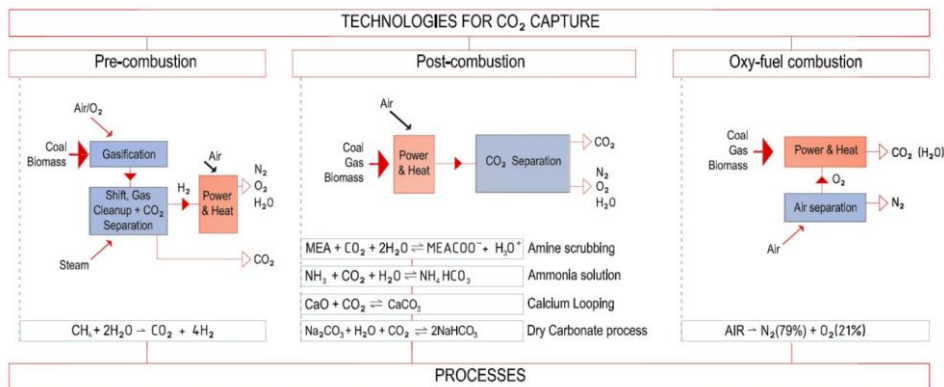
1 retrofit power plants based on no-renewable fossil fuels. Such ambitious goal is fully aligned with
 2 both the IPCC projections (CCS should contribute by about 55% to the cumulative global mitigation
 3 effort until 2100 [10]) and the IEA roadmap (1000 GW of installed Concentrated Solar power
 4 capacity by 2050 [11]).

5
 6 The present paper has the following structure. Firstly, an overview of CO₂ capture technologies is
 7 given. Different alternatives are discussed, highlighting advantages and challenges of the Dry
 8 Carbonate Process as compared to other techniques. Secondly, a case study based on the integration
 9 of a CFPP with the Dry Carbonate Process is described (layout, processes and chemistry). Based on
 10 these analyses an economic study is carried out to assess the proposed plant viability and sensitivity
 11 to different relevant parameters (price of electricity, cost of technologies, fuel cost variability, energy
 12 penalty, carbon taxes). The results obtained suggest the high interest of the proposed integration under
 13 some particular scenarios.

14 2. CO₂ capture technologies. A brief review

15 This section is devoted to an overview of the state of art regarding CO₂ capture technologies. It is
 16 structured around the three main CCS technologies (Figure 1), namely pre-combustion, post-
 17 combustion and oxy-fuel combustion processes [3].

18



19

20 Figure 1: Overview of technologies for CO₂ capture.

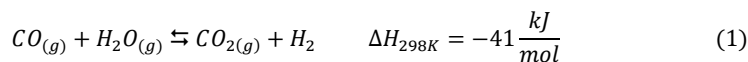
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22 2.1 Pre-combustion CO₂ capture

23 Pre-combustion CO₂ capture is based on the reaction of a fuel with oxygen or air with or without the
 24 presence of steam to produce a gaseous fuel, synthesis gas or syngas, which mainly consists of
 25 hydrogen and carbon monoxide. Carbon monoxide reacts afterwards with steam in a catalytic reactor
 26 (or shift converter) to produce CO₂ and more hydrogen. Finally, CO₂ is separated by means of
 27 physical or chemical absorption processes to obtain a hydrogen-rich fuel [10].

28

1 Syngas is usually generated from coal, biomass or natural gas by adding steam to the fuel (steam
2 reforming) or by fuel partial oxidation. When natural gas is used as primary fuel in the conventional
3 steam methane reforming (SMR) method the main reaction takes place in reformer tubes filled with
4 catalyst [12]. In the case coal or biomass are used as fuel, gasification is the main conversion
5 technology used to produce syngas. After syngas production, the water gas shift (WGS) reaction
6 (Eq.1), involves the reaction between CO and steam to yield CO₂ and H₂ as products.
7



9 The high pressure (15-40 bar) of the produced gas stream (with a CO₂ content in the range of 15-60%
10 in dry basis) facilitates the removal of CO₂ [13]. The captured CO₂ is ready to be compressed and
11 stored whereas the rich H₂-product can be used for power production through a gas turbine [14],
12 combined cycles [15] or in fuel cells [16].
13

14 The main advantage of pre-combustion capture is the production of CO₂ at elevated pressure, which
15 reduces energy consumption for compression, and the production of a carbon-free fuel [10].
16 According to the IEA GHG program [17], an efficiency penalty of 16% is expected for natural gas
17 combined cycles (NGCC) with pre-combustion CO₂ capture. This efficiency drop is caused by syngas
18 production (6%), H₂/CO₂ separation (5%), the WGS process (3%), and CO₂ compression (2%) [12].
19

20 Due to the expected efficiency drop, current research is focussed on reducing energy losses and
21 investment costs associated with CO₂ capture equipment. The most promising solution under study
22 is based on the combination of reforming and the WGS reactions with CO₂ removal in one single
23 stage, which shifts the reaction equilibrium towards the production of hydrogen. Thus, several
24 H₂/CO₂ separation technologies have emerged in the last years based on membranes and solid
25 sorbents [12]. In this regard, an modification of this process is the sorption-enhanced steam methane
26 reforming (SE-SMR), where the process is enhanced by using a CO₂ sorbent in the reactor, which
27 promotes the WGS reaction and achieves in situ CO₂ separation [18].
28

29 An option widely investigated in recent years is to integrate pre-combustion and post-combustion
30 technologies, which allows exploiting potential synergies between both technologies [19]. Thus, SE-
31 SMR-CaL and CaL enhanced gasification are being investigated. SE-SMR-CaL integration is based
32 on CO₂ capture by CaO solids, which is thermodynamically favourable at the process conditions [20].
33 According to Martinez et al. [21], the SE-SMR-CaL integration achieves much higher H₂ production
34 efficiencies (above 77%) in comparison with a conventional steam methane reforming (SMR) based
35 plant using commercially available amines for CO₂ capture.
36

37 In the case of solid fuel gasification, it is also interesting to integrate the CaL process for increasing
38 the hydrogen content in the syngas. According to Ramkumar and Fan thermodynamic analysis [22],
39 the addition of CaO as sorbent allows to attain a hydrogen purity over 99% in the absence of a water-
40 gas shift catalyst at near-stoichiometric steam to carbon (S:C) ratios, especially when operating at
41 high pressures (>21 atm) [22].

2.2 Oxy-fuel combustion

In oxy-fuel combustion a fuel is burned using pure oxygen rather than air as the primary oxidant. As a result fuel consumption is diminished and flame temperature is higher as compared to air combustion, where part of the released heat is absorbed by nitrogen. Oxy-combustion requires an air separation process to remove nitrogen from the intake air to obtain an enriched oxygen stream with an oxygen concentration as high as 95%. To avoid a too high flame temperature by directly firing the fuel with pure oxygen, the mixture is diluted with CO₂ rich recycled flue gas, or staged combustion [23,24]. In this way combustion temperature and heat transfer rate are controlled, and conventional equipment designed for conventional fuel/air combustion can be used in the coal power plant retrofitting process [25]. According to Kather et al. [26] the flue gas recirculation appropriate to yield a mixture in the boiler with combustion temperatures and heat transfer fluxes similar to those obtained with conventional coal/air-combustion is in the range of 0.65-0.75 [27]. An alternative method to control flame temperature is the use of steam injection [28]. Although oxy-fuel combustion allows reducing CO₂ emissions quite efficiently, oxygen separation from air is a high energy demanding and costly process. Thus, the main drawback for the commercial deployment of oxy-combustion is the high energy consumption for pure O₂ production in the air separation unit (ASU). Cryogenic distillation is the common technique for this purpose, which requires an energy consumption of about 200 kWh per kg of pure O₂ [29,30].

After a purification process, the almost pure CO₂ stream (~95% vol) is suitable for compression and storage or utilization [31,32]. According to Escudero et al. [33], CO₂ purification unit (CPU) specific energy consumption can be estimated as 143 kWh/tCO₂. The energy penalty associated to the integration of oxy-fuel combustion is in the range 7–13% [26,33,34].

Oxy-combustion has been successfully demonstrated in large-scale pilot projects (30 MW_e) [27,35,36]. Currently, most of the research activities on oxy-combustion are focused on pulverized coal combustion. However, Fluidized Bed (FB) combustion seems to be also an interesting alternative technology for oxy-combustion [37]. FB oxy-combustion was employed in CIUDEN project [38] with a thermal power of 30MW_{th} obtained from burning diverse fuels (petroleum coke, subbituminous coal and biomass among others) in a Circulating Fluidized Bed (CFB) boiler. Oxy-combustion using bubbling fluidized beds (BFB) has been also tested at the pilot scale [39]. A detailed review on current and proposed large scale oxy-coal combustion demonstration projects is presented in [25].

2.3 Post-combustion CO₂ capture

Post-combustion capture refers to CO₂ removal from the exhaust gas of fossil fuel power plants, which can be accomplished by using chemical solvents, solid sorbents or electrochemical processes.

In the currently mature chemical absorption technology, the solvent (typically an amine solution such as MEA) binds chemically with the CO₂. Amine absorption and stripping consists of passing the post-combustion flue gas through an aqueous amine solvent, which absorbs CO₂ by chemical reaction [40]. Then, the solvent loaded with CO₂ (the “rich” solvent) is heated up above typically 120 °C in the regenerator reactor wherein the CO₂-amine chemical reaction is reversed to release nearly pure CO₂ and regenerate the amine. The so-called “lean” solvent is recycled back to the absorber to restart the

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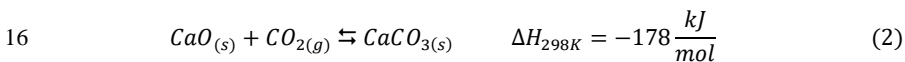
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1 process while the released CO₂ is compressed to a suitable pressure for an efficient transportation and
2 storage [41]. Amine-based PCC can efficiently remove around 90% of the CO₂ emissions.

3 In spite that CO₂ capture by chemical absorption using MEA is a well-established process in industry,
4 the commercial deployment of this technology for post-combustion CO₂ capture at large scale is
5 hindered by a combination of factors such as high energy penalty (8-12%) due to regeneration of the
6 solvent [42,43], amine toxicity [44], solvent degradation [45] and equipment corrosion [46].

7 Sorption of CO₂ by solids (either by chemical reaction or physical adsorption) is an alternative method
8 to chemical absorption with potential advantages linked to the arguably lower energy requirement for
9 regeneration and easier operation and maintenance. Suitable sorbents for CO₂ removal should meet
10 several requirements including high sorption capacity, high selectivity towards CO₂, fast kinetics,
11 mild conditions for desorption, and high multicycle stability [47].

12
13 The calcium looping (CaL) process [48] is at the basis of a 2nd generation PCC technology [47] that
14 uses CaO, typically derived from natural limestone, to capture CO₂ from flue gases by means of the
15 reversible carbonation/calcination reaction (Eq. 2):



17 The sorbent is repeatedly cycled between two CFB reactors. In the carbonator, CO₂ from the flue gas
18 is captured by carbonation of the CaO particles. Taking into account that flue gases exiting from
19 CFPP generally contain a mole fraction of CO₂ in the range 10– 15% [48,49], carbonation proceeds
20 at a satisfactory high rate at temperatures in the range 625–700°C while the reverse reaction to
21 regenerate the sorbent is carried out in the calciner under high CO₂ partial pressure, thereby at much
22 higher temperatures (900–950°C) in order to achieve complete decarbonation in a typically short
23 residence time of a few minutes [50–53]. The regenerated CaO particles are returned to the
24 carbonator while a concentrated stream of CO₂ is released from the calciner ready for compression,
25 transport and sequestration. A drawback of the process is the progressive deactivation of the
26 regenerated CaO with the number of cycles due to the harsh calcination conditions leading to marked
27 grain sintering. Thus, the CaO residual conversion at these CaL conditions is just around 0.07-0.08
28 [54,55], which requires a periodic feed of fresh limestone (make-up) to replace the poorly active
29 sorbent. The endothermicity of the calcination reaction and the temperature difference between
30 sorbent streams entering and leaving the calciner make it necessary to provide a high-energy input to
31 the calciner. In order to achieve the required calcination temperature without CO₂ dilution, Shimizu
32 and co-workers [56] proposed to oxy-fire coal (auxiliary fuel) in the calciner with O₂ provided by an
33 external air separation unit, whose estimated size would be approximately one third of that required
34 for an oxy-fuel power plant. This option serves to reach the high temperatures in the calciner typical
35 of oxy-firing while CO₂ is not diluted, albeit CaO deactivation is further enhanced by irreversible
36 CaO sulphation and ashes due to in-situ coal oxycombustion [55–58]. Recently, a combination of
37 Oxy-combustion and CaL technologies has been proposed for coal power plants with some expected
38 benefits such as the reduction of the CaL system size [59].

39
40 The CaL technology has several potential advantages when compared to amine scrubbing including
41 a higher CO₂ capture efficiency (above 90%) with minor energy penalty over the power plant (4-9%)

1 [19,60] and the low cost, wide availability and non-toxicity of natural CaO precursors such as natural
2 limestone or dolomite [61]. Even though several pilot plant projects (~ 1-2 MW_{th}) are already showing
3 promising results [52,62] the CaL technology has not yet reached a demonstration stage.

4
5 Another option for PCC is based on membrane separation, which uses the pressure difference between
6 the flue gas and the removed CO₂. The membrane technology is generally useful to treat high-
7 pressure gases [64,65] in spite of which a large number of researches have adapted it for post-
8 combustion capture [43,66,67]. Regarding efficiency penalty associated to membranes use for PCC,
9 it is estimated in the range of 4.9-8.5% [64]. Membrane separation is a promising solution to reduce
10 the costs of PCC. However, the maximum pressure ratio attainable by feed compression and/or
11 permeate vacuum is limited to approximately 10, due to cost and energy considerations [66].

12
13 A recently proposed option for PCC is the use of electrochemical processes in Molten Carbonate fuel
14 cells. Some studies show that electricity generation in the fuel cell partially compensates the penalty
15 on the original cycle in wastewater treatment plants [68] and power plants [69–71].

16
17 The development of dry CO₂ capture processes based on cheap materials operating at relatively low
18 temperatures, which would require relatively low energy for sorbent regeneration, is considered as a
19 promising pathway to advance in the deployment of CO₂ capture technologies [3,63]. In the present
20 manuscript, the use of an abundant and cheap material such as sodium carbonate (Na₂CO₃) with a
21 high dry CO₂ sorption capacity at relatively low temperatures is studied. Na₂CO₃ is the sorbent
22 employed in the Dry Carbonate Process (DCP) early proposed in [72,73] and currently being
23 demonstrated at the pilot-scale stage [74]. As Nelson et al. report [6], this capture process exhibits
24 many potential advantages. First, sorbent regeneration is achieved at relatively low temperatures
25 (100–200 °C) and it uses a dry sorbent. This helps decreasing considerably the energy required for
26 sorbent regeneration as compared to amine based absorption, wherein much energy is lost due to the
27 requirement of heating the large amounts of water in which the amine is dissolved. The DCP does
28 not require any flue gas pretreatment and the reactor materials are not subjected to high thermal
29 stresses or corrosive issues at the temperatures of operation. A further important advantage, as
30 proposed in this work, is that dry sorbent regeneration in the range of working temperatures can be
31 efficiently assisted by medium temperature solar thermal power, which significantly reduces energy
32 penalty at affordable costs.

33 **2.4 Challenges in the road to the deployment of CO₂ capture technologies**

34
35 Each one of the above reviewed PCC technologies show specific advantages but also challenges to
36 overcome at their different R&D development stages. Nonetheless, PCC is considered as the most
37 appropriate technique to be applied in the short-term for its relatively easy integration in existing
38 fossil fuel power plants [75]. PCC integration penalizes power plant performance and this hampers
39 indirectly the global CO₂ emissions reduction. The use of renewable sources such as solar thermal
40 energy or biomass to aid the process is a possibility for mitigating this penalty. An intense R&D
41 activity is being carried out to assess the feasibility of PCC-solar integration with the focus on
42 reducing solar installation costs and providing a significant fraction of the heat required for sorbent
43 regeneration [76].

1 The main drawbacks that hinder the deployment of PCC technologies are the high cost of the full
2 CCS chain and the high efficiency penalty imposed on the power plant. Further obstacles are the
3 financing of CO₂ transport infrastructure, legal and regulatory frameworks and insurance for safe
4 permanent CO₂ storage or utilization [63]. As discussed below, diverse alternatives have been
5 analysed for mitigating the efficiency penalty through the assistance of solar thermal energy mainly
6 focussed on amines and CaL based PCC systems. However, these studies fail generally to
7 demonstrate net benefits from the solar-PCC integration in the absence of external incentives [77]. A
8 main inconvenient for the integration of solar in the CaL process is that sorbent regeneration is rather
9 energy intensive requiring calcination of large flow rates of solids at very high temperatures (900–
10 950°C) [50]. On the other hand, sorbent regeneration in amine-based capture systems is carried out
11 at relatively much lower temperatures (slightly above 120 °C) [41]. Yet, regeneration of the aqueous
12 amine solution involves heating a large amount of water which requires a high energy supply [78]. In
13 this sense, the Dry Carbonate Process stands as a promising alternative since it demands a relatively
14 small amount of energy supply for sorbent regeneration. In this process the dry sorbent (Na₂CO₃) is
15 regenerated at much lower temperatures (150-200 °C) as compared to the CaL system [6,72,74]. Thus,
16 solar thermal energy requirements for sorbent regeneration would be significantly reduced, which
17 would favour the flexibility and economic viability of the solar-PCC integration.

18 **3. Integration of renewables on post-combustion carbon capture systems**

19 A main objective of R&D activities on PCC is to significantly reduce CO₂ emissions from fossil fuel
20 plants with a reduced penalty on the power plant efficiency due to the high amount of energy required
21 by the CO₂ capture processes. One way on the road to facilitate demonstration and deployment of
22 PCC technologies is the use of renewable energy sources such as solar or biomass. The energy
23 supplied by these renewable sources does not contribute to additional CO₂ emissions and is thus CO₂
24 neutral in the global process.

25 The integration of solar thermal energy in PCC technologies can be achieved through two different
26 strategies: i) by assisting sorbent regeneration, and ii) by contributing to power production to
27 minimize the efficiency penalty. Main research activities regarding solar-assisted PCC are focused
28 on amine-based CO₂ capture and the recently emerged CaL process. In order to mitigate the high
29 penalty associated to amine-based capture systems, a number of R&D activities have been carried out
30 to assess the use of solar thermal technologies:

- 31
- 32 • Parvareh et al. [76] analyzed the use of different solar thermal technologies to support amine-
33 based PCC for retrofitting CFPPs. They concluded that the large amount of thermal energy
34 required for solar integration in this PCC technology would need a huge thermal storage and
35 considerably high solar capital costs, which raises doubts on the feasibility of solar integration
36 in amine based CO₂ capture systems. In addition, the huge solar thermal energy requirement
37 for such integration to be effective is not available in most geographical locations globally.
- 38 • Mokhtar et al. [79] reported a study to reduce the energy intensity of the CO₂ separation
39 process for retrofitting existing fossil fuel power plants. Partial solar thermal energy
40 integration was assessed to reduce the penalty derived from amine-based PCC energy input
41 in a CFPP case study of 300MW_e. A main conclusion of this work is that the proposed

1 integration could be economically viable for solar collector costs of USD100/m² and if more
2 than 22% of the required solvent regeneration energy is provided by solar thermal energy.

- 3 • A techno-economic analysis of solar-assisted PCC applied to different locations in Australia
4 has been recently reported by Qadir et al. [77]. The application was divided into three
5 subsystems: the power plant (660MW_e), the amine-based PCC plant and the solar collector
6 field. Different solar technologies were compared under scenarios without and with heat
7 integration between the three subsystems. Regarding solar collectors, the integration based on
8 evacuated tube collectors performed better when heat integration between the three
9 subsystems is properly accomplished, whereas parabolic trough collectors were more effective
10 in the case without heat integration. The study concludes that process design (heat integration)
11 and climatic constraints are important considerations for the effectiveness of solar-assisted
12 PCC. However, the cases under study did not yield net benefits of using any of the solar
13 collector technologies analyzed in the absence of incentives.
- 14 • Li et al. [80] studied the feasibility of integrating solar thermal energy into amine-based PCC
15 for a 520MW_e CFPP. They concluded that, in order to achieve lower cost of electricity and
16 cost of CO₂ avoidance as compared to the case without solar assisted PCC, the price of solar
17 thermal collectors has to be lower than 150 USD/m² and 90 USD/m² for the solar trough and
18 vacuum tube, respectively. Also, the viability of solar-assisted PCC was highly dependent on
19 climate conditions.
- 20 • Cohen et al. [41] have reviewed the use of high temperature solar thermal technologies to
21 assist amine-based PCC. As a main outcome, it is concluded that using high temperature solar
22 thermal energy for direct electricity generation is more efficient than using solar energy for
23 assisting sorbent regeneration.
- 24 • A small-scale pilot study has been carried out by Wang et al. [81,82] on amine-based PCC
25 coupled with a solar thermal sub-system. Two types of solar collectors were used to gain the
26 required thermal energy of the reboiler (parabolic trough collectors and linear Fresnel
27 reflectors). Both of them could provide the required temperature heat source at the small-
28 scale of the test. The results suggested that the efficiency of parabolic trough collectors was
29 higher and less dependent on solar radiation.
- 30 • Carapellucci et al. [83] analyzed two options for integrating renewable energies into a CFPP
31 with CO₂ post-combustion capture either using an auxiliary biomass boiler or a concentrating
32 solar power (CSP) system. The obtained results for the biomass boiler integration showed that
33 the power plant capacity was increased by approximately 14% whereas the energy penalty (-
34 8%) was weakly reduced as compared to the reference case (with an efficiency of 42%).
35 Regarding the CSP system it was shown that its integration yields a 14% lower than the
36 reference case whereas the net efficiency decreased during the day to 31%.
- 37 • Sharma et al. [84] proposed a highly integrated amine-based CO₂ capture power plant in which
38 a solar thermal plant provides heat in order to avoid steam extraction from HP and IP turbines,
39 which increases power production. By means of a Heat Exchanger Network (HEN) analysis,
40 where the compressed gas energy is also utilized in the integration process, a significant
41 reduction of power plant output penalty is achieved (efficiency is increased up to 34.9 % from
42 29.4% for the base case).

Comentado [U3]: Efficiency, penalty??

1 In the case of CaL process, recent works have assessed the use of CSP to support CaL-based PCC for
2 retrofitting fossil fuel power plants:

- 3
4 • Zhang et al. [85] evaluated the energy efficiency of the CaL system when the calciner is driven
5 by a combination of oxy-fuel combustion and CSP, which provides 101 MW_{th} (a 7.4% of the
6 total energy input in the calciner). An integration of the CCR process into an ultra-supercritical
7 1019 MW_{th} power plant was proposed. In this scheme, a fraction of the CO₂ leaving the
8 calciner was used as a heat transfer fluid in the solar collectors after which it is recycled to the
9 calciner. Fossil fuel consumption in the calciner was reduced by 6.9 g/kWh compared to the
10 coal-driven case, which entails a decrease of the additional CO₂ generated and a decrease of
11 the mass flow rate of fresh limestone makeup. This scheme leads to an overall efficiency
12 penalty of 9.63% points associated to the CO₂ capture process. The thermal efficiency of co-
13 driven case is just 0.28% points below that of the conventional coal-driven case (without CSP)
14 due to the big losses of solar radiation to thermal conversion, which hinders the CSP
15 efficiency. Accordingly, increasing the CSP capacity reduces coal consumption, but it greatly
16 decreases the thermal efficiency due to the decrease of CSP efficiency.
- 17 • Zhai et al. [86] analyzed the CaL-PCC integration partially assisted by CSP for retrofitting
18 existing CFPPs in order to recover the energy of the capture system. The work analyzes the
19 integration through two different strategies, i) CFPP with solar aided CO₂ capture system
20 ((solar + CC) + PP), which uses solar energy to reduce the fuel consumption in the calciner (a
21 similar case than in [85]), and ii) solar aided CFPP plant with CO₂ capture system ((solar +
22 PP) + CC) where solar energy is used in the main cycle for increasing power production. In
23 both cases the solar thermal power available for the cycle is 88.58 MW_{th}. Results show that
24 the second case is more beneficial regarding technical and environmental aspects, whereas
25 the first case ((solar + CC) + PP) achieve a thermal efficiency slightly higher than in the ((solar
26 + PP) + CC) case (31.20% against 31.09%).
- 27 • Tregambi et al. [87] assessed the performance of coupling the CaL system to CSP for a
28 100MW_{th} CFPP with the aim of providing all the thermal energy required in the calciner by
29 renewable energy. The maximum thermal energy needed in the calciner to be provided
30 entirely by CSP was 135 MW_{th}. As a novelty, the plant allows storing the excess power
31 produced during the daytime as CaO resulting from the endothermic CaCO₃ calcination
32 reaction, which could be recovered from the exothermic CaO carbonation reaction during the
33 nighttime. They concluded that the CO₂ capture efficiency reaches a value close to 90%
34 whereas 80% of the thermal input from the CSP system to the calciner can be recovered.

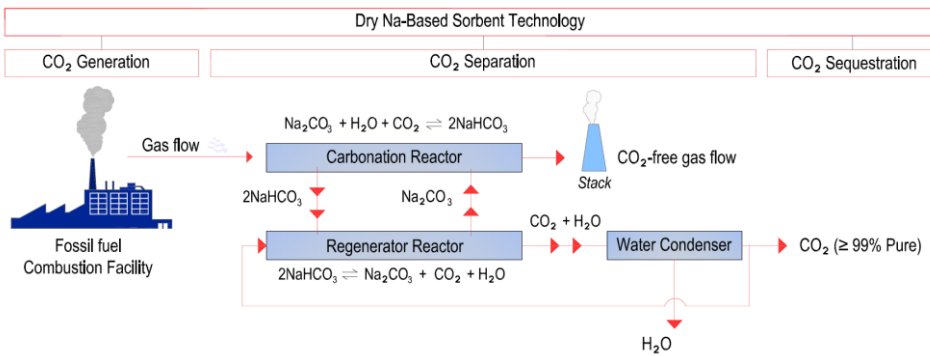
35 **4. Detailed analysis on Dry-Carbonate Process**

36 In the rest of this work the use of an abundant and cheap material such as sodium carbonate (Na₂CO₃)
37 with a high dry CO₂ sorption capacity at relatively low temperatures is analysed.

38 39 **5.14.1 Description**

40 CO₂ is captured in the Dry Carbonate Process through the chemical binding of CO₂ to Na₂CO₃ in the
41 carbonator reactor at operating temperatures below 100°C. Na₂CO₃ is converted to NaHCO₃ through

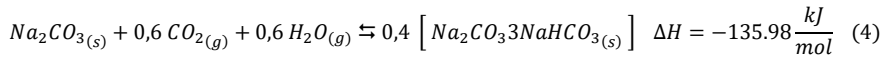
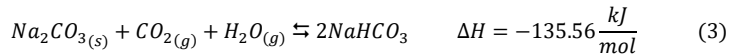
1 the chemical reaction with CO₂ in the presence of steam. The sorbent is regenerated back to its
 2 carbonate form when heated at temperatures above 100°C, thus releasing a nearly pure CO₂
 3 after steam condensation. The design of the Dry Carbonate Process takes into account the need to
 4 periodically replenish a certain amount of sorbent makeup due to particle attrition and the loss of
 5 sorbent activity by the irreversible reaction with SO₂ and HCl. It should be noted however that in
 6 post- wet flue gas desulfurization, SO₂ and HCl are present in the flue gas at very low concentrations
 7 (less than 20 ppm for SO₂ and 1 ppm for HCl), which would require a lower amount of fresh sorbent
 8 makeup flow. Figure 2 shows a schematic flow diagram of the Dry Carbonate process.
 9



10
 11 Figure 2: General scheme of the Dry Carbonate Process.

12 The Dry Carbonate Process is particularly well suited for being retrofitted into CFPPs with wet flue
 13 gas desulfurization and for natural gas-fired power plants. In the work conducted by Nelson et al.
 14 [74] it was estimated that a commercial-scale Dry Carbonate Process (a 500 MW_e nominal power
 15 plant fed with natural gas and carbon) would require an initial sorbent loading of roughly 387 tons
 16 and a makeup rate of fresh sorbent of about 0.2 tons/h. After integration of the Dry Carbonate Process,
 17 the net efficiency of the plant would suffer a drop from 40.5% to 33.4% (7.1 % penalty). In the case
 18 of power plants fed only with coal, there is a larger concentration of CO₂ in the flue gas and a larger
 19 amount of sorbent for CO₂ capture is needed whereas a similar loss of efficiency is expected.
 20

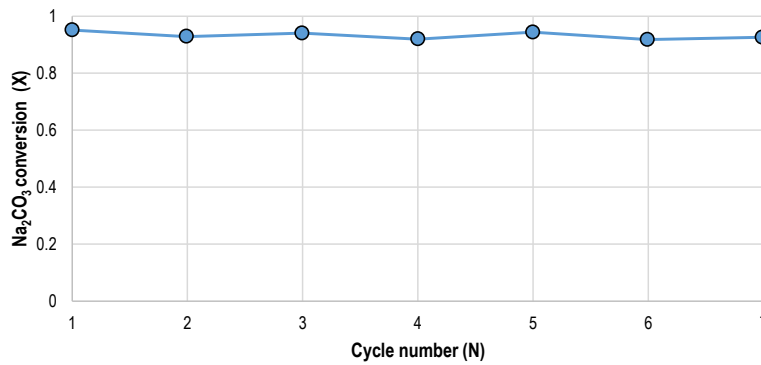
21 The reactions involved in the capture of CO₂ using Na₂CO₃ result in the reversible formation of
 22 NaHCO₃ and Wegscheider's salt (Na₂CO₃·3NaHCO₃) according to Eqs. 3-4 [74]:
 23



26
 27 Other possible reaction byproducts, such as sodium sesquicarbonate (Na₂CO₃·NaHCO₃·2H₂O) and
 28 sodium bicarbonate hydrate (NaHCO₃·2H₂O) are negligible at the reaction conditions of interest.
 29 Both forward reactions are exothermic. Therefore, heat integration is important for an efficient
 30
 31
 32

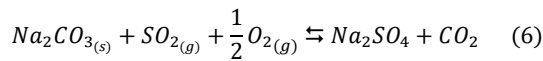
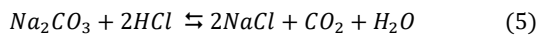
1 implementation of the process in a commercial system. Thermodynamically, the formation of
 2 Wegscheider's salt is favored under practical H₂O and CO₂ partial pressures at reaction temperatures
 3 of 70°C and above. For regeneration of the sorbent, NaHCO₃ decomposes to Na₂CO₃, H₂O and CO₂
 4 in the temperature range of 100 °C–200 °C [88] although ideally fast conversion is reached at 200°C
 5 [89].

6
 7 Multicycle carbonation/regeneration tests reported in [74] show the results plotted in Figure 3 for
 8 Na₂CO₃ conversion as a function of the cycle number (carbonation at 60°C and regeneration at
 9 160°C). Even though further thermogravimetric analysis tests should be carried out including a larger
 10 number of cycles and analyzing also the reaction kinetics, these results suggest that conversion is kept
 11 stable at a relatively high level (around 0.9), which may be explained by the relatively low
 12 temperatures used for sorbent regeneration.



14
 15 Figure 3: Na₂CO₃ conversion as a function of the cycle number (data extracted from [74]).

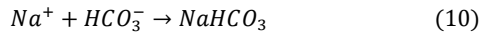
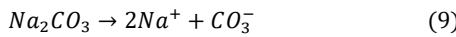
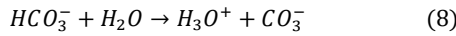
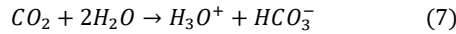
16
 17 Potential contaminants present in the flue gas, such as SO₂ and HCl, could react irreversibly with
 18 Na₂CO₃ at process conditions according to the following reactions (Eq. 5-6):



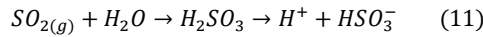
23
 24 Formation of NaCl and Na₂SO₄ reduces the capacity of the sorbent for CO₂ capture in subsequent
 25 cycles. However, the relative concentrations of HCl and SO₂ are one order of magnitude lower than
 26 the CO₂ concentration present in the flue gas following wet FGD (flue gas desulfurization) treatment,
 27 which mitigates the irreversible loss of conversion due to this issue.

5.24.2 Chemistry of the process

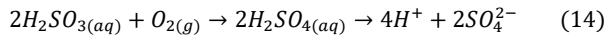
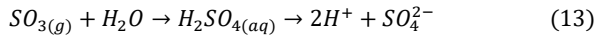
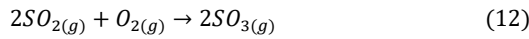
In order to gain further understanding of the dry carbonation process, the reaction mechanisms of Na_2CO_3 carbonation are detailed in this section. A possible mechanism by which Na_2CO_3 reacts with CO_2 is (Eq. 7-10) [9]:



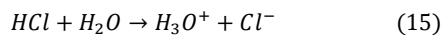
If the gas contains SO_2 other reactions would occur in the carbonation process. SO_2 can dissolve into water yielding sulfurous acid (H_2SO_3), and then the sulfurous acid dissociates, forming H^+ and HSO_3^- (Eq. 11):



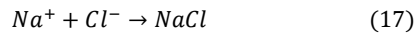
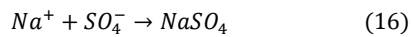
Meanwhile, before the gas is dissolved into water, part of the SO_2 can react with O_2 to form SO_3 , after which the SO_3 gas may dissolve into water to form sulfuric acid, which dissociates to H^+ and SO_4^{2-} ions leading to a reduction of the solution pH value. In addition, sulfurous acid (H_2SO_3) can also react with O_2 to form sulfuric acid. These reactions are given by Eqs. 12-14:



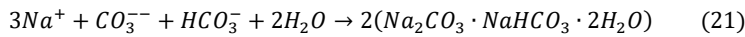
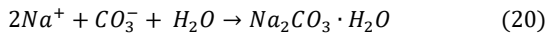
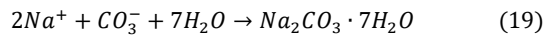
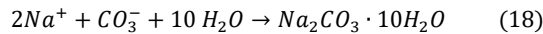
Also, chlorine present in the flue gas could react with water to form H_3O^+ and Cl^- (Eq. 15):



Besides, part of Na^+ could react with SO_4^- and Cl^- according to Eq. 16-17:



In order to model accurately the process, equilibrium reactions and salts formation were implemented in the computational model of our work. The salts formation reactions that can occur are (Eq. 18-21):



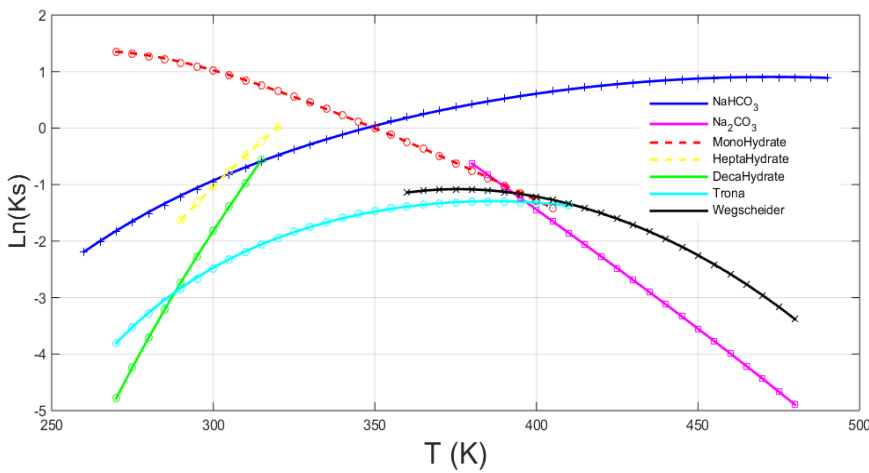
1 Thus, in addition to sodium bicarbonate (NaHCO_3) other salts can be formed from the reactions
 2 involving CO_2 , water and soda ash: sodium carbonate decahydrate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$), sodium
 3 carbonate heptahydrate ($\text{Na}_2\text{CO}_3 \cdot 8\text{H}_2\text{O}$), sodium carbonate monohydrate ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$),
 4 Wegscheider's salt ($\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$) and trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) [90]. Figure 4 shows
 5 the evolution of reaction equilibrium constants with temperature for the production of NaHCO_3 and
 6 other salts used in this work (adapted from [9]). The data was well fitted to the equation

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7
8

9 Best fitting parameters are shown in [90].

10



11

12 Figure 4: $\text{Ln}(K_s)$ values for reactions involved in NaHCO_3 production (see for additional details)

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13

14 **6.5. Case study: CFPP- Dry-carbonate process (DCP) integration**

15 **6.15.1 Baseline CFPP**

16 This section shows results from the simulation of the retrofitting of a 150 MW_e CFPP with a Dry
 17 Carbonate CO_2 capture system to assess the effects on the power plant and global system performance
 18 and to assess the feasibility of assisting sorbent regeneration by solar thermal energy.

19 Flue gas exiting the power plant is characterized by a dilute concentration of CO_2 and a large
 20 volumetric flow at ambient pressure. Thus, a typical 505 MW_e pulverized CFPP plant produces 28300
 21 m^3 of flue gas per minute with a CO_2 volume concentration between 10% and 15% [91]. In this work,
 22 a reference coal fired plant of 150 MW_e has been considered. The reference plant scheme is illustrated
 23 in Figure 5 taking as a reference the integration model developed by Ortiz et al. [92]. The main data
 24 of the CFPP are given in Table 1.

25

26

Table 1: Reference data for a 150 MW_e coal fired plant (data scaled from [48]).

Item	Magnitude	Unit
Coal consumption	61	ton/hr
Air intake	692	ton/hr
Gross power introduced with fuel	447	MW _{th}
Net power supplied	397	MW _{th}
Net Power produced	150	MW _e
Net efficiency	33.5	%

Post-combustion flue gas characteristics are detailed in Table 2:

Table 2: Flue gas flow for a 150 MW_e coal fired plant (data scaled from [48]).

Coal flue gas component	Mole Flow (kmol/hr)	Mass Flow (tons/hr)
N ₂	17154.21	529.71
CO ₂	3085.62	135.96
H ₂ O	1471.86	29.4
O ₂	781.8	27.57
CO	140.7	3.93
NO	135.36	4.47
SO ₂	37.53	2.64

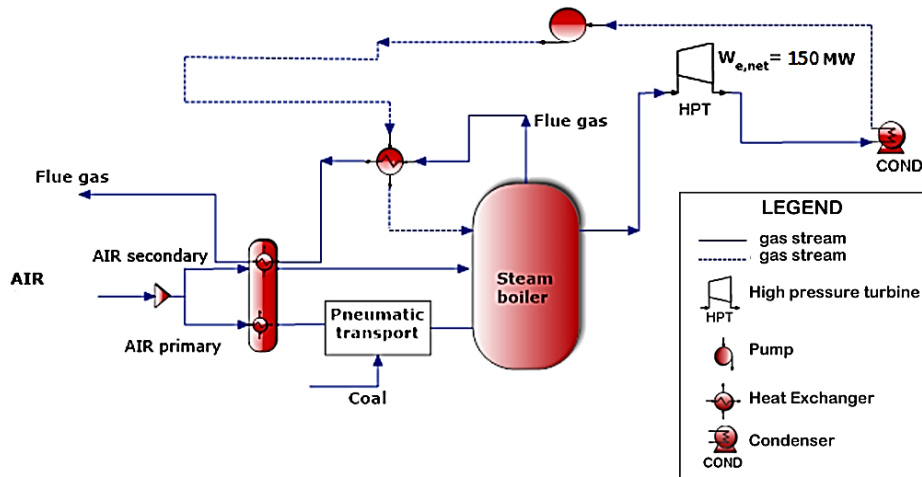


Figure 5: Reference coal fired power plant scheme used in the present work.

6.25.2 Dry Carbonate Process (DCP) integration

A schematic representation of the integrated process for CO₂ capture proposed in this work is shown in Figure 6. Simulations were done using ASPEN PLUS™ environment. Main units are indicated in the layout: for carbonation (CARB) and decarbonation (DECARB) of the sorbent, two separation units and heat exchangers for heat recovery and water condensation at the end of the process are implemented. In the carbonator, inlet streams are water (WATHOT), sodium carbonate (Na₂CO₃) and cooled flue gas (FGPLAN4). The following assumptions have been considered in the simulation in ASPEN: i) ideal gas-solid separation, ii) auxiliaries are enough to heating and cooling necessities along the plant, iii) auxiliaries electric power consumption, iv) steady state operation is assumed, v) regenerator reactor model is based on chemical and phase equilibrium through Gibbs' free energy minimization method and iv) 90% isentropic efficiency is considered in the CO₂ compressor.

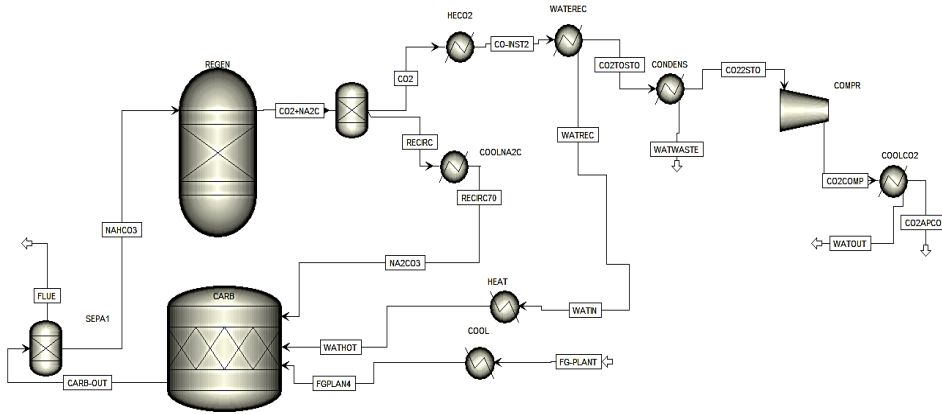


Figure 6: Dry Carbonate Process layout.

The carbonator works at 60°C and absolute pressure 1.01 bar for CO₂ sorption. Under these conditions, formation of Weigscheider' salt is thermodynamically favored. The CO₂ input flow to the carbonator (FGPLANT) is 136 ton/hr (3080 kmol/hr) while the CO₂ output flow (CARB-OUT) is 10.7 ton/hr CO₂. Efficiency of CO₂ capture in the carbonator is evaluated as:

$$\varepsilon_{ABS} = \frac{\dot{m}_{CO_2,FGPLANT} - \dot{m}_{CO_2,CARB-OUT}}{\dot{m}_{CO_2,FGPLANT}} = 0,92$$

Here ε_{ABS} is the efficiency of absorption, while $\dot{m}_{CO_2,FGPLANT}$ and $\dot{m}_{CO_2,CARB-OUT}$ represent the CO₂ mass flows of flue gas exiting the CFPP and the carbonator, respectively.

Assuming a conservative value for Na₂CO₃ conversion ($X=0.75$) in the carbonator ([74], see Figure 3), the required mas flow of Na₂CO₃ is 430 ton/hr, which yields a mass ratio Na₂CO₃/CO₂ of 3.2 kg_{Na2CO3}/kg_{CO2}. In the best scenario ($X=1$), this mass ratio would be 2.4 kg_{Na2CO3}/kg_{CO2}. Na₂CO₃ carbonation proceeds at an equimolar amount of CO₂ and H₂O, which yields a hot water requirement of at least 55.4 ton/hr. Within this amount, 27 ton/h are taken directly from the residual steam in the

1 post-combustion flue gas while the rest must be added from an external source. Table 3 shows the
 2 values of main operation parameters in the carbonator and calciner reactors.

3 Table 3: Carbonator and calciner working conditions.

	carbonator	calciner
Outlet temperature [°C]	60	140
Outlet pressure [bar]	1,01	1.01
Net heat duty [MW _{th}]	-101.240	122.480
Total feed stream CO ₂ flow [ton/h]	135.550	0
Total product stream CO ₂ flow [ton/h]	10.620	127.010
Net stream CO ₂ production [ton/h]	-124.930	127.010

4
 5 Following the proposed layout (Figure 6), the solids stream consists of Na₂CO₃·3NaHCO₃ since
 6 NaHCO₃ and H₂O (NAHCO3C) is separated in the first separation unit from air and flue gas (FLUE)
 7 and is sent to the regenerator. Sorbent regeneration is carried out in this reactor, which releases a CO₂
 8 concentrated stream. The amount of CO₂ released in the regenerator is 127 ton/h at 140°C with a
 9 100% efficiency of CO₂ stripping from the sorbent.

10
 11 From the energy balance in the regenerator, it may be calculated that a total 122.48 MW_{th} are required
 12 for maintaining the process. This heat can be obtained by burning additional coal or from another
 13 external source. In this work, the novel use of solar thermal power is proposed for that purpose.
 14 Pressurized hot water can be stored for a relatively long time at temperatures above 140°C. Table 4
 15 details the balances between the input and output flows in the calciner. It must be taken into account
 16 that part of the sorbent is lost during the overall process because of the irreversible reactions with SO₂
 17 and HCl at the process conditions (Eqs. (5) - (6)). The loss of sorbent requires a make-up flow of 3
 18 ton/h of Na₂CO₃ in order to maintain the capture efficiency in the carbonator. After the regeneration
 19 stage, Na₂CO₃ is separated from the gas stream and it is recirculated into the carbonator at 80°C.

20 Table 4: Calciner streams composition.

	CO ₂ +NA	NAHCO ₃ H
Temperature (°C)	140	60
Pressure (bar)	1.01	1.01
Mass flow (ton/hr)		
H ₂ O	50.28	1.44
CO ₂	124	0
Na ₂ CO ₃	323.25	442.7
NaHCO ₃	0	11.39
Wegscheider's salt		44.39

21
 22 From the calciner, a gas flow of 17.8 ton/h (29% steam and 71% CO₂ by weight) is sent to a train of
 23 heat exchangers/coolers for heating and H₂O recovery. Finally, a flow of 12.7 ton/hr of pure CO₂ is
 24 compressed through three intercooled stages up to 70 bar, with a global power consumption of 1.5
 25 MW_e, after which it is sent to storage. Considering the energy needed in the regenerator for sorbent
 26 regeneration, integration of the DCP yields a plant efficiency given by Eq. 22:

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Comentado [U7R6]:

$$\eta_{plant} = \frac{\dot{W}_{CFPP} - \dot{W}_{cons,DC}}{\dot{Q}_{CFPP} + \dot{Q}_{DC}} \quad (22)$$

Here η_{plant} is the plant efficiency, \dot{W}_{CFPP} and \dot{Q}_{CFPP} are the net power production and the thermal power consumptions of the CFPP, while $\dot{W}_{cons,DC}$ and \dot{Q}_{DC} are the electric power consumption and the thermal power consumption in the DCP, respectively. By considering the work for CO₂ compression (\dot{W}_{COMP}) and solids conveying (\dot{W}_{solid}), parasitic power consumption ($\dot{W}_{cons,DC}$) is given by Eq. 23:

$$\dot{W}_{cons,DC} = \dot{W}_{solid} + \dot{W}_{COMP} \quad (23)$$

Here a conservative value of $\dot{W}_{solid} = 5.5$ kWh/ton can be used for estimating the solids conveying energy [93], which yields (Eq. 24):

$$\dot{W}_{solid} = \dot{m}_{Na_2CO_3} \cdot 5,5 \frac{kwh}{ton} = 2.37 MW_{el} \quad (24)$$

being Na₂CO₃ the sodium carbonate mass flow. A summary of the global plant data is given in Table 5.

Table 5: Power balance without heat recovery.

	Power production	Power consumption
CFPP	150 MW _e	447 MW _{th}
Decarbonator		122.5 MW _{th}
COMP		15 MW _e
Wsolid		2.37 MW _e
Net Power	132.53 MW _e	
Total heat requirement		569.5 MW _{th}

By considering the extra-heat that must be supplied from coal to integrate the DCP, the global plant efficiency drops from 33.5% to 23.3%. The results obtained by imposing different carbonator and regenerator temperatures are shown in Figure 7.

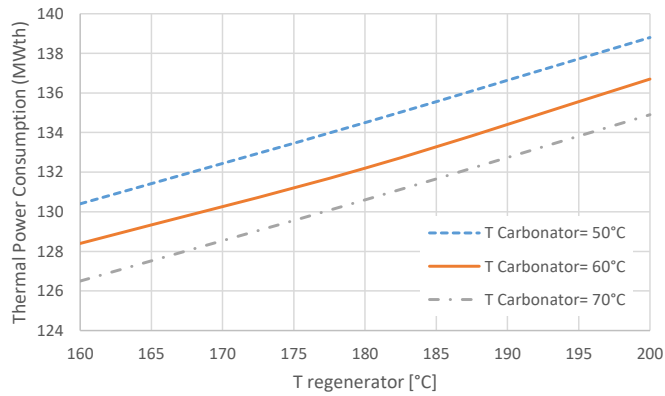
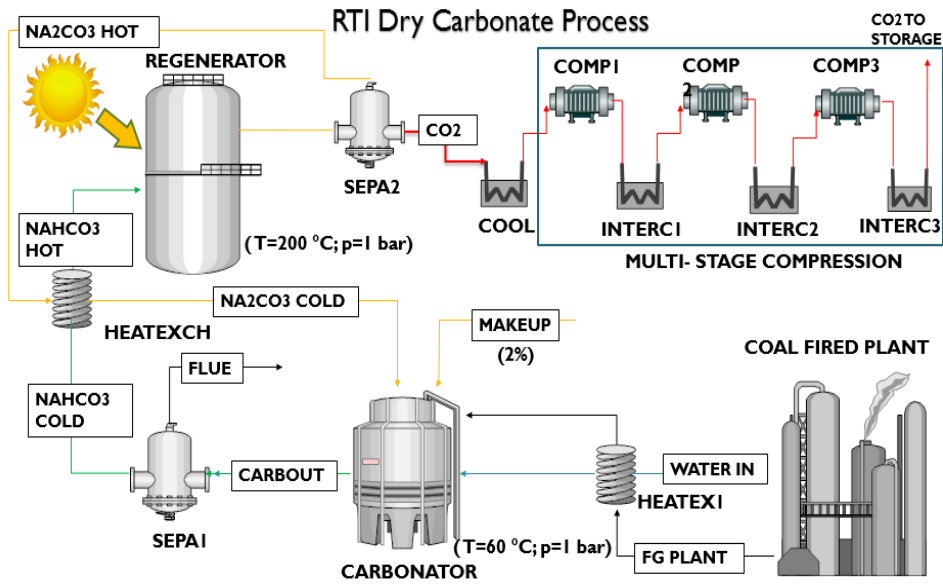


Figure 7: Thermal power required for different carbonator and regenerator temperatures.

In the temperature range 50-70 °C for the carbonator, power consumption varies within the range 126.5MW_{th} – 138.8 MW_{th}. As will be seen below, integration of solar thermal power to aid sorbent regeneration, as newly proposed in this work, serves to mitigate significantly this significant loss of efficiency.

6.3.5.3 Optimized plant configuration

The modified configuration proposed in this section is schematized in Figure 8. A solid-solid heat exchanger (HEATEXCH) has been included between the two reactors with the aim of reducing the total amount of heat required in the regenerator. This heat exchanger allows for increased temperatures in the regenerator, which enhances the reaction rate with little additional expense of thermal power. The modified configuration also leads to a reduction of the power consumption for compression by introducing a multi-stage compression with inter-refrigeration included. A sensitivity analysis using this configuration has been also carried out to analyze the variation of power required for different carbonator/regenerator temperatures (Fig. 9).



1
2

Acronyms (equipment and streams):

CARBONATOR: CO₂ capture reactor
 CARBOUT: Final product from carbonator
 CO₂: CO₂ recovered from the system
 CO₂ TO STORAGE: CO₂ to the storage system (20 °C, 75 bar)
 COAL FIRED PLANT: Coal fired plant for electricity production
 COMP1: Compressor CO₂ (1-10 bar)
 COMP2: Compressor CO₂ (10-25 bar)
 COMP3: Compressor CO₂ (25-75 bar)
 COOL: CO₂ (20°C) intercooler
 FGPLANT: Flue gas exits the coal fired plant
 NA₂CO₃ COLD: Regenerated Na₂CO₃ (80°C)
 NA₂CO₃ HOT: Regenerated Na₂CO₃ (200°C)
 NAHCO₃ COLD (fig.6): Solids exits the carbonator (60°C)

NAHCO₃ HOT: Solids entering the regenerator (140°C)
 HEATEX1 H₂O-flue gas heat exchanger
 HEATEXCH: NaHCO₃-Na₂CO₃ heat exchanger
 INTERC1: CO₂ (20°C) intercooler
 INTERC2: CO₂ (20°C) intercooler
 INTERC3: CO₂ (20°C) intercooler
 MAKE UP: Sorbent Make up
 REGENERATOR: Sorbent regenerator
 SEPA1: Solid-gas separator
 SEPA2: Solid-gas separator
 WATER IN: Water to CO₂ capture reactor

3
4
5
6

Figure 8: Optimized plant configuration proposed in this work.

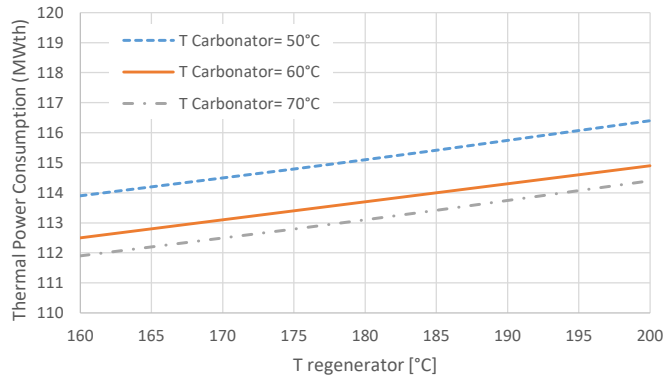


Figure 9: Power consumption for different operating conditions (including heat recovery).

In this case, the analysis shows (Figure 9) that power consumption is in the range 111.9 MW_{th} – 116.4 MW_{th}. In this new configuration, it is possible to increase temperature in the regenerator with just a slight increase of power consumption and the advantage of enhancing reaction kinetics. Thus, heat recovery reduces the heat required for sorbent regeneration by about a 10%. The heat required using this new configuration (with working conditions in the regenerator set to 200 °C and 1,01 bar) is 114 MW_{th}.

The integration of solar thermal heat for aiding sorbent regeneration is a feasible option to achieve the required temperatures in the regenerator. This renewable heat source support would mitigate significantly the operational expenditure (OPEX) penalty associated to the carbon capture system integration.

In order to minimize the power consumption of CO₂ compression a multistage compression system is proposed. Configurations with two and three stages and different compression ratios were considered, Table 6. A three-stage compression with an inter-refrigeration stage at 20°C reduces the compression power from 15 MW_e (baseline case) to 11.16 MW_e.

Table 6: CO₂ compression power

Component	two-stage compression		three-stage compression	
	Exhaust Pressure (bar)	Power (MW _e)	Exhaust Pressure (bar)	Power (MW _e)
COMP1	9	6.29	4.2	3.78
COMP2	75	6.02	17.6	3.78
COMP3	-	-	75	3.6
Global W_{comp}		12.31		11.16

1 Table 7 shows power consumption in the different parts of the system after introducing the proposed
2 modifications:

3 Table 7: Global plant energy balance.

	Power production	Power consumption
CFFP	150 MW _e	447 MW _{th}
Decarbonator		114.9 MW _{th}
COMP		11.16 MW _e
Wsolid		2.47 MW _e
Net Power	136.37 MW _e	
Total heat		561.9 MW _{th}

4
5
6 With these modifications, the global efficiency of the plant (coal power plant + CCS) is increased by
7 a 0.9% (from 23.3% to 24.2%). In the above calculations, a constant value of sorbent conversion
8 $X=0.75$ was used. Table 8 shows the effect of sorbent conversion (X) on global efficiency. This
9 parameter should be determined with further certainty from lab-scale thermogravimetric studies under
10 realistic process conditions such as the solids residence time in the reactors in future works.
11 Nevertheless, the efficiency variation is just around 1% in a wide range of sorbent conversions
12 (between 0.4 and 0.95, Table 8).

14 Table 8: Efficiency values for different sorbent conversion factors (X).

X	Na ₂ CO ₃ flow (kmol/hr)	Calciner (MW _{th})	Carbonator (MW _{th})	W _{solid} (MW _e)	Efficiency (%)
0.4	84.5	119.5	-104	4.6	23.2
0.75	42.93	114.9	-101	2.47	24.2
0.95	32.86	111	-98	1.89	24.37

15
16
17 To achieve a near to zero CO₂ emissions global system, renewable energy must be used for heating
18 the regenerator, either solar or biomass when there is no availability of solar direct irradiation, which
19 may be accomplished by storing heat. A number of storage materials for sensible storage systems are
20 listed in Table 9. Solid storage and liquid storage media are presented for indirect storage of thermal
21 energy, i.e. thermal energy from a heat transfer fluid (e.g. thermal oil, air) is transferred to a solid
22 storage medium [94] .

1 Table 9: Main properties of materials to store energy in the form of sensible heat [95,96]

	Temperature (°C)		Average density (kg/m³)	Average heat conductivity (W/(mK))	Average heat capacity (kJ/(kgK))	Thermal diffusivity (m²/s)	Volume specific heat capacity (kWh/m³)	Volume (m³)
	Cold	Hot						
Solid storage media								
Sand-rock-mineral oil	200	300	1700	1.0	1.30	4.5×10 ⁻⁷	60	22460.1
Reinforced concrete	200	400	2200	1.5	0.85	8.0×10 ⁻⁷	100	13271.9
Cast iron	200	400	7200	37.0	0.56	9.2×10 ⁻⁶	160	6155.4
Liquid storage media								
Mineral oil	200	300	770	0.12	2.6	6.0×10 ⁻⁸	55	24793.6
Synthetic oil	250	350	900	0.11	2.3	5.3×10 ⁻⁸	57	23979.1
Silicone oil	300	400	900	0.10	2.1	5.3×10 ⁻⁸	52	Out of range
Nitrite salts	250	450	1825	0.57	1.5	2.1×10 ⁻⁷	152	Out of range

2
3 For this study, the storage volume needed for supplying the heat for regeneration during 12 hours has
4 been estimated. For example, a volume of 25m x 25m x 10m is required for cast iron in order to cover
5 a storage capacity of 12 hours while if sand-rock mineral oil is used the volume needed is 50m x
6 50m x 10m (Table 9). Storage capacity has been estimated including a utilization coefficient $f_{utilization}$.
7 This factor depends on the heat conductivity of the storage medium and the operational mode of the
8 storage [95]:

$$Q_{storage} = f_{utilization} \times m \times c_p \times \Delta T_{mix/max} \quad (36)$$

9
10
11 where m is the mass [kg], c_p is the mean heat capacity [J/(kgK)] and $\Delta T_{mix/max}$ is the temperature
12 difference of the working fluid. Estimated associated costs of the solar system are included in the
13 economic sensitivity analyses. These volume sizes constrain the applicability of the integrated
14 CCS/solar solution as depending on space availability.

15
16
17 Another possibility for achieving the near to zero CO₂ emissions global system would be using
18 biomass to meet power requirements for the regenerator (114.9 MW_{th} in the Best Estimate case). By
19 considering an average heat capacity of biomass of 10.87 MJ/kg (Table 10), a biomass flow rate input
20 of 44.5 ton/h is necessary. If wood chips are used, the storage capacity for the biomass needed for
21 one week of plant operation would be around 17500 m³.

Comentado [U8]: Todavía no hemos hablado de casos...

22 Table 10: Properties of different typologies of wood chips

Wood chips	H _i [MJ/kg]	ρ[kg/m³]	H _i [MJ/ m³]
Chestnut	10,53	580	6106,24
Beech	13,45	750	10084,95
Spruce	7,90	450	3556,98
Larch	11,60	660	7654,88
Average	10,87	610	6630,29

1 Under the Carbon Emissions Reduction Target (CERT), a factor of 0.0249 kg_{CO2}/kWh is assumed for
2 wood [97]. In the case study a factor of 0.03 ton_{CO2}/MWh is considered. Thus, an additional amount
3 of 3.5 ton/h (from 10.7 ton/h to 14.2 ton/h) must be taken into account in the analysis.
4

5 **6.45.4 CFPP- Dry-carbonate process integration: Economic Analysis**

6 A detailed techno-economic analysis to assess the integration of medium temperature solar thermal
7 technology to assist regeneration of the dry sorbent has been carried out. If heat for regenerator is
8 obtained from solar thermal power the economic efficiency (defined in this case as the ratio between
9 power production -136 MW_e- and fossil fuel consumption -447 MW_{th}- without considering solar
10 thermal power) would be 30.5%. A number of assumptions according to different scenarios were
11 made for the economic analysis. These different scenarios were defined in terms of:
12

- 13 - Electricity production, to take into account the penalty on electricity generation of the
14 ancillary equipment consumption and parasitic loads (consumption in compressors, solids
15 conveying and other ancillary equipment). All these factors have been considered by an
16 electricity penalty of 10.1%.
- 17 - Variation of fuel costs, to include in the analyses the variability of fuel costs.
- 18 - Uncertainties in plant installation costs, to take into account uncertainty in the evolution of
19 equipment costs. The maximum deviation has been taken as a $\pm 9\%$ of the average installation
20 price.
- 21 - DCP costs. As for any novel technology, there is uncertainty on the installation costs and its
22 evolution. A range of $\pm 50\%$ for CCS installation cost has been considered.
- 23 - Different fixed charge factors were in addition considered for the different scenarios.
24

25 Under these considerations, three scenarios were defined:
26

- 27 - Scenario **P** (Pessimistic Scenario). The pessimistic scenario implies a combination of the
28 following factors: highest penalty in electricity generation (it has been taken as the maximum
29 error in estimating parasitic electricity losses), highest costs and a fixed charge factor of 0.15.
- 30 - Scenario **BE** (Best Estimated Scenario). In this scenario, the values derived from the
31 simulation above described were used to define the efficiency of the system. It considers a
32 capital cost of 30 M€ [6] for the CCS technology and a fixed charge factor of 0.1.
- 33 - Scenario **O** (Optimistic Scenario). This optimistic scenario considers a range of minor fuel
34 cost and minor costs of the CCS technology and plant installation. Furthermore, it considers
35 the smallest change in electricity production and the smallest fixed charge factor of 0.075.
36

37 Table 11 summarizes the data used for calculating the costs according to the different scenarios for a
38 total amount of 1089 kton/year avoided CO₂ emissions using the DCP.
39
40
41
42
43

Table 11: CO₂ emission data for different scenarios.

	REFERENCE PLANT	DRY CARBONATE (P)	DRY CARBONATE (BE)	DRY CARBONATE (O)
Power (MW _e)	150	150	150	150
CCS Power consumption (MW _e)	-	25	13.63	13
Regenerator Heat requirement (MW _{th})	-	119	114.9	111
Net power (MW _e)	150	125	136.37	137
CO ₂ Emissions (ton/hr)	136	10.7	10.7	10.7
CO ₂ Emissions (kmol/hr)	3080	243.2	243.2	243.2
CO ₂ Avoided Emissions (kton/year)		1089	1089	1089
CO ₂ Emissions (tons/ MWh _e /hr)	0.9	0.085	0.078	0.078

Along with capital investment and operating and maintenance (O&M) cost, energy consumption is a main factor that determines the viability of a CO₂ capture technology. The specific energy consumption for CO₂ avoided (SPECCA) is usually employed to quantify the additional fuel consumption (in MJ) needed to avoid the emission of 1 kg of CO₂ into the atmosphere [42] (Eq. 25):

$$SPECCA = 3600 \frac{\frac{1}{\eta_{CCS}} - \frac{1}{\eta_{ref}}}{E_{ref} - E_{CCS}} \left[\frac{MJ}{kg_{CO_2}} \right] \quad (25)$$

where η_{ref} and η_{CCS} are the power plant efficiencies, and E_{ref} and E_{CCS} are the CO₂ emissions ratios (in kg_{CO2} /MWh_{el}) without and with the DCP integrated, respectively. Table 12 shows the results obtained from the SPECCA analysis for the different scenarios:

Table 12: SPECCA Analysis for different scenarios.

Item	Scen.P	Scen. BE	Scen. O
Net Power Production (MW _e)	125	136,37	137
CO ₂ ccs (ton/hr)	10,7	10,7	10,7
E _{CCS} (kg _{CO2} /kWh _{el})	85.60	78.46	78.10
η_{CCS}	0.232	0.242	0.244
SPECCA (MJ/kg _{CO2})	5.86	5.03	4.90
η_{CCS_ECO}	0.279	0.305	0.306
SPECCA _{ECO} (MJ/kg _{CO2})	2.65	1.29	1.24

If the analysis is performed in terms of operational expenditures, and heat for regeneration of the sorbent is provided by solar (evaluated as a free energy intake from the point of view of OPEX), an operational efficiency value can be defined as $\eta_{CCS_ECO} = \text{Net Power Production with CCS (MW}_e\text{)} / \text{fossil fuel consumption (MW}_{th}\text{)}$. For operational expenditures analysis, a new SPECCA definition is used (SPECCA_{ECO}) in order to remark the difference between concepts (see Table 12):

Comentado [U9]: No se entiende...cual es la def de este nuevo specca?

The economic cost of CO₂ capture can be estimated in different ways, yet the most commonly used method contemplates incremental cost of electricity (€/kWh) and avoiding CO₂ cost (AC) expressed in terms of €/tonCO₂ avoided [98] (Eq. 26-27):

$$\Delta COE = COE_{CCS} - COE_{ref} \quad (26)$$

$$AC = \frac{\Delta COE}{\left(\frac{ton_{CO_2}}{kWh}\right)_{CCS} - \left(\frac{ton_{CO_2}}{kWh}\right)_{ref}} \quad (27)$$

Here COE is the cost of electricity, the sub-index *CCS* represents the carbon capture and storage system and the sub-index *ref* refers to the reference plant (coal fired plant). For an accurate economic analysis, the lack of imposed taxes to CO₂ emissions has been taken into consideration. The costs of electricity in the three different scenarios for the reference plant are given by Eq. 28:

$$COE = \text{fixed cost} + \text{variable cost} + \text{fuel cost} = \frac{TCR \cdot FCF}{8760 h} + VOM + \frac{FC}{\eta_{el}} \quad (28)$$

where η is the global plant efficiency ($\eta = 0.335$ for the reference plant).

Regarding the solar thermal power technology that would be used for producing the thermal power required for sorbent regeneration, a cost range between 1500-3500 €/kW [11] has been estimated for a parabolic trough plant with thermal energy storage [94]. This solar thermal technology can supply heat for regeneration of the dry sorbent at the required temperatures in the regenerator. Thus, to supply the heat required for the CCS system the expected cost has been calculated as (Eq. 29):

$$E_{SOLAR} (M\text{€}) = c_{SOLAR} \left(\frac{M\text{€}}{MW} \right) \cdot \Phi_{REGENERATOR} (MW) \quad (29)$$

where c_{SOLAR} is the solar plant cost and $\Phi_{REGENERATOR}$ is the thermal power required by the regenerator.

The summarized COE costs for the three scenarios are shown in Table 13:

Table 13: COE for different scenarios.

Item	Item	Units	Scen. P	Scen. BE	Scen. O
Fuel Cost [99]	FC	€/kWh	0.03	0.023	0.02
Capital Cost	TCR	€/kWe	1200	1100	1000
Fixed Charge Factor [99]	FCF	year ⁻¹	0.15	0.1	0.075
Variable Cost	VOM	€/kWe	0.006	0.006	0.006
COE _{ref}		€/kWh	0.116	0.087	0.074

Table 14 shows the COE and investment costs for the three scenarios considered to facilitate the analysis on the effect of solar thermal power cost (in the range between 1500 €/kW_{th} and 3500 €/kW_{th}). These include the cost of the heat storage system. Regarding the cost of electricity with a

1 CCS system, electric efficiency depends on power consumption for the different scenarios. Table 15
 2 shows the variation of COE for the different solar thermal power costs.
 3

4 Table 14: COE for CCS system (as function of Solar Capital Costs).

Item	Item	Units	Scen. PE	Scen. BE	Scen. O
Net Power Production		MW _e	125	136.37	137
η_{el}			27.9	29.9	30.2
η_{system}		%	22.1	24.2	24.37
Dry Carb. Capital cost [6]	TCR	M€/ MW _e	0.32	0.223	0.148
Solar Capital Cost [100]	TCR	M€/MW _e	1.5		
COECCS		€/kWh	0.165	0.115	0.095
AC		€/ton _{CO2}	60.416	34.245	25.421
Solar Capital Cost [100]	TCR	M€/ MW _e	2		
COECCS		€/kWh	0.174	0.121	0.099
AC		€/ton _{CO2}	64.223	41.188	30.629
Solar Capital Cost [100]	TCR	M€/ MW _e	2.5		
COECCS		€/kWh	0.182	0.127	0.103
AC		€/ton _{CO2}	73.736	48.132	35.837
Solar Capital Cost [100]	TCR	M€/ MW _e	3		
COECCS		€/kWh	0.191	0.132	0.108
AC		€/ton _{CO2}	83.249	55.076	41.045
Solar Capital Cost [100]	TCR	M€/ MW _e	3.5		
COECCS		€/kWh	0.199	0.138	0.112
AC		€/ton _{CO2}	92.762	62.020	46.253

5

6 Table 15: Δ COE (€/kWh_{el}) for different costs of solar thermal field.

Solar Thermal cost (€/kW _t)	Scen. P	Scen. BE	Scen. O
1500	0.0492	0.0281	0.0209
2000	0.0578	0.0339	0.0252
2500	0.0664	0.0396	0.0295
3000	0.0749	0.0453	0.0337
3500	0.0835	0.0510	0.0380

7

8 The costs of the other components and reactors are estimated in the range between 20 and 40 M€ [6].
 9 Finally, maintenance and operation costs are assumed as 10% of the total investment cost. The
 10 investment cost of the CCS system is given by Eq. 30:

11

$$E_{TOT} = E_{SOLAR} + E_{DRYCARBONATE} + E_{O\&M} \quad (30)$$

12

13

1 where E_{TOT} is the total investment cost, E_{SOLAR} is the solar plant installation cost, $E_{DRYCARBONATE}$ is
 2 the carbon capture system installation cost and $E_{O\&M}$ represents the cost due to operation and
 3 maintenance. Total CFPP retrofitting investment cost are shown in Table 16 as a function of
 4 investment costs for the three scenarios and solar field prices considered.

5

6 Table 16: Total CFPP retrofitting investment cost calculated by considering several CSP plant
 7 prices.
 8

Solar Thermal Cost 1.5 M€/ MW _e				
	Units	Scen. P	Scen. BE	Scen. O
ESOLAR	M€	179.25	172.35	166.5
EDRY	M€	40	30	20
EO&M	M€	21.92	20.23	18.65
ETOT	M€	241.17	222.58	205.15
Solar Thermal Cost 2 M€/ MW _e				
	Units	Scen. P	Scen. BE	Scen. O
ESOLAR	M€	239	229.8	222
EDRY	M€	40	30	20
EO&M	M€	27.9	25.98	24.2
ETOT	M€	306.9	285.78	266.2
Solar Thermal Cost 2.5 M€/ MW _e				
	Units	Scen. P	Scen. BE	Scen. O
ESOLAR	M€	298.75	287.25	277.5
EDRY	M€	40	30	20
EO&M	M€	33.87	31.725	29.75
ETOT	M€	372.62	348.975	327.25
Solar Thermal Cost 3 M€/ MW _e				
	Units	Scen. P	Scen. BE	Scen. O
ESOLAR	M€	358.5	344.7	333
EDRY	M€	40	30	20
EO&M	M€	39.85	37.47	35.3
ETOT	M€	438.35	412.17	388.3
Solar Thermal Cost 3.5 M€/ MW _e				
	Units	Scen. P	Scen. BE	Scen. O
ESOLAR	M€	418.25	402.15	388.5
EDRY	M€	40	30	20
EO&M	M€	45.82	43.21	40.85
ETOT	M€	504.07	475.36	449.35

9

10

11

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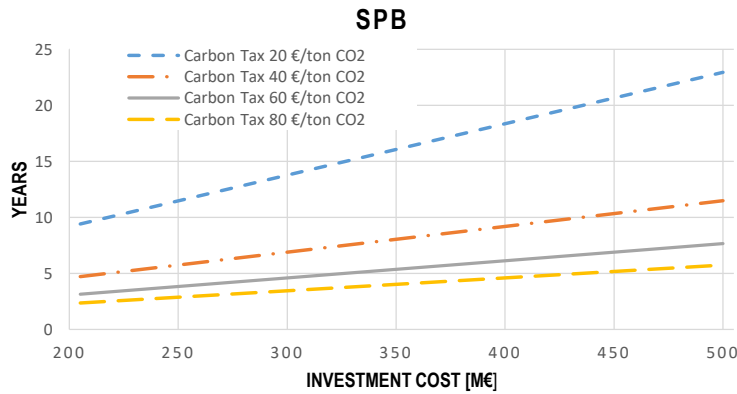
1 After the economic evaluation of electricity costs and avoided CO₂ emissions with the DCP assisted
 2 by medium temperature solar thermal power, net present value (NPV) and Simple Pay Back (SPB)
 3 are analyzed with the goal of assessing the effects of carbon taxes and installation funds for
 4 renewables technologies. To carry out these analyses, carbon taxes are assumed as fixed through the
 5 next years in the worst scenario (Scenario P) while they are assumed to increase in future years for
 6 the optimistic scenario (Scenario O). Additionally, European or National funds could be received by
 7 the integration of solar thermal power to reduce CO₂ emissions. The net gain from avoided CO₂
 8 emissions is given by Eq. 31:

$$E_{CO_2,AVOIDED} = (ton_{CO_2,ref} - ton_{CO_2,CCS}) \cdot c_{CO_2} \quad (31)$$

11 where $E_{CO_2,AVOIDED}$ is the avoided cost due to the avoided emission of CO₂, $ton_{CO_2,ref}$ and $ton_{CO_2,CCS}$
 12 are the CO₂ emissions without and with the DCP integrated, respectively, while c_{CO_2} is the carbon tax
 13 expressed in €/ton_{CO₂}. The energy simple payback period, SPB, is the time to recover the initial
 14 investment in energy savings. SPB is calculated as the ratio of capital costs to the annual energy cost
 15 savings (Eq. 32):

$$SPB = \frac{E_{TOT}}{E_{NET,GAIN,year}} \quad (32)$$

19 where E_{TOT} is the total investment of the plant while $E_{NET,GAIN,year}$ represents the annual economic
 20 gain due to the avoided emissions. Figure 10 illustrates the SPB curves for the three scenarios as
 21 function of total CFPP retrofitting capital cost.



24 Figure 10: SPB curves according to the three scenarios as function of CFPP retrofitting capital costs.

25 The net present value (NPV) is calculated as the discounted cash flow minus the capital cost (Eq. 33):

26

27

28

$$NPV = \sum_{n=0}^n \frac{E_{NET,GAIN,year}}{(i+1)^n} - E_{TOT} \quad (33)$$

where n represents the year number and i represents the discount rate. Figure 11 illustrates the variation of NPV as a function of the carbon taxes value for fixed discount rate ($i=0.1$) and different values of investment cost.

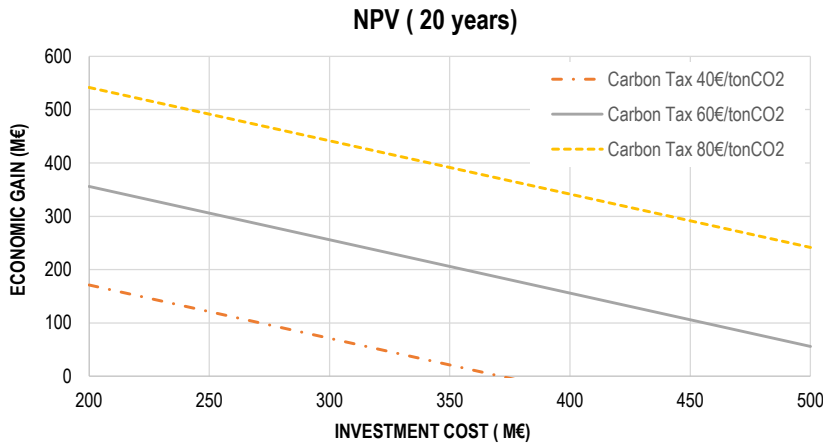


Figure 11: NPV for different carbon tax values and different investment costs.

As can be seen, NPV changes substantially under different situations of carbon taxes. In addition for solar installations there are available funds that could be considered (European or National funds) that would favor retrofitting of the plant but they have not been included in this analysis.

If the economic profit for the avoided CO₂ emissions is not enough to balance the additional investment cost an increase of electricity price ($\Delta PRICE_{EL}$) is required. The annual revenues due to this incremental cost is given by Eq. 34:

$$E_{INCR} = \Delta PRICE_{EL} \left(\frac{\text{€}}{\text{kWh}} \right) \cdot P_{NET,year} \left(\frac{\text{MWh}}{\text{year}} \right) \quad (34)$$

where E_{INCR} , expressed in M€/year, represents the revenues due to the incremented cost of selling electricity while $P_{NET,year}$ is the total electric energy per year produced by the plant. Thus, the total yearly revenue ($E_{TOT,REV}$) would be (Eq. 35):

$$E_{TOT,REV} = E_{NET,GAIN,year} + E_{INCR} \quad (35)$$

The required rise of electricity price associated to each case is shown in Table 17:

Table 17: Required increment of electricity sale price for maintaining a fixed value of IRR=0.1

	Total Investment Cost (M€)	E_{incr} (M€/year)	Δ Electricity price (c€/kWh)
Without Carbon Tax	200	23.5	1.967
	300	35.2	2.947
	400	47	3.934
	500	58.8	4.922
Carbon Tax 20 €/tonCO ₂	200	0	0
	300	11.6	0.971
	400	23.4	1.959
	500	35.2	2.947
Carbon Tax 40€/tonCO ₂	200	0	0
	300	0	0
	400	0	0
	500	11.5	0.963

6.5.5 Heat storage for near zero CO₂ emissions

The use of heat storage for solar has been considered in the previous analyses by taking into account solar equipment costs. If biomass is alternatively employed, operating costs derive from the various stages of the supply chain (cutting, chipping, transportation). On average, a total cost of 50 €/ton [101] for M40 (M40= 40% of humidity) wood chip can be estimated whereas the total cost would be 85 €/ton [102] for M20 wood chip. In the case study the LHV is near a M40 wood chip class. If a wood chip price of 60 €/ton is assumed, it would result a biomass annual cost of 31.18 M€. Under a scenario of 60 €/ton CO₂ for carbon taxes a yearly revenue of 32.31 M€ could be achieved. For these calculations, a total investment cost within the range of 80-110 €/kW [103] is considered for the biomass system, where O&M costs are estimated as a 40% of the capital costs.

6.5.6 Discussion

The above results suggest a potential interest of the DCP for CO₂ capture. The energy penalty that results from retrofitting a CFPP with this CCS technology (~9%) is similar to that estimated for other technologies such as pre-combustion CO₂ capture (~16%), amines scrubbing (~8-12%), membranes (~5-8.5%) and Calcium Looping (~4-9%). However, because of the low temperature needed to regenerate the sorbent, a CO₂ neutral solar facility could be efficiently integrated to supply the heat required, which would reduce coal consumption and operation costs significantly. Solar energy integration would serve to decrease the energy penalty just to CO₂ compression and ancillaries consumption, which leads to a near to zero CO₂ emissions power plant. The solar-CCS system penalty is estimated as just 3-4% points, with a SPECCA of only around 2 MJ/kg, which is well below the SPECCA values reported for other CO₂ capture technologies. Previous works based on thermodynamic analysis of the DCP report an energy consumption of about 3 MJ/kg [8], which is in the range of the results obtained in this work.

Comentado [U10]: Cuidado con esto...

Comentado [U11]: Cuidado con esto...

Comentado [U12]: No entiendo...arriba queremos decir que el solar ayuda a reducir significativamente el specca...y a hora decimos que en trabajos previos sin solar el specca es similar?

1 The results obtained from the economic analysis strongly suggest the economic viability of using the
2 DCP to retrofit a CFPP. Since the DCP is an emerging CCS technology, cost estimations are based
3 on assumptions based on diverse scenarios. Thus, for a 150 MW_e CFPP, the most optimistic scenario
4 leads the total investment cost of 205 M€ whereas for the pessimistic scenario the calculated
5 investment is 449 M€. If medium temperature solar energy is used to assist the DCP, the estimated
6 costs are in the range between 25 and 46 €/tonCO₂ (avoided CO₂) and from 0.095 to 0.112 € per kWh_e.
7 According to Zhao et al. [8], the total capital cost of an Integrated Gasification Combined Cycle
8 (IGCC) plant with a pre-combustion CO₂ capture system is about 1775-2567\$/kW, the cost of a CFPP
9 with a MEA system for post-combustion CO₂ capture would be about 1798\$/kW, that of an oxy-
10 combustion plant would be about 1810 \$/kW whereas that of a membrane/catalytic plant would be
11 2082 \$/kW. Considering the results obtained for the optimistic case, the total investment cost of the
12 proposed solar assisted DCP is estimated in the range of 1500-3300 \$/kW as function of solar facility
13 cost. For that, the Dry Carbonate Process investment cost of 160-320€/kW, which is in the line of
14 previous works [6,8].

15
16 It is important to point out that the above analysis is based on different assumptions for a novel
17 integration scheme. However, the preliminary results obtained show an interesting potential to be
18 further explored by a deeper analysis in future works. Future works should address in further depth a
19 comparison between different CFPP-DCP-solar integration schemes to minimize energy penalty and
20 investment costs. Since the carbonation reaction is exothermic, a proper use of the released energy is
21 fundamental. Moreover, further work on the multicycle sorbent behavior at realistic process
22 conditions is needed.

24 7.6. Conclusions

25 This paper is devoted in its first part to provide an overview of the currently most studied CO₂ capture
26 systems. The performance of CCS technologies is assessed, highlighting advantages, drawbacks and
27 challenges. In a second part a novel analysis is carried out for the integration of medium temperature
28 solar thermal energy into the Dry Carbonate Process to assist sorbent regeneration. The Dry
29 Carbonate Process to capture CO₂ is based on the use of a cheap, abundant and non-toxic material
30 (Na₂CO₃) as dry sorbent at relatively low temperatures for both carbonation and sorbent regeneration.
31 Our work shows that, when coupled with a medium temperature solar thermal power technology
32 including thermal storage, the integration yields a nearly zero CO₂ emissions with a reduced global
33 penalty in the power plant and avoiding also the generation of hazardous waste. The efficiency of the
34 power plant coupled to the Dry Carbonate Process to capture CO₂ is decreased from 33.5% to 24.2%
35 if fossil fuel is used to supply the heat for regeneration of the sorbent. This penalty is due to the
36 amount of heat required for sorbent regeneration plus the power spent for CO₂ compression and solid
37 conveying. If solar thermal power is used for sorbent regeneration, the penalty drops remarkably and
38 the global efficiency, defined in terms of operational expenditures, is just decreased from 33.5% to
39 30%. Since additional fossil fuel would not be needed for sorbent regeneration most of this penalty
40 is due to compression of the captured CO₂. A cost estimation of CO₂ capture by means of the Dry
41 Carbonation Process coupled to solar thermal power (for the optimistic scenario) ranges from 25 to
42 46 €/tonCO₂ (avoided CO₂) and from 0.095 to 0.112 € per kWh_e produced (compared to 0.087 €/kWh_e

Comentado [U13]: Dependerá del tamaño de planta, no?

Comentado [U14]: Arriba, sin solar, hay que poner las mismas unidades

Comentado [U15]: Arriba, sin solar, no se dicen estos costes. Habría que ponerlos para resaltar la mejora con solar

Comentado [U16]: Que son estos costes?...cuales son sin solar?

Comentado [U17]: No se entiende la comparación...son estos Kwe?...parece que estamos comparando con los valores de arriba de ~0.1 €/kWe...cuales son los costes de estas tecnología por €/tonCO₂

Comentado [u18]: Revisar los valores que hay y dejar claro que es cada cosa

Comentado [U19]: La comparación es muy confusa...hay que dejarla más clara, quizás hacer una tabla y decir claramente que es cada coste

1 for the reference plant) as depending on the cost of the solar thermal technology. Thus, the highest
2 costs are associated to the solar energy system. Although there is room for technology improvement
3 and additional cost reductions could be expectedly achieved, the proposed integration based on solar
4 thermal power and the Dry Carbonation Process can be considered as a promising technology as
5 compared to other carbon capture technologies and renewable energy integrations recently proposed
6 in the literature.

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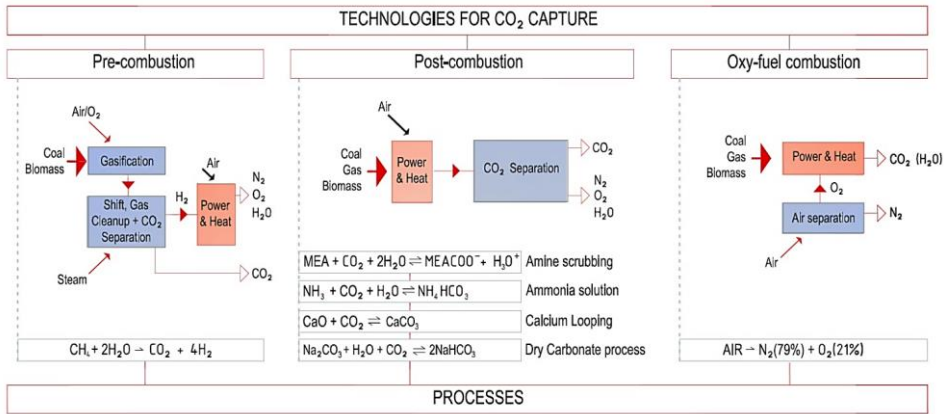
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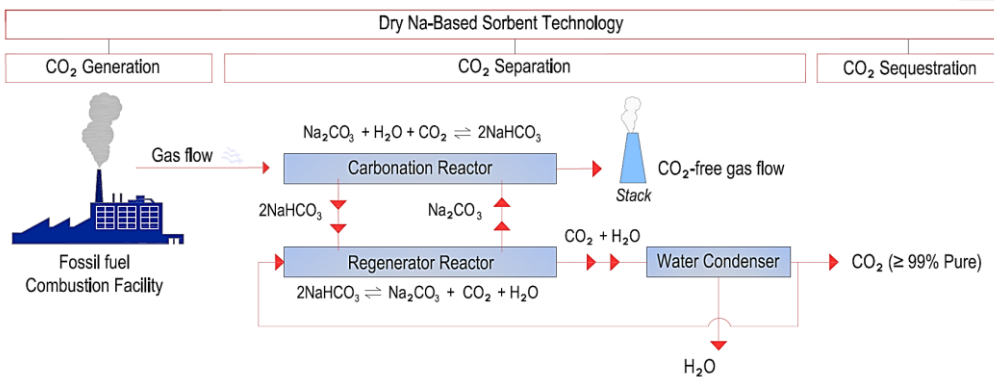
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Figure 1: Overview of technologies for CO2 capture.



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Figure 2: General scheme of the Dry Carbonate Process.

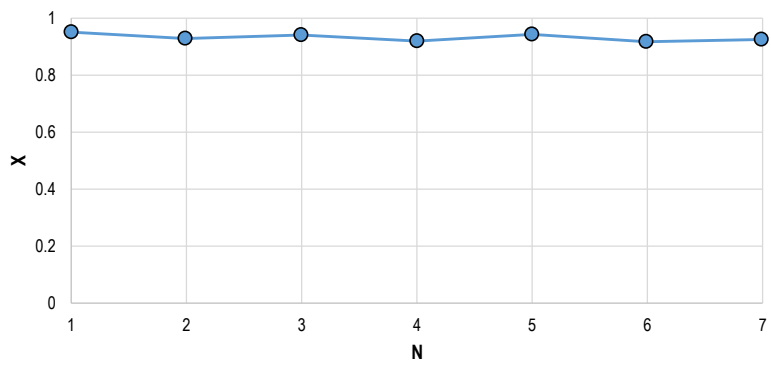
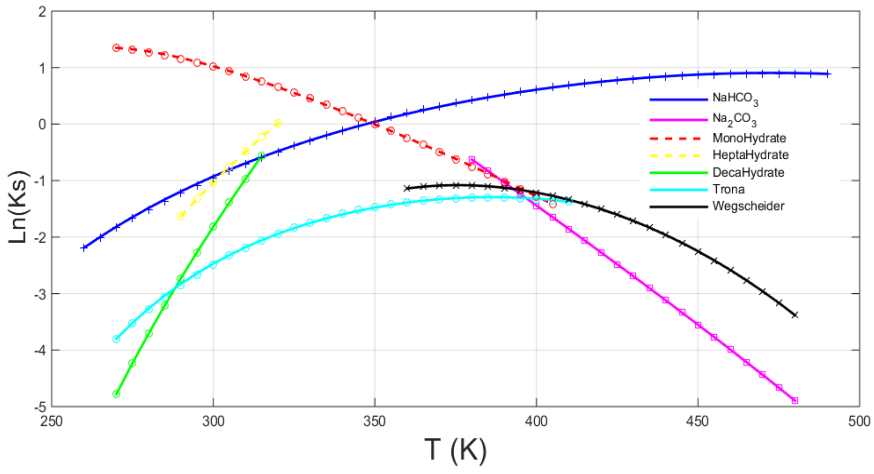


Figure 3: Na_2CO_3 conversion as a function of the cycle number (data extracted from [74]).

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4 Figure 12: $\ln(K_s)$ values for reactions involved in NaHCO_3 production from raw trona

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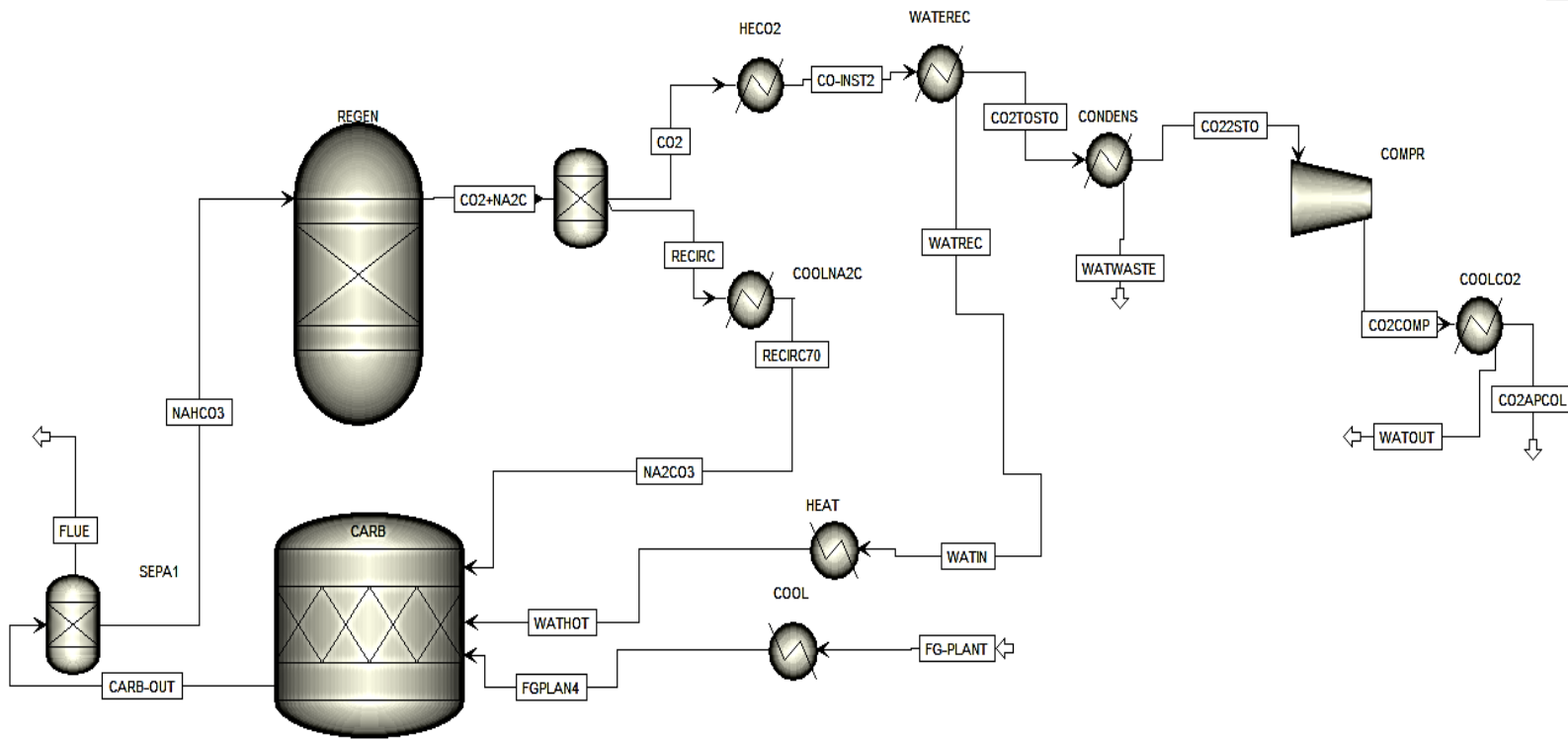


Figure 6: Dry Carbonate Process layout.

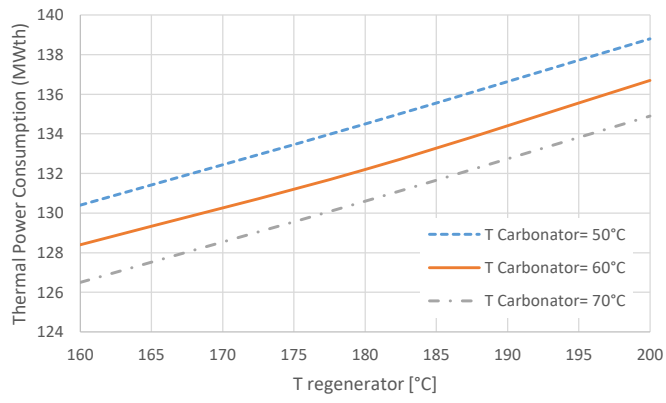
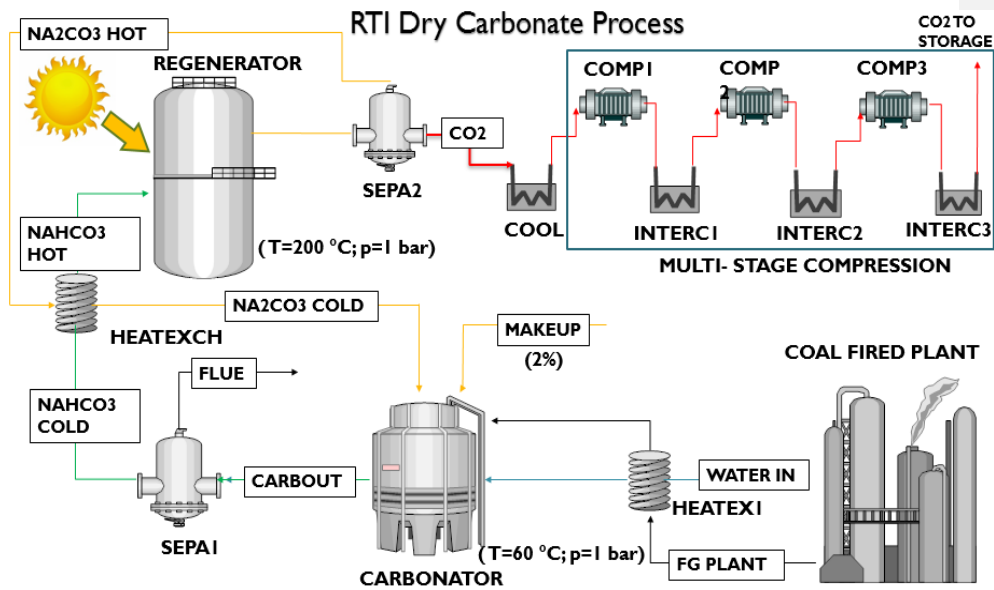


Figure 7: Thermal power required for different carbonator and regenerator temperatures.



Acronyms (equipment and streams):

CARBONATOR: CO₂ capture reactor
 CARBOUT: Final product from carbonator
 CO₂: CO₂ recovered from the system
 CO₂ TO STORAGE: CO₂ to the storage system (20 °C, 75 bar)
 COAL FIRED PLANT: Coal fired plant for electricity production
 COMP1: Compressor CO₂ (1-10 bar)
 COMP2: Compressor CO₂ (10-25 bar)
 COMP3: Compressor CO₂ (25-75 bar)
 COOL: CO₂ (20°C) intercooler
 FGPLANT: Flue gas exits the coal fired plant
 NA₂CO₃ COLD: Regenerated Na₂CO₃ (80°C)
 NA₂CO₃ HOT: Regenerated Na₂CO₃ (200°C)
 NAHCO₃ COLD (fig.6): Solids exits the carbonator (60°C)

NAHCO₃ HOT: Solids entering the regenerator (140°C)
 HEATEX I H₂O-flue gas heat exchanger
 HEATEXCH: NaHCO₃-Na₂CO₃ heat exchanger
 INTERC1: CO₂ (20°C) intercooler
 INTERC2: CO₂ (20°C) intercooler
 INTERC3: CO₂ (20°C) intercooler
 MAKE UP: Sorbent Make up
 REGENERATOR: Sorbent regenerator
 SEPA1: Solid-gas separator
 SEPA2: Solid-gas separator
 WATER IN: Water to CO₂ capture reactor

Figure 8: Optimized plant configuration proposed in this work.

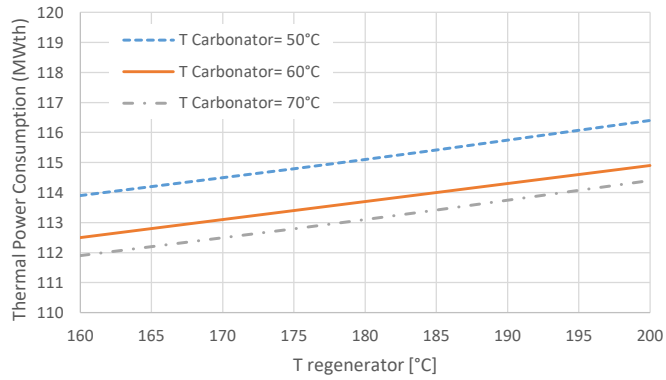


Figure 9: Power consumption for different operating conditions (including heat recovery).

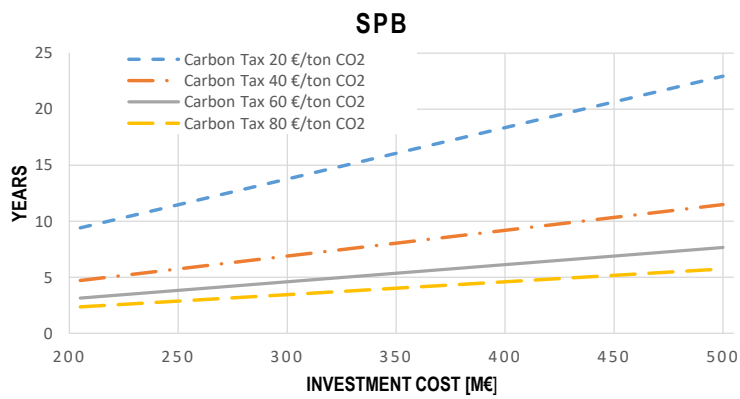


Figure 10: SPB curves according to the three scenarios as function of CFPP retrofitting capital costs.

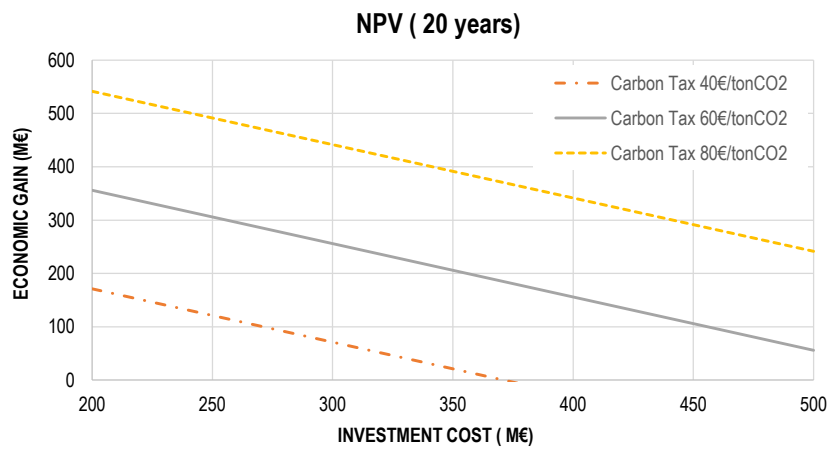


Figure 11: NPV for different carbon tax values and different investment costs.

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Table 1: Reference data for a 150 MW_e coal fired plant (data scaled from [48]).

Item	Magnitude	Unit
Coal consumption	61	ton/hr
Air intake	692	ton/hr
Gross power introduced with fuel	447	MW _{th}
Net power supplied	397	MW _{th}
Net Power produced	150	MW _{el}
Net efficiency	33.5	%

Table 2: Flue gas flow for a 150 MW_e coal fired plant (data scaled from [48]).

Coal flue gas component	Mole Flow (kmol/hr)	Mass Flow (tons/hr)
N ₂	17154.21	529.71
CO ₂	3085.62	135.96
H ₂ O	1471.86	29.4
O ₂	781.8	27.57
CO	140.7	3.93
NO	135.36	4.47
SO ₂	37.53	2.64

Table 3: Carbonator and calciner working conditions.

	carbonator	calciner
Outlet temperature [°C]	60	140
Outlet pressure [bar]	1,01	1.01
Net heat duty [MW]	-101.240	122.480
Total feed stream CO ₂ flow [ton/h]	135.550	0
Total product stream CO ₂ flow [ton/h]	10.620	127.010
Net stream CO ₂ production [ton/h]	-124.930	127.010

Table 4: Calciner streams composition.

	CO ₂ +NA	NAHCO ₃ H
Temperature (°C)	140	60
Pressure (bar)	1.01	1.01
Mass flow (ton/hr)		
H ₂ O	50.28	1.44
CO ₂	124	0
Na ₂ CO ₃	323.25	442.7
NaHCO ₃	0	11.39
Wegscheider's salt		44.39

Table 5: Power balance without heat recovery.

	Power production	Power consumption
CFFP	150 MW _{el}	447 MW _{th}
Decarbonator		122.5 MW _{th}
COMP		15 MW _{el}
Wsolid		2.37 MW _{el}
Net Power	132.53 MW _{el}	
Total heat requirement		569.5 MW _{th}

Table 6: CO₂ compression power

Component	two-stage compression		three-stage compression	
	Exhaust Pressure (bar)	Power (MW)	Exhaust Pressure (bar)	Power (MW)
COMP1	9	6.29	4.2	3.78
COMP2	75	6.02	17.6	3.78
COMP3	-	-	75	3.6
Global W_{comp}		12.31		11.16

Table 7: Global plant energy balance.

	Power production	Power consumption
CFFP	150 MW _{el}	447 MW _{th}
Decarbonator		114.9 MW _{th}
COMP		11.16 MW _{el}
W _{solid}		2.47 MW _{el}
Net Power	136.37 MW _{el}	
Total heat		561.9 MW _{th}

Table 8: Efficiency values for different sorbent conversion factors (X).

X	Na ₂ CO ₃ flow (kmol/hr)	Calciner (MW _{th})	Carbonator (MW _{th})	W _{solid} (MW _{el})	Efficiency (%)
0.4	84.5	119.5	-104	4.6	23.2
0.75	42.93	114.9	-101	2.47	24.2
0.95	32.86	111	-98	1.89	24.37

Table 9: Main properties of materials to store energy in the form of sensible heat [95,96]

	Temperature (°C)		Average density (kg/m ³)	Average heat conductivity (W/(mK))	Average heat capacity (kJ/(kgK))	Thermal diffusivity (m ² /s)	Volume specific heat capacity (kWh _{th} /m ³)	Volume (m ³)
	Cold	Hot						
Solid storage media								
Sand-rock-mineral oil	200	300	1700	1.0	1.30	4.5×10 ⁻⁷	60	22460.1
Reinforced concrete	200	400	2200	1.5	0.85	8.0×10 ⁻⁷	100	13271.9
Cast iron	200	400	7200	37.0	0.56	9.2×10 ⁻⁶	160	6155.4
Liquid storage media								
Mineral oil	200	300	770	0.12	2.6	6.0×10 ⁻⁸	55	24793.6
Synthetic oil	250	350	900	0.11	2.3	5.3×10 ⁻⁸	57	23979.1
Silicone oil	300	400	900	0.10	2.1	5.3×10 ⁻⁸	52	Out of range
Nitrite salts	250	450	1825	0.57	1.5	2.1×10 ⁻⁷	152	Out of range

Table 10: Properties of different typologies of wood chips

Wood chips	H _i [MJ/kg]	ρ[kg/m ³]	H _i [MJ/ m ³]
Chestnut	10,53	580	6106,24
Beech	13,45	750	10084,95
Spruce	7,90	450	3556,98
Larch	11,60	660	7654,88
Average	10,87	610	6630,29

Table 11: CO₂ emission data for different scenarios.

	REFERENCE PLANT	DRY CARBONATE (P)	DRY CARBONATE (BE)	DRY CARBONATE (O)
Power (MWel)	150	150	150	150
CCS Power consumption (MWel)	-	25	13.63	13
Regenerator Heat requirement (MWth)	-	119	114.9	111
Net power (MWel)	150	125	136.37	137
CO ₂ Emissions (ton/hr)	136	10.7	10.7	10.7
CO ₂ Emissions (kmol/hr)	3080	243.2	243.2	243.2
CO ₂ Avoided Emissions (kton/year)		1089	1089	1089
CO ₂ Emissions (tons/ MW _{th} /hr)	0.9	0.085	0.078	0.078

Table 12: SPECCA Analysis for different scenarios.

Item	Scen.P	Scen. BE	Scen. O
Net Power Production (MW)	125	136,37	137
CO ₂ ccs (ton/hr)	10,7	10,7	10,7
E _{ccs} (kg _{CO2} /kWh _{el})	85.60	78.46	78.10
η _{ccs}	0.232	0.242	0.244
SPECCA (MJ/kg _{CO2})	5.86	5.03	4.90
η _{ccs_eco}	0.279	0.305	0.306
SPECCA _{eco} (MJ/kg _{CO2})	2.65	1.29	1.24

Table 13: COE for different scenarios.

Item	Item	Units	Scen. P	Scen. BE	Scen. O
Fuel Cost [99]	FC	€/kWh	0.03	0.023	0.02
Capital Cost	TCR	€/kWe	1200	1100	1000
Fixed Charge Factor [99]	FCF	year ⁻¹	0.15	0.1	0.075
Variable Cost	VOM	€/kWe	0.006	0.006	0.006
COE _{ref}		€/kWh	0.116	0.087	0.074

Table 14: COE for CCS system (as function of Solar Capital Costs).

Item	Item	Units	Scen. PE	Scen. BE	Scen. O
Net Power Production		MW _e	125	136.37	137
η_{el}			27.9	29.9	30.2
η_{system}		%	22.1	24.2	24.37
Dry Carb. Capital cost [6]	TCR	M€/MW	0.32	0.223	0.148
Solar Capital Cost [100]	TCR	M€/MW	1.5		
COECCS		€/kWh	0.165	0.115	0.095
AC		€/ton _{CO2}	60.416	34.245	25.421
Solar Capital Cost [100]	TCR	M€/MW	2		
COECCS		€/kWh	0.174	0.121	0.099
AC		€/ton _{CO2}	64.223	41.188	30.629
Solar Capital Cost [100]	TCR	M€/MW	2.5		
COECCS		€/kWh	0.182	0.127	0.103
AC		€/ton _{CO2}	73.736	48.132	35.837
Solar Capital Cost [100]	TCR	M€/MW	3		
COECCS		€/kWh	0.191	0.132	0.108
AC		€/ton _{CO2}	83.249	55.076	41.045
Solar Capital Cost [100]	TCR	M€/MW	3.5		
COECCS		€/kWh	0.199	0.138	0.112
AC		€/ton _{CO2}	92.762	62.020	46.253

Table 15: ΔCOE (€/kWh_{el}) for different costs of solar thermal field.

Solar Thermal cost (€/kW _t)	Scen. P	Scen. BE	Scen. O
1500	0.0492	0.0281	0.0209
2000	0.0578	0.0339	0.0252
2500	0.0664	0.0396	0.0295
3000	0.0749	0.0453	0.0337
3500	0.0835	0.0510	0.0380

Table 16: Total CFPP retrofitting investment cost calculated by considering several CSP plant prices.

Solar Thermal Cost 1.5 M€/MW				
	Units	Scen. P	Scen. BE	Scen. O
ESOLAR	M€	179.25	172.35	166.5
EDRY	M€	40	30	20
EO&M	M€	21.92	20.23	18.65
ETOT	M€	241.17	222.58	205.15
Solar Thermal Cost 2 M€/MW				
	Units	Scen. P	Scen. BE	Scen. O
ESOLAR	M€	239	229.8	222
EDRY	M€	40	30	20
EO&M	M€	27.9	25.98	24.2
ETOT	M€	306.9	285.78	266.2
Solar Thermal Cost 2.5 M€/MW				
	Units	Scen. P	Scen. BE	Scen. O
ESOLAR	M€	298.75	287.25	277.5
EDRY	M€	40	30	20
EO&M	M€	33.87	31.725	29.75
ETOT	M€	372.62	348.975	327.25
Solar Thermal Cost 3 M€/MW				
	Units	Scen. P	Scen. BE	Scen. O
ESOLAR	M€	358.5	344.7	333
EDRY	M€	40	30	20
EO&M	M€	39.85	37.47	35.3
ETOT	M€	438.35	412.17	388.3
Solar Thermal Cost 3.5 M€/MW				
	Units	Scen. P	Scen. BE	Scen. O
ESOLAR	M€	418.25	402.15	388.5
EDRY	M€	40	30	20
EO&M	M€	45.82	43.21	40.85
ETOT	M€	504.07	475.36	449.35

Table 17: Required increment of electricity sale price for maintaining a fixed value of IRR=0.1

	Total Investment Cost (M€)	E _{incr} (M€/year)	Δ Electricity price (c€/kWh)
Without Carbon Tax	200	23.5	1.967
	300	35.2	2.947
	400	47	3.934
	500	58.8	4.922
Carbon Tax 20 €/tonCO2	200	0	0
	300	11.6	0.971
	400	23.4	1.959
	500	35.2	2.947
Carbon Tax 40€/tonCO2	200	0	0
	300	0	0
	400	0	0
	500	11.5	0.963