

# Study of a Drop–Tube Carbonator Reactor for CSP–Calcium Looping Based on a Heterogeneous Reaction Model

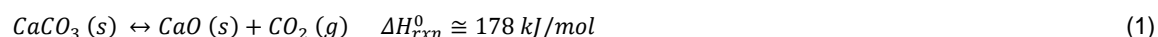
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Calcium-looping (CaL) is a competitive thermochemical energy storage (TCES) alternative allowing uninterrupted power production from solar heat. In this work, a model-based approach of the very fast carbonation reaction ( $\text{CaO (s)} + \text{CO}_2 \text{ (g)} \rightarrow \text{CaCO}_3 \text{ (s)}$ ) is employed to simulate a drop-tube as the carbonator reactor. A one-dimensional (1D) heterogeneous plug flow reactor (PFR) model for gas and solid phase is developed at steady state conditions. The model handles gas and solids as two distinct phases characterized by individual physical properties each. Model simulations export useful information about crucial process variables variation along the reactor. A case study of carbonator operation is examined through process simulation subjected to different  $\text{CO}_2/\text{CaO}$  molar ratios at the inlet of the reactor. In this way, the capabilities of the model are demonstrated related to different operating conditions providing insights for preliminary designs of similar reactors.

## 1. Introduction

Renewable energy sources contribute to global sustainability by massively cutting greenhouse gases emissions and helping to mitigate climate changes. Among others, solar energy stands as a free and endless source of energy that can be converted into electricity by means of a concentrated solar power plant (CSP). Thermal energy storage (TES), phase change materials (PCM) and thermochemical energy storage (TCES) systems are established as the most interesting and applicable energy storage technologies for CSPs (Chacartegui et al., 2016). The calcium-looping process proved as a promising technology for high energy storage efficiency in concentrating solar power plants through thermochemical energy storage (Karasavvas et al., 2018). The high energy density of the reversible and high endothermic/exothermic calcination-carbonation reaction system (Eq(1)), as well the low price, nontoxicity and wide availability of natural CaO precursors have driven the interest towards this application.



In SOCRATCES project (SOCRATCES Project, 2019), a prototype plant is being designed and constructed to demonstrate the proof of concept of the CSP–CaL integration. In the prototype operation, solar energy is exploited in the calcination section where natural limestone ( $\text{CaCO}_3$ ) decomposes towards CaO and  $\text{CO}_2$  (Eq(1)) in the calciner reactor. Thus, the produced solids (CaO) react back with the gas  $\text{CO}_2$  in the carbonator to form  $\text{CaCO}_3$  through the exothermic carbonation reaction, which allows recovering great amount of thermal energy and produce electricity at the power block (Figure 1). Carbonator reactor can be a drop-tube, known for his wide range of applicability in fast gas-solid reaction systems like  $\text{CO}_2$  capture in cement industry (Plou et al., 2019). Several studies related to mathematical model development of drop-tube reactors implemented in different applications have been published before. Gasification of biomass (Kasule et al., 2012), cooper oxidation (Schöfß et al., 2016), or calcium oxide carbonation in  $\text{CO}_2$  capture processes (Spinelli et al., 2018) are some indicative examples. This work encompasses the development of a one-dimensional (1D) steady-state mathematical model for the carbonation reaction, focused on CSP–CaL applications. The model is used as a

tool for the reactor simulation, where useful results are extracted for design purposes under the framework of SOCRATCES prototype erection. The model generally describes carbonator operation as a drop-tube, by calculating energy, mass, and momentum balances under several operating conditions and regimes.

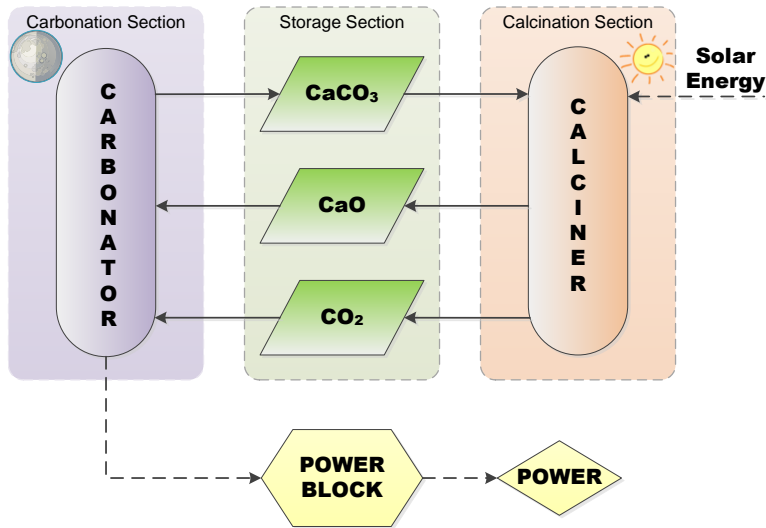


Figure 1: Basic block diagram of SOCRATCES prototype.

## 2. SOCRATCES reactor description

The proposed carbonator reactor resembles a drop tube. It is divided into two sections of two meters length each (Figure 2). The inner diameter of the reactor ( $\sim 0.16$  m), and the total length ( $\sim 4$  m) was set in order to achieve high solids residence times.

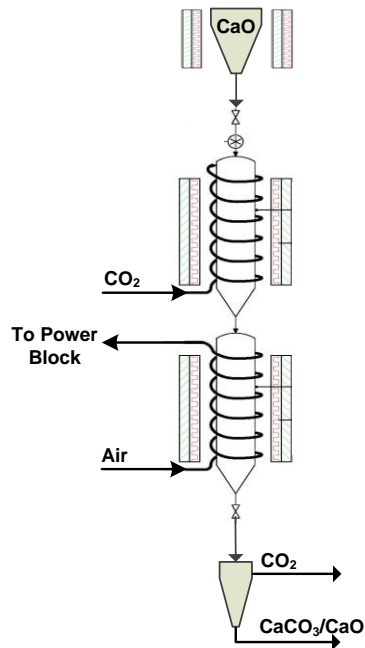


Figure 2: Conceptual carbonator layout for the down-flow of  $\text{CaO}$  solids.

Gas ( $\text{CO}_2$ ) and solids ( $\text{CaO}$ ) enter from the top of reactor, while the product as well the unconverted reactants are discharged in an extension vessel at the bottom (Figure 2). Before the injection, the calcined solids are stored in a heated tank ( $200\text{--}600$  °C) on top of the reactor (Figure 2).  $\text{CO}_2$  is provided by pressurized bottles, while  $\text{CaO}$  particles enter the reactor via a dosing screw feeder located between the top vessel and the

inlet of the reactor. For cooling purposes, the reactor is encircled by a set of helical gas coils that work as a heat exchanger and remove the produced heat released by the exothermic reaction. Fresh air is the heat transfer fluid passing 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 (Figure 2). 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 (~600-850 °C).

### 3. Drop-tube reactor mathematical model description

The mathematical model of the carbonator was developed to describe the physical and chemical processes taking place inside the reactor. The model is one-dimensional (1D) at steady state conditions that simulates a single-stage carbonator reactor as an industrial drop-tube. A Euler-Euler approach is implemented to describe the gas-solid system, which means that each phase (gas & solid phase) is treated separately and owns a finite volume-fraction at the reactor. Also, the plug flow assumption has been considered for both phases as experimentally proved for a spiral-shaped entrained flow carbonator reactor (Plou et al., 2019), as well for the carbonation of fine CaO particles in a drop-tube. (Turrado et al., 2018). In this model, mass, momentum and energy balance equations for solid and gas phase are considered separately. The mass balance of a component under the plug flow assumption is given by the generic equation below (Eq(2)), where,  $C$ , denotes the component concentration,  $u$ , the velocity of the flowing ingredient,  $D$ , the diffusivity coefficient,  $\dot{R}$ , the rate of mass consumption or generation, and  $\nabla$  is the differential operator in Cartesian coordinates.

$$\frac{dC}{dt} + \nabla (uC) = D \nabla^2 C + \dot{R} \quad (2)$$

Pressure along the reactor, voidage of gas phase, velocity and temperature profiles of each phase as well as conversion of reactants, are the state variables derived from the mass, energy and momentum equations. Drag, buoyancy and friction forces (i.e., friction forces between gas-wall and solids-wall) are calculated for both phases, while momentum losses are computed due to mass transfer rate from one phase to another. The CO<sub>2</sub> is modelled as a compressible gas obeying the law of ideal gases. The model takes also into account the modifications of particles characteristics as the carbonation reaction proceeds. The solid phase density continuously varies between the density of pure CaO and CaCO<sub>3</sub> linearly with CaO conversion. Moreover, each phase encompasses their own physiochemical properties which may vary as reaction occurs.

The gas-solid heterogeneous reaction rate has been previously inferred within the framework of SOCRATCES project and the kinetics were calculated using the Prout-Tompkins model (Eq(3)) to fit experimental data (Ortiz et al., 2018).  $X$ , denotes the mass conversion of CaO and  $r$ , the carbonation reaction rate depending on the temperature of particles surface and pressure of gas phase. The kinetic data deduced for particle sizes of around 45-75 μm and refers to SOCRATCES prototype operating conditions (i.e. 1-1.7 bar & ~800-900 °C).

$$\frac{dX}{dt} = f(X)r(T, P) \quad (3)$$

The heat produced due to the exothermic reaction is initially transferred from solids surface to the gas phase and then to the wall. For that purpose, the relative heat transfer terms and heat transfer coefficients have been computed separately (VDI Heat Atlas, 2010). In this way, the surplus heat which hinders reaction rate is removed out of the system. No a priori wall temperature profile is assumed in this model, but a constant wall temperature is considered. Theoretically, the actual wall temperature profile can be introduced into the model once experimental information is acquired from real plant operation, while parameters tuning will enhance model predictive capabilities towards the scale-up of the process.

#### 3.1 Model assumptions

The one-dimensional (1D) mathematical model of carbonator reactor is at steady state and simulates gas and solids as two separate phases. Consequently, the radial dispersions of mass, energy and momentum are neglected at the present study. Mass, energy, and momentum transport terms are developed for gas and solid phase. The entrained-flow system is assumed to be very dilute in the solid phase such that the particle-wall and particle-particle interactions may be neglected. Subsequently, the conductive heat transfer between single particles and particles to wall is neglected too. Solids are assumed to be spherical with a uniform size, while no temperature variations are considered within the bulk of the particle. Also, kinetic energy and work forces of the system are considered unimportant in comparison to the thermal energy due to the high temperature of the reactor.

The mathematical problem is a DAE (Differential and algebraic equations) system which consists of 11 first-order differential and 38 algebraic equations integrated simultaneously by a first-order backward finite difference

method. In this work the mathematical model is numerically computed by a solver for stiff differential equations with a multistep integration option. The developed system of DAE is treated as an initial value problem. Initial values are set for each differential variable initiating integration process.

#### 4. Results and discussion

In this section, the carbonator reactor is simulated via the model presented before under different inlet conditions. The base case input data implemented to the model are presented here after (Table 1).

Table 1: Base case input data for carbonator simulation.

Carbonator variable/parameter	Value
Inlet reactants temperature (°C)	600
Reactor pressure (kPa)	101.32
Initial CaO flow rate (kg/h)	12.70
Initial CO <sub>2</sub> flow rate (kg/h)	10.00
Reactor diameter (m)	0.16
Reactor length (m)	4.0
Solids average diameter (m)	75·10 <sup>-6</sup>
Reactor wall temperature (°C)	500
Maximum sorbent conversion (-)	15 % and 70 %

The dimensions of the reactor are pre-determined due to a priori reactor design. The operating conditions are pre-defined in accordance with the scheduled carbonator operation for 10 kW<sub>th</sub> thermal energy released due to the exothermic carbonation reaction. The same conditions are implemented both for a “low” maximum sorbent conversion (i.e., sintered CaO after multiple cycles,  $X_{CaO,max} \sim 15\%$ ) and for a “high” maximum sorbent conversion (i.e., fresh CaO,  $X_{CaO,max} \sim 70\%$ ). The capabilities of the model are demonstrated in terms of several process variables profiles along the reactor length (Figure 3 and Figure 4).

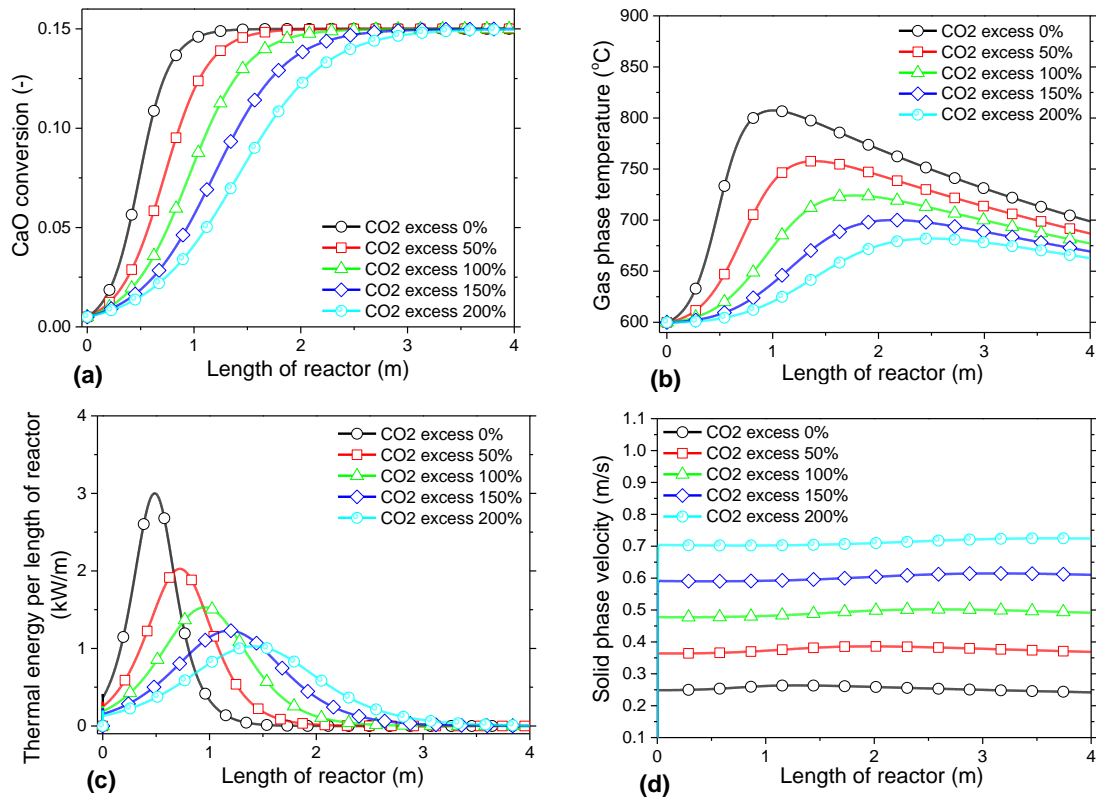


Figure 3: Process variables profiles under different CO<sub>2</sub> excess at the inlet of carbonator for sintered CaO with respect to the: (a) CaO conversion,  $X_{CaO}$ ; (b) Gas phase temperature,  $T_g$ ; (c) Thermal energy production rate due to reaction,  $Q_{rxn}$ ; (d) Solid phase velocity,  $v_p$ .

Among the most significant variables of the process constitute the sorbent conversion,  $X_{CaO}$ , gas phase temperature,  $T_g$ , rate of produced thermal energy due to reaction,  $Q_{rxn}$  and solid phase velocity,  $v_p$ . The sorbent conversion designates the extent of reaction, while  $Q_{rxn}$  indicates about the reaction rate and the zone of reactor where carbonation is accomplished. Reactor temperature is exhibited by the gas phase temperature ( $T_g$ ), while solid phase velocity,  $v_p$ , provides insights about the residence time of particles. Negligible deviation between solid and gas phase velocity and temperature is observed in these solids' sizes order of magnitude ( $\sim 30\text{-}75\ \mu\text{m}$ ), while a noteworthy difference is inferred for more coarse particles ( $>100\ \mu\text{m}$ ) (not shown in the graphs).

Five different  $\text{CO}_2$  ratios at the inlet of the reactor are examined with respect to the variables mentioned before (Figure 3). As seen, in all cases, the maximum sorbent conversion (15 %) is achieved (Figure 3a). However, the greater the  $\text{CO}_2$  excess, the higher the solid phase velocity and thus the shorter the residence time in the reactor (Figure 3d). This has an important effect in the profile of CaO conversion, which induces a delay in the maximum conversion approach. Temperature of reactor increases as exothermic reaction occurs until a maximum value, and then drops as is completed (Figure 3b). Carbonation performs a very abrupt reaction rate leading to the completion within the first 2 meters of the reactor in all cases. As long as the  $\text{CO}_2$  excess increases, reaction rate performs a smoother profile (Figure 3c).

In case of using fresh material (CaO) passing through the reactor, a different approach in carbonation reaction is observed. In particular, the equilibrium temperature ( $\sim 890\ ^\circ\text{C}$ ) is reached almost at all  $\text{CO}_2$  ratios, hindering the reaction progress (Figure 4b). Once temperature of reactants approximates equilibrium temperature, reaction rate diminishes near to zero and then, further conversion depends on the cooling rate of the reactor. For that reason, sorbent final conversion is continuously boosted towards higher values as  $\text{CO}_2$  excess also increases, acting as a heat sink that cools the reactor. However, after a critical  $\text{CO}_2$  excess value ( $\sim 150\%$ ), the lower residence time of solids (Figure 4d) surpasses the privilege of the better cooling (due to higher  $\text{CO}_2$  excess) and leads eventually to lower final conversions (Figure 4a). Also, the region of reactor that carbonation occurs, broads further as  $\text{CO}_2$  excess increases at the inlet (Figure 4c).

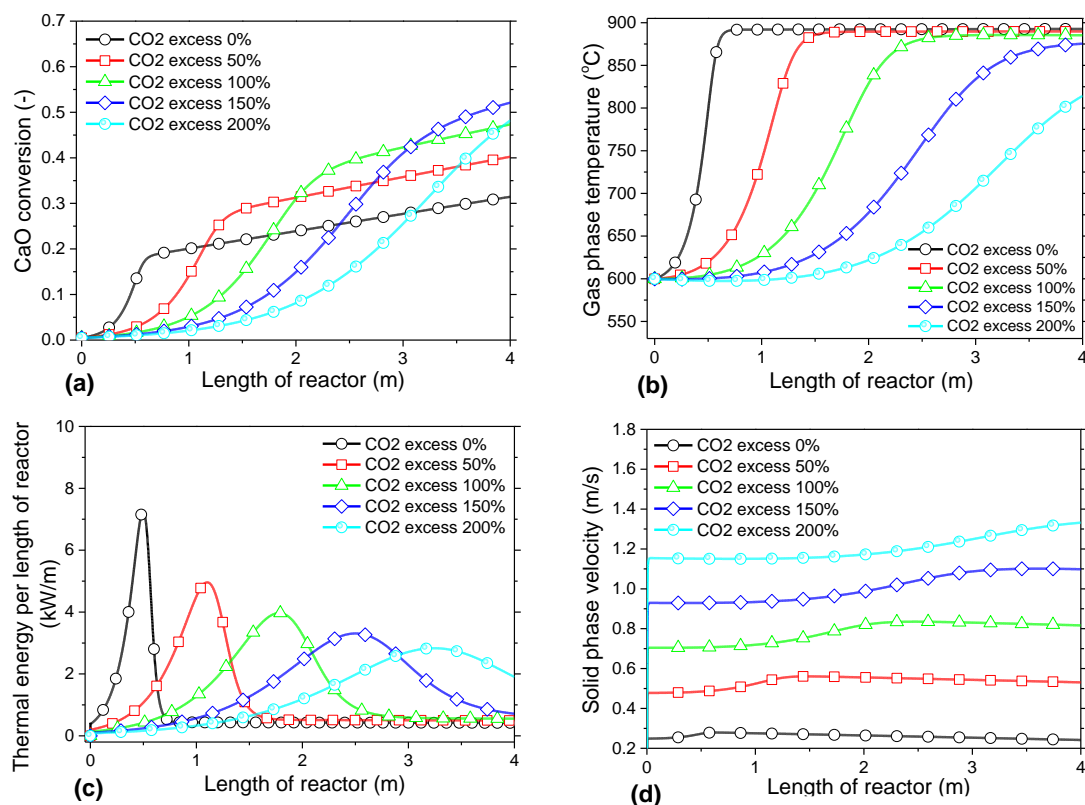


Figure 4: Process variables profiles under different  $\text{CO}_2$  excess at the inlet of carbonator for fresh CaO with respect to the: (a) CaO conversion,  $X_{CaO}$ ; (b) Gas phase temperature,  $T_g$ ; (c) Thermal energy production rate due to reaction,  $Q_{rxn}$ ; (d) Solid phase velocity,  $v_p$ .

## 5. Conclusions

In this study, a one-dimensional drop-tube carbonator model for CSP-Calcium looping has been developed to simulate carbonation reaction. The model provides the main trends of reactor performance under sintered and fresh CaO material. CO<sub>2</sub> excess at the inlet of the reactor was examined by means of the sorbent conversion, temperature profile of carbonator, rate of produced heat due to exothermic reaction and solid phase velocity profile along the reactor. Kinetics and operating conditions were determined previously due to SOCRATCES project requirements. For sintered CaO, the maximum sorbent conversion is obtained (~15 %), while for the fresh one, an adequate reaction performance within the actual length of reactor is observed (~52 %). The CO<sub>2</sub> excess seems to highly affect reaction rate and carbonation yield. In particular, it determines the residence time of solids inside the reactor and consequently the sorbent conversion profile (sintered CaO). Also, CO<sub>2</sub> absorbs the surplus heat of reaction which hinders carbonation improvement (fresh CaO). This very first carbonator modeling approach stands as a tool for entrained-flow design studies and can be further used as a provision for scale-up via experimental validation and tuning of model parameters.

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