This Project has received funding from European Commission by means of Horizon 2020,
the EU Framework Programme for Research and Innovation, under Grant Agreement no.727348

Grant Agreement No. 727348

Project Acronym:

SOCRATCES

Project title:

SOlar Calcium-looping integRAtion for Thermo-Chemical Energy Storage.

DELIVERABLE D2.4

Final carbonator model report

Funding scheme:	Research and Innovation Action (RIA)		
Project Coordinator:	USE		
Start date of the project:	01.01.2018	**Duration of the project:**	36 months
Contractual delivery date:	30.06.2019		
Actual delivery date:	01.06.2019		
Contributing WP:	WP2		
Dissemination level:	*Public*		
Authors:	CSIC		
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Version:	V2		
Document name	**SOCRATCES_Deliverable_D2.4**		

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EXECUTIVE SUMMARY

Deliverable name: Final carbonator model report

Work Package number/title: 2/carbonation

Author/contributors: CSIC/USE, UNIZAR, CERTH, AUTH

Contents of the deliverable

The deliverable has the following structure: the first section summarizes the work carried out within each WP task. Later on, the main decisions taken facing the prototype construction (WP6) are described, namely, selected materials and expected kinetics, final reactor design, Process Flow Diagram (PFD) of the carbonator side and potential heat integration between carbonator and Stirling. A briefly detailed overview of the deliverable follows:

- **List of Tables**

A list summarizing the five tables within this deliverable can be found in page 5.

- **List of Figures**

A list summarizing the twenty-two figures within this deliverable can be found in page 6.

- **Introduction**

The WP2 aims to make a depth assessment on carbonation reaction and to develop at lab-scale the carbonator (reactor), which subsequently will be constructed within the WP6. The main objectives of the carbonation WP are to make an in-depth assessment of the carbonation reaction, develop a carbonator reactor at lab-scale, implement experiments for the understanding of the carbonation reaction and its kinetics, all of which will subsequently provide useful data for the carbonator model development and eventually the construction of the prototype reactor in the WP6. In order to achieve the best carbonator operation conditions, analysis is carried out at lab-scale conditions and scaled up by means of mathematical modelling. The carbonator is simulated using computer-aided programs like MATLAB, CFD and EES.

- **Summary of the work carried out. Main results**

    - Task 2.1: Carbonation kinetics

A kinetic model has been proposed within the frame of this project and published in open source in reference (Ortiz et al., 2018). In this kinetic model, the reversibility of the reaction and the heterogeneous character of the process has been considered. Thus, a complete kinetic model, that takes into consideration the experimental conditions required for using this reaction in thermochemical storage application, has been proposed. This is a significant contribution, from both the scientific and technical point of view and relevant to the objectives of SOCRATCES. The model has been tested and applied to a number of experimental data with successful results.

    - Task 2.2 : Carbonator development

This section summarizes the work have been done by CERTH and UNIZAR in terms of mathematical model development for carbonator reactor, simulation activities and sensitivity analysis studies. During the models development, an extensive literature review in similar reaction systems and designs was conducted in order to comprehend the different chemical and physical phenomena taking place in this particular process. Thus, a review in carbonation kinetics was conducted and interpreted, while the modelling methodology of the carbonator reactor was developed. The main scope of the mathematical models development was by one side to understand carbonation reaction process, principles of physical and chemical transport phenomena taking place, and conditions under which reaction is favored. Then by the mechanistic model development, reactor's dimensions and geometry were determined based on preliminary simulation results as well as the operating conditions under which reaction performs a desirable CaO conversion. In this way, reactor's operating conditions and dimensions were initially defined, in terms of privileging thermodynamic efficiency, yield and reaction rate.

- Task 2.3 : Heat integration

The work carried out is complementary to the carbonator models proposed within the task 2.2 (section 1.2), in which complex fluid dynamics mechanisms were included. Likewise, carbonation kinetics results from task 2.1 are considered for the modelling. Thus, all the carbonator models proposed within the WP2, each one developed and oriented from a specific perspective compose a complete framework about the reaction behaviour and the implications facing the prototype construction.

The scope of the model developed is to provide a useful tool to evaluate the heat transfer from the highly exothermic carbonation, providing in this way worthy information for the carbonator design (WP2) as well as for the prototype design within the EPC task (WP6). In addition, the model will be tuned within the experimental campaigns (WP7) to provide valuable information for the scaling-up of the technology.

A proper understanding of the heat transfer mechanisms is needed to properly analyze the heat released in the carbonator reactor and its capacity for power generation. Among the possibilities for carbonator-power cycle integration, which was analyzed in the Deliverable 4.1, an indirect power cycle integration is considered for the SOCRATCES prototype.

- **Main WP2 decisions and recommendations for WP6**

Important decisions for the project have been taken from the work carried out in WP2. Thus, the reactor design and the kinetics studies developed have served as the basis for the selection of the materials that best fits the project's objectives. The carbonator modelling tasks (task 2.2 and task 2.3) support the carbonator design activity and the operating conditions selected to meet the objectives of the reactor and allow a correct integration with the rest of the components of the whole Thermochemical Energy Storage (TCES) system proposed in SOCRATCES.

- **Next steps**

The next steps to follow within the WP are defined, mainly related to provide scientific support during the Engineering (WP5, WP6) and validation (WP7) tasks. This includes:

- Evaluation of different mathematic models for carbonation kinetics.
- Studying the effect of steam addition at low concentrations (5-10 vol.%)
- Carbonation kinetics will be tested, and kinetics parameters will be refined in the real prototype plant conditions.
- The mass flow rates of CO_2, CaO and air must be optimized from the proposed carbonator mathematical models in order to maximize the heat release to the Stirling.

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INTRODUCTION

This deliverable summarizes the work carried out under the Work Package -WP- 2 (Carbonator) during the first half of SOCRATCES, as well as the main decisions taken about materials, reactors and operating conditions. The WP2 aims to make a depth assessment on carbonation reaction and to develop at lab-scale the carbonator (reactor), which subsequently will be constructed within the WP6. Main tasks are summarized in Table 1.

Table 1: Task within the WP2

Task.	Title	Lead partner	Related deliverable(s)	Partners involved
2.1	Carbonation kinetics	CSIC	D2.1 y D2.4	CSIC, USE. ZAR, AUTH, CNR, CLX
2.2	Carbonator development	CERTH	D2.2 y D2.4	AUTH, USE, CSIC, CERTH, ZAR, CNR
2.3	Heat integration	USE	D2.3 y D2.4	TOR, ZAR, AUTH, CLX

The main objectives of the carbonation WP are to make an in-depth assessment of the carbonation reaction, develop a carbonator reactor at lab-scale, implement experiments for the understanding of the carbonation reaction and its kinetics, all of which will subsequently provide useful data for the carbonator model development and eventually the construction of the prototype reactor in the WP6. In order to achieve the best carbonator operation conditions, analysis is carried out at lab-scale conditions (TGA and small-scale fixed bed reactors, or -optional- DRX, XPS, SEM, TEM) and scaled up by means of mathematical modelling. The carbonator is simulated using computer-aided programs like MATLAB, CFD and EES.

Important decisions for the project have been taken from the work carried out in WP2. Thus, the reactor design and the kinetics studies developed have served as the basis for the selection of the materials that best fits the project's objectives. The carbonator modelling tasks (task 2.2 and task 2.3) support the carbonator design activity and the operating conditions selected to meet the objectives of the reactor and allow a correct integration with the rest of the components of the whole Thermochemical Energy Storage (TCES) system proposed in SOCRATCES.

During the reported period no major issues occurred and the work on carbonation evolves as expecting. All the deliverables have been submitted on time and the milestones were reached.

The deliverable has the following structure: the first section summarizes the work carried out within each WP task. Later on, the main decisions taken facing the prototype construction (WP6) are described, namely, selected materials and expected kinetics, final reactor design, Process Flow Diagram (PFD) of the carbonator side and potential heat integration between carbonator and Stirling. Finally, the next steps to follow within the WP are defined, mainly related to provide scientific support during the Engineering (WP5, WP6) and validation (WP7) tasks.

1. SUMMARY OF THE WORK CARRIED OUT AND MAIN RESULTS (M1-M18)

1.1. Carbonation kinetics

A kinetic model has been proposed within the frame of this project and published in open source in reference (Ortiz et al., 2018). In this kinetic model, the reversibility of the reaction and the heterogeneous character of the process has been considered. Thus, a complete kinetic model, that takes into consideration the experimental conditions required for using this reaction in thermochemical storage application, has been proposed. This is a significant contribution, from both the scientific and technical point of view and relevant to the objectives of SOCRATCES. The model has been tested and applied to a number of experimental data with successful results. Thus, the kinetics of carbonation of three limestones with different particle size distribution (GRANICARB 0.1/0.8, d_{50}= 211 µm; OMYACARB 10 BE, d_{50}= 6.46 µm; and ESKAL 60, d_{50}= 60 µm) and one dolomite (DOLOMITA PPS, d_{50}= 6.70 µm) have been studied by CSIC using thermogravimetry. AUTH performed carbonation experiments on DOLOMITA PPS, OMYACARB 10 BE and GRANICARB 0.1/0.8 (sieved in order to obtain particles in the range 45-75 µm) on a continuous flow fixed bed reactor. Additionally, the reactor bed was diluted using inert quartz material to avoid hot spots and limestone particles agglomeration to simulate the dispersed phase in a downer reactor. Experimental data obtained independently by AUTH and CSIC were fitted successfully fitted with the proposed kinetic equation. Main results regarding the proposed kinetic model and experiments performed by CSIC and AUTH were reported in detail in the public deliverable D2.1 (Carbonation Kinetics). Moreover, additional results have been presented to the consortium partners in the internal reports covering m1-m6 and m1-m12.

The effect of several experimental parameters (temperature, CO_2 pressure, type of sample, sample particle size) on the carbonation kinetics were investigated, as they were considered relevant to the thermochemical application in SOCRATCES. Figure 1 shows, as way of example, a carbonation isotherm experiment carried out by CSIC. Several series of experiments at different temperatures, in the range 300-900°C, under either pure CO_2 or 70%vol.CO_2:30%vol He atmosphere were performed by thermogravimetry to evaluate the carbonation kinetics of the samples selected for the application.

The fitting of the proposed kinetic model to some experimental results, as a way of example, is shown in Figure 2 and Figure 3. It should be taken into consideration that the higher the temperature the closer to the equilibrium and, therefore, the slower the carbonation. Moreover, for the carbonation experiments carried out at temperatures far from equilibrium, an overshoot in the mass signal is observed. This effect is attributed to the very fast carbonation reaction that takes place at these temperatures (see Figure 3). In general, the kinetic model was able to fit satisfactorily all experimental curves, validating the model for describing experimental data within a very broad range of experimental conditions.

Particle size also played a significant role on carbonation kinetics. Thus, it was observed that, for a given temperature, carbonation rate increases as particle size decreases. Nonetheless, all samples provided a very fast kinetics during the kinetic-controlled stage of the reaction. Moreover, dolomite samples carbonated at higher than limestone samples.

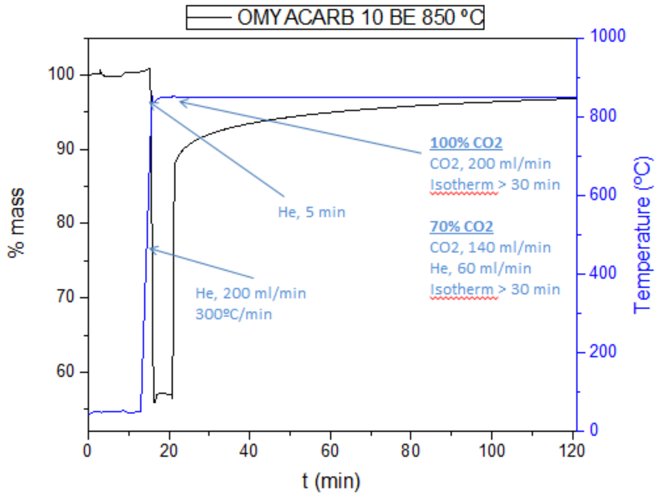

Figure 1. – OMYACARB 10 BE thermogram showing the time evolution of temperature and mass for a typical isothermal experiment of carbonation.

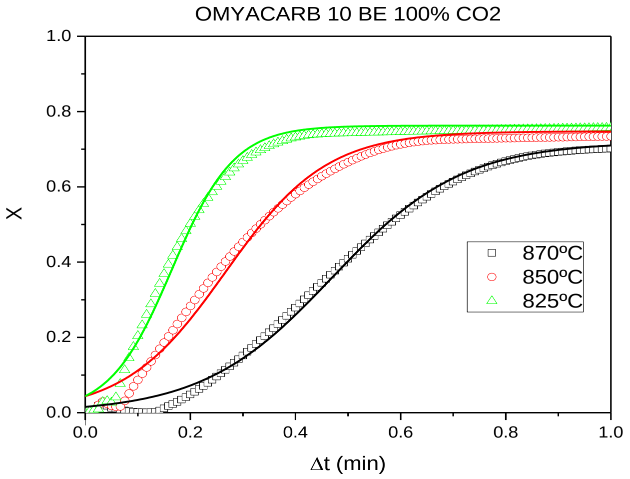

Figure 2. – Conversion vs time plot for OMYACARB 10 BE carbonated at 825°C, 850°C and 870°C under pure CO₂. The symbols correspond to experimental data and the solid lines correspond to the fit to the kinetic model.

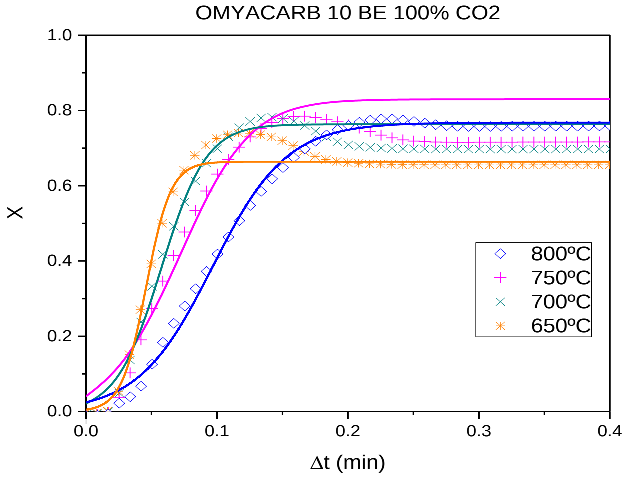

Figure 3. –Conversion vs time plot for OMYACARB 10 BE carbonated at 650°C, 700°C, 750°C and 800°C under pure CO₂. The symbols correspond to experimental data and the solid lines correspond to the fit of the kinetic model.

The results obtained by AUTH using fix bed reactor confirmed results obtained with thermogravimetric apparatus while the suggested model also fitted the experimental curves. (see Figure 4).

In any case, the model predicts reasonably well the experimental results for all samples studied, as shown in Figure 5, especially at temperatures near the equilibrium.

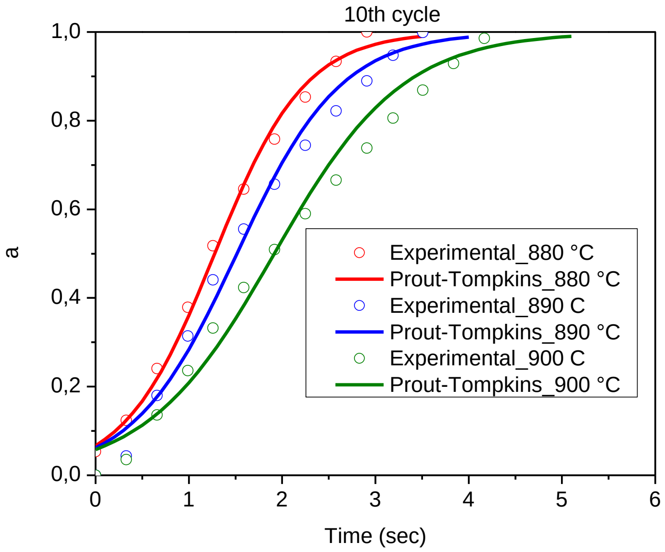

Figure 4. – Experimental carbonation conversion (normalized) during kinetically controlled regime as a function of time for the three studied temperatures and fit curves by the equation 9. (Material: GRANICARB 0.1/0.8 (OMYA) (45-75 µm); Carbonation: 100%CO_2, 600ml/min, 3 min; Calcination: 100%/N_2, 200ml/min, 3 min; T=880, 890, 900°C, P=1.7 atm)

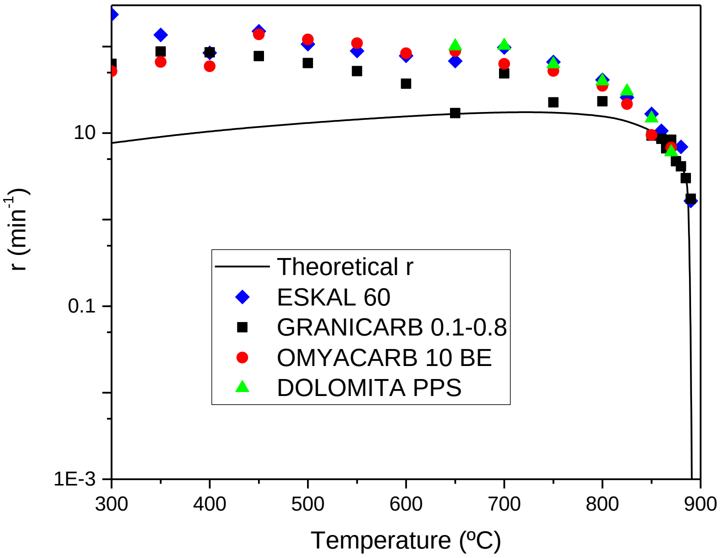

Figure 5. – Reaction rate values for all the samples studied by CSIC, carbonated at different temperatures under pure CO_2. Solid line corresponds to expected reaction rate values given by the kinetic model. The symbols correspond to the reaction rate values obtained by the fit of the conversion vs time plots to this model.

Calcination in several CO_2 and N_2 mixtures (and also pure N_2 and CO_2 separately) were studied by CSIC and AUTH in order to determine the influence of the calcination atmosphere with regards to carbonation reaction. No relevant influence of the calcination atmosphere was found in the experimental conditions employed, at least regarding first CaO carbonation.

Regarding the multicycle activity of the materials, the effective conversion decreases with the cycle number due to CaO sintering. This effect is more pronounced for the limestones than for the dolomite since the presence of MgO grains in dolomite after the first calcination hinders CaO sintering. It can be stablished that the effect of particle size on CO_2 uptake is much more relevant than that of the experimental conditions employed to perform the calcination/carbonation cycles.

1.2. Carbonator development

Several carbonator models have been already proposed in the literature (Alonso et al., 2009; Martínez et al., 2016; Ortiz et al., 2015; Romano, 2012). Most of them consider Fluidized Bed (FB) reactors as originally proposed for the CaL process for its application to capture CO_2 (Shimizu et al., 1999). FB is a widely used technology in the industry, which allows reducing the risk that faces implementing the CaL process. In the case of fine particles, with an important industrial interest that is being analyzed within SOCRATCES, fluidization is however difficult to achieve (Valverde Millán, 2013). As an alternative downer reactors are presented as potential candidates (Spinelli et al., 2018).

The carbonator reactor as a downer works as follows: CaO particles coming the storage tank enter by the top of the carbonator and react with CO_2 according to the carbonation reaction. The heat released in the carbonation is used to preheat the inlet CO_2 stream coming from the storage tank (in the first carbonation section) and to run a Stirling engine (in the second section) for power production. In the upper section a stream of CO_2 flows bottom-up while it is preheated from 25ºC. The external wall is maintained at constant temperature (880ºC) to ensure an adequate reaction extent. The preheated CO_2 enters the inner tube (the reactor) at the top. At this point the CO_2 stream is mixed with the preheated CaO particles coming from the storage vessel. The stream of CO_2 and solids flows through the carbonator reactor from top to bottom while the carbonation reaction takes place. In the lower section of the reactor, HTF coming from the power cycle enters at the bottom of the annulus space and flows bottom-up while absorbs heat from the CO_2/solids stream.

This section summarizes the work have been done by CERTH and UNIZAR in terms of mathematical model development for carbonator reactor, simulation activities and sensitivity analysis studies. During the models development, an extensive literature review in similar reaction systems and designs was conducted in order to comprehend the different chemical and physical phenomena taking place in this particular process. Thus, a review in carbonation kinetics was conducted and interpreted, while the modelling methodology of the carbonator reactor was developed. The main scope of the mathematical models development was by one side to understand carbonation reaction process, principles of physical and chemical transport phenomena taking place, and conditions under which reaction is favored. Then by the mechanistic model development, reactor’s dimensions and geometry were determined based on preliminary simulation results as well as the operating conditions under which reaction performs a desirable CaO conversion. In this way, reactor’s operating conditions and dimensions were initially defined, in terms of privileging thermodynamic efficiency, yield and reaction rate.

1.2.1 Model development and results analysis (CERTH)

CERTH analysed the carbonator reactor performance through the development of two different kinds, and level of detail, mathematical models, such as models that integrate heat, mass and momentum balances with reaction kinetics and CFD models studying the hydrodynamics and the different model assumptions under no reaction conditions.

Final conversion of the sorbent and temperature profile of the carbonator constitute some of the most crucial process variables that affect both the carbonator performance and the final decisions for the prototype construction. Specifically, the main scope of the carbonator mathematical model development is to understand the performance and the behavior of the reactor under different operating conditions and simultaneously conform with different technical and physical constraints. Also, the mathematical models development will serve as a tool for the validation of them in WP7 by fine-tuning model parameters, where prototype experiments in the carbonator will be performed. In this way also, carbonation kinetics will be tested, and kinetics parameters will be refined in the real prototype plant conditions. Below it summarizes the work under the execution of Task 2.2 "*Carbonator development*".

Within the Deliverable D2.1, a 1-D heterogeneous steady state drop-tube carbonator model is described and presented by CERTH. Specifically, this model handles solids and gas as two distinct phases (gas and solid phase), with each phase characterized by individual physical properties (i.e., gas and solid phase density, specific heat, molecular weight etc.). The model is based on a Euler-Euler approach, which means a segregated manipulation of each phase with the conservation of mass, energy, and momentum being used to couple them. Thus, the two phases are handled as fluids, and the plug flow assumption has been considered for both. Each phase possesses a finite volume fraction in each reactor section and the sum of them consist the total volume of the reactor. Mass (continuity equations), energy (first law of thermodynamics) and momentum (equation of Newtons second law) balances constitutes Navier – Stokes equations, simplified in one dimension, and solved for both phases. Kinetics are acquired from deliverable D2.1 (Carbonation kinetics) and the first WP2 internal report, where two different ("slow" and "fast") carbonation kinetic regimes has been described. As experimentally proven previously by AUTH and CISC, the "slow" kinetics describe better for the fresh CaO, while fast kinetics simulate better the performance of sintered CaO. Under this assumption, the proper kinetics are selected for the two different materials (fresh and sintered CaO) for the simulation activities later. In this stage of the model development, the helical coiled heat exchanger is not integrated into the aforementioned model due to the lack of significant data which they would result in very uncertain results. Instead, a boundary condition of a constant wall temperature or a variant wall temperature profile is employed as a more viable solution to assess only the phenomena taking place inside the reactor. This kind of carbonator model can be used also with high accuracy in more dense solids systems in which pressure and velocities variation have an important impact on the reactor's performance. The solution of the model calculates the profile of several crucial variables along the reactor, such as: reactants conversion, pressure, gas and solid phase temperature, velocity and density, volume fraction of each phase and different variables related to heat transfer from the inner side to the outer of the reactor.

Table 2 shows the methodology that have been followed for carbonator model development and the main assumptions.

Table 2: Methodology and assumptions of the carbonator model.

<table>
<tr><th>PARTNER</th><th>CERTH</th></tr>
<tr><td>EQUIPMENT</td><td>CARBONATOR</td></tr>
<tr><td>SOFTWARE</td><td>Matlab</td></tr>
<tr><td>SCOPE</td><td>Detailed simulations of carbonator reactor to assess performance and quantify heat sources.</td></tr>
<tr><td colspan="2">METHODOLOGY</td></tr>
<tr><td colspan="2">Chemical reactions kinetics: Deliverable 2.1 and 1st WP2 internal report.</td></tr>
<tr><td colspan="2">Fluid-dynamics: Continuity equations: Gas and solid phase balances (Euler-Euler approach), Momentum balance for gas and solid phase.</td></tr>
<tr><td colspan="2">Energy balances: Heat transfer: Heat transfer rate from solid phase to gas and from gas phase to wall by convection and radiation.</td></tr>
<tr><td colspan="2">ASSUMPTIONS</td></tr>
<tr><td colspan="2">• The downer reactor is modelled at steady state.
• Constant wall temperature conditions and a variant wall temperature profile along the reactor is considered.
• 1-D heterogeneous plug flow model for the gas and solid phase with respect to the reactor length. Discretization of 0.8 mm.
• The radial dispersions of mass, momentum and energy are neglected.
• The entrained-flow system is assumed to be very dilute in the solid phase such that the particle-wall and interparticle interactions may be neglected. Consequently, the conductive heat transfer between single particles and particles and wall is neglected.
• The ideal gas law is assumed for the gas phase.
• Solids assumed to be spherical, and uniform size and temperature inside them is considered.
• The reaction kinetics are described by a Prout-Tompkins model (D2.1 or 1st WP2 internal report).
• Kinetic energy and work forces of the system are negligible in comparison to the thermal energy due to high temperature in the carbonator.
• Gas phase physical properties (heat capacity, thermal conductivity and viscosity) are calculated from ASPEN PLUS properties (IDEAL).
• Solid phase heat capacity is assumed constant (ASPEN PLUS properties) while density varying between density of CaO and $CaCO_3$ as a function of conversion. Porous material</td></tr>
</table>

Table 2 illustrates initial input conditions of the model and model outputs. The model of the downer carbonator consists of 44 algebraic equations (Eqns. (9)-(17), (21)-(54), and 11 differential equations (Eqns. (1)-(8), (18)-(20)), and the number of variables involved is 60. Further details on the model equations can be found in the Deliverable D2.2. The problem is a DAEs (Differential and algebraic equations) system comprised by 11 first-order differential and 44 algebraic equations which are integrated simultaneously by a first-order backward finite difference method. In this work the mathematical model is coded in Matlab environment and numerically solved by a Matlab solver for stiff differential equations with a multistep solver option.

Table 3: **Inputs and outputs of carbonator simulation (CERTH)**

PARTNER	**CERTH**
EQUIPMENT	CARBONATOR
SOFTWARE	Matlab
INPUT	**OUTPUT**
• Mass flow rate of CaO • Mass flow rate of CO_2 • Pressure • Voidage • Superficial velocity • Solid phase temperature • Gas temperature • Solid phase velocity • Gas phase velocity • Solid phase density • Gas phase density	• CaO and CO_2 conversion profile • Pressure variation along the reactor • Reaction rate variation along the reactor • Gas and solid phase temperature profile • Voidage variation along the reactor • Gas and solid phase velocity profile • Gas and solid phase density variation along reactor • Produced heat per meter due to reaction • Total produced heat due to reaction • Transferred heat per meter from solid to gas phase to wall • Total transferred heat from gas phase to wall

In the second section preliminary development of a 2-D axisymmetric CFD-based model for the carbonator is presented by CERTH, which will provide useful insights for the coupled dynamics of the entrained solids and reactor flow as well as a more accurate way to predict thermal coupling of the particles with the reactor environment. Currently, the CFD-based model development does not include implementation of reaction dynamics. Also, via the CFD-based carbonator model, the main assumption of the plug flow of each phase will be investigated. Eventually, the axisymmetric CFD-based model intends to be coupled simultaneously with the carbonation reaction source terms to be solved for different operating conditions and then be compared to the other models. In this way, the CFD study is intended as an auxiliary tool both for the proper carbonator design and for verification of the 1-D carbonator models by CERTH and ZAR.

The most important outputs of the model constitute the CaO and CO_2 conversion profile along the reactor, carbonator temperature profile (gas and solid phase), variation of velocity (gas and solid phase) and energy source terms. The latter refers to the energy produced due to the exothermic carbonation reaction which stands as the main output of the model results. As deduced from the model, carbonator performance is critically affected by operating variables such as reactor's wall temperature T_w, CO_2 excess at the inlet of reactor, CaO mass flow rate and sorbent condition. The latter is stipulated by the number of calcination/carbonation cycles (i.e., 69.1 % for the first cycle and 15 % after the 10th cycle) and referred as fresh or sintered material. This has an impact also on the kinetics of carbonation as the sintered CaO performs a more rapid reaction rate (1st WP2 internal report and D2.1).

A comparative study of the thermal energy produced in the carbonator is performed. The impact of constant wall temperature, CO_2 excess in the reactor and variant wall temperature profile is examined subjected to the thermal energy produced (Figure 6). Wall temperature profile as well as CO_2 excess have an important role in the final produced energy. In the constant wall temperature strategy, the lower the temperature (i.e., 600 °C) the higher the final sorbent conversion and thus the produced energy (4.4-7.2 kW$_t$). CO$_2$ excess, has a severe impact on the residence time of solids in the reactor. Thus, the higher the CO$_2$ flow rate, the less the produced energy (3.8-6.7 kWth). On the other hand, after the interpretation of the results until now, a manually defined wall temperature profile was introduced to the model, in order to simulate a more realistic state of the real unit operation. Thus, a high wall temperature value was considered at the first carbonator section (800 °C) to preheat reactants and initialize the reaction, and then a lower value at the second section (500-700 °C), in order to regulate the removed heat released by the exothermic reaction. Profile 1 (800→500 °C) performs the better results in terms of the released heat (~7.6 kW$_{th}$).

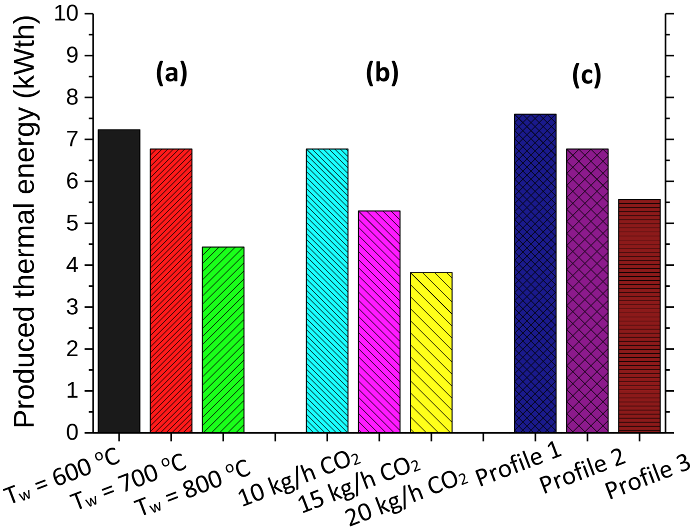

Figure 6. **Produced thermal energy due to carbonation reaction under different strategies: (a) Reactor's wall temperature analysis; (b) CO$_2$ excess analysis; (c) Variant wall temperature profile analysis.**

The expected thermal energy released by carbonation in the SOCRATCES prototype (10kW$_t$) can be produced via specific operating conditions under sintered CaO material. Below are presented some identical input data for the simulation activities performed.

Table 4: Base case input data for carbonator simulation under sintered CaO and CaO mass flow rate analysis.

Carbonator variable/parameter	Value
Inlet reactants temperature (°C)	200
Reactor pressure (kPa)	101.32
Initial CaO flow rate (kg/h)	10-80 kg/h
Initial CO$_2$ flow rate (kg/h)	10.00
Reactor diameter (m)	0.1514
Reactor length (m)	4.0
Solids average diameter (m)	$60 \cdot 10^{-6}$
Reactor wall temperature (°C)	700 °C
Maximum sorbent conversion (-)	15.0 %

As a result, there is an incremental trend of produced thermal energy as CaO mass flow rate increases (Figure 7). The desirable amount of energy (10kW$_{th}$) is produced when CaO rate is around 75-80 kg/h with the given conversion (15 %). Also a heuristically defined wall literature profile (Profile 1 in Figure 7) for 80 kg/h CaO performs similar results.

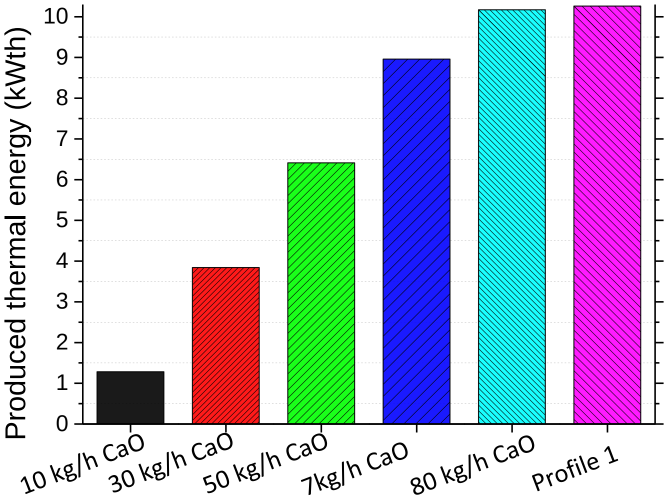

Figure 7. Produced thermal energy due to carbonation reaction under different sintered CaO mass flow rates.

Finally, CERTH developed also a 2-D / axisymmetric CFD-based model which, in currently on-going work, will incorporate carbonation kinetics strongly coupled to the flow, heat and solids stream dynamics. In this way, a different carbonator model will become available, based on multi-physics CFD methods with, the prospect to verify a number of assumptions of the other two models (i.e., plug flow) and to give insights for better prediction of heat transfer coefficients. Also, the enhanced spatial detail of the CFD-based studies will comprise an additional valuable tool for the improved prototype carbonator design and construction.

1.2.2 Model development and results analysis (UNIZAR)

The University of Zaragoza (UNIZAR) has also developed a carbonator model which results are complementary to those provided by the CERTH's model (Section 1.2.1). In this new model, a 1-D steady state drop-tube carbonator rsector has been implemented. The gas phase is treated as a fluid with a plug flow assumption, while solids are modelled as a dilute entrained flow. Velocities of solids are calculated from the terminal velocity of a falling particle in a medium. Pressure is assumed constant. Conversion profile of the sorbent is calculated via the residence time of gas and solids in the reactor using the same kinetics as the kinetics described in D2.1. Also, it is included the necessary condition of reaching 400 °C in the solids in order to start the reaction. Furthermore, the UNIZAR model includes a heat transfer model for both the inner part of the reactor and the outer part. It considers (i) heat transfer between the solids and the gas, (ii) heat transfer between the cloud of gas plus particles and the inner wall of the reactor, (iii) heat transfer between the inner wall of the reactor and the outer wall of the reactor, (iv) heat transfer between the outer wall of the reactor and the outer wall of the helical coils, (v) heat transfer between the outer and inner walls of the coils, (vi) heat transfer between the inner wall of the coils and the cooling fluid, and (vii) heat transfer between the wall of the furnace and the outer wall of the coils. The model calculates the conversion of sorbent, the temperature profiles along the reactor and the power required in the furnaces.

The following table summarizes the study cases that UNIZAR was asked to simulate, according to the data provided by CERTH. All of them have also the following input data provided by CERTH as in model described in section 1.2.1: inner diameter of carbonator = 0.1541 m, outer diameter of carbonator = 0.1682 m, inner diameter of coils = 10.92 mm, outer diameter of coils = 12.7 mm, number of coils = 10, distance between the wall of the furnace and the outer wall of the coil = 3.6 cm, material between the wall of the furnace and the outer wall of the coil = air, diameter of the particles = 60 microns, inlet temperature of CaO = 200 °C, mass flow of CO_2 at coil's inlet = 10 kg/h, fixed temperature of the outer wall of the reactor = 850 °C, and inlet temperature of CO_2 at the carbonator's inlet = the temperature of CO_2 at the coil's exit.

Table 5: Study of cases for the UNIZAR's carbonator model

	Base case	Case 1	Case 2	Case 3	Case 4
T_{in} CO_2 at coil's inlet [°C]	25	200	25	25	25
T_{in} Air at coil's inlet [°C]	25	25	200	25	25
Mass of CaO [kg/h]	80.0	80.0	80.0	16.2	80.0
Mass of air [kg/h]	10	10	10	10	50
Residual conversion of CaO (X_K) [-]	0.150	0.150	0.150	0.691	0.150

The following figures show the results of the cases presented in the table above. As the furnaces that will be constructed for the carbonator (both, the one of the upper carbonator and the one of the lower carbonator) are divided in 3 pieces, the power provided (or removed) is computed according to these 3 sections for each furnace. Each of these pieces may provide a maximum of 14.8 kW. In none of the simulated cases is required a power greater than this for a furnace's piece.

Figure 8 shows the results for the base case. It can be seen that the gas entering at about 857 °C is rapidly cooled down by the solids. Then, the cloud of gas plus particles has to be heated by the furnace up to reaching 400 °C to start the reaction. After the first meter of the reactor, the temperature inside the reactor increases above 850 °C, and therefore the furnaces must provide a negative heat power. This means that furnaces should be stopped, and heat has to be released to the atmosphere (or transferred to a cold fluid in a future commercial installation) in order to maintain the outer wall of the reactor at 850 °C. At this point the reaction is already completed as can be seen in the figure. Thus, the heat provided to the CO_2 during the preheating stage, as well as the heat provided to the air directed to the Stirling engine, mainly comes from the furnaces and not from the exothermal heat of the reaction. This can be seen in the peaks of furnaces' power at the entrance of the coils. Importantly, the carbonator operation strategy will try to minimize the power provide by the furnaces, or what is the same, maximize the heat transfer from the carbonation thermal power.

According the simulations, the total power provided by the furnaces is 9.7 kW, while the exothermal heat released during the carbonation is 10.7 kW. However, the heat provided to the air fluid only amounts to 2.42 kW.

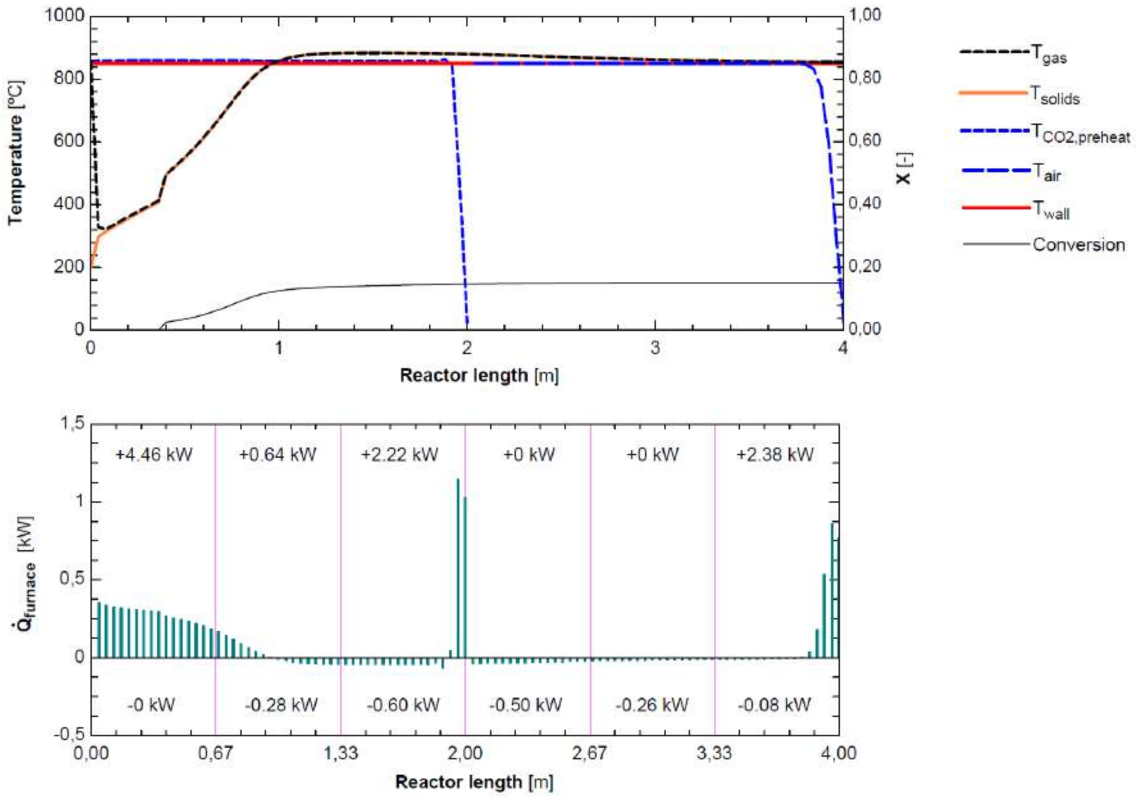

Figure 8. – Base case for the UNIZAR's carbonator model. Temperature profiles and furnace's power.

Similar results take place in Case 1 and Case 2. The only difference is the amount of heat provided by the furnaces at the entrance of the coils, as the fluids enter at 200 °C instead of 25 °C. This can be seen in Figure 9 and Figure 10.

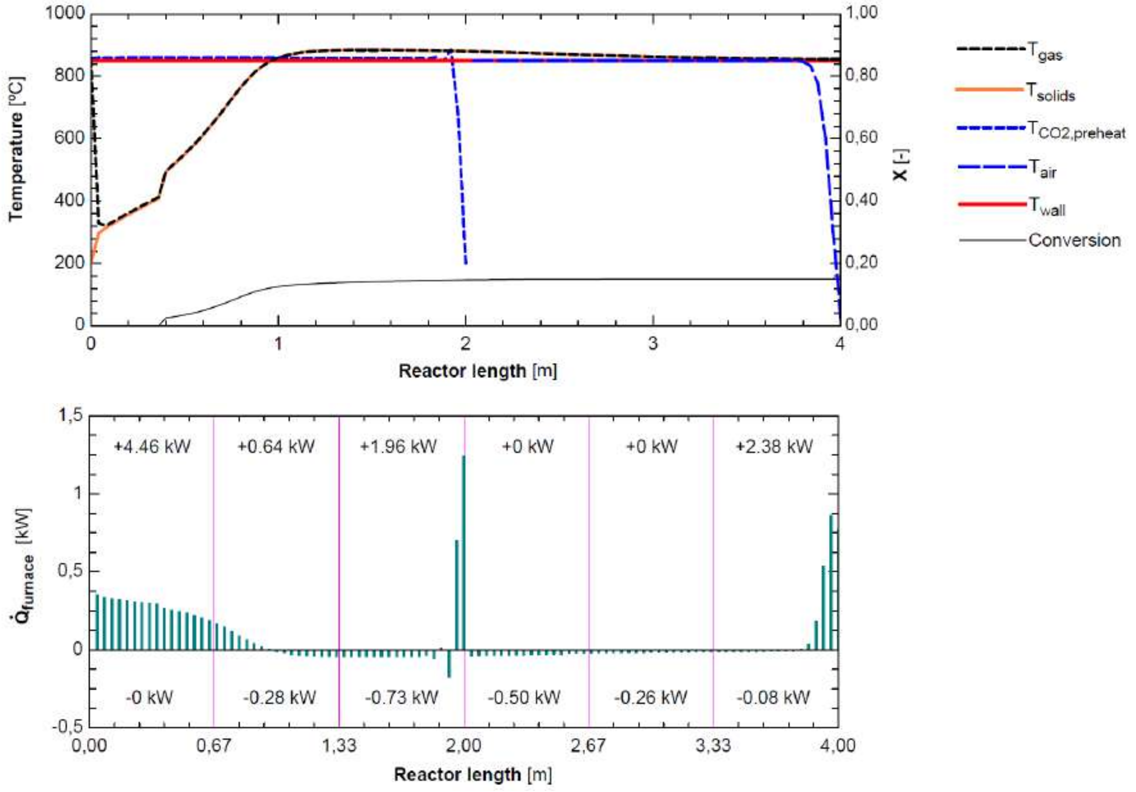

Figure 9. – Case 1 for the UNIZAR's carbonator model. Temperature profiles and furnace's power.

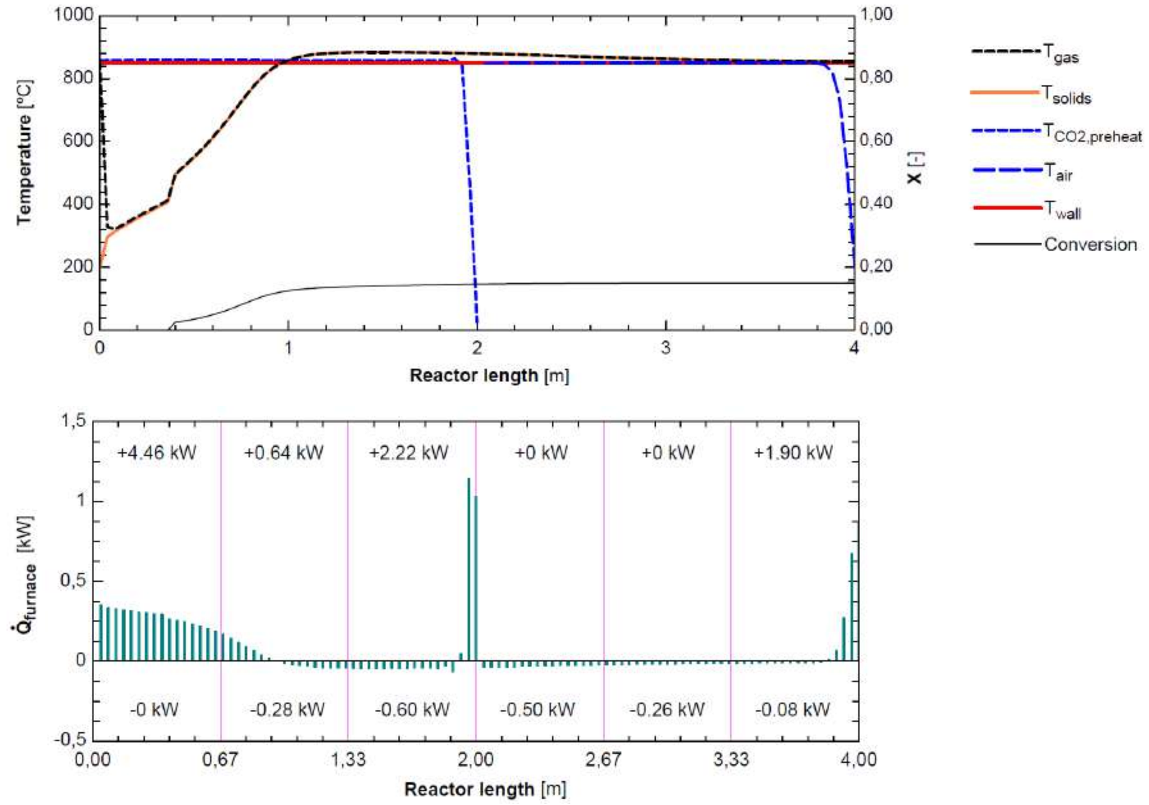

Figure 10. – Case 2 for the UNIZAR's carbonator model. Temperature profiles and furnace's power.

In Case 3, the amount of solids that enter at a low temperature is highly reduced, and therefore the temperature of 400 °C needed to start the carbonation reaction already takes place at the very beginning of the carbonator. Because the kinetics integrated in the carbonator model is not suitable for low temperatures, the initial conversion given at time 0 is highly overestimated and not realistic. Thus, the temperature inside the carbonator instantly increases above 850 °C, and the reaction is inhibited throughout the entire reactor. Under this scenario, continuous heat released to the atmosphere is necessary and the furnaces would only operate to heat the fluids entering the coils at the entrance.

In general, this kind of behaviour in which a high peak of power is provided by the furnaces at the entrance of the coils is due to the restriction of maintaining the outer wall of the furnace at 850 °C, which seems not realistic.

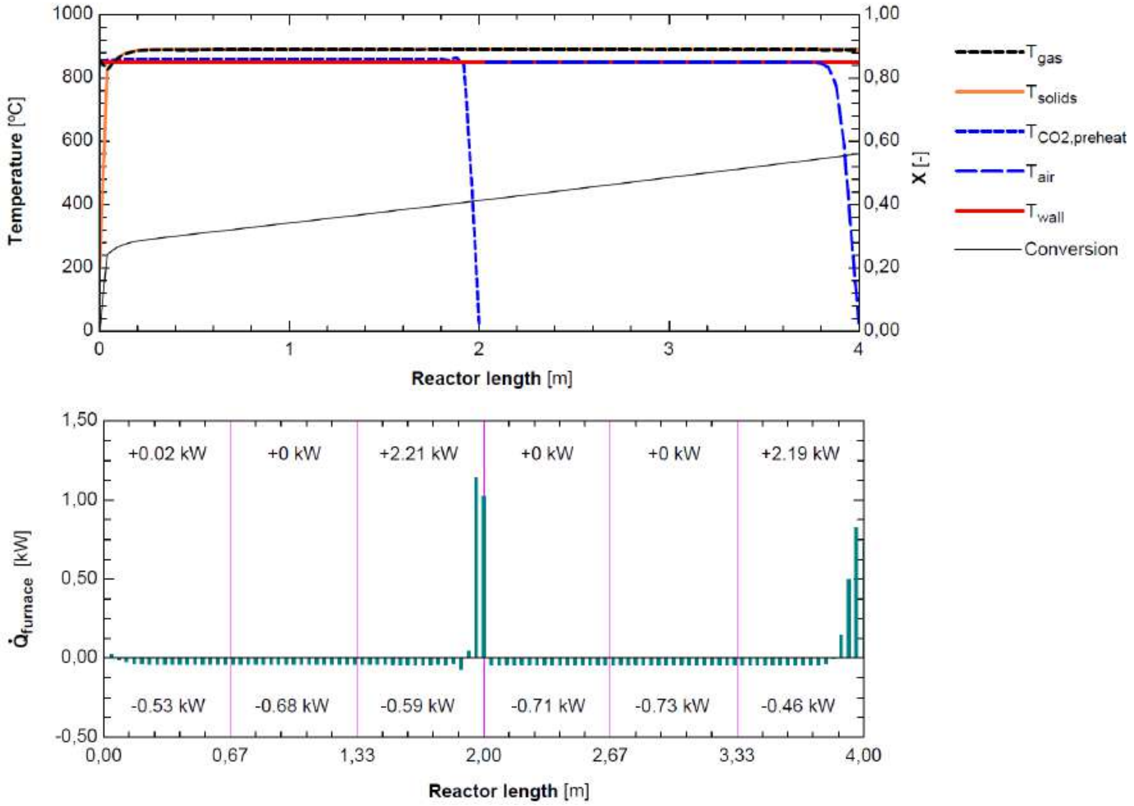

Figure 11. – Case 3 for the UNIZAR's carbonator model. Temperature profiles and furnace's power.

The last study case increases the amount of air that flows through the coil up to 50 kg/h, in order to provide a greater flow to the Stirling engine. The only difference compared to the base case is that the heat provided by the furnaces must increase accordingly. In this case, the third piece of the lower furnace should provide 11.4 kW, which is still below the maximum power output that the furnaces may provide (14.8 kW). However, all this heat that is sent to the Stirling engine for the power production is actually coming from the furnaces and not from the exothermal carbonation, so different control strategies have to be defined in order to take advantage of the heat provided by the carbonation reaction.

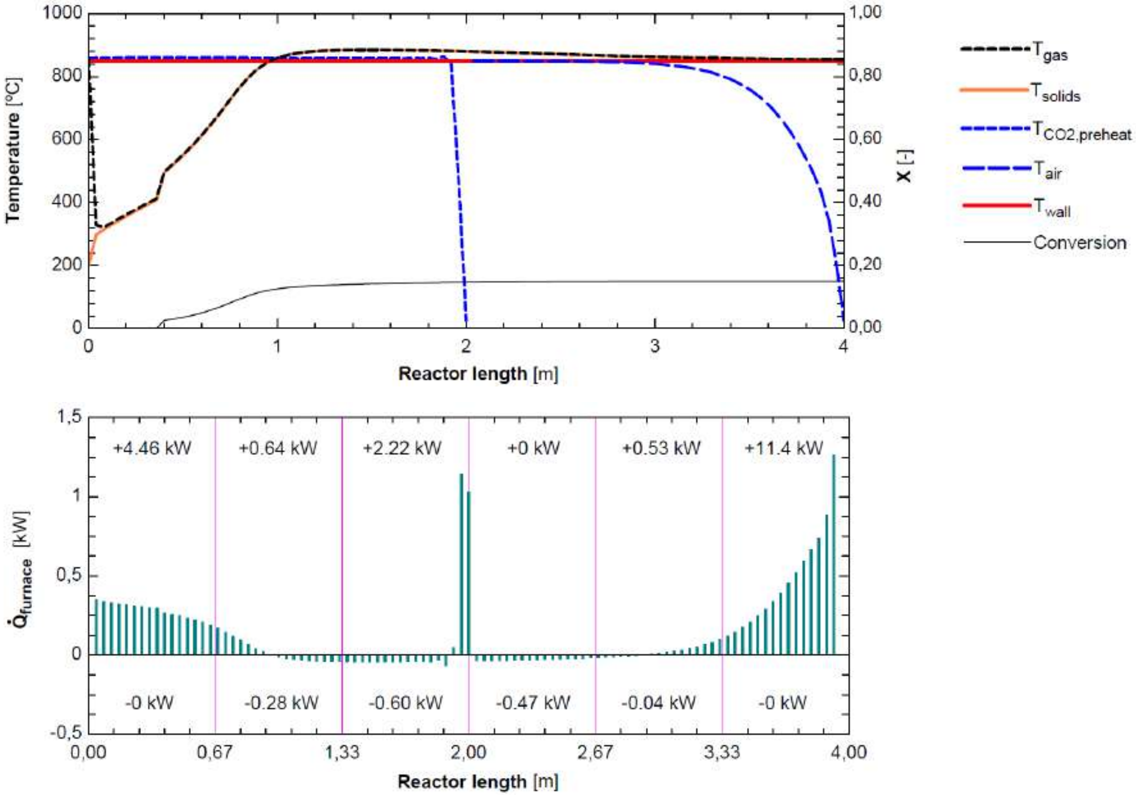

Figure 12. – Case 4 for the UNIZAR's carbonator model. Temperature profiles and furnace's power.

1.3. Heat integration

1.3.1 Introduction

This section summarizes the work under execution in *Task 2.3 "Heat integration"*. A carbonator heat transfer model has been developed along the WP2 (task 2.3) to evaluate the carbonator behaviour under relevant operation conditions for the SOCRATCES project. The model considers carbonation kinetics and heat transfer mechanisms within a 1-D reactor model. Carbonator size, operating conditions (P, T) or even changes in CaO precursors can be analysed from this model. The work carried out is complementary to the carbonator models proposed within the task 2.2 (section 1.2), in which complex fluid dynamics mechanisms were included. Likewise, carbonation kinetics results from task 2.1 are considered for the modelling. Thus, all the carbonator models proposed within the WP2, each one developed and oriented from a specific perspective compose a complete framework about the reaction behaviour and the implications facing the prototype construction.

The scope of the model developed is to provide a useful tool to evaluate the heat transfer from the highly exothermic carbonation, providing in this way worthy information for the carbonator design (WP2) as well as for the prototype design within the EPC task (WP6). In addition, the model will be tuned within the experimental campaigns (WP7) to provide valuable information for the scaling-up of the technology.

A proper understanding of the heat transfer mechanisms is needed to properly analyze the heat released in the carbonator reactor and its capacity for power generation. Among the possibilities for carbonator-power cycle integration, which was analyzed in the Deliverable 4.1, an indirect power cycle integration is considered for the SOCRATCES prototype.

1.3.2 Carbonator heat transfer model

The model considers the carbonation kinetics and the heat transfer mechanisms in the context of a 1-D reactor model. Open and closed-loop power cycles schemes can be modelled (i.e. for air and CO_2 streams as HTF respectively -see Deliverable D4.1-) and at different inlets temperatures.

The heating up process of the HTF through the external spiral is simulated assuming annulus flow in 2 concentric pipes and matching the residence time and the heat transfer of the spiral pipe by adjusting the external dimeter. Main hypothesis and assumptions can be consulted in the Deliverable 2.3.

The energy balance is calculated in each control volume: “ge” (external flow), “gi” (internal flow), as well as in the external and internal surfaces of the reactor wall. The external wall temperature is kept at a constant value in the preheating section, which is calculated by the model in order to achieve the desired CO_2 temperature at the reactor inlet (800ºC in the base case). Energy balance equations as well as all the correlations employed for calculating the heat transfer coefficients are described in depth in the Deliverable D2.3.

Conduction heat transfer occurs through the reactor wall (steel). The model considers heat transfer by convection between the external annulus space and the CO_2 stream in the preheating and in the power cycle sections, and between the reactor wall and the CO_2/solids stream. There are two walls at the concentric annular duct (Figure 13) and both are involved in heat transfer to the CO_2 flowing across the annulus space. The thermal boundary condition for the upper section (preheating of CO_2) consists of a uniform temperature at both walls. A fully developed laminar flow in a circular tube annulus with one surface insulated and the other at constant temperature is the most suitable condition for both walls of the upper section (Incropera et al., 2007). A fully developed laminar flow in a circular tube annulus with uniform heat flux kept at both surfaces is used as the thermal boundary condition for the Stirling engine section (bottom section of the reactor) (Incropera et al., 2007).

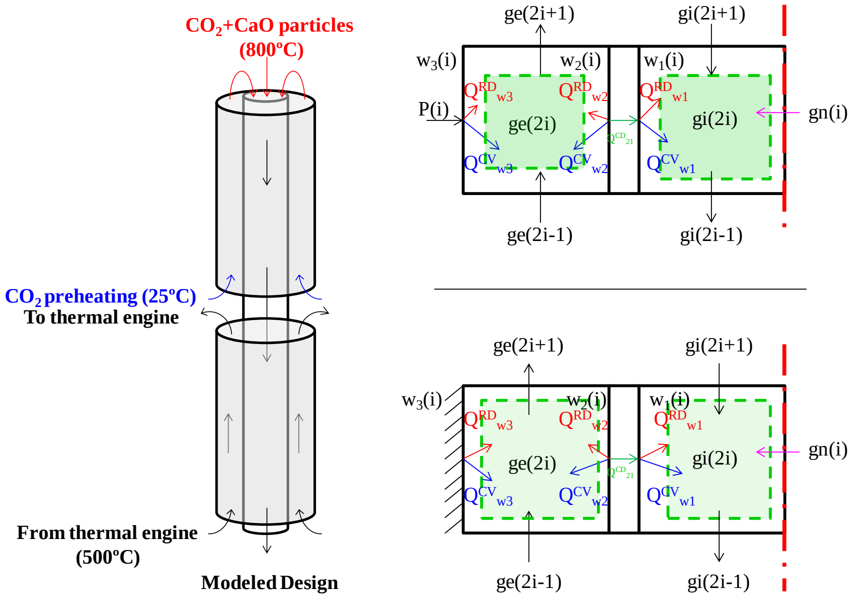

Figure 13. Left) Carbonator reactor scheme; Right) control volumes for the energy balance in each carbonator section: gn: reaction enthalpy released; w: wall; i: interior; e: exterior; g: gas.

Radiation plays an important role in the heat transfer mechanisms, being one order of magnitude higher than convection effects (Deliverable D2.3), mainly because the low gas velocity (natural convection). In order to model the thermal radiation exchanged between the

CO_2/solids cloud and the reactor wall, the CO_2/solids emission (ε_{g+p}) and absorption (α_{g+p}) coefficients must be carefully evaluated. The total emissivity of CO_2 can be determined using the "weighted sum of gray gases model'' (Leckner, 1972). The emissivity and absorptivity of the CO_2 stream are calculated from correlations presented in (Siegel, 2001). Further details can be found in the Deliverable D2.3. Remarkably, the calculated variation of the emissivity is low in the expected temperature wall range (500-900ºC). The emissivity of a cloud of limestone suspended in a CO_2 stream is calculated based on VDI Heat Atlas, Part K (Springer, 2010). It allows calculating the heat flux from the gas-particle mixture to the wall, which in addition requires a proper evaluation of the gas emissivity and absorptance.

The energy released in the exothermic carbonation reaction is transferred to the CO_2-particles stream and then to the carbonator reactor wall. Depending of the residence time of the CaO particles and temperature of the streams the heat from carbonation can be totally released in the first section of the carbonator, along the whole reactor or not totally released if the particles residence time is not high enough for the reaction to be fully achieved. The carbonation kinetics model is taken from the work carried out within the task 2.1 (Ortiz et al., 2018) as described in section 1.1. The pre-exponential factor $\boldsymbol{a_2}$ (a_2=42255-74666 s^{-1}) has been inferred from SOCRATCES experimental tests (low and high kinetics as described in section 1.2.1). Under the specific conditions considered in this paper (calcination and carbonation under full CO_2 atmosphere at 950ºC and 800ºC respectively), most of the carbonation occurs in the fast reaction-controlled stage while the contribution from the diffusion-controlled stage is negligible (Benitez-Guerrero et al., 2017). A conservative residual conversion value of X_k=0.15 is considered for the simulations, in the same way than in the others modelling tasks (section 1.2). Further information about integrating the carbonation kinetics and the heat transfer model can be found in the Deliverable D2.3.

Several case studies have been simulated and discussed to illustrate the potential of the model to be used as tool to support the carbonator design, complimentary to the other specific models developed within SOCRATCES and that together define the complete design framework. All these simulations consider operating conditions at SOCRATCES prototype scale (10 kW_t). In additions the model will be compared and tuned against real data in WP7 to provide information facing the scale-up of the process. Thus, the heat transfer model could be useful for evaluating the carbonator behaviour as a downer at MWs scale.

In agreement with the simulations carried out in tasks 2.2 (section 1.2 of the present document), it was assumed a CO_2 mass flow entering the carbonator of 10 kg/h. Solids and gas inlets temperature was assumed as 800ºC. CO_2 was considered as HTF to the Stirling engine. Further information on simulations inputs can be found in Deliverable D2.3. The mass flow rate of CaO entering the carbonator as well as the HTF inlet temperature are considered key parameters to improve the heat integration between carbonator and power cycle. Firstly, 5 kg/h of CaO and 10 kg/h of HTF (CO_2) coming from the power cycle at 500ºC are considered.

Figure 14 shows the temperature profile along the carbonator reactor. CaO particles enters the carbonator at 800ºC considering previous preheating. Importantly, this is different than simulated by UNIZAR (section 1.2.1) and therefore a comparison analysing the effect of this parameter can be done. As shown, almost the entire reaction occurs in the first section of the carbonator, which means that the heat provided for the Stirling under these conditions comes just from the sensible heat of the hot CO_2 and CaO. This situation should be optimized in order to maximize the heat release to the Stirling. Under these conditions, the CO_2 exits the carbonator at more than 600ºC. This hot CO_2 could be recirculated to the carbonator inlet to increase the temperature of the materials entering the carbonator, and therefore enhancing the thermal power released to the Stirling. On the other hand, CO_2 exits the carbonator to the Stirling at 750ºC. This temperature seems appropriate to run the Stirling Engine according the simulations carried out within the WP4 and WP5 as well as considering recommendations from the Stirling manufacturer. Figure 15 shows the power balance along the reactor. Negative values obtained at the top of the reactor represents that heat in excess is released to the preheated CO_2, which involves cooling needs (as predicted in simulations from section 1.2.1). This extra cooling means heat losses to the Stirling engine, and therefore it must be avoided by regulating the process streams mass flows or varying the strategy of temperature profiles within the carbonator according to development of reactions. Moreover, the total amount of the released power in the carbonator (blue line) is around 1.8 kW_t, which is lower than the expected one according to the SOCRATCES objective (10 kW_t). This small amount of power release involves an HTF mass flow rate to the Stirling Engine at 760ºC as low as 10 kg/h. According the models proposed by the carbonator-Stirling integration within the WP4 and WP5, this mass flow is insufficient to properly operate the Stirling engine.

A Stirling model was developed within the WP2-WP4 and WP5 to evaluate the overall heat integration between the carbonator and the Stirling engine. Further details on the Stilring modelling can be found in the Deliverable D5.1. Figure 16 shows the Stirling power output and HTF outlet temperature as a function of HTF mass flow coming from the carbonator for several rpm at the Stirling. An HTF inlet temperature of 750ºC was assumed. As can be seen in Figure 16, an air mass flow of HTF at 750ºC as high as 150 kg/h would be necessary to produce around 1 kWe of electric power. This mass flow is notably higher than the one obtained from the initial carbonator simulations (10 kg/h, Figure 14). These results on the Stirling output are corroborate by the Stirling supplier. According to the manufacturer, 0.2 kW could be produced with an air mass flow of around 72 kg/h at 500ºC.

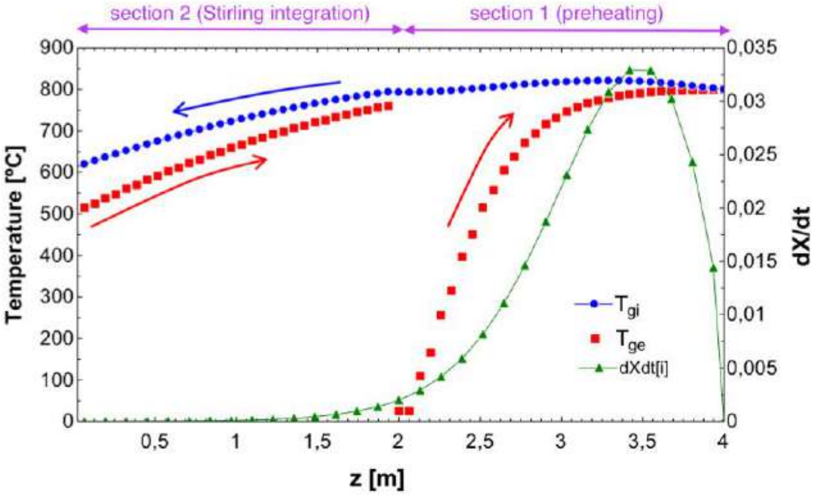

Figure 14. Temperature (ºC) profile for the carbonator reactor and the annulus flows (Stirling and pre-heating); and the derivative of the conversion reaction vs reactor height (m)

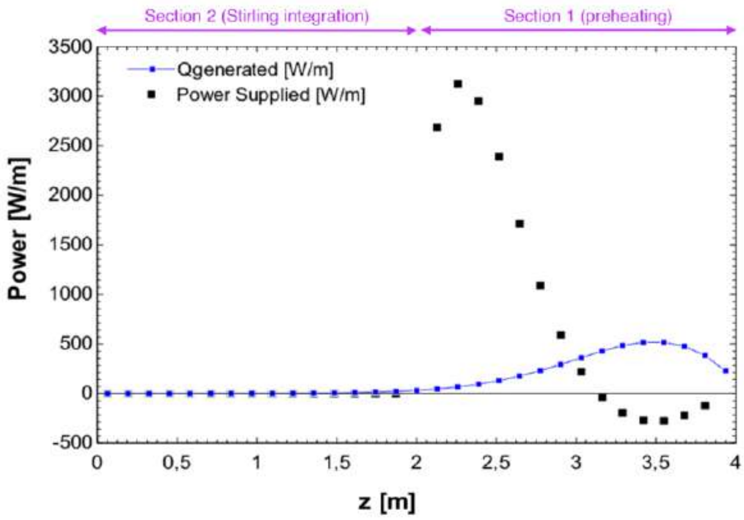

Figure 15. Power supplied (black) and power released by the carbonation reaction (blue) to maintain the external wall temperature at 800ºC.

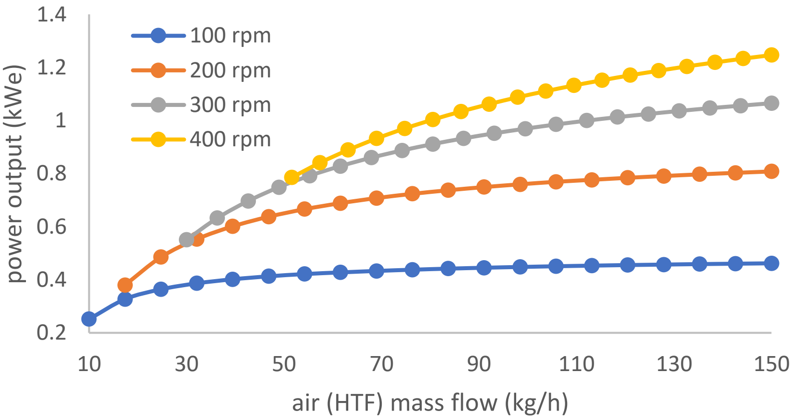

Figure 16. Stirling power output as a function of HTF mass flow coming from the carbonator.

A possibility to increase the thermal power release in the carbonator -and therefore the electricity generation at the Stirling – is introduce a certain amount of fresh limestone in the process to increase the value of the average CaO conversion. At this regard, a conservative value of CaO conversion of X=0.15 was assumed in the simulations. In the case of fine particles as used in the SOCRATCES prototype (of size ~60 μm), for which carbonation in the fast reaction-controlled phase is not limited by pore plugging, this residual value could be as high as ~0.5 (Benitez-Guerrero et al., 2017).

Another possibility to increase the thermal power released is increase the amount of CaO entering the carbonator, which was also simulated along sensitivity analyses in section 1.2. In this case the CaO/CO_2 ratio takes an important role. Due the stochiometric, by increasing the CaO mass flow, the CO_2 mass flow should be increased to ensure complete carbonation (up to $X_{average}$). On the other hand, the higher CO_2 mass flow the lower particles residence time. Larger CO_2 mass flow could distribute the reaction heat released in a more equal way between the two carbonation sections but taking in mind the limit to ensure a certain particles residence time to reach $X_{average}$. In this line, a new simulation was developed in which the CaO and the CO_2 mass flow rate was increased to 25.5kg/h and 20 kg/h respectively.

Figure 17 shows the carbonator temperature profile under these conditions. The CO_2 stream enters at the bottom of the preheating section (reactor height 2 m) at 25ºC and it is heated up to achieve 869ºC at the outlet, just before entering the carbonator at the top. CaO particles at

730ºC are mixed with the CO_2 stream. The mixture enters the carbonator at 800ºC. As may be seen, CaO particles leave the first 2 m of the reactor with a carbonation degree X~ 0.072 indicating that carbonation up to half of the residual value (X=0.15) takes place in the preheating section. This means that CaO particles exits the first 2 m of reactor after having already reached half of their maximum conversion in the fast reaction-controlled phase. The mass flow rate of the HTF sent to thermal engine is 45.5kg/h.

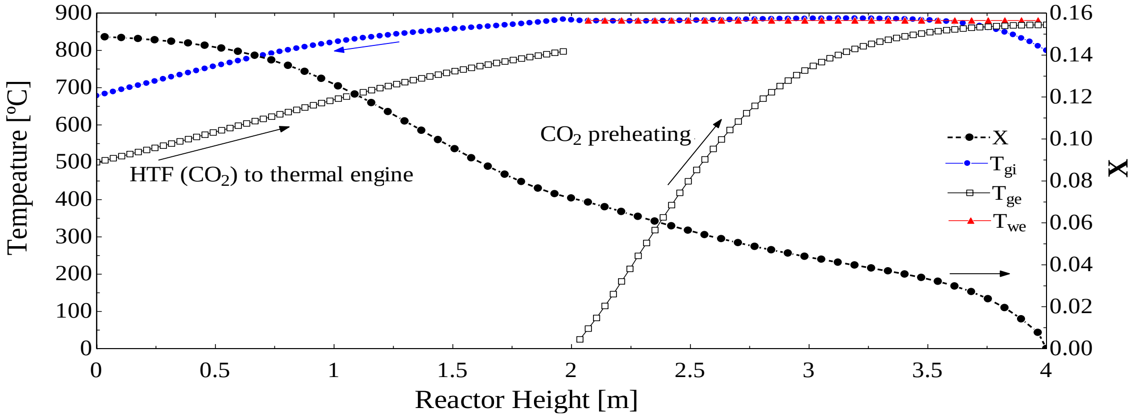

Figure 17. Carbonator reactor temperature profile (ge: external gas; gi internal gas; w3: external wall). The carbonation degree is also represented as a function of the reactor height.

The gas and solids residence time (~7s under conditions simulated in Figure 17) depends mainly on the CO_2 mass flow rate and its temperature, which affects its density. Figure 18 shows the CaO conversion when increase both CaO and CO_2 mass flow by multiplying the base case values for a factor in the range of 0.875-2. As can be seen, by increasing the mass flow rates of all components 1.5 times, the particles residence time is not high enough to complete the reaction, and therefore a part of energy is not released. Thus, the CO_2 mass flow rates should be optimized to ensure a complete reaction.

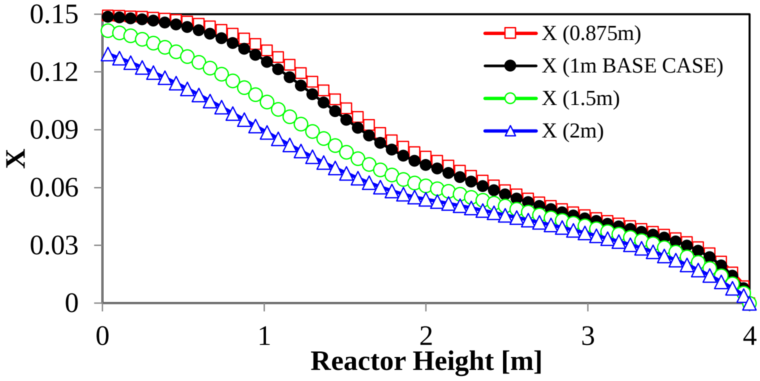

Figure 18. Carbonation degree (CaO conversion X) as a function of the reactor height for different mass flow rate simulated.

Simulations results from Figure 18 shows a maximum thermal power release by the carbonation of ~ 6 kWt. To reach the expected value of 10 $kW_{t,}$ a mass flow of CaO and CO_2 of ~ 80 kg/h and ~ 15 kg/h could be needed. This is fully aligned with the results obtained by CERTH in task 2.2 (Figure 7). New heat transfer simulations based on open-loop power cycle integrations (with air as HTF) will be carried out in next months.

Finally, the effect of the CaO particle size was assessed during task 2.3. As described in section 1.1, the CaO particle size is a critical parameter because it influences the reactivity and the carbonation conversion as well as the radiation heat transfer mechanism. By using fine particles the CaO conversion (and therefore the system efficiency) can be highly enhanced (Benitez-Guerrero et al., 2017). In these particles attrition is not very relevant although the agglomeration can be an important effect to consider because the intensity of the Van de Wall forces (Castellanos et al., 2001). Regarding heat transfer, the lower the particle size the higher emissivity of the mixture and this favours the radiation mechanism over convection. According to simulations results carried out within task 2.3, the effect of the particle size in the SOCARTECS reactor is not too relevant in the range of 30-120 µm.

2. Main WP2 decisions and recommendations for WP6

2.1. Materials and expected kinetics

From the work carried out by CSIC and AUTH on this task, and after several meetings of the entire consortium about the challenges to be faced on the real application, such as optimum material recovery, it was stablished that the most suitable material for SOCRATCES is ESKAL 60 limestone given its narrow and well defined particle size distribution which perfectly match the requirements of commercially available cyclones, taking into account that for all the studied samples, carbonation take place in less than 1 minute (in some cases, the kinetic controlled regime has finished in less than 5 seconds).

A kinetic model that takes into consideration the heterogeneous and reversible character of the reaction has been proposed. This model is able to predict the behaviour of the different materials (limestone and dolomite) under different experimental conditions relevant to SOCRATCES application. The proposed model seems to fit the carbonation reaction with just some deviations for low temperatures experiments due, probably, to the difficulties in controlling the temperature in the experiments because of the high exothermicity of the process. In any case, the experimental rates are above those predicted by the model, which is favourable for the project purpose.

The kinetics observed at the lab-scale fixed-bed reactor by AUTH is expected to be verified at the prototype carbonation reactor. As mentioned before, the carbonation kinetics are similar regardless the type of limestone used. Therefore, the kinetic analysis can be used for ESKAL 60 sample, although it was derived from experiments on GRANICARB sample. The calculated pre-exponential factor for the 2nd cycle is equal to 52700 s^{-1} while for the 10th cycle is 67700 s^{-1}. This difference could be ascribed to the non-isothermal conditions in the reactor mainly for the fresh material as well as to structural transformations of the material during cycles. It is recommended that the value of 52700 s^{-1} to be adopted as the “worst case scenario” in order to avoid overestimations in the reactor design. Note that this value is in agreements with those employed for the carbonator modelling (sections 1.2 and 1.3).

2.2. Final reactor design

The reactor type (entrained bed, fluidized bed, etc.) geometry and operation conditions (pressure, temperature, gas and solids velocities, etc.) highly conditions the heat transfer from the reactor bulk to the HTF (air) and therefore the power production.

An entrained flow reactor (downer) is proposed as carbonator within the SOCRATCES prototype. This configuration allows using fine particles, which is a key point within the project scope. In the conceptual design, the reactor will be able to handle particles with average size around 60 µm. Figure 19 shows the preliminary design scheme of the carbonator reactor and the integration with the Stirling engine, as proposed by CERTH.

The carbonator reactor is designed as a drop tube divided into two sections of two meters length each, comprising a four meters long reactor. The inner diameter of the reactor (0.1514 m), and the total length (~4 m) was set in order to achieve high solids residence times. Gas (CO_2) and solids (CaO) reactants are entering from the top, and the mixture of the unconverted CaO and CO_2, and the $CaCO_3$ product are discharged from the bottom. Specifically, CaO particles are stored in a storage vessel in the top of the reactor, while normally a furnace will surround the vessel to preheat solids. CO_2 gas and CaO particles will enter the reactor while mass flow rate of each component will be controlled via a dosing system (i.e., screw feeder) that will be set and established between CaO storage vessel on the top and first section of carbonator (not shown in the figure). It is expected that solids will enter the carbonator at temperature around 200ºC and therefore the screw feeder must be properly traced-heated and tested to this end. Each carbonator section will be encircled by helical coils in order to remove the produced heat during the exothermic reaction. Air is selected as HTF and evolves through the cooling coils, as it performs a cheap and abundant source of heat sink. The produced hot air is later used to provide heat to the power block. The entire reactor segments are surrounded by two furnaces blocks, that ensure the preheating of the overall system at temperatures at which carbonation reaction is triggered (~400-600^oC). Finally, solids will be collected in a downward vessel in the bottom of the reactor (Figure 19).

The carbonator design should avoid as much as possible the utilisation of the furnaces. Also, as recommended by UNIZAR and USE, it should be tried to carry out the carbonation reaction mostly in the lower carbonator, as it is where the heat is provided to the fluid of the Stirling engine. The mass flow rates of CO_2, CaO and air must be optimized in order to maximize the heat release to the Stirling. In general, current scenarios in which the outer wall of the carbonator is kept at a fixed temperature only leads to use the exothermal heat from the reaction to heat the solids and gas inside the carbonator, rather than for the power production in the Stirling engine.

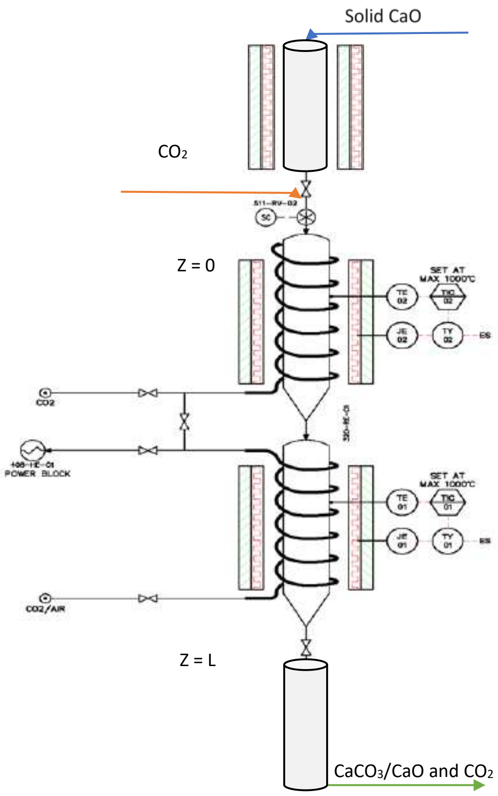

***Figure 19*. Conceptual carbonator scheme for the SOCRATCES prototype (figure developed by CERTH).**

Figure 20 shows the Process Flow Diagram (PFD) of the carbonator side. The main equipment of carbonation section involves the two reactors compartments, the top and the bottom vessel, the reactors furnaces and the furnace of the top vessel. Also, utility equipment (i.e., mass Flow controllers, valves, pressure and temperature transmitters etc.) are included. Fresh air (0-50 kg/h) is used as the Heat Transfer Fluid (HTF) inside the coils to remove the produced heat from the second part of reactor's walls, as the reaction is accomplished mainly in that section regarding the simulation activities performed in WP2. CO_2 is expanded from pressurized storage and after pressure regulation it passes through the coils towards the inlet of reactor (0-30 kg/h). N_2 is used either to fluidize solids at the top vessel (0-10 l/min), or to measure differential pressure between the top vessel and the inlet of reactor and between the intel and outlet of reactor. The amount of N_2 (0-3 l/min) used to measure PDT is also passing through the reactor and is used to measure CO_2 conversion via a CO_2 analyser at the discharge stream. In this way, and via knowing initial flow rates of components, an in-line CaO conversion system is established at the system. It is expected that N_2 concentration in the carbonator will be lower than 5%v/v and therefore the carbonation will occur in an almost pure CO_2 atmosphere as one of the key points of the carbonator as thermochemical energy storage systems against carbonator as post-combustion CO_2 capture. Other atmospheres could be tested within the experimental campaign (WP7).

The mass flow rates of CaO/CO_2 considered at nominal and off-design conditions has been discussed in detail in within the WP2 and WP6. As shown by simulation results within tasks 2.2 and 2.3 (sections 1.2 and 1.3 of the present document), around 80 kg/h of CaO should enter the carbonator when testing the reactor with sintered CaO ($X \sim 0.15$). CaO mass flow rate at the reactor can be vary between 5-80 kg/h depending on the material condition. For fresh CaO material, less mass flow rate is required for the same amount of produced thermal energy compared with the sintered material. CO_2 mass flow rate ranges between 5-30 kg/h covering the whole cases. Reactor's wall temperature can be controlled via a controller and adjusted at proper temperatures for the reaction initiation and regulation (400-800 ^{o}C). The HTF mass flow rate evolving to the Stirling engine should be as high as 70 kg/h at ∼700ºC to allows a certain power generation in the engine. Possible discrepancies between these values and the considered in the simulations/design will be further analyse in next weeks.

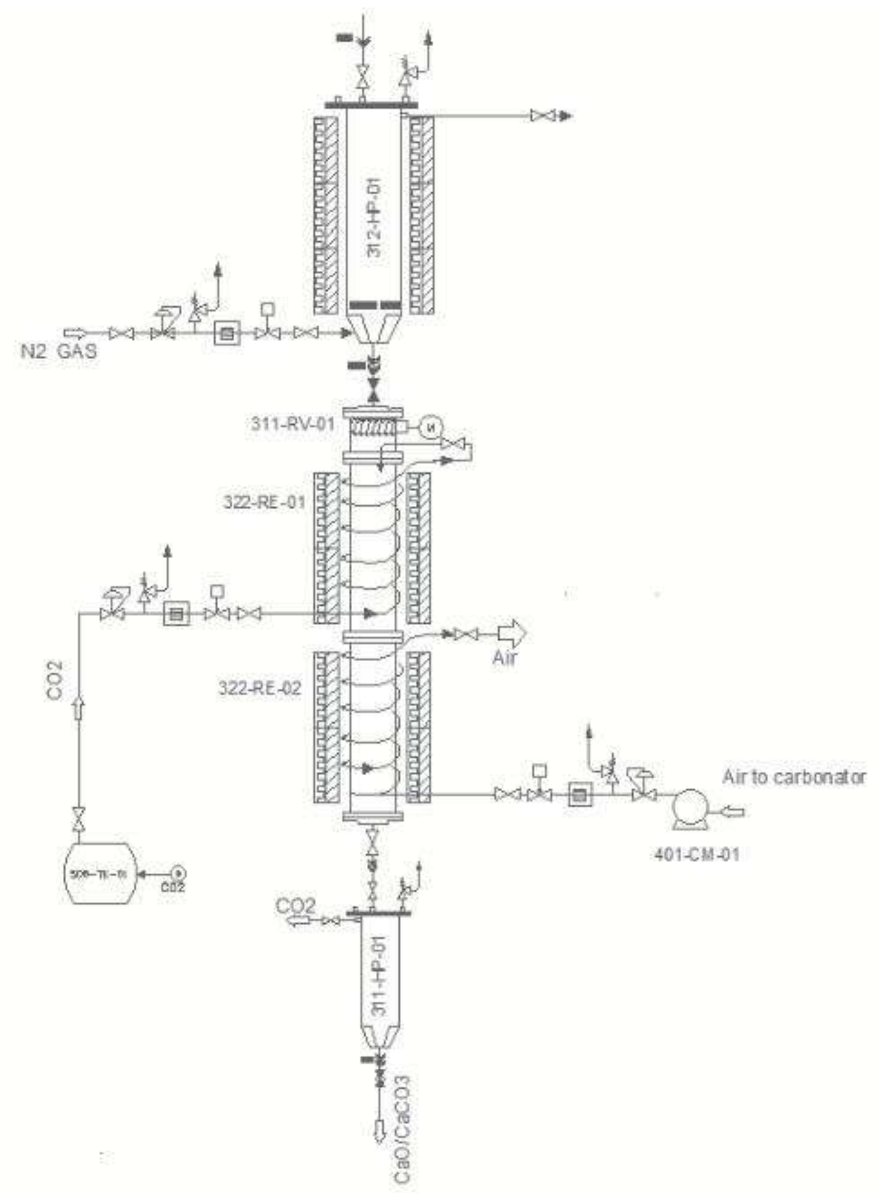

***Figure 20*. Process Flow Diagram (PFD) of the carbonator side.**

Several heat integration options have been proposed on the carbonator-Stirling integration to enhance the power production at the engine.

i) The hot CO_2 could be recirculated to the carbonator inlet to increase the temperature of the materials entering the carbonator, and therefore enhancing the thermal power released to the Stirling (Figure 21, left). Thus, the CO_2 entering the carbonator spiral (upper section) would be a mixture between CO_2 recirculated and CO_2 coming from the storage tank. Ideally, the mass flow of CO_2 coming from the storage tank would be the same that is consumed in the reaction. This would reduce notably the CO_2 storage tank size. However, the viability of integrating a CO_2 recirculation at high temperature should be evaluated from an engineering complexity point of view within the WP6.

ii) The hot CO_2 sent to the storage trend could be used to preheat the CO_2 entering the upper part of the carbonator (Figure 21, right).

iii) Integrating a gas-gas air preheater taking advantage of the air leaving the Stirling to be vented to the atmosphere (Figure 22).

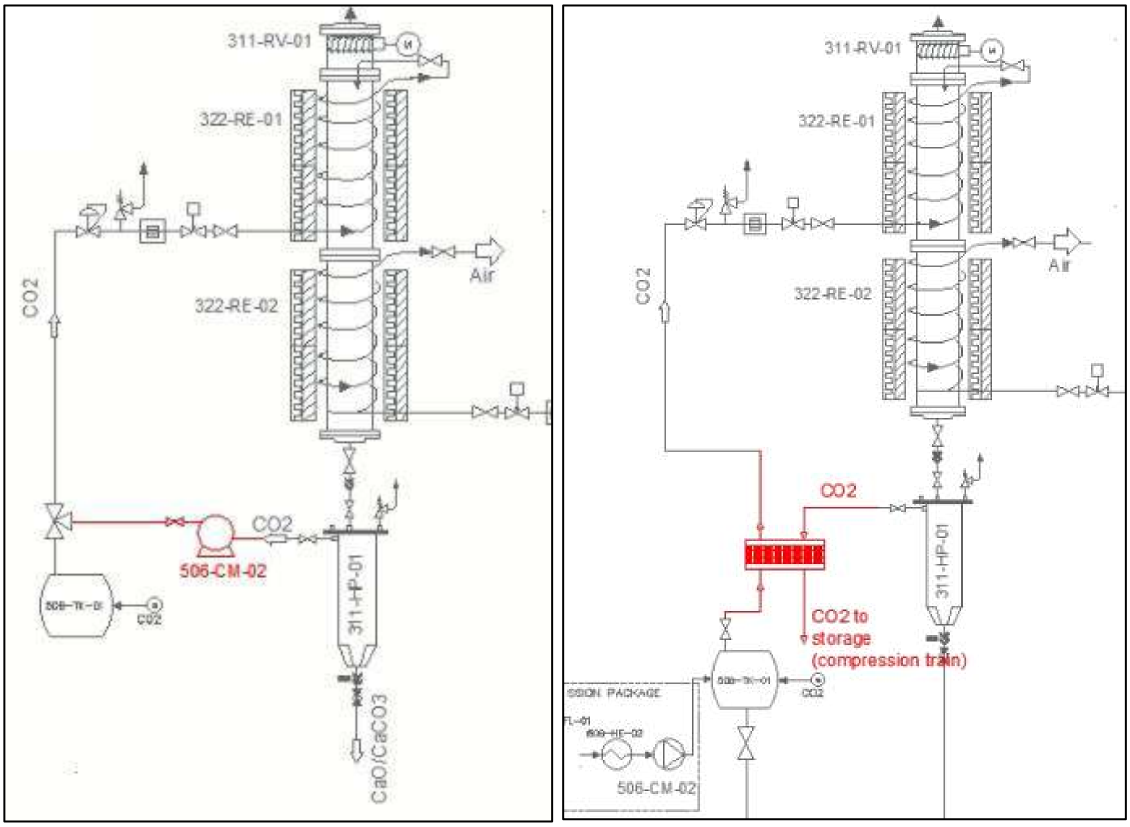

Figure 21. **Potentials heat integration on the carbonator side**

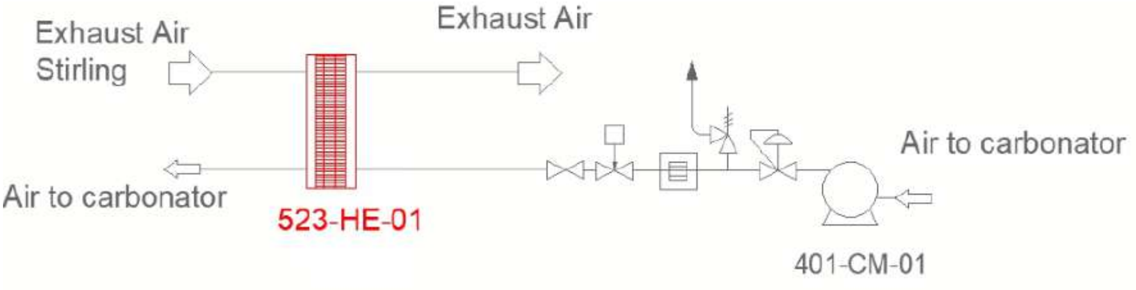

Figure 22. **Potentials heat integration between carbonator and Stirling engine**

2.3. Operation

The carbonator will be operated at isothermal conditions, keeping constant the temperature by using electric heaters in order to make independent and fully controllable the carbonation processes and to assure stable operating conditions. The operation conditions and strategy are described in detail in Deliverable D5.1. As a summary, the different operation strategies considered for the carbonator are: start-up; full load and part-load; and shutdown.

3. NEXT STEPS

Future plans on task 2.1 include studying the effect of steam addition at low concentrations (5-10 vol.%) and the evaluation of different mathematic models for carbonation kinetics.

The mathematical models development will serve as a tool for the validation of them in WP7 by fine-tuning model parameters, where prototype experiments in the carbonator will be performed. In this way also, carbonation kinetics will be tested, and kinetics parameters will be refined in the real prototype plant conditions. The mass flow rates of CO_2, CaO and air must be optimized from the proposed carbonator mathematical models in order to maximize the heat release to the Stirling.

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