

# Carbon capture and utilization for Sodium Bicarbonate production assisted by solar thermal power

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## Abstract

In this paper, a novel carbon capture and utilization process is proposed. It is based on using a fraction of the captured carbon dioxide to produce sodium bicarbonate ( $\text{NaHCO}_3$ ), a widely used product in the chemical and food industries. The process couples the Dry Carbonate process for  $\text{CO}_2$  capture with  $\text{NaHCO}_3$  production. Raw material is trona or sodium sesquicarbonate dehydrate ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ ) which is a relatively abundant mineral composed by approximately 46% sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and 35% sodium bicarbonate ( $\text{NaHCO}_3$ ) by weight. In the process trona is firstly converted into  $\text{Na}_2\text{CO}_3$  in a fluidized bed reactor operated at 180-200°C and 1 bar. Heat required in the fluidized bed reactor for decomposing trona can be supplied by renewable sources such as low/medium temperature solar energy or biomass. A fraction of the  $\text{Na}_2\text{CO}_3$  generated is recirculated for  $\text{CO}_2$  capture by means of the dry carbonate process. The rest is converted to  $\text{NaHCO}_3$  in a carbonating tower through the reaction with  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . After separation of  $\text{NaHCO}_3$  and other salts from water,  $\text{NaHCO}_3$  is suitable for direct sale. The use of renewable sources for the energy required at the sorbent regenerator and trona decomposition yields a near-zero  $\text{CO}_2$  emissions global system. As case of study,  $\text{CO}_2$  capture coupled to  $\text{NaHCO}_3$  production has been analysed for a 15  $\text{MW}_{\text{el}}$  coal fired power plant. Heat required in the carbon capture process penalizes the global system efficiency by a 10.2%, which is reduced just to the electricity parasitic consumption for solids transport and  $\text{CO}_2$  compression (~3%) if renewable energy sources are integrated. From an economic perspective, the penalty in electricity consumption is fully compensated by the new by-product sales. Taking into account the reduction of electricity sales and current prices of trona and  $\text{NaHCO}_3$  a return of investment is obtained in the range between 3 and 8.7 years with an internal rate of return over 12%. These values improve the current forecast of any other carbon capture and storage process up to date, which suggests a high interest of the proposed conceptual integrations for regions where trona is widely available.

## Keywords:

$\text{CO}_2$  capture, Coal fired power plant, CCS, CCU, Dry carbonate process, Trona, Sodium bicarbonate.

## 1. Introduction

2

4 A complete replacement of fossil fuels by renewable energies is not feasible in the short-term. Thus,  
6 fossil fuel power plants should be urgently retrofitted with CO<sub>2</sub> capture and sequestration (CCS)  
8 processes as a necessary measure to limit global warming below 2°C [1]. CCS would allow continuing  
10 the use of fossil fuel until a deeper penetration of renewable energy sources into the grid is attained  
12 in an orderly fashion. CO<sub>2</sub> capture and utilization (CCU) for commercial purposes would help  
14 mitigating capture costs that mainly hinder the commercial deployment of state of the art CO<sub>2</sub> capture  
16 technologies. Current anthropogenic CO<sub>2</sub> emissions (around 35 Gt/y) largely exceed the amount of  
18 CO<sub>2</sub> used in chemical processes (~200 Mt/y). However, promoting CO<sub>2</sub> utilization routes for the  
20 production of valuable chemicals could be a starting point to promote the deployment of CO<sub>2</sub> capture  
technologies [2]. According to International Energy Agency (IEA) projections, the CCS share of  
cumulative emissions reduction to achieve the 2°C target would require about 3500 large-scale CCS  
projects in operation by 2050. Only about 15 large-scale CCS commercial projects are in operation  
to this date of which Boundary Dam in Canada is the only coal fired power plant applying CCS in  
the power sector. Yet, it is estimated that abandoning CCS in the power sector would increase the  
investment required over 40% in the 2°C scenario [3]. Moreover, post-combustion capture  
technologies have the greatest potential for reduction of CO<sub>2</sub> emissions in the short term because they  
can be retrofitted to existing fossil fuel power plants and are also applicable to other industrial  
processes.

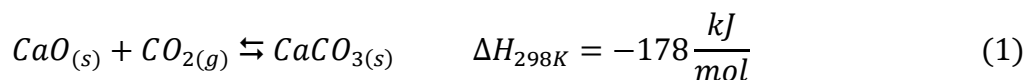
22 Up to date the only post-combustion capture technology commercially available at the necessary  
24 large-scale of coal fired power plants is based on chemical absorption by amines dissolved in water.  
26 In this post-combustion capture system, the exhaust gases stream from the power plant is passed  
28 through an absorber column where it comes into contact with the liquid amine flowing downwards,  
30 which allows CO<sub>2</sub> to be chemically absorbed by the amine. The CO<sub>2</sub> rich amine solvent is then  
32 pumped to a regenerator, where heat is supplied to reverse the chemical reaction and release relatively  
34 pure CO<sub>2</sub> for its compression, transport and storage while the CO<sub>2</sub> lean liquid amine is pumped back  
36 into the absorber to be reused [4]. Although temperatures for CO<sub>2</sub> desorption are not high (~ 130°C)  
sorbent regeneration in this process requires a relatively high amount of energy to heat the large  
volume of water where amines are dissolved. Thus, the energy required per ton of CO<sub>2</sub> captured is  
about 3.3 GJ/ton<sub>CO2</sub> for an advanced monoethanolamines (MEA) system whereas 3.9 GJ/ton<sub>CO2</sub> are  
required for a typical aqueous MEA system [5]. On the other hand, post-combustion capture by MEA  
suffers from other serious issues related to toxicity, corrosion and degradation [6]. Furthermore,  
amines have a relatively high cost (>1000 €/ton), which is a major problem taking into account the  
large scale of commercial CCS applications [1,7].

38 Thus, there is a need to develop novel post-combustion capture processes using cheap, widely  
40 available and non-toxic materials at reduced cost and energy penalty. In this line, novel amine-based  
42 solid sorbents based on direct steam stripping desorption have shown an improved performance [8].  
44 In ref. [9] an organic solvent was added to a CO<sub>2</sub> rich, aqueous ammonia/CO<sub>2</sub> solution under room  
46 temperature and pressure conditions. The sorbent was regenerated by using low-temperature heat,  
48 with a reduced thermal energy requirement. In ref. [10] novel absorbents were studied using both  
single and mixed amine-based absorbents. Experimental results indicate that most absorbents tested  
have a poor performance as compared to MEA except for aqueous 2-(2-Aminoethylamine)ethanol  
(AEEA), which shows a promising performance. Ref. [11] presents a review about the impact of  
uncertainty in the sorbent thermo-physical properties on the design and operation of components and  
processes involved in CO<sub>2</sub> capture.

50 CO<sub>2</sub> capture processes using dry solid sorbents capable of capturing CO<sub>2</sub> from flue gas streams by  
physical adsorption show potential advantages compared with other conventional CO<sub>2</sub> capture

2 systems using aqueous amine solvents [12]. Thus, a variety of promising adsorbents such as activated  
3 carbonaceous materials, microporous/mesoporous silica or zeolites, carbonates, and polymeric resins  
4 have been proposed in the recent literature [12]. As a common feature, these solid sorbents require  
5 very small amounts of heat for regeneration although their capture capacity is generally low. Ref [13]  
6 proposes the use of power plant's waste heat for CO<sub>2</sub> capture by nanomaterials properly designed to  
overcome the competitive adsorption of CO<sub>2</sub> and H<sub>2</sub>O.

8 The Calcium-Looping process is a promising 2<sup>nd</sup> generation post-combustion process validated at the  
9 pilot level (1-2 MW<sub>th</sub>) that uses Calcium Oxide (CaO) derived from cheap (~10 €/ton) and abundant  
10 natural limestone to capture CO<sub>2</sub> from flue gas. The process is based on the reversible  
carbonation/calcination chemical reaction at high temperatures [14]:



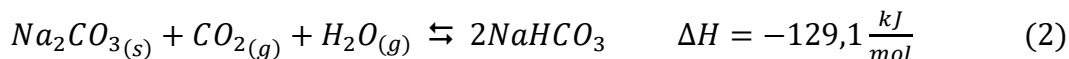
14 Carbonation proceeds at a satisfactory fast rate at temperatures in the range 625–680°C while the  
15 reverse calcination reaction should be carried out at 900–950°C under high CO<sub>2</sub> partial pressure [14].  
16 The dry sorbent is repeatedly cycled between two reactors. In one reactor (carbonator) carbonation  
17 of CaO particles serves to capture CO<sub>2</sub> from the flue gas. The carbonated particles are then circulated  
18 into another reactor (calciner) where sorbent regeneration takes place by calcination. To close the  
19 cycle, the regenerated CaO particles are returned back into the carbonator, leaving a concentrated  
20 stream of CO<sub>2</sub> in the calciner ready for compression, transport and sequestration. However, a main  
21 drawback of this process is the progressive deactivation of CaO particles mainly due to marked  
22 sintering in the high temperature calcination stage, which requires a large make-up of fresh limestone  
23 thus increasing the energy penalty of the process taking into account the high temperatures at which  
24 it must be carried out to enhance the reaction kinetics.

26 Concerning the penalty imposed by the capture system, ref [15] examines potential design routes for  
27 the capture, transport and storage of CO<sub>2</sub> in power plants. Around 90% of operational carbon  
28 emissions could be captured with an energy penalty between 14 and 300% and rises by 27-142% of  
29 electricity cost [16]. However, CO<sub>2</sub> capture system integration, with an adequate heat and work  
30 integration would result in significant energy savings [17]. The CO<sub>2</sub> capture installation requires  
31 large amounts of heat for solvent regeneration in appropriate quantity and quality, a cooling system  
32 to discharge waste heat and additional power to drive CO<sub>2</sub> compressor and auxiliary equipment  
33 (pump, fans). In [18] the steam to CCU is extracted from IP/LP crossover pipe showing the high  
34 impact of the design IP/LP crossover pressure on the power unit efficiency.

36 Integration with solar could be a driving factor to favor CO<sub>2</sub> capture implementation at the  
37 commercial scale. Ref [19] studies flexible operation of solvent-based capture for three types of  
38 plants obtaining the highest revenue to electricity ratio in the case where solar repowering was used  
39 for power boosting. Ref [20] analyzes the use of solar energy to provide the energy of the capture  
40 system. A CaL based capture system assisted by solar energy is assessed in [20] for reducing the  
41 global system efficiency penalty.

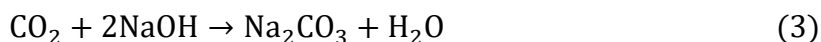
44 CCS feasibility could be fostered by integration of the capture system with other processes and  
45 valuable chemicals. Ref [21] suggests a method for combining CCS and biofuel production using  
46 CO<sub>2</sub> as a feedstock. [22]. A significant part of the cost for CCS is related to the compression of the  
47 captured CO<sub>2</sub>, however the conditions for carbon capture and utilization (CCU) can reduce the  
48 parasitic energy consumption. Ref [27] addresses the critical technologies in CO<sub>2</sub> capture, transport,  
49 utilization and storage and proposes technical priorities by evaluating critical indexes such as the  
50 objective contribution rate and technical maturity.

2 Among the carbon capture technologies in a research and development (R&D) phase [23], one of the  
4 most promising CO<sub>2</sub> capture processes is the dry carbonate process, which uses Na<sub>2</sub>CO<sub>3</sub> (sodium  
6 carbonate also known as soda ash) as sorbent to separate CO<sub>2</sub> from others flue gases. The process is  
based on the reversible chemical reaction [24]:



8 Equal molar quantities of CO<sub>2</sub> and H<sub>2</sub>O are produced during sorbent regeneration, and pure CO<sub>2</sub>  
10 suitable for use or sequestration is available after condensation of the H<sub>2</sub>O. In contrast with the  
Calcium-Looping process, the carbonation reaction in the dry carbonate process takes place  
12 efficiently at relatively low temperatures (60-70°C), which is below the typical flue gas temperature.  
At these temperatures, the capture efficiency can be as large as 90%. Moreover, the required sorbent  
14 regeneration temperature is not high (120-200°C) allowing the use of medium temperature heat  
sources. Na<sub>2</sub>CO<sub>3</sub> is an abundant and relatively cheap (~100 €/ton) natural mineral lacking serious  
16 problems of degradation, toxicity or corrosiveness at the working temperatures of the process [1,25].  
The research triangle institute (RTI) has designed and constructed a Dry Carbonate based prototype  
18 unit [26] showing a number of potential advantages over MEA systems such as [30] : i) lower total  
regeneration energy requirement; ii) less energy requirement also to operate due to lower pressure  
20 drop; iii) Modest temperatures of operation and noncorrosive reactants allowing standard equipment  
and materials of construction; iv) more stable and cheaper sorbent than amines.

22 Reaction (2) is also at the basis of the Solvay process to produce sodium bicarbonate (NaHCO<sub>3</sub> also  
24 known as baking soda) through the reaction of calcium carbonate, sodium chloride, ammonia, and  
carbon dioxide in water. In this process (Solvay), the initial reaction of CO<sub>2</sub> with an aqueous solution  
26 of sodium hydroxide to produce sodium carbonate is:



30 Further addition of CO<sub>2</sub> yields NaHCO<sub>3</sub> through reaction (2), which at sufficiently high concentration  
precipitates out of the solution. Sodium hydroxide (NaOH) is mainly produced from electrolysis  
32 (2NaCl(aq) + 2H<sub>2</sub>O(l) → H<sub>2</sub>(g) + Cl<sub>2</sub>(g) + 2NaOH(aq), ΔH<sub>298K</sub>= 422 kJ/mol) [27]. This involves a  
certain amount of waste energy to produce NaHCO<sub>3</sub> as benefit. NaHCO<sub>3</sub> is also produced  
34 commercially by a similar method using Na<sub>2</sub>CO<sub>3</sub> obtained from naturally occurring mineral trona,  
which is dissolved in water and treated with CO<sub>2</sub> [25]. This process avoids the use of electrolysis for  
36 NaOH production, but a little amount of energy is still required for trona dissociation (133,9 kJ/mol).

38 In the present manuscript a novel CCU concept is introduced, which combines the production of  
NaHCO<sub>3</sub> with the dry carbonation process for CO<sub>2</sub> capture and is assisted by renewable energy  
40 sources for sorbent regeneration (solar thermal power or biomass). The structure of the manuscript is  
the following. First, the current state of the art technology for sodium bicarbonate production from  
42 trona decomposition is described. Then the concept of CO<sub>2</sub> capture and sodium bicarbonate  
production for CO<sub>2</sub> fixation in a valuable chemical product is described. Na<sub>2</sub>CO<sub>3</sub>, CO<sub>2</sub> and H<sub>2</sub>O are  
44 obtained from trona decomposition. These three components, together with a relevant fraction of CO<sub>2</sub>  
from the capture system are used for sodium bicarbonate production. The integration scheme is  
46 applied to a small 15 MW<sub>el</sub> coal power plant or, equivalently, to a fraction of the flue gas from a  
bigger size plant. The novel concept of this manuscript consists of the synergistic combination of the  
48 dry carbonate process with sodium bicarbonate production starting from a raw natural material such  
as trona. This study shows that the penalty imposed by the capture system can be mitigated from the  
50 production of a valuable material such as sodium bicarbonate with an economic return. The results

obtained in this preliminary analysis demonstrate the environmental and economic interest of the proposed concept

## 2. Trona mineral

Trona consists mainly of sesquicarbonate sodium (systematic name is trisodium hydrogencarbonate) having the chemical formula:



As specified in Table 1, natural trona is composed of approximately 46%  $Na_2CO_3$  and 35%  $NaHCO_3$  being relatively abundant in nature. They are widely distributed around the world. Among other places they are found in Wyoming [28,29], Tanzania [30], Namib [31], Turkey [32], China [33]. Calcination and dehydration of raw trona in industrial processes are applied for different purposes: to eliminate carbonate for reducing acid consumption if an acidic treatment is to be applied, to decrease the weight of the material for reducing transportation costs in the case that it involves hydration in large quantities, or as a necessary step in a chemical process such as the production of  $Na_2CO_3$ , which is the main focus of the current manuscript.

In the production of  $Na_2CO_3$  from trona, the monohydrate process is the most commonly used method. The first step of this method is thermal decomposition of the mineral, which yields  $Na_2CO_3$  via the following reaction [34,35]:

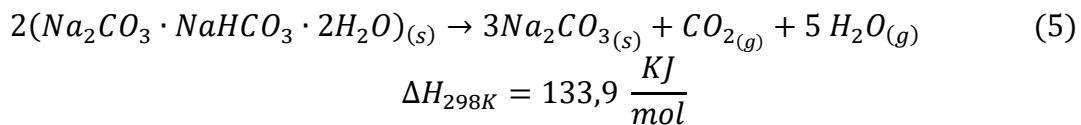
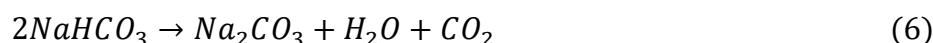


Table 1. Natural trona composition [34]

Component	Wt%
$Na_2CO_3$	46,53
$NaHCO_3$	34,82
$Na_2SO_4$	0,568
insolubles	2,98
hydration water	14,92
others	0,182

Trona-phase equilibrium diagrams for low and high temperature regions have been analysed in detail in [36]. Trona is stable at temperatures up to 57 °C under dry conditions. Intermediate salts such as wegschiderite ( $Na_2CO_3 \cdot 3NaHCO_3$ ) and sodium monohydrate ( $Na_2CO_3 \cdot H_2O$ ) are produced between 57 °C and 160 °C [34,37]. Above 160 °C, trona decomposes into  $Na_2CO_3$  and  $NaHCO_3$ .  $NaHCO_3$  decomposes to  $Na_2CO_3$ ,  $H_2O$  and  $CO_2$  in the temperature range of 100°C–200 °C [38]. Reaction kinetics is fast at 200°C [39]:



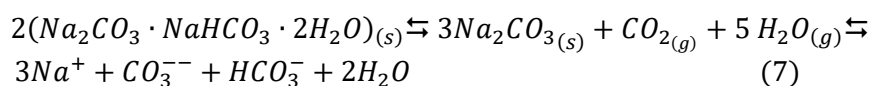
Thus, the final decomposition of trona generates  $Na_2CO_3$ ,  $CO_2$  and  $H_2O$ .

## 3. Sodium bicarbonate production

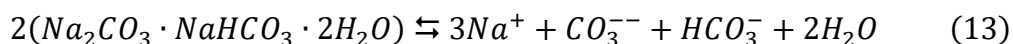
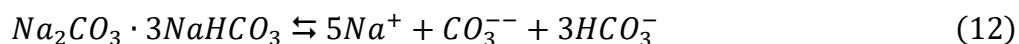
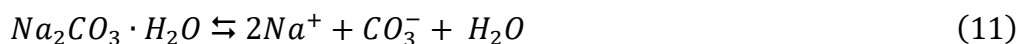
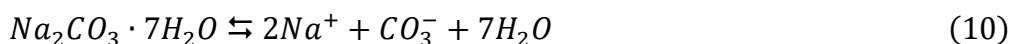
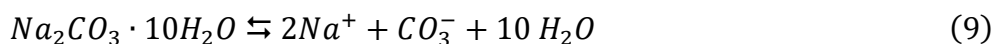
The novel concept presented in this manuscript combines CO<sub>2</sub> capture and the production of NaHCO<sub>3</sub> at low temperature using for both processes natural trona as raw material. CO<sub>2</sub> capture is realized via the reaction expressed by Eq. (2). This section briefly reviews NaHCO<sub>3</sub> production from raw trona as currently applied in industry and the reactions involved that will be used in this work.

In the NaHCO<sub>3</sub> production process, crushed raw trona is fed into a vertical hollow tubular vessel with a perforated bottom that separates an upper fluidizing chamber from a lower plenum chamber. A gas stream is introduced into the plenum chamber through the perforated bottom to fluidize crushed trona. Part of the charge remains in suspension while the decomposition gases such as H<sub>2</sub>O and CO<sub>2</sub> are redirected to the carbonator for NaHCO<sub>3</sub> production. The fluidized bed reactor acts both as a calciner for the crushed trona and as a separator to remove fine particles of crushed trona from the coarse portion of the charge remaining in fluid suspension in the fluidized bed reactor. Thus, fine particles of crushed trona become entrained in the effluent gas and exit the fluidized bed before they become calcined. The thermal energy required to achieve the conversion of crude trona to Na<sub>2</sub>CO<sub>3</sub> is supplied by heating the fluidizing gas or by placing heating means within or around the bed in order to attain a temperature of 125°- 225°C [40]. The next step is to take the intermediate Na<sub>2</sub>CO<sub>3</sub> solution into a centrifuge, which separates the liquid from the crystals. The crystals are then dissolved in a soda ash solution made by the manufacturer in a rotary dissolver, thereby becoming a saturated solution. This solution is filtered to remove any non-soluble materials and is then pumped through a feed tank to the top of a carbonating tower. Purified CO<sub>2</sub> is introduced into the bottom of the tower and held under pressure. As the saturated sodium solution moves through the tower, it cools down and reacts with CO<sub>2</sub> to form NaHCO<sub>3</sub> crystals. These crystals are collected at the bottom of the tower and transferred to another centrifuge, where the excess solution (filtrate) is filtered out. The crystals are then washed in a bicarbonate solution, forming a cake-like substance ready for drying. The filtrate removed from the centrifuge is recycled to the rotary dissolver, where it is used to saturate more intermediate soda ash crystals. The washed filter cake is then dried on either a continuous belt conveyor or in a vertical tube drier.

A key step in the process occurs in the carbonating tower. Here, the saturated Na<sub>2</sub>CO<sub>3</sub> solution moves from the top of the tower downwards. As it falls, the solution cools down and reacts with CO<sub>2</sub> to form NaHCO<sub>3</sub> crystals. After filtering, washing, and drying, the crystals are sorted by particle size and packaged appropriately. Trona decomposition and Na<sub>2</sub>CO<sub>3</sub> carbonation involve several reactions. Dissociation reactions of trona and NaHCO<sub>3</sub> are:



In the process, a number of other salts can be also formed such as sodium carbonate decahydrate (Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O), sodium carbonate heptahydrate (Na<sub>2</sub>CO<sub>3</sub>·7H<sub>2</sub>O), sodium carbonate monohydrate (Na<sub>2</sub>CO<sub>3</sub>·H<sub>2</sub>O) and Wegscheider's salt (Na<sub>2</sub>CO<sub>3</sub>·3NaHCO<sub>3</sub>). Thus, other possible reactions are:





To model the dependence of the equilibrium constants (Ks) for the dissociation reactions of the different salts involved in NaHCO<sub>3</sub> production we have used a polynomial equation:

$$\ln K_s = A + \frac{B}{T} + C \ln(T) + D T \quad (15)$$

which provides a good fit to experimental curves shown in [36] ( $R^2 > 0.99$ ). Best fittings parameters are given in Table 2.

Table 2. Best fitting parameters used in the model for the equilibrium constant  $K_s$  (Eq. 15) of the reactions involved in NaHCO<sub>3</sub> production from raw trona.

	A	B	C	D
REACTIONS				
$CO_2 + 2H_2O \rightleftharpoons H_3O^+ + HCO_3^-$	231.47	-12092.7	-36.78	0
$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$	216.05	-1243.7	-35.48	0
$NaHCO_3 \rightleftharpoons Na^+ + HCO_3^-$	-63.26	-1308.41	13.48	-0.034
$Na_2CO_3 \rightleftharpoons 2Na^+ + CO_3^{2-}$	-548.32	18070.74	94.75	-0.165
$Na_2CO_3 \cdot H_2O \rightleftharpoons 2Na^+ + CO_3^{2-} + H_2O$	281.77	-9970.6	-44.56	0.0221
$Na_2CO_3 \cdot 7H_2O \rightleftharpoons 2Na^+ + CO_3^{2-} + 7H_2O$	484.91	-18935	-80.12	0.114
$Na_2CO_3 \cdot 10H_2O \rightleftharpoons 2Na^+ + CO_3^{2-} + 10 H_2O$	1165.01	-37.81	-200.08	0.335
$2(Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O) \rightleftharpoons 3Na^+ + CO_3^{2-} + HCO_3^- + 2H_2O$	277.24	-14523.8	-41.0	0.0085
$Na_2CO_3 \cdot 3NaHCO_3 \rightleftharpoons 5Na^+ + CO_3^{2-} + 3HCO_3^-$	-1209.46	29113.05	213.72	-0.363

For example, at 200°C, it is  $K_s > 1$  for the NaHCO<sub>3</sub> dissociation reaction and hence the reaction is shifted to dissociation while for Na<sub>2</sub>CO<sub>3</sub> dissociation it is  $K_s < 1$  indicating that Na<sub>2</sub>CO<sub>3</sub> dissociation is not thermodynamically favored at this temperature. Equilibrium between carbonate and bicarbonate ions in the aqueous solution determines the stable solid phase in a saturated solution and the corresponding solubility concentrations of carbonate and bicarbonate. This equilibrium is strongly affected by the CO<sub>2</sub> partial pressure. At  $T < 80$  °C ( $K_{sNaHCO_3} < 1$ ) and ambient CO<sub>2</sub> partial pressure, solid bicarbonate (nahcolite) is the thermodynamically stable solid [41]. Equilibrium between the dissolved bicarbonate and dissolved carbonate establishes itself by sorption of CO<sub>2</sub>.

#### 4. Integration of NaHCO<sub>3</sub> production and CO<sub>2</sub> capture

In this section a novel concept of integration of the NaHCO<sub>3</sub> production process above described and the dry carbonate CO<sub>2</sub> capture process is presented. The integration is originally conceived for its application in a coal fired power plant (CFPP), which is retrofitted with the dry carbonate process using Na<sub>2</sub>CO<sub>3</sub> for CO<sub>2</sub> capture, although it can be used in other industrial applications with CO<sub>2</sub> emissions. The flow diagram of this integration is shown in Figure 1. Part of the Na<sub>2</sub>CO<sub>3</sub> produced by trona calcination is used as sorbent make-up in the CO<sub>2</sub> capture process while a fraction of the CO<sub>2</sub> released from sorbent regeneration, together with the fraction of CO<sub>2</sub> derived from trona dissociation (0.5 mol<sub>CO2</sub>/mol<sub>trona</sub>), is utilized to produce in the carbonating tower NaHCO<sub>3</sub> suitable for sale. As Figure 1 shows H<sub>2</sub>O is used in the calciner for trona decomposition and carbonation of the flue gas stream. H<sub>2</sub>O is generated in the carbonating tower during NaHCO<sub>3</sub> production and in the NaHCO<sub>3</sub> regenerator. An optimized integration would recirculate these hot water streams between these systems, regenerator to carbonator in the CCS system, and from the carbonating tower to the calciner in the NaHCO<sub>3</sub> production system. Calcination of trona and sorbent regeneration are assisted by medium temperature heat, which could be available from renewable sources such as solar thermal or biomass. If these renewable sources are used, the global system (power plant plus capture of CO<sub>2</sub>,

part of which is stored and the rest used for  $\text{NaHCO}_3$  production) becomes a near zero  $\text{CO}_2$  emissions system.

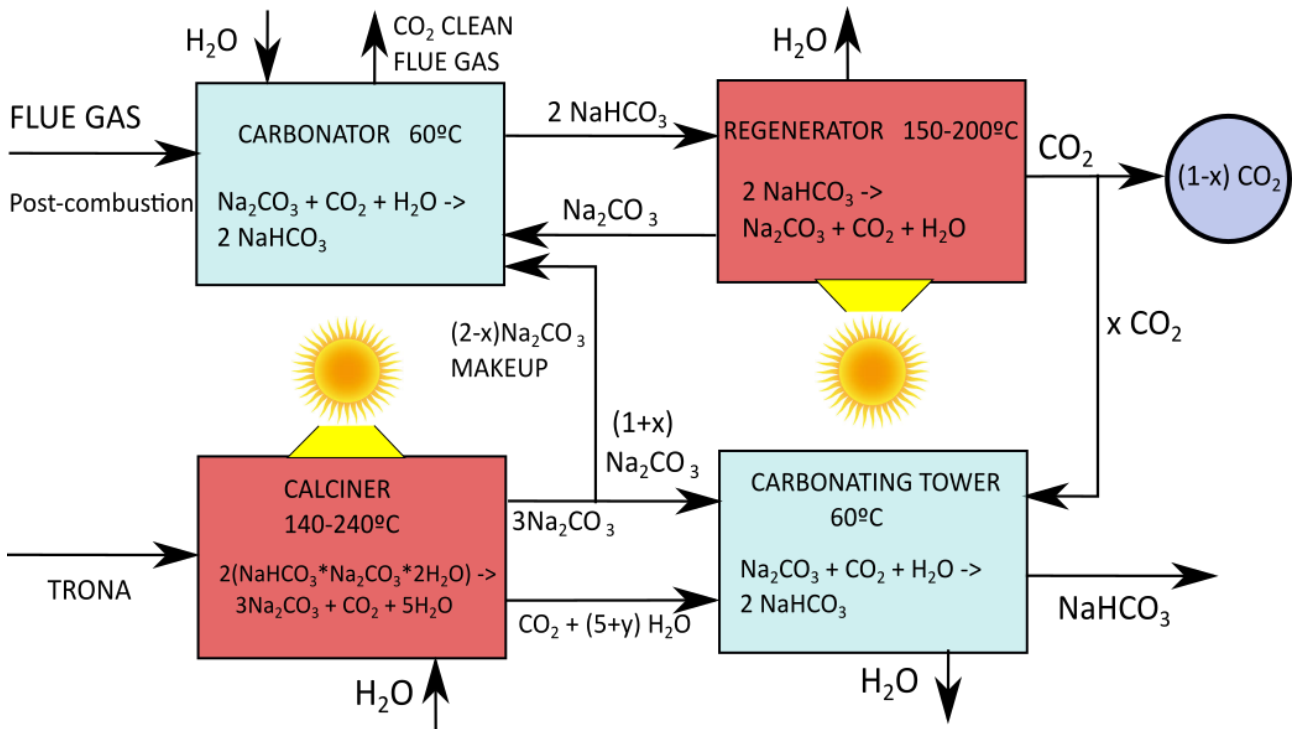


Figure 1. Flow diagram of the research triangle institute (RTI) dry carbonate process for  $\text{CO}_2$  capture coupled to  $\text{NaHCO}_3$  production using raw trona and assisted by medium temperature solar thermal power.

Figure 2 illustrates a Sankey diagram where the different routes followed by the  $\text{CO}_2$  are detailed.

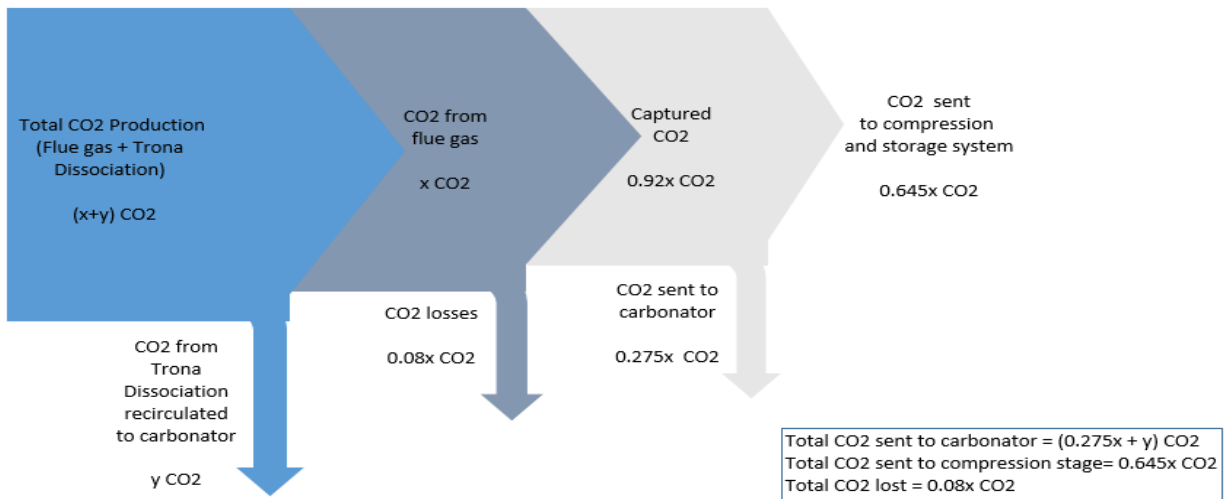


Figure 2. Sankey diagram of  $\text{CO}_2$  routes in the overall process

As Figure 2 shows an amount of about 35% of  $\text{CO}_2$  produced by the CFPP is employed for  $\text{NaHCO}_3$  production while the rest is sent to the compression system and could be stored or eventually utilized for others purposes.



## Reference power plant

This section describes the main characteristics of the CFPP used in this work as reference case. CFPP flue gases are characterized by a dilute concentration of CO<sub>2</sub> at large volumetric flow and ambient pressure, which poses a technological challenge for CO<sub>2</sub> capture. For the 15 MW<sub>el</sub> generated in the pulverized coal-fired (PC) power plant used in our study, the exhaust gases stream is 830 m<sup>3</sup> per minute with a CO<sub>2</sub> concentration between 10% and 15% in volume [42]. Assuming standard performance of equipment, the pulverized coal-fired boiler combusts 6.1 tons per hour (tph) of coal and generates 44.7 MW<sub>th</sub> (HHV). The boiler output provides 39.7 MW<sub>th</sub>, which yields a boiler efficiency of 88.6%. Since the present work is focused on the postcombustion system analysis and given the complexity and proprietary nature of power plant steam turbine cycles, a general 42% thermal to electric steam cycle efficiency is assumed [43], which leads to 16.67 MW<sub>el</sub> generated. In addition, a 10% in-house power plant electricity is consumed resulting in a net electrical generation of 15 MW<sub>el</sub> delivered to the grid.

The relatively small size of the reference CFPP (15 MW<sub>el</sub>) has been chosen with the purpose of storing the captured CO<sub>2</sub> in tanks of reasonable volume to be ready for utilization. This size can be representative of small coal power plants or for dealing with a fraction of the exhaust gases of bigger plants. Main data for a plant of this reference CFPP are shown in Table 3. Composition of the flue gas from the plant used for the analysis is detailed in Table 4.

Table 3: Power consumption for the reference CFPP [42,43]

Item	Magnitude	Unit
Coal consumption	6.1	t/h
Air in	69.2	t/h
Gross power introduced	44.7	MW <sub>th</sub>
Net power introduced	39.7	MW <sub>th</sub>
Net Power Produced	15	MW <sub>el</sub>
Net efficiency	33.5	%

Table 4: Flue gas flow composition from the reference CFPP [42,43].

Coal flue gas component	Mole Flow(kmol/h)	Mass Flow(t/h)
N <sub>2</sub>	1715.42	52.97
CO <sub>2</sub>	308.56	13.60
H <sub>2</sub> O	147.19	2.94
O <sub>2</sub>	78.18	2.76
CO	14.07	0.39
NO	13.54	0.45
SO <sub>2</sub>	3.75	0.26

The use of the dry carbonate process in a CFPP for CO<sub>2</sub> capture is described in [10]. An optimized integration with solar thermal energy is schematized in figure 3. Alternatively, the heat source could be either biomass or coal. Overall, the dry carbonate process yields a CO<sub>2</sub> removal efficiency of 92% (assuming a fixed value for Na<sub>2</sub>CO<sub>3</sub> conversion to NaHCO<sub>3</sub> of X=0.75) and utilizes 43 ton/hr of Na<sub>2</sub>CO<sub>3</sub> as CO<sub>2</sub> sorbent to remove 12.5 t/h of CO<sub>2</sub> in a continuous cycle. A heat exchanger (HEATEX1) between the flue gas leaving the power coal plant and the flow exiting the carbonator is used for cooling the flue gas. Another heat exchanger (HEATEXCH) is interposed between the

incoming and the outgoing flow in the regenerator. Both heat exchangers serve to increase significantly the total efficiency of the plant. They allow to reduce the heat required for sorbent regeneration by about 10% with a thermal flow exchanged of 1,45 MWth (0.8 MWth+ 0.65 MWth). This makes possible working with different operating conditions in the regenerator (200 °C in the best case scenario and 140°C with solar radiation support). With this configuration the heat requirement, in the case the working condition in the regenerator are set equal to  $T=200\text{ }^{\circ}\text{C}$  and  $p=1,01$  bar, is about 11,4 MWth (the theoretical value for the heat required using  $\Delta H = 129,09 \frac{\text{kJ}}{\text{mol}}$  at  $T=298$  K is 10,25 MWth ).

The  $\text{Na}_2\text{CO}_3$  make-up flow rate is 0.3 ton/hr, the heat required for  $\text{Na}_2\text{CO}_3$  regeneration is around 11.4 MWth and the power consumption for  $\text{CO}_2$  compression and solid conveying is 1.58 MWeI (Table 5). Power demand for solid separation in two stages centrifugation can be estimated as 0.3 MWeI by taking as reference a high efficiency centrifuge used as salt separator. Thus, the total efficiency of the CFPP retrofitted with the dry carbonate process drops from 33.5% to 24% due to the penalty in power and additional heat required. If medium temperature solar thermal energy is used as energy input for sorbent regeneration, and taking thus into account only the penalty in power consumption, the economic efficiency, defined in basis of the operation costs including fuel, decreases just to about 30%.

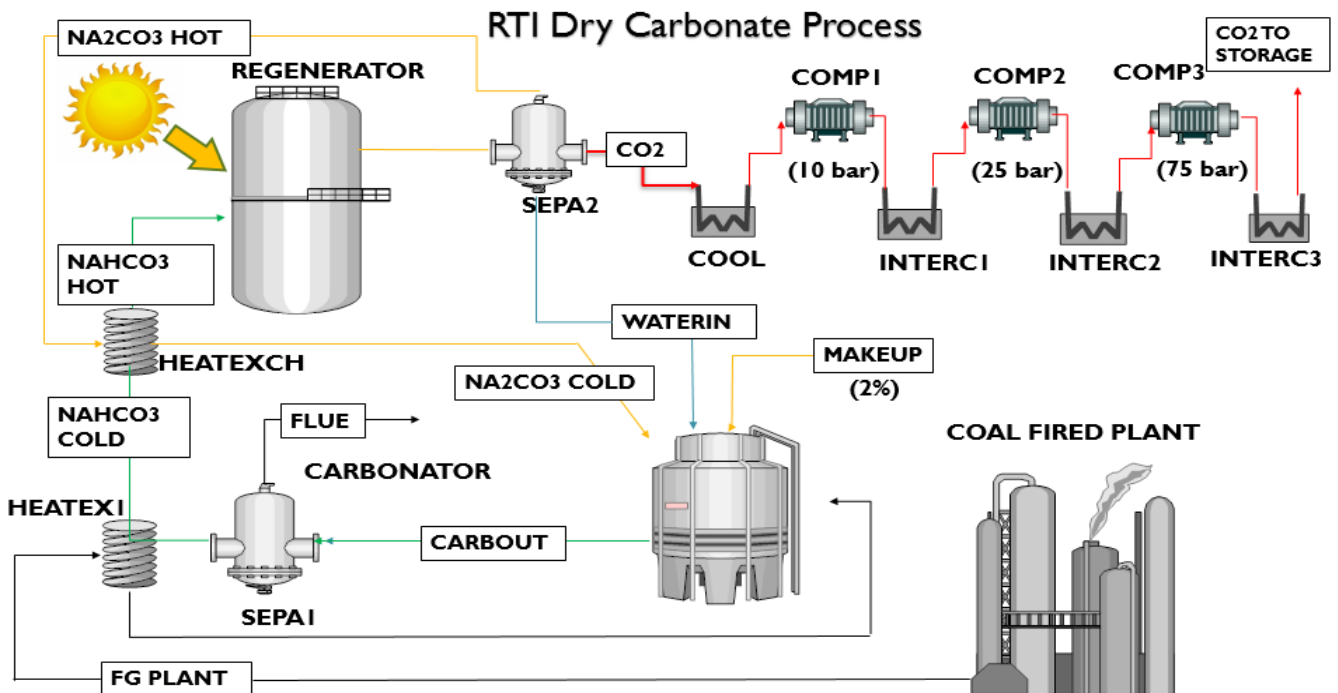


Figure 3. Integration of the RTI dry carbonate process into a CFPP for  $\text{CO}_2$  capture [44].

Table 5. Power consumption for a 15  $\text{MW}_{\text{el}}$  CFPP with integrated RTI dry carbonate process for  $\text{CO}_2$  capture.

	Power production	Power consumption
CFPP	15 $\text{MW}_{\text{el}}$	44.7 $\text{MW}_{\text{th}}$
Regenerator		11.4 $\text{MW}_{\text{th}}$
COMP		1.33 $\text{MW}_{\text{el}}$
Wsolid		0.25 $\text{MW}_{\text{el}}$
Centrifugation		0.3 $\text{MW}_{\text{el}}$
Net Power	13.12 $\text{MW}_{\text{el}}$	
Total heat requirement		56.1 $\text{MW}_{\text{th}}$

To achieve a near zero CO<sub>2</sub> emissions global system, renewable energy must be used for heating the calciner, either solar or biomass. In the case of solar, and to take into account its discontinuous availability, different options for heat storage can be considered such as: i) heat storage using tanks with pressurized water/steam. For instance a thermal storage of about 3 hours of steam can be obtained with the support of three tanks of 350 m<sup>3</sup>; ii) molten salts tanks; iii) synthetic oils; iv) a combination with a biomass boiler for supporting heat requirements of the post-combustion system.

Regarding the required CO<sub>2</sub> storage volume, a total flow rate of 68000 m<sup>3</sup>/h in the carbonator must be processed. Assuming a residence time of 15 s, a total storage volume of 270 m<sup>3</sup> would be sufficient for the carbonator working at low pressure. This can be achieved in practice using a CO<sub>2</sub> storage tank of 6 m in diameter and 10 m high, which is affordable with current technologies. For greater power a sequence of standardized tanks could be used.

## 5. Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> production from trona

This section analyses production of Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> from trona decomposition in a fluidized bed reactor working at 220 °C and 1 bar using solar thermal power as heat source. A schematic layout of the process is shown in figure 4. For the temperatures needed in this application, medium temperature parabolic troughs collectors coupled with a thermal energy storage system (i.e. with pressurized water tanks), are suitable to provide the necessary energy input.

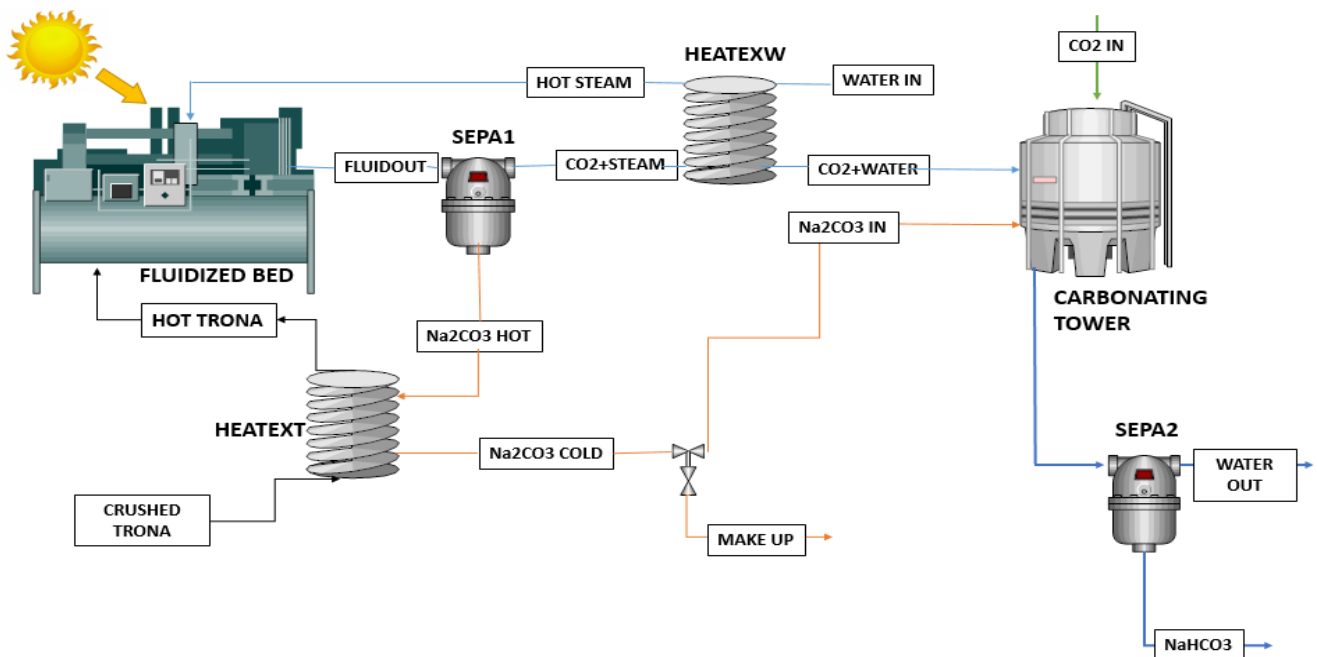


Figure 4. Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> production from trona assisted by solar energy.

As seen in figure 4, the stream of trona (CRUSHED TRONA), initially at 25°C and 1 bar, passes, before entering the fluidized bed reactor, through a solid–solid heat exchanger (HEATEXT) where it exchanges heat with the effluent Na<sub>2</sub>CO<sub>3</sub> stream from the fluidized bed reactor (Na<sub>2</sub>CO<sub>3</sub> HOT), which raises trona temperature up to 127°C. Another heat exchanger (HEATEXW) transfers heat from the gases and water vapor stream (CO<sub>2</sub>+STEAM) exiting the fluidized bed reactor to the water stream (WATER IN) entering the fluidized bed, which raises up its temperature to 205 °C. The total heat recovered by means of these heat exchangers amounts is 1.85 MW<sub>th</sub> as detailed in Table 6. Flow rates of the streams entering and exiting the fluidized bed reactor are summarized in Table 7.

Table 6. Heat exchanged in NaHCO<sub>3</sub> production according to Fig. 3.

	MW <sub>th</sub>	T <sub>incold</sub> (°C)	T <sub>outhot</sub> (°C)	T <sub>inhot</sub> (°C)	T <sub>outcold</sub> (°C)
HEATEXCT	1.15	20	95	219	205
HEATEXW	0.7	20	40	219	127
Total Thermal Power	1.85				

Table 7. Flow rates of streams entering and exiting the fluidized bed reactor in the NaHCO<sub>3</sub> production according to Fig. 3.

	Units	TRONA	WATIN	FLUIDOUT
TRONA	kmol/h	84.709	0	0
WATER	kmol/h	0.387	85	307.5
CO <sub>2</sub>	kmol/h	0.002	0	42.5
WEGSC(S)	kmol/h	0.096	0	0
NaHCO <sub>3</sub>	kmol/h	0.198	0	0
Na <sub>2</sub> CO <sub>3</sub>	kmol/h	0	0	127.5
Mole Flow	kmol/h	146.391	85	613.5
Temperature	°C	127	204	219
Pressure	bar	1.01	1.01	1,01
Vapor Fraction		0	1	0.733
Solid Fraction		1	0	0.267
Mass Density	kg/cum	2029	0.454	1.209
Average Molecular Weight		224	18.015	43.81

4 The heat required in the fluidized bed reactor for decomposing 19.2 t/h of trona is 5.1 MW<sub>th</sub> at 220°  
 (the theoretical value to decompose 85 kmol/h of trona at T= 25 ° C is 3.15 MW<sub>th</sub> from the reaction  
 6 enthalpy  $\Delta H_{298K} = 133.9 \frac{KJ}{mol}$  [11][25]). Such amount of heat, which can be provided by medium  
 temperature solar thermal power, warrants the production of 13.55 t/h of Na<sub>2</sub>CO<sub>3</sub> (Na<sub>2</sub>CO<sub>3</sub> COLD in  
 8 Fig. 6) plus 1.85 ton/h of CO<sub>2</sub> and 4 t/h of water (CO<sub>2</sub> + STEAM) of which 300 kg/h are used as  
 makeup in the dry carbonate process for CO<sub>2</sub> capture (MAKE UP) while the rest is sent to a  
 10 carbonating tower (Na<sub>2</sub>CO<sub>3</sub> IN) to produce sodium bicarbonate (NAHCO<sub>3</sub>) using a 3.75 t/h stream  
 of pure CO<sub>2</sub> from the carbon capture system (CO<sub>2</sub> IN) and the CO<sub>2</sub> and water streams released from  
 12 the fluidized bed reactor (CO<sub>2</sub> + STEAM). From the Na<sub>2</sub>CO<sub>3</sub> carbonation reaction (Eq. 2) it turns out  
 that 20.75 t/h of NaHCO<sub>3</sub> are produced at a total flow rate of about 9.5 m<sup>3</sup>/h. In this way, a commercial  
 14 chemical product is produced using captured CO<sub>2</sub> from the power plant with a higher economic value  
 than the raw mineral.

16

## 18 Overall system efficiency

20 The CFPP efficiency is reduced due to the heat employed for the production of NaHCO<sub>3</sub>, albeit an  
 economic revenue is obtained. Considering the 5.1 MW<sub>th</sub> needed in the fluidized bed reactor, the total  
 22 heat requirement is 61.2 MW<sub>th</sub> (Table 8).

24 Table 8. Heat requirement in different components for the production of NaHCO<sub>3</sub>.

	T ( ° C )	Thermal Power consumption
CFFP	850	44.7 MW <sub>th</sub>
Regenerator	200	11.4 MW <sub>th</sub>
Fluidized bed reactor	220	5.1 MW <sub>el</sub>
Total heat requirement		61.2 MW <sub>th</sub>

26 By avoiding storage of part of the CO<sub>2</sub> captured for half a day (considering 12 hours of daylight) the  
 total power consumption for compression decreases to 0.879 MW<sub>el</sub> (Table 9).

28

Table 9. Compression power for NaHCO<sub>3</sub> production.

Component	W <sub>comp</sub> ( MW <sub>el</sub> )
Compressor 1 ( 4.2 bar )	0.295
Compressor 2 ( 17.5 bar )	0.289
Compressor 3 ( 75 bar )	0.295
Total W <sub>comp</sub> ( from 1 to 75 bar )	0.879

For the reference CFPP with integrated CO<sub>2</sub> capture, and considering a power consumption of 0.247 MW<sub>el</sub> for solids conveying and 0.3 MW for centrifuge stages, the global efficiency penalty is -10.2 % over the baseline plant and the mean global electricity production is decreased by -9%. It results in a net efficiency of the global plant of 23 %:

$$\eta_{NET} = \frac{13,123 MW_{el} \cdot 12h + 13,574 MW_{el} \cdot 12h}{56,1 MW_{th} \cdot 12h + 61,2 MW_{th} \cdot 12h} = 0.23 \quad (16)$$

$$\eta_{NET_{el}} = \frac{13,123 MW_{el} \cdot 12h + 13,574 MW_{el} \cdot 12h}{15 MW_{el} \cdot 24h} = 0.89 \quad (17)$$

If the low temperature heat required in the calciner and regenerator is provided from renewables a near zero emissions system is obtained. By using solar energy for heating, that penalty on the original plant economic efficiency amounts to only 3%, which is associated to the parasitic power consumption of the post-combustion system.

## 6. Economic Analysis

For the economic analysis of the integrated process different scenarios are defined to analyze the competitiveness of the technology[45]. These scenarios are defined in terms of:

- NaHCO<sub>3</sub> production, to take into account the variability of demand in the market.
- Variation of trona costs, taking into account trona cost variability.
- Variation of NaHCO<sub>3</sub> sale prices on the market.
- Different plant installation costs. To consider uncertainty in equipment cost evolution a maximum deviation has been considered for the scenario. The variation range was taken as  $\pm 9\%$  of the average installation price.

Attending to these criteria three scenarios are considered:

**Scenario P** (Pessimistic Scenario): it takes into consideration a combination of diverse factors such as the highest penalty in electricity generation (it has been taken as the maximum error in estimating parasitic electricity losses), the highest plant installation costs, the highest cost of trona, and lowest sale price of NaHCO<sub>3</sub> in the market.

**Scenario BE** (Best Estimation Scenario): In this scenario the values derived from the simulation above described were used to define the efficiency of the system. It considers a capital cost of 3 M€ for the CCS technology [25]. This scenario uses current values of trona cost and NaHCO<sub>3</sub> sale price in the market.

**Scenario O** (Optimistic Scenario): this optimistic scenario implies minor trona and plant installation costs.

Considering that the price of trona is in the range 80-120 \$/ton [46] and that the sale price of NaHCO<sub>3</sub> is around 200-240 \$/ton, the economic profit for production of NaHCO<sub>3</sub> can be calculated as:

$$E_P = p_{\text{NaHCO}_3} \cdot \dot{m}_{\text{NaHCO}_3} - p_{\text{trona}} \cdot \dot{m}_{\text{trona}} \quad (18)$$

Here  $E_P$  is the economic profit derived from  $\text{NaHCO}_3$  production,  $p_{\text{NaHCO}_3}$  and  $p_{\text{trona}}$  are the selling price of  $\text{NaHCO}_3$  and purchase price of trona, respectively, and  $\dot{m}_{\text{NaHCO}_3}$  and  $\dot{m}_{\text{trona}}$  are the  $\text{NaHCO}_3$  and trona mass flow rates, respectively. Table 10 shows the prices calculated for the different scenarios considered.

Table 10. Different prices for different scenarios.

	Units	Scen. P	Scen. BE	Scen. O
$p_{\text{trona}}$	€/ton	120	100	80
$p_{\text{NaHCO}_3}$	€/ton	200	220	240
$\Delta_{\text{Gain}}$	€/ton	80	120	160
$E_{\text{GAIN}}$	€/day	22000	32000	44000

The investment cost of the solar technology is in the range 2.5-3.5 M€/MW<sub>th</sub> for a parabolic trough collectors plant with thermal energy storage [47] whereas the fluidized bed reactor cost is about 0.25 M€/MW<sub>th</sub> with an error margin of +/-25% [48]. Operation & maintenance costs are taken as 10 % of the baseline cost. The costs of other components of the solar field are estimated as 15% of the solar capital expenditures. Table 11 summarizes the investment costs of the plant for the different scenarios considered and according to different prices of the solar thermal technology. The total investment cost ( $E_{\text{TOT}}$ ) takes into account the cost of solar technology ( $E_{\text{SOLAR}}$ ), the cost of the fluidized bed reactor used for trona conversion ( $E_{\text{FLUID}}$ ), the cost of reactors for dry carbonate process ( $E_{\text{DRY}}$ ) and the cost of operation & maintenance ( $E_{\text{O&M}}$ ).

Table 11: Total investment cost:  $\text{NaHCO}_3$  production + Solar Thermal.

Solar Thermal 2.5 M€/MW				
	Units	Scen. P	Scen. BE	Scen. O
$E_{\text{SOLAR}} (\text{FLUID+DECARB})$	M€	42.5	41.25	40.5
$E_{\text{DRY}}$	M€	4	3	2
$E_{\text{FLUID}}$	M€	1.9	1.5	1.15
$E_{\text{O&M}}$	M€	4.84	4.58	4.37
$E_{\text{TOT}}$	M€	51.34	48.83	46.87
	Units	Scen. P	Scen. BE	Scen. O
Solar Thermal 3 M€/MW				
$E_{\text{SOLAR}} (\text{FLUID+DECARB})$	M€	51	49.5	48.6
$E_{\text{DRY}}$	M€	4	3	2
$E_{\text{FLUID}}$	M€	1.9	1.5	1.15
$E_{\text{O&M}}$	M€	5.69	5.4	5.18
$E_{\text{TOT}}$	M€	60.69	57.9	55.78
	Units	Scen. P	Scen. BE	Scen. O
Solar Thermal 3.5 M€/MW				
$E_{\text{SOLAR}} (\text{FLUID+DECARB})$	M€	59.5	57.75	56.7
$E_{\text{DRY}}$	M€	4	3	2
$E_{\text{FLUID}}$	M€	1.9	1.5	1.15
$E_{\text{O&M}}$	M€	6.54	6.23	5.98
$E_{\text{TOT}}$	M€	70.04	66.98	64.68

As can be seen in Table 11 the total investment costs are highly dependent on solar installation costs. Total investment of the CCU system varies from 15.3 M€ to 37.15 M€ and is strongly affected by the

solar technology cost. Table 12 shows the total investment costs and estimated annual profit for different scenarios and different solar technology costs.

Table 12: Total Investment costs and yearly revenue for scenarios of analysis.

TOTAL INVESTMENT	SCENARIO P	SCENARIO BE	SCENARIO O
SOLAR THERMAL COST 2.5 M€/MW	51.34 M€	48.83 M€	46.87 M€
SOLAR THERMAL COST 3 M€/MW	60.69 M€	57.90 M€	55.78 M€
SOLAR THERMAL COST 3.5 M€/MW	70.04 M€	66.98 M€	64.69 M€
ANNUAL ECONOMIC PROFIT	8.08 M€	11.58 M€	15.08 M€

Using these data, CCU investment's simple payback period (SPB) can be evaluated. SPB is the time for recovering the initial investment, which is given by:

$$SPB = \frac{E_{TOT}}{E_p} \quad (19)$$

Figure 5 shows estimated SPB values for the different scenarios as a function of solar thermal technology investment cost and for a constant production of 7470 ton/month of NaHCO<sub>3</sub>.

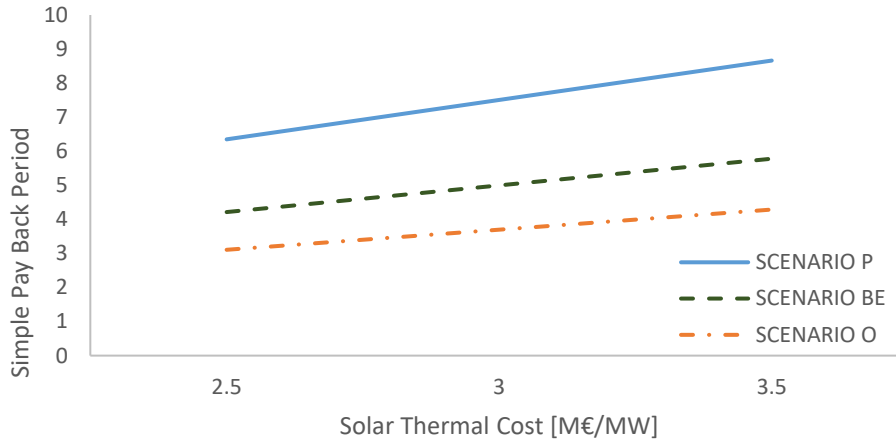


Figure 5. SPB as a function of solar thermal technology costs for the different scenarios analyzed.

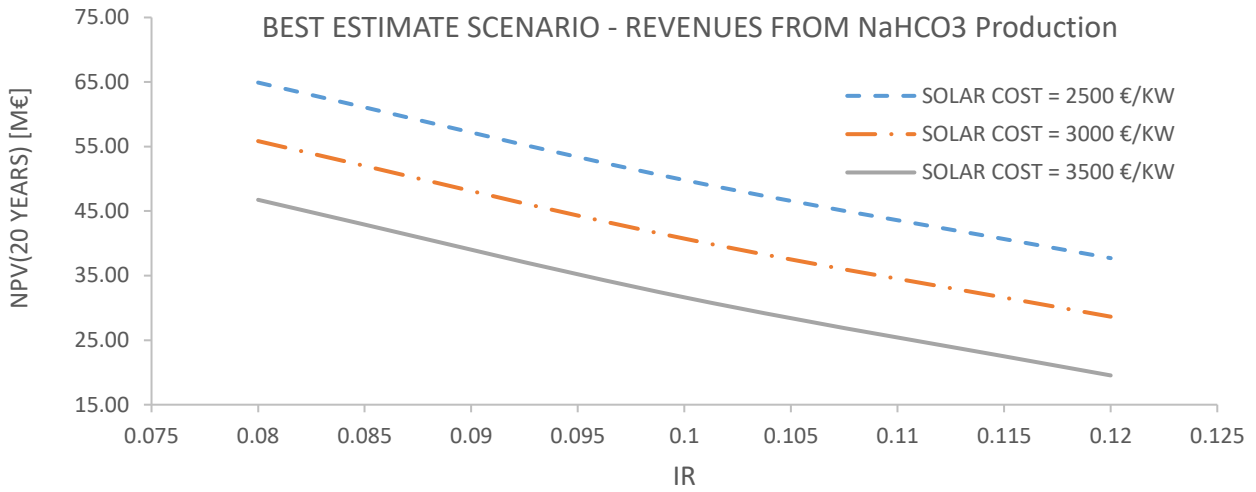
Figure 5 shows that relatively short SPB periods are obtained. In the worst case (Pessimistic Scenario) the SPB period is equal to 8.7 years while in the best case it amounts to only 3 years (Optimistic Scenario). These values suggest a high interest of the integration proposed in this paper, combining the dry carbonate CO<sub>2</sub> capture and sodium bicarbonate production using trona as raw material where it is available. However, the SPB does not address the time value of money, inflation, project lifetime or operation. For this reason, it is important to evaluate internal rate of return (IRR), which can be evaluated from the definition of net present value (NPV). NPV is the sum of the discounted cash flow minus the total investment cost:

$$NPV = \sum_{k=0}^N \frac{E_{NET,GAIN,year}}{(IR + 1)^k} - E_{TOT} \quad (20)$$

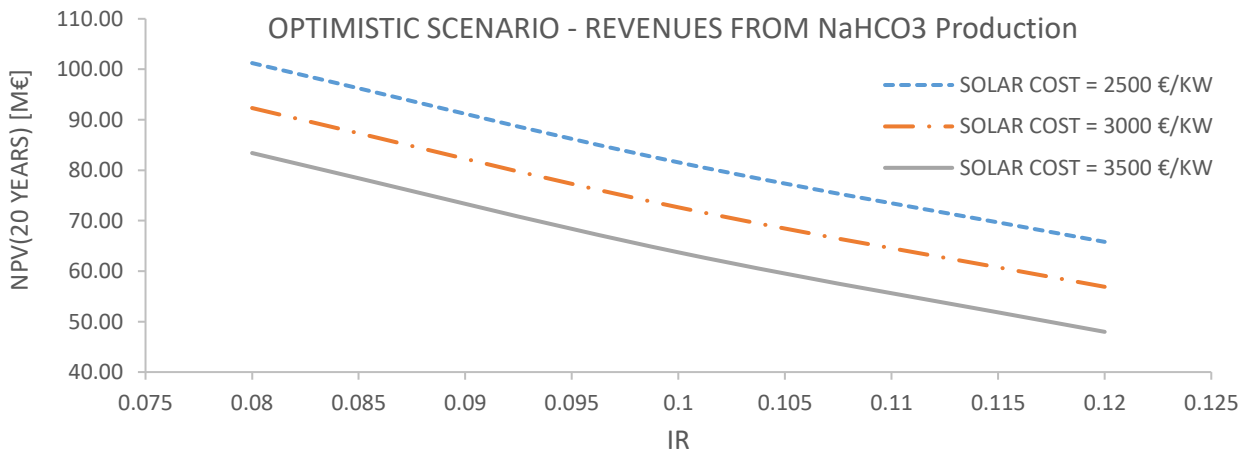
where  $k$  represents the year number,  $N$  is the total number of years, and  $IR$  is the discount rate. Assuming different values of the discount rate NPV value is calculated for the different scenarios and as function of the solar thermal technology cost. Figures 6, 7 and 8 show the NPV calculated curves as a function of the discount rate and for different solar thermal technology costs for a life plant of 20



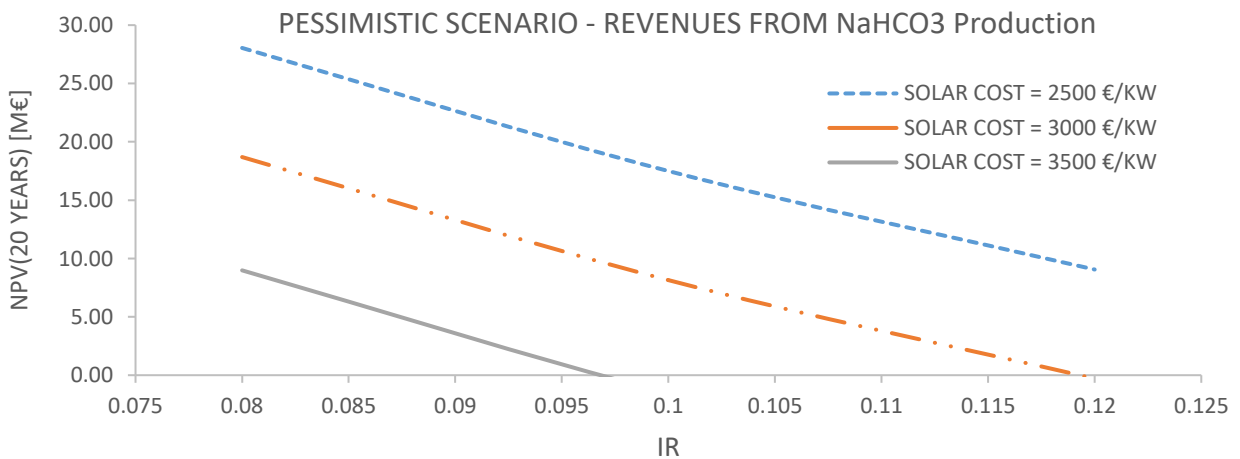
2 years. It can be seen how consistent revenues from the sale of  $\text{NaHCO}_3$  are obtained for realistic values of the discount rate ( $\text{IR}=0.08 - 0.12$ ) in all the Scenarios.



4  
6 Figure 6. Best Estimate Scenario: NPV in 20 years as function of internal rate value and solar thermal technology costs.

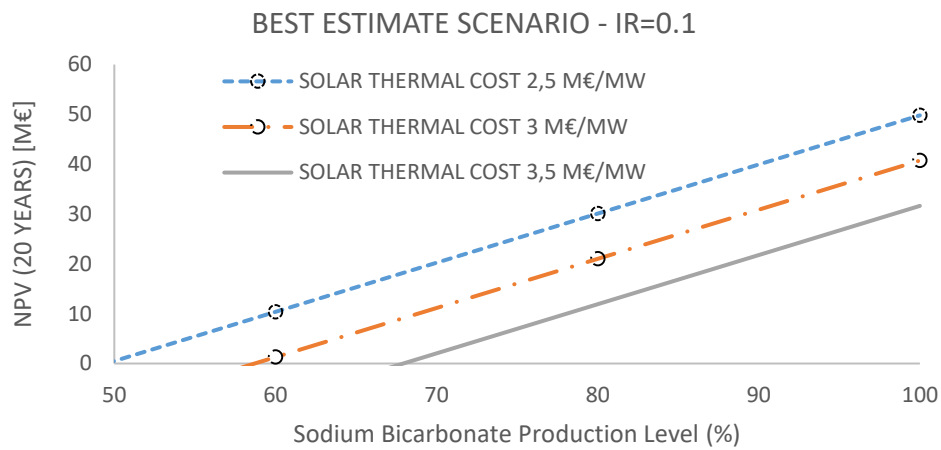


8  
10 Figure 7. Optimistic Scenario: NPV in 20 years as function of internal rate value and solar thermal technology costs.



12  
14 Figure 8. Pessimistic Scenario: NPV in 20 years as function of internal rate value and solar thermal technology costs.

The internal rate of return (IRR) is the discount rate at which NPV is equal to zero or, in other words, the rate at which an investment breaks even. It can be seen in Figures 6 and 7 that high values of internal rate of return ( $IRR > 0.12$ ) are obtained, while for the pessimistic scenario the value of  $IRR = 0.12$  is reached for a solar thermal cost of 3 M€/MW. Considering the life of the plant equal to 20 years the investment would be always of interest having current ordinary IR values of 0.08-0.1. Moreover, considering an IR of 0.1 higher values of NPV are obtained. Also considering a solar technology cost of 3.5 M€/MW<sub>th</sub>, it results a NPV value of 31.6 M€ with an investment cost of 67 M€ referred to the best estimate scenario. These values have been obtained assuming a constant production for sale of NaHCO<sub>3</sub>. Figure 9 shows NPV values as a function of the produced NaHCO<sub>3</sub> for the Best Estimate Scenario and using a fixed discount rate value ( $IR = 0.1$ ).



12

14 Figure 9. NPV in 20 years as function of NaHCO<sub>3</sub> production and solar technology costs for a fixed discount rate  $IR = 0.1$ .

16 As shown in Figs. 8 a minimum production of sodium bicarbonate per month is needed to ensure the return of the investment cost ( $NPV = 0$ ). In the worst case, which comprises the maximum cost of solar thermal technology, at least 5080 ton/month (68%) of sodium bicarbonate must be produced to cover the investment with a discount rate of  $IR = 0.1$ . On the other extreme, for the best case (a minimum cost of solar thermal technology), a production of 3585 ton/month would be needed.

## 22 Carbon taxes

24 The previous analysis does not include any benefit in terms of taxes due to avoided CO<sub>2</sub> emissions. However, this technology would dramatically reduce emissions of the plant, which would result in additional cost savings that would increase the interest of the investment. Table 13 summarizes the data used for calculating the costs according to the different scenarios for a total amount of 108.9 kton/year avoided CO<sub>2</sub> emissions using the dry carbonation system.

28

Table 13: CO<sub>2</sub> emission data for different scenarios.

	REFERENCE PLANT	DRY CARBONATE (P)	DRY CARBONATE (BE)	DRY CARBONATE (O)
Power (MWel)	15	15	15	15
CCS Power consumption (MWel)		2.5	1.6	1.5
Regenerator Heat requirement (MWth)		11.9	11.4	11.1
Net power (MWel)	15	12.5	13.35	13.5
CO <sub>2</sub> Emissions (tons/hr)	13.5	1.07	1.07	1.07
CO <sub>2</sub> Emissions (kmol/hr)	308	24.32	24.32	24.32
CO <sub>2</sub> Avoided Emissions (kton/year)		108.9	108.9	108.9
CO <sub>2</sub> Emissions (tons/ MWhel)	0.9	0.085	0.08	0.079

2 The carbon tax is assumed as constant during the next years in the worst scenario (Scenario P) while  
 4 is supposed that will increase in the future years for the optimistic scenario (Scenario O). Average  
 6 values of carbon tax are taken into account for the analysis. The gain from avoided CO<sub>2</sub> emission is  
 8 given by:

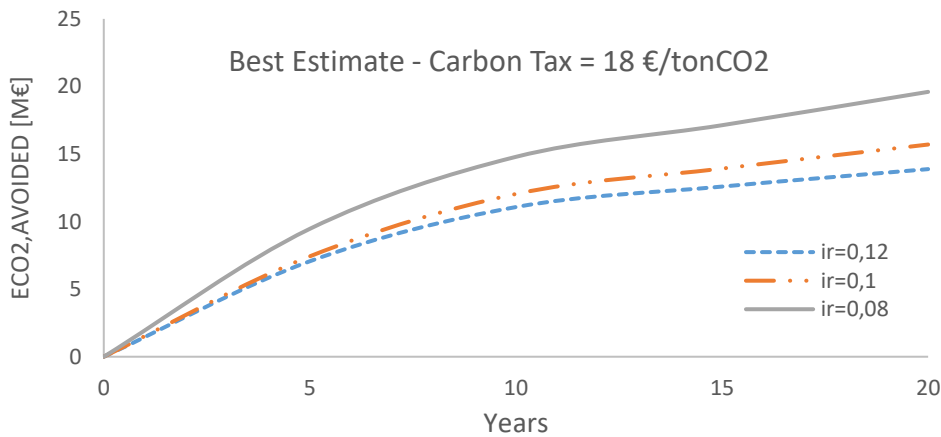
$$E_{CO_2,AVOIDED} = (ton_{CO_2,ref} - ton_{CO_2,CCS}) \cdot c_{CO_2} \quad (21)$$

10 Where  $c_{CO_2}$  is the carbon tax expressed in €/ton<sub>CO<sub>2</sub></sub>. The economic benefits derived from CO<sub>2</sub> avoided  
 12 emissions under the different carbon tax scenarios are shown in Table 14.

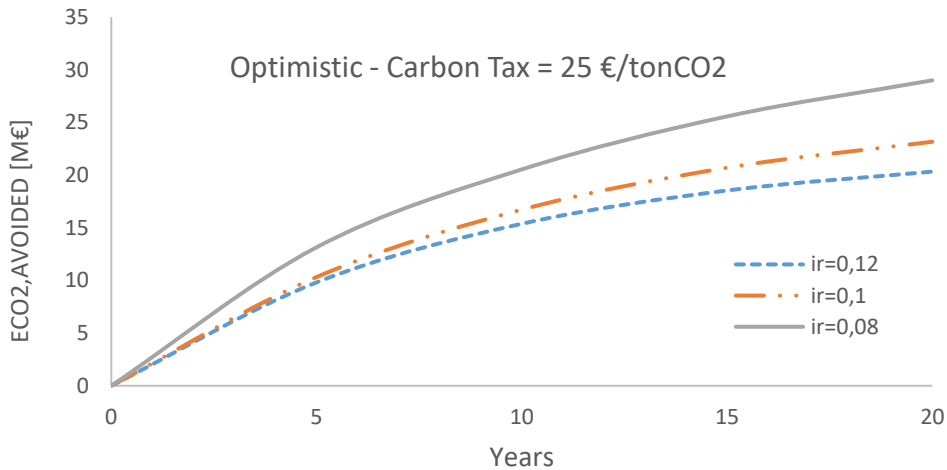
12 Table 14: Revenues due to CO<sub>2</sub> emission reduction for different scenarios (20 years).

	SCENARIO P	SCENARIO BE	SCENARIO O
Carbon Tax	10 €/ton <sub>CO<sub>2</sub></sub>	18 €/ton <sub>CO<sub>2</sub></sub>	25 €/ton <sub>CO<sub>2</sub></sub>
Yearly Economic Gain	1.09 M€/year	1.96 M€/year	2.72 M€/year
IR =0.08	10.89 M€	19.60 M€	29.00 M€
IR =0.1	8.72 M€	15.70 M€	23.18 M€
IR =0.12	7.71 M€	13.88 M€	20.33 M€

14 Figures 10, 11 and 12 show the economic impact due to CO<sub>2</sub> avoided emission for different scenarios  
 16 and different values of IR.



18 Figure 10. Best Estimated Scenario: Economic Gain due to CO<sub>2</sub> avoided emissions.



20 Figure 11. Optimistic Scenario: Economic Gain due to CO<sub>2</sub> avoided emissions.

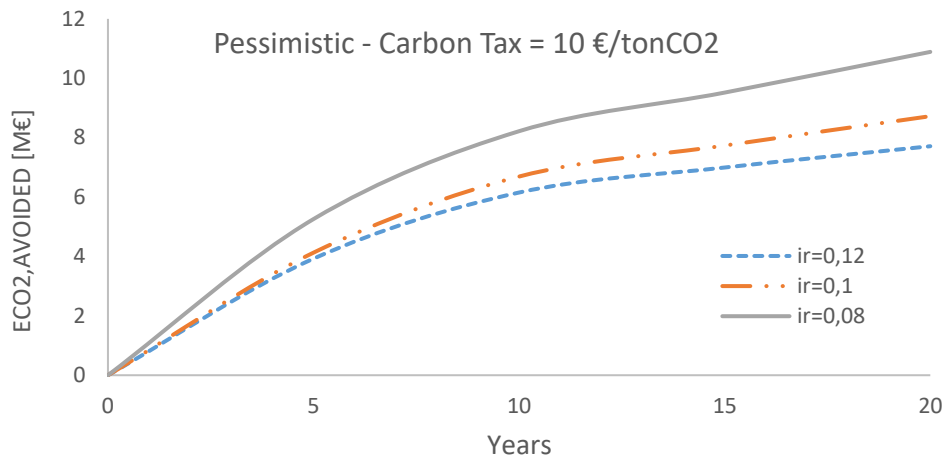


Figure 12. Pessimistic Scenario: Economic Gain due to CO<sub>2</sub> avoided emissions.

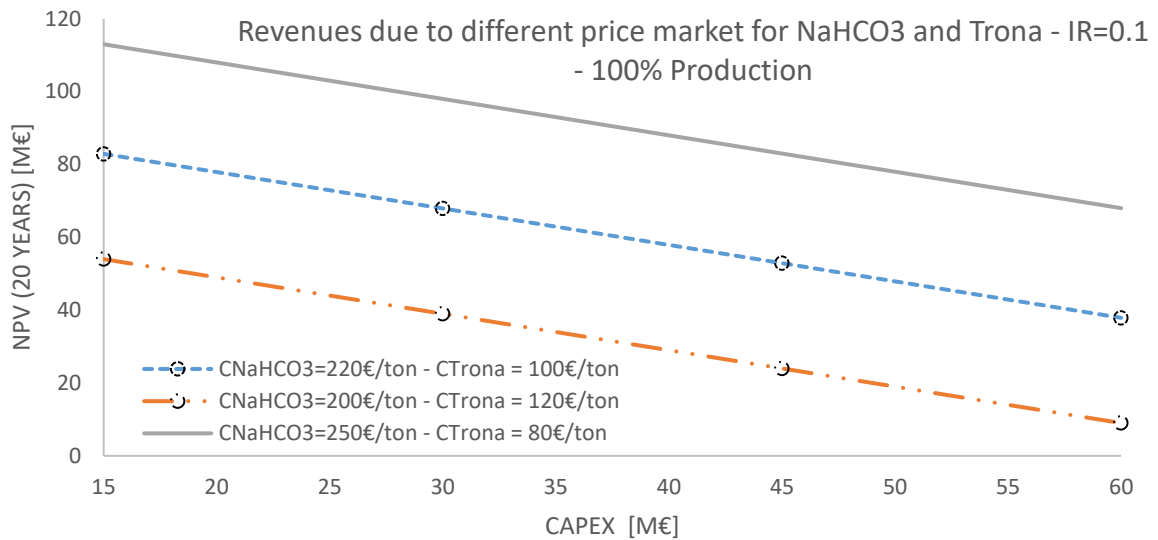
Under carbon taxes scenarios the NPV of the CCU investment can be recalculated adding cost savings due to carbon taxes. Results, considering a production level of 7470 ton/month, are shown in Table 15, where only in the worst case (Pessimistic Scenario, maximum cost of solar thermal technology and IR=0.12) NPV negative values are obtained. Considering the Best Estimate Scenario, with a mean cost of solar technology (3M€/MW), and IR 0.1, the NPV goes up to 56.4 M€ in 20 years.

Table 15: NPV(20 years) values including savings from CO<sub>2</sub> emission reduction.

IR	SOLAR COST(M€/MW)	SCENARIO P	SCENARIO BE	SCENARIO O
0,08	2.5	38.93	84.51	130.24
	3	29.58	75.44	121.33
	3.5	19.87	66.34	112.41
0,1	2.5	26.22	65.50	104.73
	3	16.87	56.43	95.82
	3.5	7.6	47.33	86.90
0,12	2.5	16.77	51.58	86.14
	3	7.42	42.51	77.23
	3.5	-2.29	33.41	68.31

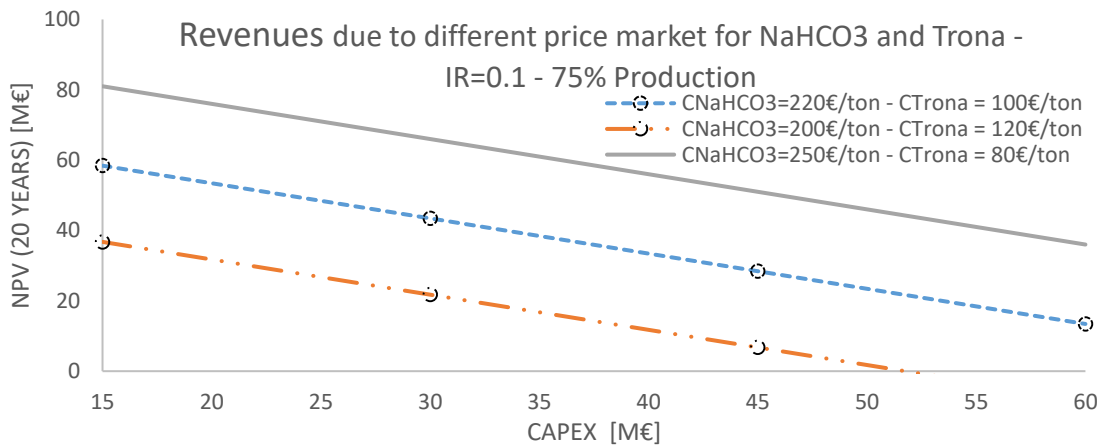
### Sodium bicarbonate prices

In figures 13 to 15 NPV data are plotted for different investment costs as a function of the sale price of NaHCO<sub>3</sub> and trona in the market and taking into account a variable production (from 50% to 100%). A fixed IR=0.1 is considered in these analyses.



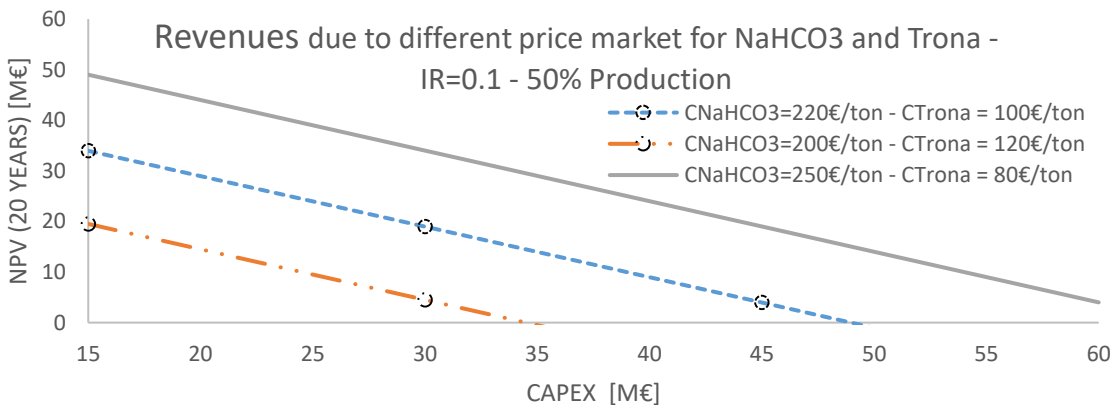
2 Figure 13. NPV in 20 years as function of investment costs and NaHCO<sub>3</sub> price with 100% of NaHCO<sub>3</sub> total production.

4



6 Figure 14. NPV in 20 years as function of investment costs and NaHCO<sub>3</sub> price with 75% of NaHCO<sub>3</sub> total production.

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10 Figure 15. NPV in 20 years as function of investment costs and NaHCO<sub>3</sub> price with 50% of NaHCO<sub>3</sub> total production.

12

14 Figures 13 to 15, give a map of CCU investment profitability as function of sodium bicarbonate price and demand (linked to production). In this sense, production capacity depends on solar energy input. For periods without solar resource availability thermal storage can be used to assure CO<sub>2</sub> capture and

sodium bicarbonate production. The use of biomass would maintain the near zero emissions condition and could support capture when the stored thermal energy is not able to deal with it. Another important factor to consider is how NaHCO<sub>3</sub> demand could vary on the market. For example, if the demand raises constantly, production could be maintained at the maximum capacity but it must be kept in mind that a massive introduction of the concept proposed in this paper necessarily would affect to the sodium bicarbonate production price by reducing it. In any case this is not pretended to be a global solution but one for locations with trona availability. From an economic perspective, the market is expected to grow at 4% per year in the next few years and will reach 4.2 million tonnes by 2018 driven mainly by the Asia region and China in particular. The European market is expected to grow a 2% per year [49]. A plant of 15 MW<sub>el</sub> could produce about 40 kton of NaHCO<sub>3</sub>. Thus, such production would have a relatively low impact at the global scale although the local sale impact could be significant. Independently of sodium bicarbonate sale, the CC system results in a permanent CO<sub>2</sub> fixing in the sodium bicarbonate and its integration with renewables (solar, biomass) drives to a near CO<sub>2</sub> emissions technology. In addition, CO<sub>2</sub> avoided emission reduction has an economic return where carbon taxes are applied.

## Conclusions

In this work a novel Carbon Capture and Utilization concept is presented based on the integration of a CO<sub>2</sub> post-combustion system using the dry carbonate process assisted by renewables for sodium bicarbonate production. Results suggest a potentially high interest of the integration. Main aspects of the concept are:

- Sodium bicarbonate is produced for sale and for make-up in the dry carbonate CO<sub>2</sub> capture process.
- An abundant, non-toxic and cheap raw material (trona) is used.
- When coupled with renewables for heating, biomass or medium temperature solar thermal, technology to regenerate the sorbent and calcination of trona, the global system results in a near to zero CO<sub>2</sub> emissions technology with a reduced penalty in power generation.
- NaHCO<sub>3</sub> production could allow permanent CO<sub>2</sub> storage.
- As concept application it has been applied to the flue gases stream equivalent to a small coal power plant of 15 MW, or for a fraction of flue gases of a bigger coal power plant.
- Energy analysis show a minor penalty in power consumption (<3%).
- According to the economic analysis with different Scenarios the Simple Pay Back time (SPB) for the integrated solution has very short periods (8.7 years in the worst case and 3 years in the best case) remarking the interest of the concept.
- The preliminary study shows an interesting potential for advancing in this technology in further studies (kinetics, sorbent deactivation, optimization of integration, equipment design, byproducts usage, etc...).
- When heat supply is based on solar, the proposed technology requires heat storage or support from other sources as biomass to work continuously. Various storage technologies (phase change liquid, thermal oils, molten salt) are already present on the market and a thorough study on the relative volumes of accumulation and on the exploitation of renewable sources is required to define in the best way the effective feasibility of this system.

## Nomenclature

2

### Components

CARBONATING TOWER	CO <sub>2</sub> capture and NaHCO <sub>3</sub> production reactor
CARBONATOR	CO <sub>2</sub> capture reactor
COAL FIRED PLANT	Coal fired plant for electricity production
COMP1	Compressor CO <sub>2</sub> (1-10 bar)
COMP2	Compressor CO <sub>2</sub> (10-25 bar)
COMP3	Compressor CO <sub>2</sub> (25-75 bar)
COOL	CO <sub>2</sub> (20°C) intercooler
FLUIDIZED BED	Fluidized bed reactor
HEATEX1	H <sub>2</sub> O-flue gas heat exchanger
HEATEXCH	NaHCO <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub>
HEATEXT	Trona - Na <sub>2</sub> CO <sub>3</sub> heat exchanger
HEATEXW	H <sub>2</sub> O - steam+CO <sub>2</sub> heat exchanger
INTERC1	CO <sub>2</sub> (20°C) intercooler
INTERC2	CO <sub>2</sub> (20°C) intercooler
INTERC3	CO <sub>2</sub> (20°C) intercooler
REGENARATOR	Sorbent regenerator
SEPA1	Solid-gas separator
SEPA2	Solid-gas separator

### Streams

CARBOUT	Final product from carbonator
CO2	CO <sub>2</sub> recovered from the system
CO2 IN	CO <sub>2</sub> entering the system
CO2 TO STORAGE	CO <sub>2</sub> to the storage system (20 °C, 75 bar)
CO2+STEAM	CO <sub>2</sub> and steam (220°C)
CO2+WATER	CO <sub>2</sub> and water( 95 °C)
CRUSHED TRONA	Crushed Trona
FGPLANT	Flue gas exits the coal fired plant
FLUE	Flue gas exits the carbonator
FLUID OUT	Chemical products exits the fluidized bed reactor
HOT STEAM	Super heated steam (205°C)
HOT TRONA	Hot Trona (125°C) entering the fluidized bed reactor
MAKE UP	Sorbent Make up
NA2CO3 COLD (Fig.5)	Regenerated Na <sub>2</sub> CO <sub>3</sub> (80°C)
NA2CO3 COLD (Fig.6)	Cooled Na <sub>2</sub> CO <sub>3</sub> (40 °C)
NA2CO3 HOT (Fig.5)	Regenerated Na <sub>2</sub> CO <sub>3</sub> (200°C)
NA2CO3 HOT (Fig.6)	Hot Na <sub>2</sub> CO <sub>3</sub> (220°C)
NA2CO3 IN	Chemical products enteing the NaHCO <sub>3</sub> production reactor
NAHCO3	NaHCO <sub>3</sub> produced by the system

NAHCO <sub>3</sub> COLD	Solids exits the carbonator ( 60°C)
NAHCO <sub>3</sub> HOT	Solids entering the regenerator(140°C)
WATER IN (Fig.5)	Water CO <sub>2</sub> capture reactor
WATER IN (Fig.6)	Cold water (35 °C)
WATER OUT	Process water

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## 2 **Figures Captions**

4 Figure 1. Flow diagram of the research triangle institute (RTI) dry carbonate process for  
6 CO<sub>2</sub> capture coupled to NaHCO<sub>3</sub> production using raw trona and assisted by medium  
temperature solar thermal power.

8 Figure 2. Sankey diagram of CO<sub>2</sub> patterns in the overall process

10 Figure 3. Integration of the RTI dry carbonate process into a CFPP for CO<sub>2</sub> capture [44].

12 Figure 4. Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> production from trona assisted by solar energy.

14 Figure 5. SPB as a function of solar thermal technology costs for the different scenarios  
analyzed.

16 Figure 6. Best Estimate Scenario: NPV in 20 years as function of internal rate value and  
18 solar thermal technology costs.

20 Figure 7. Optimistic Scenario: NPV in 20 years as function of internal rate value and solar  
thermal technology costs.

22 Figure 8. Pessimistic Scenario: NPV in 20 years as function of internal rate value and solar  
24 thermal technology costs.

26 Figure 9. NPV in 20 years as function of NaHCO<sub>3</sub> production and solar technology costs  
for a fixed discount rate IR=0.1.

28 Figure 10. Best Estimated Scenario: Economic Gain due to CO<sub>2</sub> avoided emissions.

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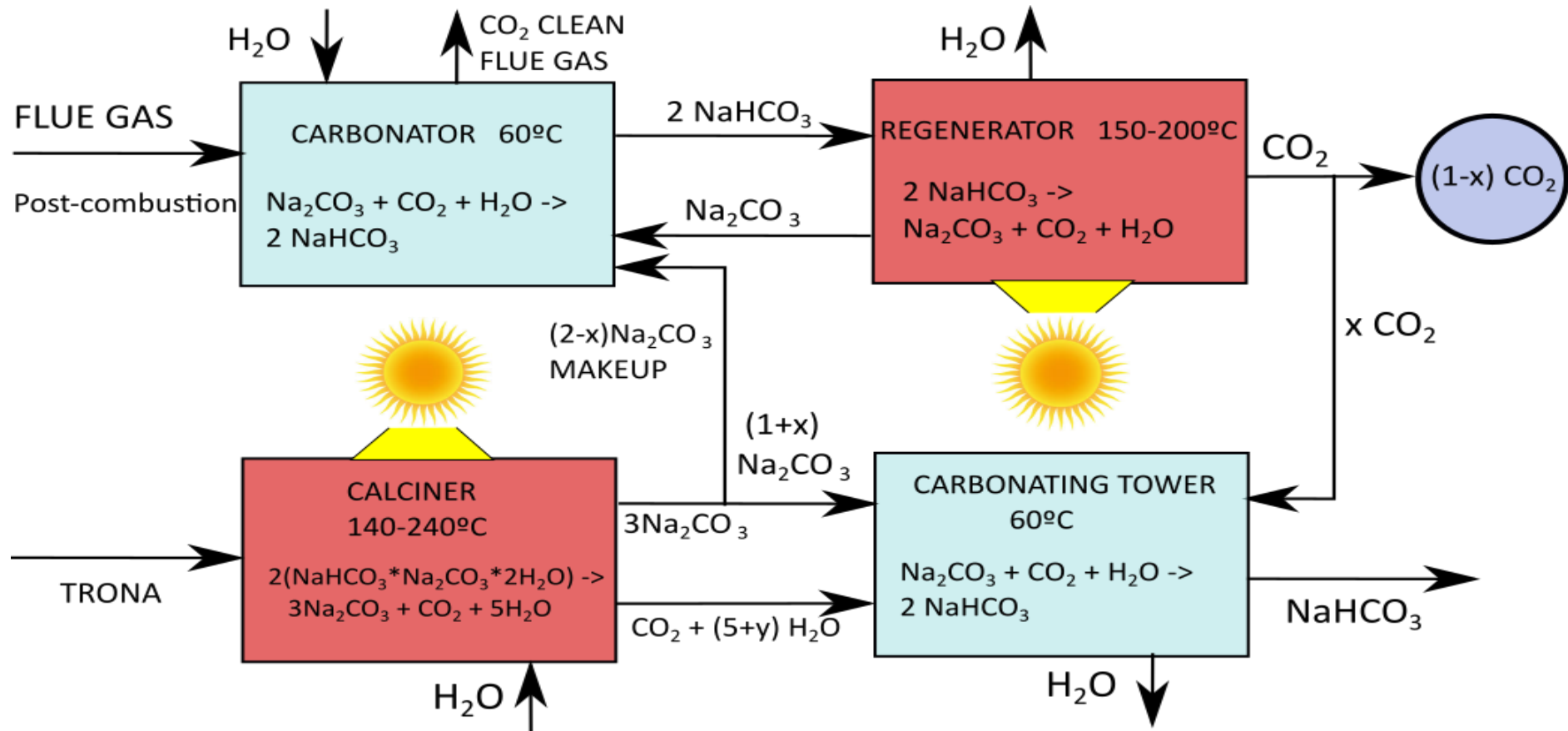
## Tables Captions

- 2 Table 1. Natural trona composition [20].
- 4 Table 2. Best fitting parameters used in the model for the equilibrium constant  $K_s$  (Eq. 15)  
6 of the reactions involved in  $\text{NaHCO}_3$  production from raw trona.
- 8 Table 3: Power consumption for the reference CFPP [42,43]
- 10 Table 4: Flue gas flow composition from the reference CFPP [42,43].
- 12 Table 5. Power consumption for a 15  $\text{MW}_{el}$  CFPP with integrated RTI dry carbonate process  
14 for  $\text{CO}_2$  capture.
- 16 Table 6. Heat exchanged in  $\text{NaHCO}_3$  production according to Fig. 3.
- 18 Table 7. Flow rates of streams entering and exiting the fluidized bed reactor in the  $\text{NaHCO}_3$   
20 production according to Fig. 3.
- 22 Table 8. Heat requirement in different components for the production of  $\text{NaHCO}_3$ .
- 24 Table 9. Compression power for  $\text{NaHCO}_3$  production.
- 26 Table 10. Different prices for different scenarios.
- 28 Table 11: Total investment cost:  $\text{NaHCO}_3$  production + Solar Thermal.
- 30 Table 12: Total Investment costs and yearly revenue for scenarios of analysis.
- 32 Table 13:  $\text{CO}_2$  emission data for different scenarios.
- 34 Table 14: Revenues due to  $\text{CO}_2$  emission reduction for different scenarios (20 years).
- 36 Table 15: NPV(20 years) values including savings from  $\text{CO}_2$  emission reduction.

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# Figures

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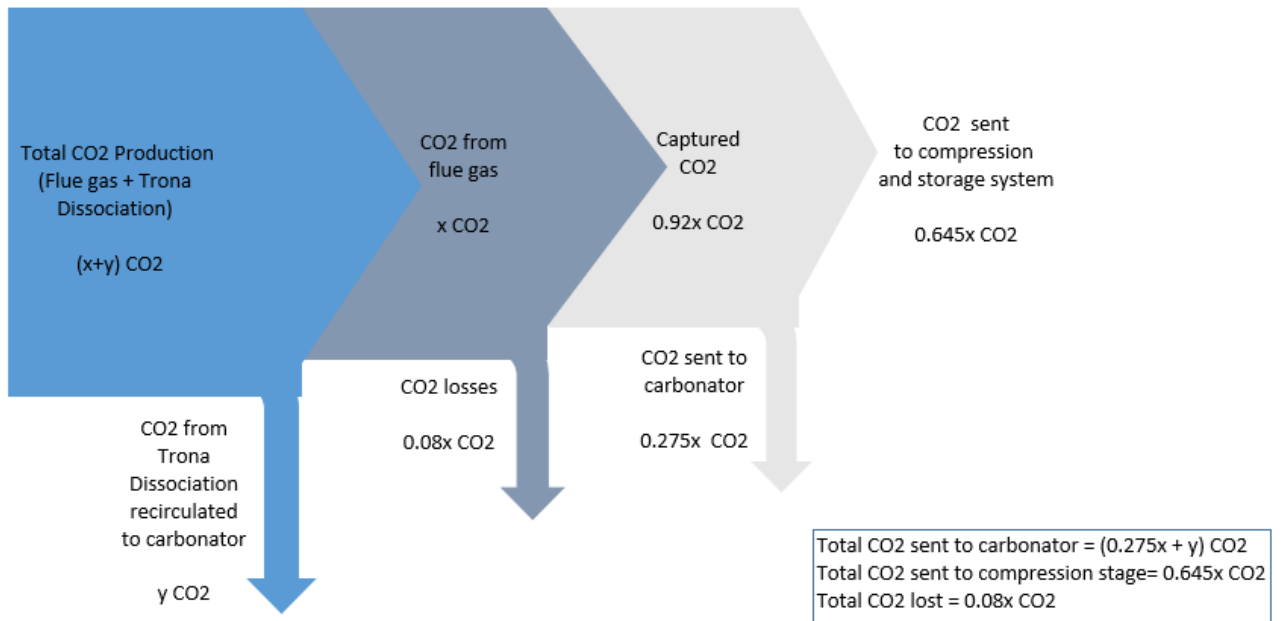
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Figure 2. Sankey diagram of CO<sub>2</sub> routes in the overall process

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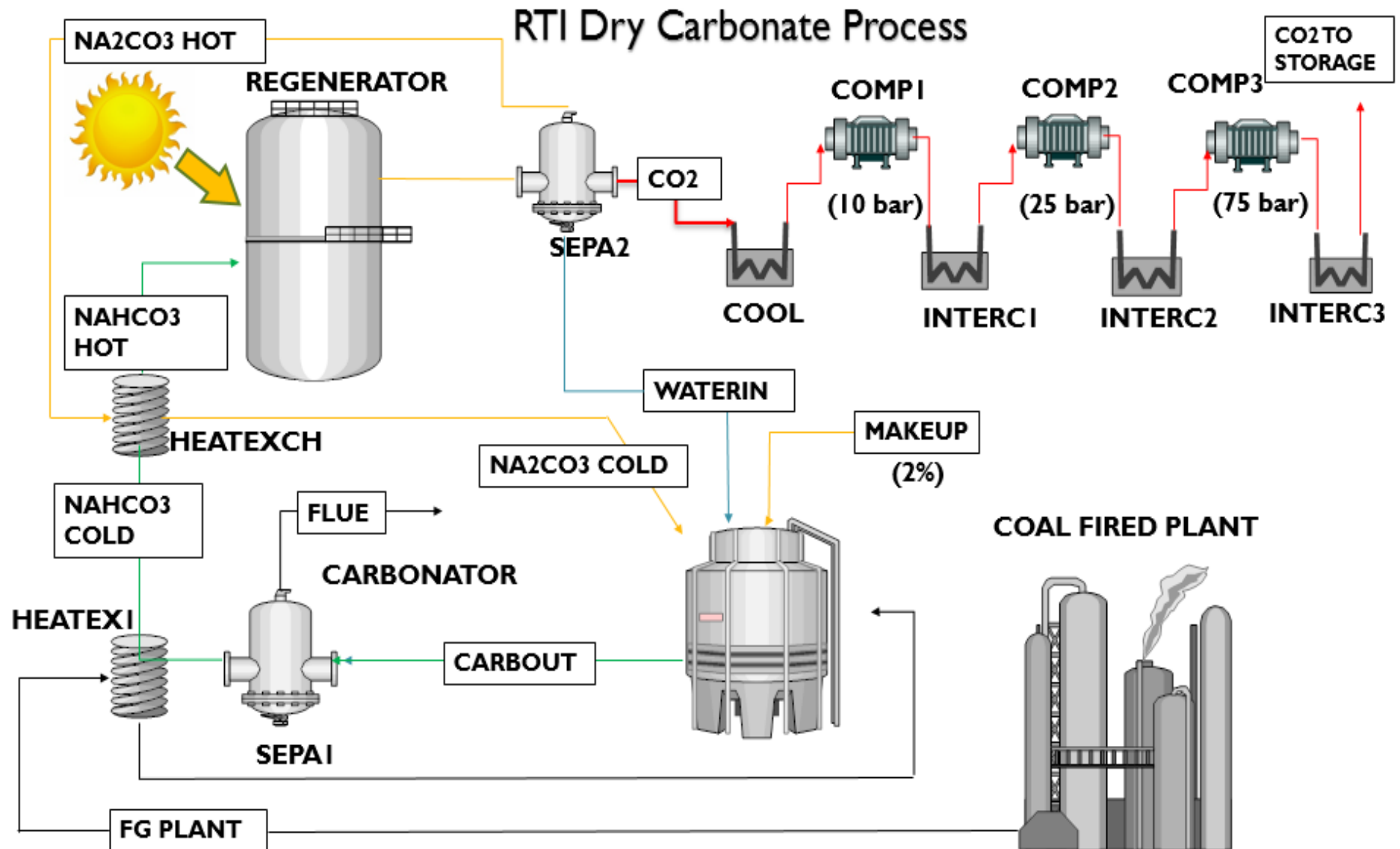
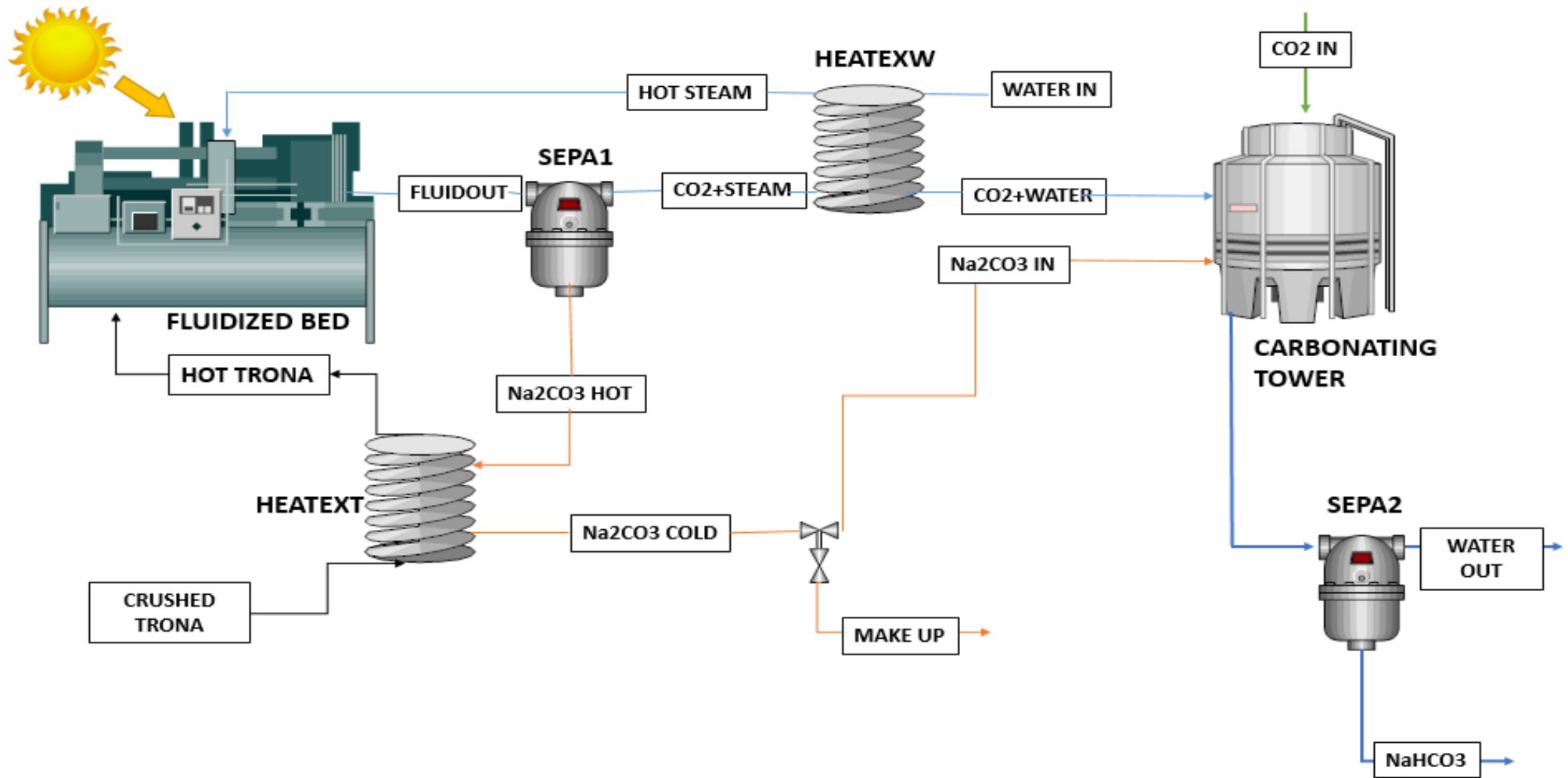


Figure 3. Integration of the RTI dry carbonate process into a CFPP for CO<sub>2</sub> capture [44].

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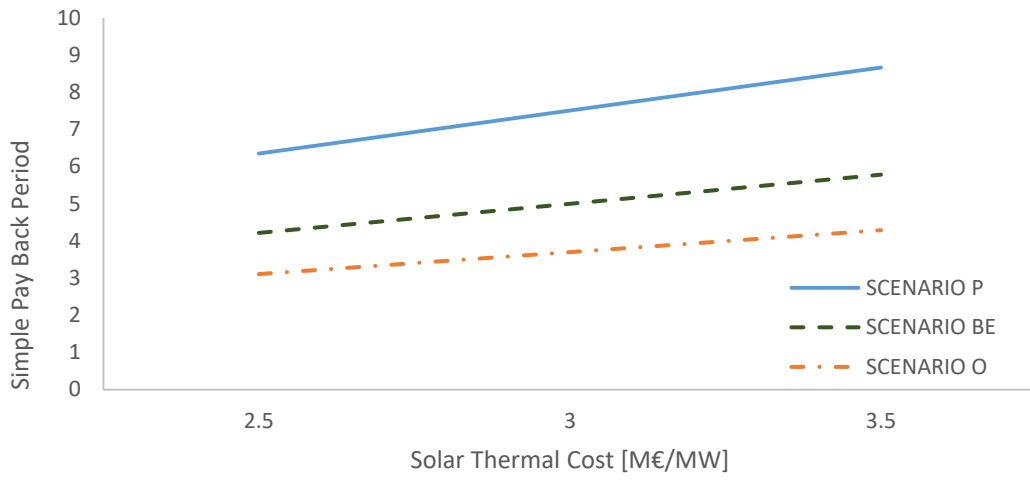
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Figure 4.  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  production from trona assisted by solar energy.

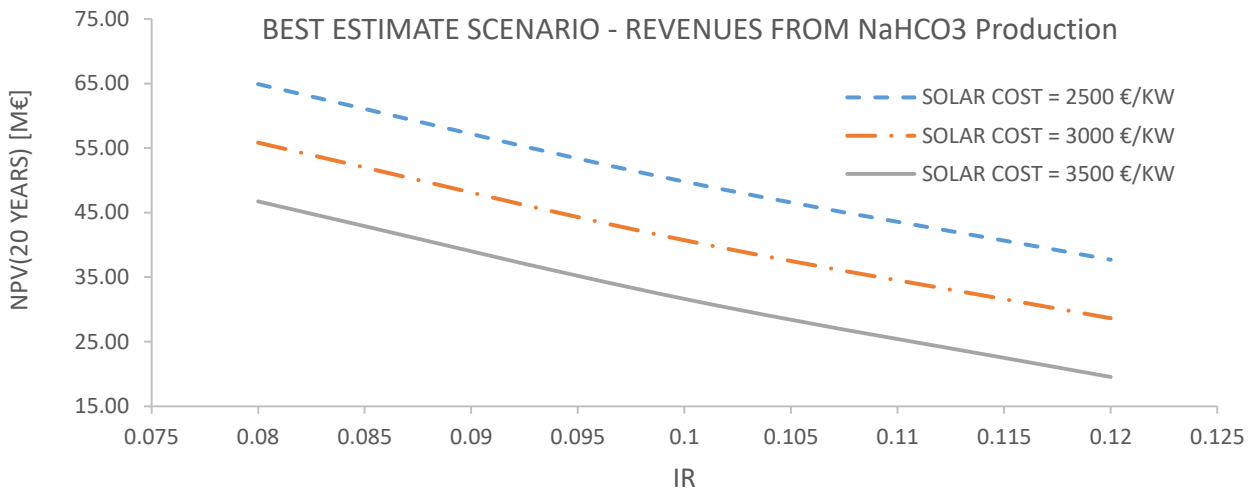
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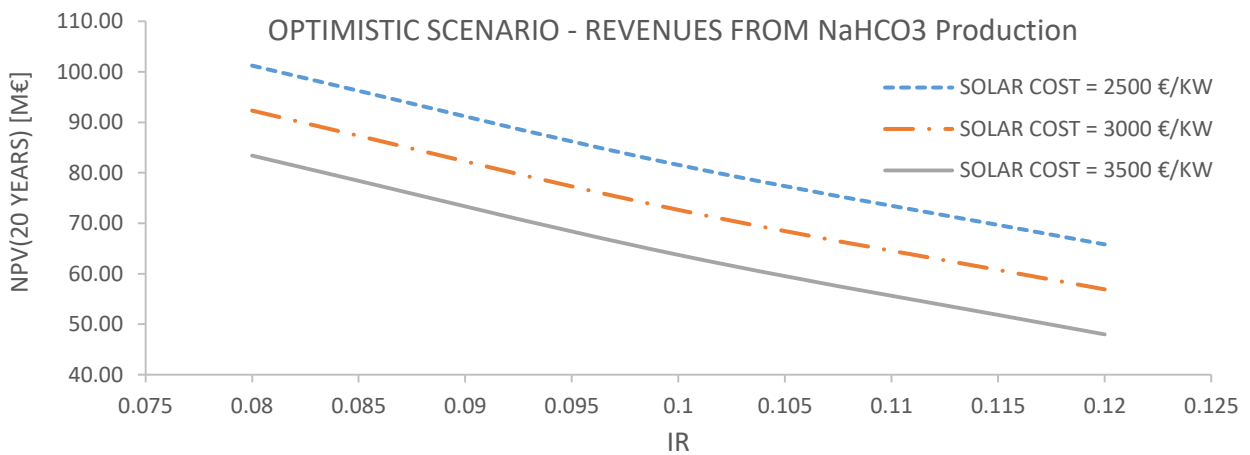
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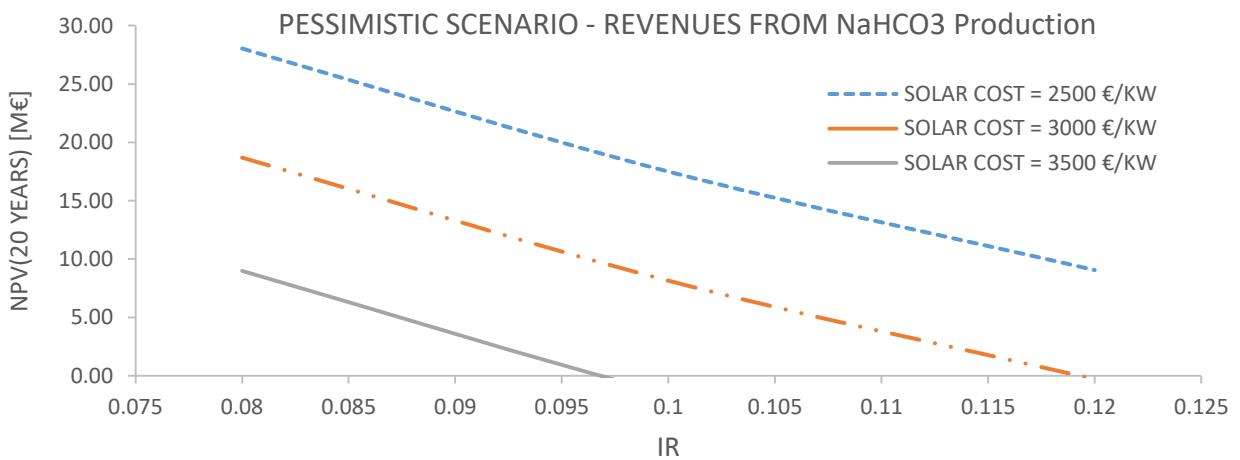
4 Figure 5. SPB as a function of solar thermal technology costs for the different scenarios analyzed.



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Figure 6. Best Estimate Scenario: NPV in 20 years as function of internal rate value and solar thermal technology costs.



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Figure 7. Optimistic Scenario: NPV in 20 years as function of internal rate value and solar thermal technology costs.



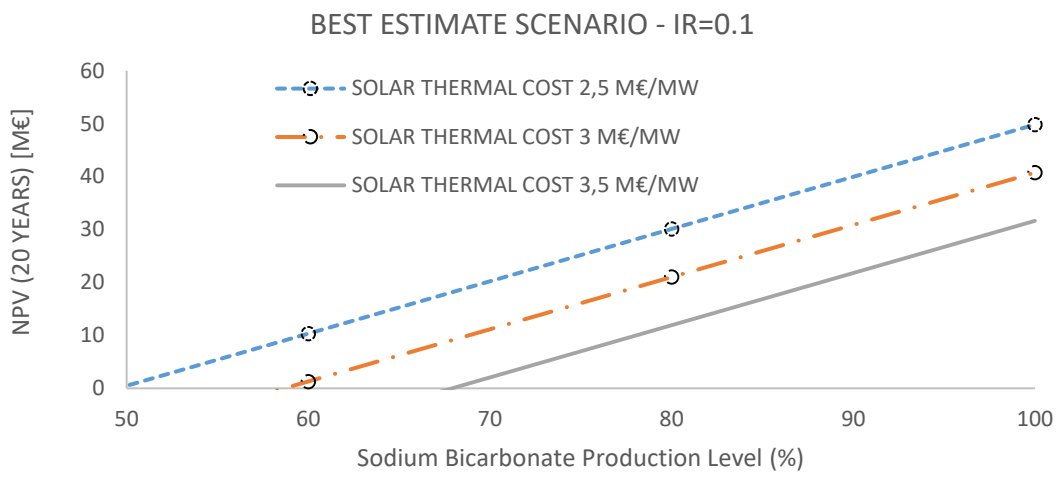
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Figure 8. Pessimistic Scenario: NPV in 20 years as function of internal rate value and solar thermal technology costs.

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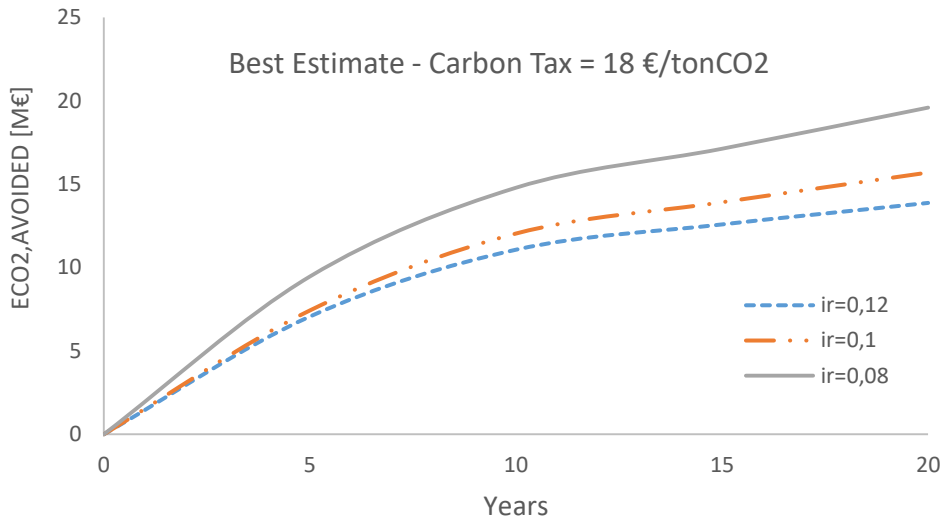


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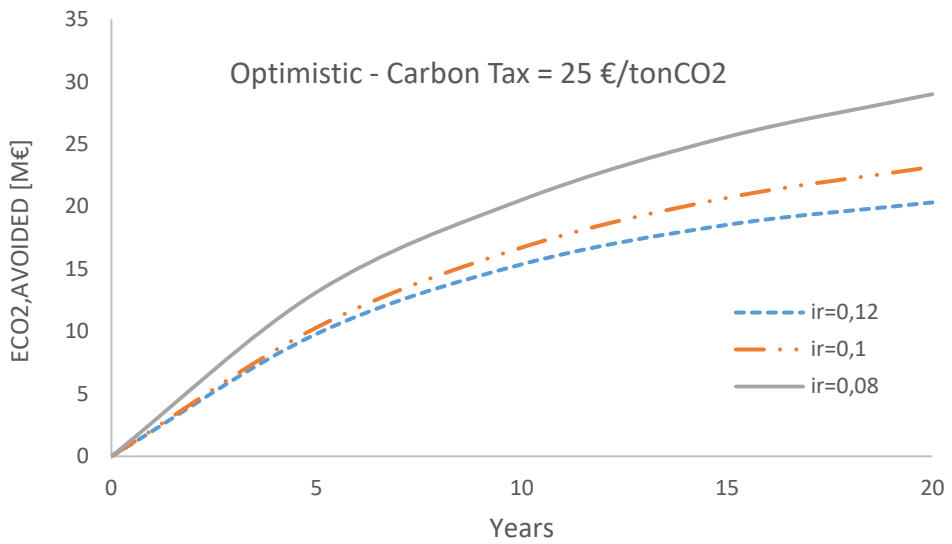
Figure 9. NPV in 20 years as function of  $\text{NaHCO}_3$  production and solar technology costs for a fixed discount rate  $IR=0.1$ .

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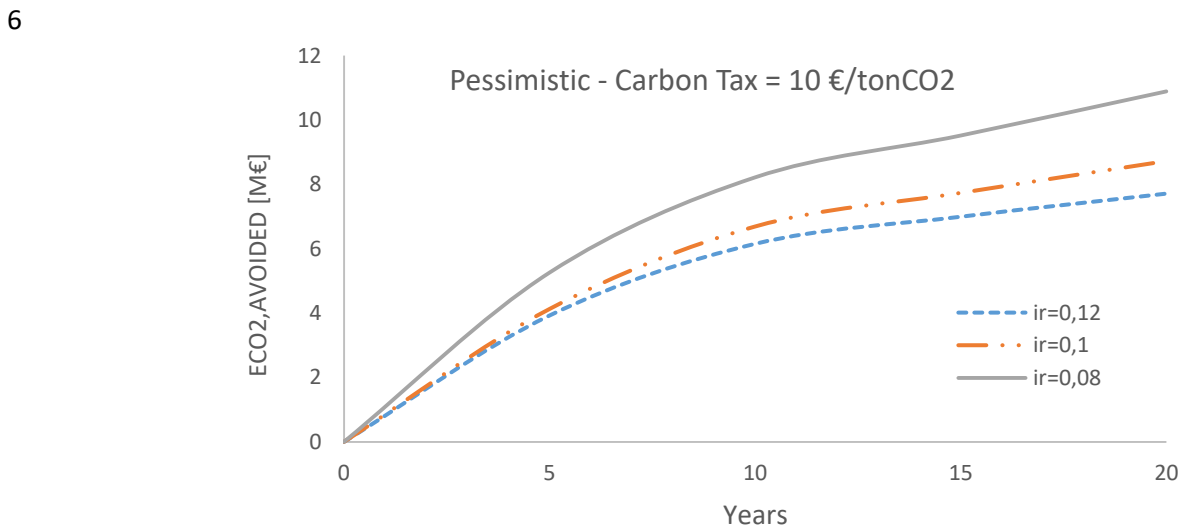
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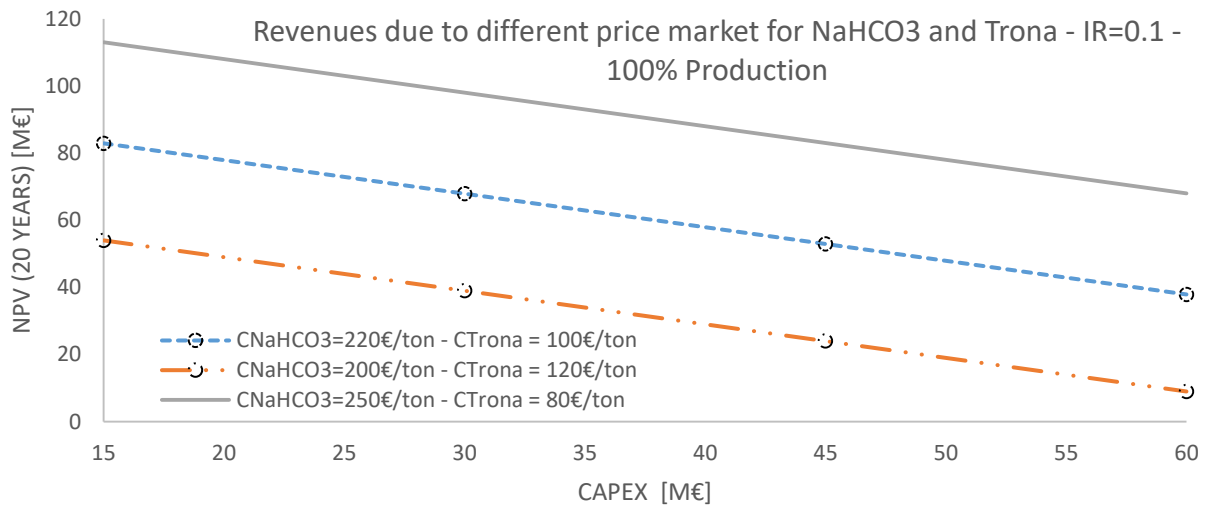
2 Figure 10. Best Estimated Scenario: Economic Gain due to CO<sub>2</sub> avoided emissions.



4 Figure 11. Optimistic Scenario: Economic Gain due to CO<sub>2</sub> avoided emissions.

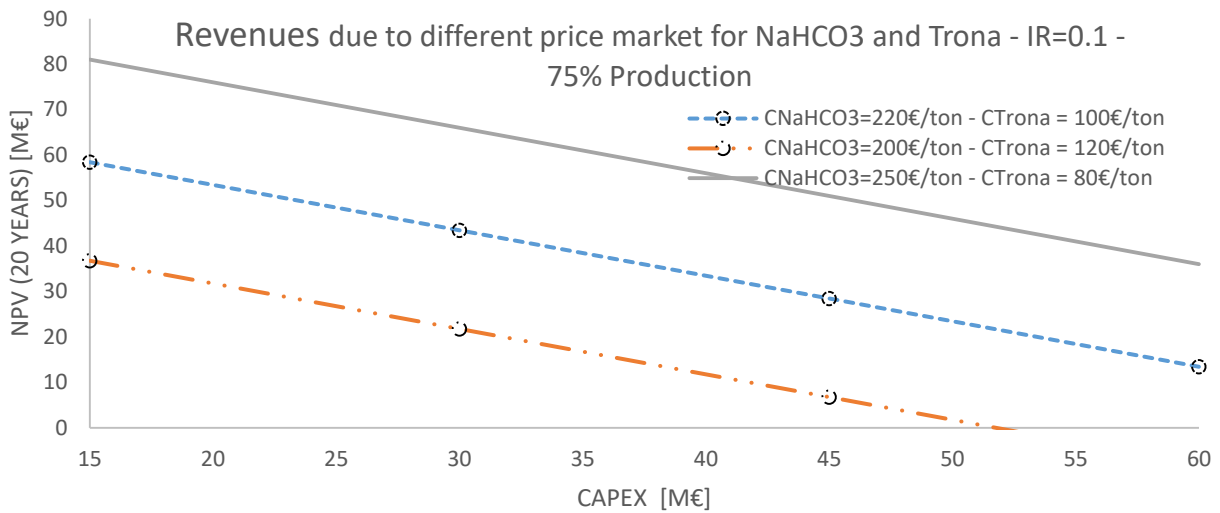


6 Figure 12. Pessimistic Scenario: Economic Gain due to CO<sub>2</sub> avoided emissions.



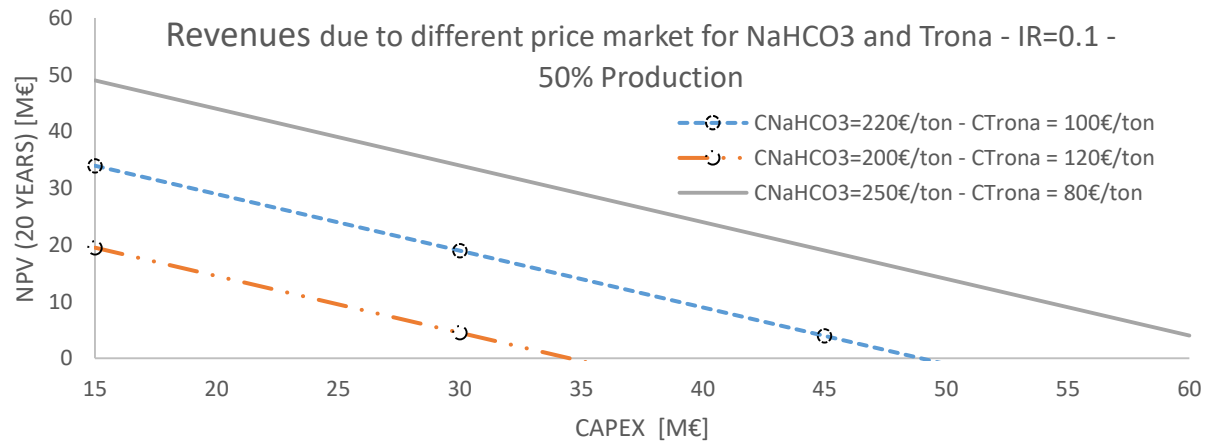
2 Figure 13. NPV in 20 years as function of investment costs and NaHCO<sub>3</sub> price with 100% of NaHCO<sub>3</sub> total production.

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6 Figure 14. NPV in 20 years as function of investment costs and NaHCO<sub>3</sub> price with 75% of NaHCO<sub>3</sub> total production.

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10 Figure 15. NPV in 20 years as function of investment costs and NaHCO<sub>3</sub> price with 50% of NaHCO<sub>3</sub> total production.

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## 2 Tables

Table 1. Natural trona composition [20].

Component	Wt%
Na <sub>2</sub> CO <sub>3</sub>	46,53
NaHCO <sub>3</sub>	34,82
Na <sub>2</sub> SO <sub>4</sub>	0,568
insolubles	2,98
hydration water	14,92
others	0,182

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6 Table 2. Best fitting parameters used in the model for the equilibrium constant  $K_s$  (Eq. 15) of the reactions involved in NaHCO<sub>3</sub> production from raw trona.

	A	B	C	D
REACTIONS				
$CO_2 + 2H_2O \rightleftharpoons H_3O^+ + HCO_3^-$	231.47	-12092.7	-36.78	0
$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{--}$	216.05	-1243.7	-35.48	0
$NaHCO_3 \rightleftharpoons Na^+ + HCO_3^-$	-63.26	-1308.41	13.48	-0.034
$Na_2CO_3 \rightleftharpoons 2Na^+ + CO_3^{--}$	-548.32	18070.74	94.75	-0.165
$Na_2CO_3 \cdot H_2O \rightleftharpoons 2Na^+ + CO_3^{--} + H_2O$	281.77	-9970.6	-44.56	0.0221
$Na_2CO_3 \cdot 7H_2O \rightleftharpoons 2Na^+ + CO_3^{--} + 7H_2O$	484.91	-18935	-80.12	0.114
$Na_2CO_3 \cdot 10H_2O \rightleftharpoons 2Na^+ + CO_3^{--} + 10 H_2O$	1165.01	-37.81	-200.08	0.335
$2(Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O) \rightleftharpoons 3Na^+ + CO_3^{--} + HCO_3^- + 2H_2O$	277.24	-14523.8	-41.0	0.0085
$Na_2CO_3 \cdot 3NaHCO_3 \rightleftharpoons 5Na^+ + CO_3^{--} + 3HCO_3^-$	-1209.46	29113.05	213.72	-0.363

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Table 3: Power consumption for the reference CFPP [42,43]

Item	Magnitude	Unit
Coal consumption	6.1	t/h
Air in	69.2	t/h
Gross power introduced	44.7	MW <sub>th</sub>
Net power introduced	39.7	MW <sub>th</sub>
Net Power Produced	15	MW <sub>el</sub>
Net efficiency	33.5	%

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Table 4: Flue gas flow composition from the reference CFPP [42,43].

Coal flue gas component	Mole Flow(kmol/h)	Mass Flow(t/h)
N <sub>2</sub>	1715.42	52.97
CO <sub>2</sub>	308.56	13.60
H <sub>2</sub> O	147.19	2.94
O <sub>2</sub>	78.18	2.76
CO	14.07	0.39
NO	13.54	0.45
SO <sub>2</sub>	3.75	0.26

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Table 5. Power consumption for a 15 MW<sub>el</sub> CFPP with integrated RTI dry carbonate process for CO<sub>2</sub> capture.

	Power production	Power consumption
CFPP	15 MW <sub>el</sub>	44.7 MW <sub>th</sub>
Regenerator		11.4 MW <sub>th</sub>
COMP		1.33 MW <sub>el</sub>
Wsolid		0.25 MW <sub>el</sub>
Centrifugation		0.3 MW <sub>el</sub>
Net Power	13.12 MW <sub>el</sub>	
Total heat requirement		56.1 MW <sub>th</sub>

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Table 6. Heat exchanged in NaHCO<sub>3</sub> production according to Fig. 3.

	MW <sub>th</sub>	T <sub>incold</sub> (°C)	T <sub>outhot</sub> (°C)	T <sub>inhot</sub> (°C)	T <sub>outcold</sub> (°C)
HEATEXCT	1.15	20	95	219	205
HEATEXW	0.7	20	40	219	127
Total Thermal Power	1.85				

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Table 7. Flow rates of streams entering and exiting the fluidized bed reactor in the  $\text{NaHCO}_3$  production according to Fig. 3.

	Units	TRONA	WATIN	FLUIDOUT
TRONA	kmol/h	84.709	0	0
WATER	kmol/h	0.387	85	307.5
$\text{CO}_2$	kmol/h	0.002	0	42.5
WEGSC(S)	kmol/h	0.096	0	0
$\text{NaHCO}_3$	kmol/h	0.198	0	0
$\text{Na}_2\text{CO}_3$	kmol/h	0	0	127.5
Mole Flow	kmol/h	146.391	85	613.5
Temperature	$^\circ\text{C}$	127	204	219
Pressure	bar	1.01	1.01	1,01
Vapor Fraction		0	1	0.733
Solid Fraction		1	0	0.267
Mass Density	kg/cum	2029	0.454	1.209
Average Molecular Weight		224	18.015	43.81

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Table 8. Heat requirement in different components for the production of  $\text{NaHCO}_3$ .

	T ( $^\circ\text{C}$ )	Thermal Power consumption
CFFP	850	44.7 $\text{MW}_{\text{th}}$
Regenerator	200	11.4 $\text{MW}_{\text{th}}$
Fluidized bed reactor	220	5.1 $\text{MW}_{\text{el}}$
Total heat requirement		61.2 $\text{MW}_{\text{th}}$

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Table 9. Compression power for  $\text{NaHCO}_3$  production.

Component	$W_{\text{comp}}$ ( $\text{MW}_{\text{el}}$ )
Compressor 1 ( 4.2 bar )	0.295
Compressor 2 ( 17.5 bar )	0.289
Compressor 3 ( 75 bar )	0.295
Total $W_{\text{comp}}$ ( from 1 to 75 bar )	0.879

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Table 10. Different prices for different scenarios.

	Units	Scen. P	Scen. BE	Scen. O
$p_{trona}$	€/ton	120	100	80
$p_{NaHCO_3}$	€/ton	200	220	240
$\Delta_{Gain}$	€/ton	80	120	160
$E_{GAIN}$	€/day	22000	32000	44000

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Table 11: Total investment cost: NaHCO<sub>3</sub> production + Solar Thermal.

Solar Thermal 2.5 M€/MW				
	Units	Scen. P	Scen. BE	Scen. O
ESOLAR (FLUID+DECARB)	M€	42.5	41.25	40.5
EDRY	M€	4	3	2
EFLUID	M€	1.9	1.5	1.15
EO&M	M€	4.84	4.58	4.37
ETOT	M€	51.34	48.83	46.87
	Units	Scen. P	Scen. BE	Scen. O
Solar Thermal 3 M€/MW				
ESOLAR (FLUID+DECARB)	M€	51	49.5	48.6
EDRY	M€	4	3	2
EFLUID	M€	1.9	1.5	1.15
EO&M	M€	5.69	5.4	5.18
ETOT	M€	60.69	57.9	55.78
Solar Thermal 3.5 M€/MW				
	Units	Scen. P	Scen. BE	Scen. O
ESOLAR (FLUID+DECARB)	M€	59.5	57.75	56.7
EDRY	M€	4	3	2
EFLUID	M€	1.9	1.5	1.15
EO&M	M€	6.54	6.23	5.98
ETOT	M€	70.04	66.98	64.68

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2 Table 12: Total Investment costs and yearly revenue for scenarios of analysis.

TOTAL INVESTMENT	SCENARIO P	SCENARIO BE	SCENARIO O
SOLAR THERMAL COST 2.5 M€/MW	51.34 M€	48.83 M€	46.87 M€
SOLAR THERMAL COST 3 M€/MW	60.69 M€	57.90 M€	55.78 M€
SOLAR THERMAL COST 3.5 M€/MW	70.04 M€	66.98 M€	64.69 M€
ANNUAL ECONOMIC PROFIT	8.08 M€	11.58 M€	15.08 M€

4 Table 13: CO<sub>2</sub> emission data for different scenarios.

	REFERENCE PLANT	DRY CARBONATE (P)	DRY CARBONATE (BE)	DRY CARBONATE (O)
Power (MWel)	15	15	15	15
CCS Power consumption (MWel)		2.5	1.6	1.5
Regenerator Heat requirement (MWth)		11.9	11.4	11.1
Net power (MWel)	15	12.5	13.35	13.5
CO <sub>2</sub> Emissions (tons/hr)	13.5	1.07	1.07	1.07
CO <sub>2</sub> Emissions (kmol/hr)	308	24.32	24.32	24.32
CO <sub>2</sub> Avoided Emissions (kton/year)		108.9	108.9	108.9
CO <sub>2</sub> Emissions (tons/ MWhel)	0.9	0.085	0.08	0.079

6 Table 14: Revenues due to CO<sub>2</sub> emission reduction for different scenarios (20 years).

	SCENARIO P	SCENARIO BE	SCENARIO O
Carbon Tax	10 €/ton <sub>CO2</sub>	18 €/ton <sub>CO2</sub>	25 €/ton <sub>CO2</sub>
Yearly Economic Gain	1.09 M€/year	1.96 M€/year	2.72 M€/year
IR =0.08	10.89 M€	19.60 M€	29.00 M€
IR =0.1	8.72 M€	15.70 M€	23.18 M€
IR =0.12	7.71 M€	13.88 M€	20.33 M€

8 Table 15: NPV(20 years) values including savings from CO<sub>2</sub> emission reduction.

IR	SOLAR COST(M€/MW)	SCENARIO P	SCENARIO BE	SCENARIO O
0,08	2.5	38.93	84.51	130.24
	3	29.58	75.44	121.33
	3.5	19.87	66.34	112.41
0,1	2.5	26.22	65.50	104.73
	3	16.87	56.43	95.82
	3.5	7.6	47.33	86.90
0,12	2.5	16.77	51.58	86.14
	3	7.42	42.51	77.23
	3.5	-2.29	33.41	68.31