Numerical Tools for a BFB Calciner Reactor: CFD and Thermodynamic Models

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Abstract

Calcium Looping (CaL) process has emerged over the past few years as a CO2 post-combustion capture technology. Based on the reaction between a Ca-based sorbent and CO2 an apparatus consisting of two interconnected fluidized bed reactors is utilized. Within the first reactor (carbonator) CO2 is captured by CaO sorbents in the form of CaCO3, while in the second reactor (calciner) CaCO3 is regenerated to form fresh CaO. Several CFD and thermodynamic models have been developed so far individually, mainly for the carbonator unit, in order to interpret the physical mechanisms taking place. The present work focuses on the presentation of a CFD model aiming at the successful simulation of the calciner unit. The applied CFD model covers the calcination reaction kinetics and drag force modeling; two reaction rates, based on Labiano and Martínez theory, respectively, and two drag models, an homogeneous and an EMMS based model, are used and compared. The main objective of the CFD model is its validation against available experimental data, i.e. the calciner efficiency and CO2 mole fraction leaving the calciner, as derived by the University of Stuttgart for the case of a lab-scale bubbling reactor. As a further step, the CFD model results are used as an input in a coupled thermodynamic modeling approach, and a parametric investigation for the optimization of parameters, such as temperature and bed inventory, governing the operation of the whole cycle is performed. The developed model is expected to be a helpful tool for the scale-up of the calciner.

Keywords: Calcium looping; CO2 capture; Process modeling; CFD; Calcination

1. Introduction

Fossil fuel combustion is one of the major contributors to the greenhouse effect, due to the release of large amounts of CO2, especially in coal-fired power plants. Attempts have been made to separate...
CO₂ from flue gases by means of different technologies and techniques. CO₂ capture and sequestration (CCS) is considered as a potential technology that would make deep cuts in greenhouse gas emissions from fossil fuels use in power plants and other industrial facilities in the mid to long term (Metz et al. 2005). According with the CCS concept, CO₂ is removed from flue gases before entering the atmosphere and is stored underground in large geological deposits (Olajire. 2010). All CO₂ capture technologies along with the CCS concept have a lot of applications in industry (Dean et al. 2011, Kuramochi et al. 2012) over the past decades. However, they have not yet been commercially implemented in large-scale installations and their role has not been tested, especially in emerging economies.

Among the CCS post-combustion technologies Calcium Looping (CaL) process has received a lot of attention recently and is considered as a promising option for carbon capture compared to MEA scrubbing and oxy-fuel (Abanades et al. 2007). Firstly proposed by (Shimizu et al. 1999) the calcium looping process is based on the reversible reaction between a CaO-based sorbent and CO₂. The sorbent particles are continuously recirculated between the two interconnected fluidized bed reactors, i.e. the carbonator and the calciner, operating under atmospheric pressure. In the former (carbonator), CO₂ reacts with lime solids (CaO) to form limestone (CaCO₃). The sorbent’s regeneration and release of CO₂ takes place in the latter reactor (calciner), mainly in a pure CO₂ or CO₂/H₂O atmosphere (Martínez et al. 2012).

The decomposition of the limestone, which follows the chemical equation CaCO₃→CaO+CO₂, is strongly endothermic, thus it is conducted under high temperatures (around 900 °C, but below 950 °C). As a result, the simultaneous fuel combustion in the calciner reactor is required for supplying the heat of reaction. In order to secure high CO₂ concentrations in the out-coming gas, pure O₂ stream is used as oxidizing agent. The process flow sheet diagram, of the calcination reaction, is depicted in Fig. 1.

![Fig 1. Calcination process flow sheet](image-url)
The understanding of the calcination kinetics has been the object of several research studies. A wide variety of correlations regarding the calcination rate have been applied so far; among them are a) the shrinking core model, which considers that the limestone calcination occurs at an interaction boundary between CaCO$_3$-CaO particles, which moves constantly towards the centre of CaCO$_3$ particles (Dennis and Hayhurst 1987, Silcox et al. 1989), and b) the homogeneous reaction model, which assumes an homogeneous reaction throughout the sorbent (Borgwardt 1985). Based on the above mentioned models most recent correlations have been presented by (García-Labiano et al. 2002), using a particle model known as "Changing grain size model" (CGSM), and by (Martínez et al. 2012). Both correlations are used and evaluated in the present work.

For the sufficient limestone calcination in a low cost and reasonable reactor size, except for a proper reaction rate prediction, sufficient residence times and a good gas-solid contact are required. This is best achieved in fluidized bed reactors (FB) (Alonso et al. 2009, Ylätalo et al. 2012). The development and implementation of CFD models can play a significant role in the design optimization of such reactors. This is attributed to their inherent ability to provide detailed information for complicated issues, such as inert material concentration in the bed, particles residence time, reactants mixing efficiency and temperature distribution, with a reduced cost when compared to experimental campaigns. Therefore, CFD modeling can play an important role in the up-scale procedure and efficient design not only of a calciner reactor, but generally of a dual fluidized bed (DFB) system.

The modeling approach used in the present study, for the 3D simulation of the multiphase flow, is the Two-Fluid-Model (TFM) (Nikolopoulos et al. 2010a, Nikolopoulos et al. 2010b). This technique is coupled with the sophisticated EMMS (Energy Minimization Multi-Scale) drag model scheme for the calculation of the drag forced exerted on the solid phase (particles), by the gas one. However, the accuracy of such numerical models and their high computational cost should be further evaluated and optimized.

The approach that is mainly followed for the calciner modeling in thermodynamic terms, is based on the hypothesis of equilibrium inside the reactors, an approach close to reality because of the high levels of operating temperature that promote the dominance of equilibrium against other factors such as kinetics of the reaction. However, simulation of calcination process, relied on the kinetic rates of the most dominant reactions that take place (i.e. calcination, combustion and desulfurization) can provide important information, not easily measured. This can be subsequently used for the most efficient design and operation of the whole system. Such an approach can also take into consideration, except for the reaction kinetics, the governing granulate hydrodynamics and sorbent activity.

Up to time being, the calcium looping main processes cannot be comprehensively addressed neither by the CFD analysis, nor by simple process modeling tools. On the one hand, CFD tools are not able to sufficiently model large scale units due to the induced complexities and the excessive computational cost. On the other hand, although thermodynamic tools have in principle relatively small computational cost and can effectively simulate even large scale units, phenomena that occur in the reactor, relevant to hydrodynamics cannot be taken into consideration at first hand.
This study tries to fill this gap, as it is a first attempt of the combination of these two numerical tools for the calcination process. A CFD model for a bubbling calciner reactor is proposed, taking into account both reaction kinetics and drag force modeling. Moreover, the thermodynamic model of the same calciner reactor is described, using as an input data from the CFD model, which prove to increase the accuracy of the whole approach compared to stand alone approximations. Additionally, a sensitivity analysis of some important operating parameters, including temperature and bed inventory is performed, in order to determine the set of parameters for an optimum operation.

2. CFD analysis

2.1 Model Description
The unit modeled in the present paper, Fig. 2a, is a bubbling calciner, part of a dual fluidized bed (DFB) system located at USTUTT installations. This DFB system comprises of a carbonator, named as DIVA, which continuously loops CaO particles to capture CO$_2$ in the form of CaCO$_3$ and the calciner (regenerator), herein referred as ELWIRA, where the CaCO$_3$ is calcined and CO$_2$ is released in a concentrated form ready for storage. Only the calciner riser is modeled in the present work, as a full loop simulation has been conducted for the carbonator case in previews works (Nikolopoulos et al. 2010a, Nikolopoulos et al. 2010b, Charitos et al. 2011, Nikolopoulos et al. 2012). Due to the fact that the particles in the two reactors are the same, the hydrodynamics of the calciner have been investigated indirectly through the simulation of the carbonator. In addition, this study focuses on the calcination kinetics and a CFD model is implemented as the decomposition of the limestone takes place at the bottom zone of the riser.

The apparatus has a height of 3.49m and a diameter of 0.1495m. Fluid gas consisting of a mole fraction of 36.7% CO$_2$ and 63.3% N$_2$ enters the bottom of the riser, i.e. the distributor, with a superficial gas velocity equal to 1.35m/s resulting in a gas flow rate equal to 0.001716963 kg/s.

The sorbent used in the simulation is a limestone. Solid particles with a mean diameter of 350μm and density equal to 1800 kg/m$^3$ (Geldard B) are fluidized upwards by the fluid gas, while the solids inventory being equal to approximately 6.445 kg. Fresh sorbent material enters the calciner from the carbonator at a height of 0.97m, with a rate measured by USTUTT equal to around 38.25 kg/h and a mass/mole fraction of CaCO$_3$ equal to 20.83%/12.85% respectively. In order to keep the solid inventory constant, the solid particles are exiting the riser with a mass flow rate equal to the one entering the calciner, i.e. 38.25 kg/h.
An unstructured numerical grid is implemented with full respect to the geometry of USTUTT’s hot calciner. The 3D calculation domain which consists of 31877 tetrahedral elements is depicted in Fig. 2b. The mean ratio of the equivalent cell size to particles diameter is around to 33, which is considered to be a reasonable ratio, for having quite accurate results, at least in terms of drag force calculation. The boundary conditions for BFB walls are set to the no slip condition for the gas phase and to the partial slip condition (Johnson and Jackson. 1987) for the solid phase. The specularity coefficient is set to 0.6 (Almuttahar and Taghipour 2008, Atsonios et al. 2011, Benyahia et al. 2000, Zhang and VanderHeyden 2001).

Regarding the spatial discretization schemes for the momentum and volume fraction equations the second-order accuracy QUICK scheme is used. For the transient calculations, a variable time step is set ranging from 1-100 μs in order to achieve convergence at each time step, while for time discretization a bounded second order implicit scheme is applied. The phase coupled SIMPLE algorithm is used for pressure–velocity coupling, while for the determination of scalars at grid faces values the Green-Gauss node based approximation is adopted. The set of time dependent equations is solved using the commercial software package ANSYS Fluent 14.0 (FLUENT 2010).
For the calculation of the drag force exerted on the solid phase (sorbent) from the gas phase an homogeneous drag force model (Gidaspow) and an heterogeneous model (EMMS) are implemented and compared. Different reaction rates for the decomposition of the limestone from the most updated available literature have been implemented and their results are compared against available experimental data.

2.2 Drag Force Model

In this work two models calculating the drag force exerted on the solid particles by the gas phase are implemented and compared; the conventional Gidaspow drag force model and the heterogeneous EMMS model.

The conventional model by (Gidaspow 1994) correlates the (Wen and Yu 1996) and (Ergun 1952) equations for drag calculation, depending on the solid phase fraction in a control volume.

\[
\beta = \begin{cases} 
\frac{3}{4} C_{D0,f} \rho_s e_s e_s \frac{|u_g - \bar{u}_s|}{d_s} e_{g}^{-2.65}, & \varepsilon_s \leq 0.2 \\
150 \frac{e_s}{\varepsilon_s} |u_g - \bar{u}_s| + 1.75 \rho_s e_s \frac{|u_g - \bar{u}_s|}{d_s}, & \varepsilon_s > 0.2 
\end{cases}
\]

However, (Wang et al. 2008) proposed that (Wen and Yu 1996) correlation is only reliable when the particles are homogeneously dispersed inside a control volume. However, in FB risers particles usually aggregate in heterogeneous formations referred as clusters. According to him, Wen and Yu correlation should be modified with the introduction of a new variable \((H_d)\), taking into account the effect of heterogeneous spatial distribution of solid phase in a control volume. This is reflected to the calculation of the drag coefficient, by the incorporation of \(H_d\) index as follows:

\[
\beta = \frac{3}{4} C_{D0,f} \rho_s e_s e_s \frac{|u_g - \bar{u}_s|}{d_s H_d} e_{g}^{-2.65}
\]

The calculation of the heterogeneity index \((H_d)\) according with the EMMS (Energy Minimization Multi-Scale) scheme has been described in the work of (Nikolopoulos et al. 2010a, Nikolopoulos et al. 2010b).

2.3 Reaction Rate

Two reaction rate correlations for the calcination reaction are applied in the present work; the one is based on (García-Labiano et al. 2002) approach, which incorporates the adsorption theory in the "Changing grain size model" (CGSM) and the other a correlation is developed by (Martínez et al. 2012), based on the Shrinking Core Model (SCM) with a kinetic rate constant derived by USTUTT.

For both cases the same values for \(X_{co2^{(in)}}\) and \(T\) were used as boundary conditions of the problem setup. The parameters \(X_{calc}\) and \(X_{co2^{(out)}}\) are computed numerically for each computational cell and at
each time step and as soon as they reach an almost constant value their time averaged values are compared against the corresponding parameters measured and provided by USTUTT, depicted in Table 1. However, the commercial program ANSYS Fluent gives results only for the time averaged mean mass fractions of the solid and gas species. Thus, the mass fractions of the reference process data are given as well in Table 1 in order to be easily compared with the numerically computed averaged values.

**Table 1** Values for calcination reaction parameters

<table>
<thead>
<tr>
<th>Reference case process data</th>
<th>Carbonate</th>
<th>Calcite</th>
<th>CO2 (in)</th>
<th>N2 (in)</th>
<th>CO2 (out)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X_carb</td>
<td>12.85%</td>
<td></td>
<td>36.86%</td>
<td>63.14%</td>
<td>50.31%</td>
</tr>
<tr>
<td>Y_carb</td>
<td></td>
<td>20.83%</td>
<td>47.84%</td>
<td>52.16%</td>
<td>61.40%</td>
</tr>
<tr>
<td>X_calc</td>
<td>4.722%</td>
<td></td>
<td>8.126%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y_calc</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>1193 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**2.3.1 García-Labiano reaction rate correlation (CGSM)**

Proposed by (García-Labiano et al. 2002) this model incorporates the adsorption mechanism based on the "Changing Grain Size" (CGSM) particle model. According to CGSM model each solid particle is composed of non-porous spherical grains, each one of them having a uniform initial radius, $r_0$. The rate of decomposition of each particle per unit of particle volume is given by the following correlation:

$$ RR = k_S (1 - \theta) f(P_{CO2}) $$  \hspace{1cm} (3)

The specific surface $S_e$ at a time instant $t_2$ is a function of the initial specific surface area $S_0$, the initial radius of the grains, $r_0$, and the radius of the unreacted core, $r_2$. The initial conditions correspond at the time instant $t=0$ before the start of the calcination. For reasons of simplicity, the present study assumes that $S_0 = S_e$.

$$ S_e = S_0 \left(\frac{r_2}{r_0}\right)^2 $$  \hspace{1cm} (4)

The CO2 partial pressure is calculated according to the following mathematical expression (Fuertes et al. 1993, Hu and Scaroni 1996):

$$ f(P_{CO2}) = (1 - \frac{P_{CO2}}{P_{eq}})^b $$  \hspace{1cm} (5)

with $1 < b < 2$. In the present work a value of $b=1$ was considered as the most appropriate for the calculations, in accordance with the work of (García-Labiano et al. 2002).
The equilibrium decomposition pressure $P_{eq}$ is calculated as (Silcox et al. 1989),

$$P_{eq} = 4.137 \times 10^{12} e^{(-20474/T)} \tag{6}$$

while the partial pressure of $P_{CO_2}$ is calculated as part of the solution of the CFD model for each cell in the 3-D computational domain.

The parameter $\theta$ expresses the fraction of active sites occupied by CO$_2$ given by an appropriate adsorption isotherm. The Freundlich isotherm is applied in the present work, i.e.

$$\theta = cP_{CO_2}^{1/\mu} \tag{7}$$

with $n = 2$

The kinetic rate constant, $k_c$, and the isotherm adsorption constant, $c$, are calculated according to Arrhenius law-based expressions:

$$k_c = k_0 e^{-E_c/RT} \tag{8}$$

$$c = c_0 e^{-E_a/RT} \tag{9}$$

The constants used in the above-mentioned expressions, Table 2, are dependent on the type of limestone calcined. Due to lack of experimental data for the specific limestone used, these values were taken from the work of García-Labiano for the Mequinenza limestone case (García-Labiano et al. 2002).

**Table 2** Values for the calcination reaction parameters

<table>
<thead>
<tr>
<th>Mequinenza limestone</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_c$</td>
<td>2.54 E+2</td>
</tr>
<tr>
<td>$\varepsilon_c$</td>
<td>1.31 E+5</td>
</tr>
<tr>
<td>$c_0$</td>
<td>3.70 E-7</td>
</tr>
<tr>
<td>$E_a$</td>
<td>-9.0 E+4</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>0.60</td>
</tr>
<tr>
<td>$S_0$</td>
<td>0.50 E+6</td>
</tr>
</tbody>
</table>

However, García-Labiano’s model is based on fresh limestones (limestones neither yet calcined nor carbonated), while the experimental data derived by USTUTT, Table 1, refer to a limestone which
has undergone several calcination-carbonation cycles. Thus, the reaction rate calculated is considered to have an overestimated value for the specific sorbent used. In order to achieve a more realistic value for the reaction rate a correcting factor was used, \( f_N = 0.08 \).

In the work of Martínez et al. (2012) it is reported that the value of the calcination reaction rate can decreased considerably (almost 10%) after several carbonation-calcination cycles (around to ten 10).

2.3.2 Martínez reaction rate correlation

A reaction rate correlation proposed by Martínez et al. (2012), based on the Shrinking Core Model (SCM), was also implemented in the present work. The general form of the calcination rate is given by the following expression:

\[
\frac{d(X_{\text{calc}} - X_{\text{calc}})}{dt} = RR = k_c \left(1 - \frac{X_{\text{calc}}}{X_{\text{calc}}}\right)^2 (C_{eq} - C_{CO_2})
\]

where

- \( X_{\text{carb}} \) is the CaCO\(_3\) content entering the calciner (mol of CaCO\(_3\) / mol of Ca),
- \( X_{\text{calc}} \) is the CaCO\(_3\) content exiting the calciner (mol of CaCO\(_3\) / mol of Ca),
- \( C_{CO_2} \) is the concentration of CO\(_2\) in the gas phase (kmol/m\(^3\)),
- \( C_{eq} \) is the equilibrium concentration of CO\(_2\) in the gas phase (kmol/m\(^3\)) and
- \( k_c \) is the kinetic rate constant of the CaCO\(_3\) calcination (m\(^3\) kmol\(^{-1}\) s\(^{-1}\)).

The equilibrium concentration of CO\(_2\) is calculated as follows:

\[
C_{eq} = \frac{1.462E + 11e^{-\frac{19130}{T}}}{T}
\]

where \( T \) is temperature calculated in K.

The kinetic rate constant is calculated according to Arrhenius law, given by the expression [8]. However, in the present work a specific value based on experimental data for the specific limestone calcined was delivered by USTUTT. That is \( k_c = 8.6 \times 10^{-2} \) (m\(^3\) kmol\(^{-1}\) s\(^{-1}\)).

The parameters \( X_{\text{calc}} \) and \( X_{CO_2} \) (out) are computed numerically for each computational cell and time step, which means that they are local variables. On the other hand, the \( X_{\text{carb}} \) parameter is a global variable, which means that it keeps a constant value (\( X_{\text{carb}} = 0.1285 \)) throughout space (at each numerical cell) and time.

2.4 Process modeling methodology

The thermodynamic analysis of the process at the ELWIRA reactor is accomplished in two case studies:

1) The first one has the same input parameters with the case study that is described in CFD analysis before, where only calcination is assumed to take place during the reaction. In this case, a
A continuous stirred tank reactor (CSTR) is used in order to calculate the carbonated solids decomposition accompanied by a solids/gas separator that represents the cyclone of the reactor.

For the reaction rate calculation, an algorithm in FORTRAN code has been set up, coupled with ASPEN Plus™, the simplified block diagram of which is shown in Fig. 3. The total quantity of CaO in the control volume (i.e. the reactor bed) is determined by the sum of the corresponding value at the previous time step, plus the CaO produced by from the calcination reaction in the reactor at the given time step and the difference of the lime entering the control volume with that of exiting. The time-loop ends when the time becomes equal to the solids residence time in the control volume, being determined by the following equation:

\[ t_{res} = \frac{\text{solids inventory, } N_{Ca} \text{ (kmol)}}{\text{solids recirculating, } n_{Ca} \text{ (kmol/s)}} \]  

(12)

The CO\(_2\) molar concentration at the reactor outlet, which is used at the next time step for the calculation of the mean CO\(_2\) concentration along the bed, is calculated according to CO\(_2\) mass balance in the control volume. For the reaction rate calculation, the (García-Labiano et al. 2002) approach, as described above, is chosen. Unlike the CFD analysis that is based on the mechanisms and phenomena that occur in small scale, the thermodynamic one examine the process in its entirety. Thus, for the partial pressure of CO\(_2\) that is required for the reaction rate calculation [eq 5], the average value along the bed is obtained. Since in the beginning of the calcination process only the \(P_{CO2}\) at the reactor inlet is known, the information about the fluctuation of CO\(_2\) molar concentration along the bed that is obtained from the CFD analysis is very useful for the accomplishment of the process simulations.

This first case of the thermodynamic analysis is essential in order to check the accuracy of the model for the prediction of the process outputs. The contribution of the CFD analysis to the setup of this thermodynamic model is of high importance, since useful information is obtained from this, are used as an input, i.e. the height of bed \((H_b)\), from which the bed volume is determined and the CO\(_2\) concentration spatial function along the bed’s height (i.e. linear) (see Fig. 6a), which is used for the calculation of its mean partial pressure of CO\(_2\) spatial distribution.
It should be mentioned that the majority of input data in this study such as the operating conditions (temperature, $X_{\text{carb}}$ and inlet flow rates) and reactor parameters such as bed inventory and solid residence time are obtained from the corresponding experimental campaign. The CFD analysis has contribution to the indication of CO$_2$ concentration behavior along the bed (i.e. linear one) and the more precise bed volume. In case that no such experimental data are available (as for the case of large scale units under in the design phase), all the aforementioned data can be provided exclusively from the CFD analysis.

2) In the second case study, a fuel combustion step is as well included, so that isothermal conditions within the reactor are sustained. The process flow sheet diagram of the model developed in ASPEN Plus™ is shown in Fig. 4.
The calciner modeling comprises of a continuously stirred tank reactor, where the calcination reaction takes place in a stoichiometric ratio (RSTOIC reactor) for the fuel combustion along with a cyclone for gas-solid separation.

The combustible fuel is assumed to be methane, the selection of which is owed to two main reasons:

1. The reactor that is investigated in this study is a pilot scale bubbling fluidized bed and the implementation of other fuel types, but natural gas cannot be technically supported. Hence, the comparison with experimental data in this pilot reactor can be performed in future, only if methane is considered as fuel.

2. Other phenomena or reactions that are related to solid fuels and occur in an industrial scale calciner like desulfurization, combustion efficiency or effect of ash on combustion characteristics and mixing, are too complicated and cannot be supported in detail by this study's approach.

Regarding the combustion modeling, it is assumed a complete CH$_4$ conversion in the RSTOIC reactor and the flow rate of the required fuel is set as enough to secure autothermal conditions in the calciner ($Q_{cal}=0$). The oxygen equivalence ratio is set equal to 1.05.

A major issue in the calciner modeling, including both calcination and combustion reactions, is the determination of the CO$_2$ concentration value that is taken into account at the calcination reaction rate. This is the only operational parameter that determines the calcination reaction rate and varies significantly in space and time. This is due to the fuel combustion mechanism, where CO$_2$ is produced and O$_2$ is consumed at the same time, increasing considerably the rate of carbon dioxide concentration, ($\frac{dC_{CO_2}}{dt}$). In this study, a first attempt to take into account calcination and combustion reactions in the calciner simultaneously beyond the equilibrium methodology is made, so the $y_{CO_2}$ after the complete methane combustion is considered for the reaction rate calculation.
3. Results and Discussion

3.1 CFD modelling
3.1.1 Kinetics of Calcination Reaction

Two reaction rates based on Labiano and Martínez study respectively were applied and evaluated against experimental data derived by USTUTT. In both cases, as a first approximation the Gidaspow conventional scheme was implemented for the calculation of the drag force exerted on the solid particles.

Numerical results using García-Labiano’s correlation

Figs. 5a and 5b, depict the corresponding spatial distributions of CO$_2$ and CaCO$_3$ mass fractions at a time instant $t_1=67.42$ sec after the start of calcination and for a time averaging equal to $t_{1\text{aver}}=8.5$ sec, with the implementation of the reaction rate based on Labiano approach along with a correction factor equal to $f_N=0.08$, as aforementioned. The distribution of CO$_2$, depicted in Fig. 6., which was used as an input for the thermodynamic model, is linear along the bed, The height of the bubbling bed, which is an additional important parameter used as an input for the thermodynamic model is approximately $H_b=0.43$m, Fig. 6c.

**Fig 5a.** CO$_2$ mean mass fraction at plane X=0, for a time averaging equal to $t_{1\text{aver}}$.  
**Fig 5b.** CaCO$_3$ mean mass fraction at plane X=0, for a time averaging equal to $t_{1\text{aver}}$.  

![Image of CO$_2$ and CaCO$_3$ mass fractions](image-url)
Numerical results using Martínez’s correlation

The following Figures, depict the corresponding spatial distributions at time $t_2=67.58$ sec after the start of calcination and for a time averaging of $t_{2\text{aver}}=8.5$ sec, with the implementation of the reaction rate based on Martínez approach and with a kinetic rate constant calculated for the specific sorbent used in ELWIRA unit.
The results of the CFD simulation for each reaction rate used above and the corresponding experimental data are presented in the following table. As comparison data for $Y_{CO2}$, the CO$_2$ averaged mass fraction at a height $z=1.4$m from the bottom of the riser was taken, where $Y_{CO2}$ has reached an almost constant value.

<table>
<thead>
<tr>
<th>Experimental Data</th>
<th>García-Labiano correlation, $f_N=0.08$</th>
<th>Martínez correlation (exponential factor derived from USTUTT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y_{calc}$</td>
<td>8.126%</td>
<td>5.66%</td>
</tr>
<tr>
<td>$Y_{CO2}$</td>
<td>61.4%</td>
<td>63.73%</td>
</tr>
</tbody>
</table>

From table [3], it is concluded that the reaction rate based on Labiano theory with $f_N=0.08$ gives results closer to the experimental data. The reaction rate based on Martínez failed to reproduce accurate results and it seems to be inappropriate for a CFD analysis. The most plausible explanation for this lies on the fact that the reaction rate based on Martínez theory is considered to be not applicable for a CFD model. This is owed to the inclusion of the parameter $X_{carb}$, which is a global and not local parameter.

In the case of process modeling this is not a problem as all the parameters are calculated globally. However, in the case of the CFD analysis the reaction is calculated locally for each cell at the computational grid. With this globally measured parameter used in the expression for the reaction rate ($X_{carb}$), the calculated reaction rate at each computational cell is greater than the real one and as a result the calculated CO$_2$ is higher than the actual one. For all the above reasons the flow in the case of the Martínez reaction rate could not reach steady state conditions with an acceptable accuracy in terms of CO$_2$ calculation. The results presented in the case of the specific reaction rate do not correspond to a steady solution. However, they were presented in order to demonstrate the high amount of CO$_2$ released with the implementation of the Martínez reaction rate. The respective results for the Labiano reaction rate presented correspond to steady state conditions.

### 3.1.2 Drag Force Model Implementation

Two drag force model schemes were evaluated against experimental data. The EMMS minimization problem was solved prior to the CFD simulation and the results for the heterogeneity index were properly introduced in the numerical problem. The results are presented in the following table for the same time averaging. As it can be seen, Table 4, the implementation of EMMS scheme does not affect significantly the derived results, when compared to the ones produced with the Gidaspow’s application, as the values of $Y_{CO2}$ are almost equal for both drag schemes used. However, at the bubbling bed area the CO$_2$ averaged mean mass fraction profiles are different for Gidaspow and EMMS drag schemes implemented. This is owed to the fact that the hydrodynamics of the solid and subsequently of the gas phase flow depend on the drag force scheme implemented. The results for the EMMS case are of higher accuracy and as a result the advanced EMMS scheme is considered to be more appropriate for the calculation of the drag force exerted on the solid particles.
Table 4 Comparison between Gidaspow and EMMS drag schemes

<table>
<thead>
<tr>
<th></th>
<th>Reference case process data</th>
<th>Results for Labiano Case with ( f_N = 0.08 ) and EMMS</th>
<th>Results for Labiano Case with ( f_N = 0.08 ) and Gidaspow</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Y_{calc} )</td>
<td>8.126%</td>
<td>5.78%</td>
<td>5.66%</td>
</tr>
<tr>
<td>( Y_{co2} )</td>
<td>61.4%</td>
<td>63.19%</td>
<td>63.73%</td>
</tr>
</tbody>
</table>

Fig 8a. \( \text{CO}_2 \) averaged mean mass fraction at plane X=0, for a time averaging \( t_{aver} \), with Gidaspow drag scheme.

Fig 8b. \( \text{CO}_2 \) averaged mean mass fraction at plane X=0, for a time averaging \( t_{aver} \), with EMMS drag scheme.

From all cases studied it is concluded that due to bubbling formation - the calciner operates under the bubbling fluidized bed regime - there is a reduction in the efficiency of the limestone regeneration, due to high concentration of \( \text{CO}_2 \) entrapped, thus reducing significantly the calcination rate. This drawback of a bubbling fluidized reactor is as well observed during the experimental campaigns, conducted by USTUTT personnel. Therefore, it should be stressed out that such a calciner should operate in the fast and not in the bubbling regime. Moreover, it is concluded that the decomposition most of the limestone happens at the bottom zone of the riser. This is depicted in Fig. 9, where the reaction rate gets a maximum value at this area.
3.2 Process modelling

The model accuracy against the corresponding data provided by the experiments is depicted in Fig. 10 where the temporal evolution of sorbent regeneration is shown, reflected by the decrease of limestone content in the sorbents ($X_{calc}$) and the increase of CO$_2$ mole fraction ($y_{CO2}$) in the gas outlet. The proposed calcination model based on (García-Labiano et al. 2002) is considered to be quite accurate as there is a good agreement with the corresponding experimental values of $X_{calc}$ and CO$_2$ volume fraction at the reactor outlet ($y_{CO2}$). Additionally, the $X_{calc}$ and the resulting CO$_2$ concentration values at the exit of the calciner show an almost linear dependency on solids residence time. It should be pointed out that the equilibrium approach at this case study predicts complete regeneration of the limestone (Vorrias et al. 2013), which is quite far from the reality, as it is depicted from the experimental data.

![Fig 9. Reaction Rate of Calcination for Labiano Case](image)

**Fig 9.** Reaction Rate of Calcination for Labiano Case

![Fig 10.](image)

**Fig 10.** Temporal evolution of CO$_2$ molar fraction and $X_{calc}$ in the calciner outlet and comparison with the corresponding experimental values.
The sensitivity analysis that follows refers to the first case study (inlet gas mixture of CO\textsubscript{2} /N\textsubscript{2}), where the combustion effect on the calciner operation, is not considered. Fig. 11 presents the impact of mass of bed on the calcination process. A linear increase of the calcination efficiency, with the bed inventory is observed, as it is illustrated by the CO\textsubscript{2} concentration at the outlet and the $X_{\text{calc}}$ drop. At the same time, under real conditions, where fuel combustion should be as well considered, the elevated bed inventories, as the sorbents decomposition is performed with higher rate, more fuel is required in order to overbalance the heat required for calcination. On the other hand, greater bed inventories imply greater reactor size, an issue that increases the capital investment cost and is associated with higher power consumptions for the fluidizing agent boosting, increasing in turn the operational cost.

![Fig 11. Effect of bed inventory on the calcination process ($X_{\text{carb}}=12.85\%$, $T_{\text{calc}}=1173\text{K}$). The black and grey bullets refer to the corresponding values of the base case.](image)

The following sensitivity analysis refers to the model case that takes into account the fuel combustion in the reactor. The effect of the operational temperature on the process is depicted in Fig. 12. The shape of fuel demand curve resembles to an exponential curve (Fig. 12a). This behavior of fuel demand, as the calciner temperature increases, is justified by the increase of both the sensible heat and the reaction heat, the values of which are greater at elevated temperatures owed to the endothermic nature of the reaction. The calcination efficiency is considerably enhanced for temperatures greater than 870 \textdegree C, as it is illustrated by the descending behavior of $X_{\text{calc}}$ and the specific heat demand curves, (Fig. 12b).
4. Conclusions

This study presents the approaches for the modeling of a lab scale bubbling reactor (calciner) using CFD and process simulation tools.

In the frame of the CFD analysis the calcination kinetics and drag force modeling were investigated. Firstly, two reaction rates obtained through the most recent literature were implemented. The one based on Labiano theory proved to be more appropriate for a CFD simulation than the one based on Martínez study. Subsequently, the influence of the drag force model on the numerical results was investigated. The two drag force models implemented, an homogeneous and an heterogeneous one, indicated that in the case of the bubbling calciner the drag force scheme does not have great influence on the numerical results. However, the results for the EMMS case are of higher accuracy and as a result the advanced EMMS scheme is considered to be more appropriate for the calculation of the drag force exerted on the solid particles. Finally, in all cases investigated there was a reduction in the efficiency of the calcination due to the formation of bubbles, which is attributed to the fact that \( \text{CO}_2 \) is trapped inside the bubbles.

From the process modeling analysis, a CaL process model that incorporates a rigorous approach for the calcination reaction is presented showing a very good agreement with the experimental data related to the \( X_{\text{calc}} \) and \( y_{\text{CO}_2} \) at the calciner outlet. The kinetic-based approach for calcination modeling in lab scale reactor was proved more accurate than the equilibrium-based approach that is mainly followed in such cases. The simulations reveal that bed inventories in the reactors strongly affect the performance of the process. Higher capture rates in the carbonator impose higher bed inventory in the calciner in order to achieve a certain \( X_{\text{calc}} \) value. A minimum calcination temperature for sufficient sorbents decomposition is suggested at 870\( ^\circ \)C.

This a first try that couples these two numerical tools (CFD and process modeling) for the better comprehension of the Calcium loop process. A modified and more detailed approach will be followed in future studies so that to be very useful for large scale and industrial applications.
Acknowledgements

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Nomenclature

c  isotherm adsorption constant
C_{D0,f}  static drag coefficient in the dilute phase, -
d_s  particle diameter, m
E_{calc}  calciner efficiency, -
E_{carb}  carbonator efficiency, -
E_{CO2}  total carbon capture efficiency, -
f_{active}  fraction of active particles
F_{CO2}  CO_2 flow rate, kmol/s
F_0  fresh limestone flow rate, kmol/s
F_{Ca}  Ca solids looping flow rate, kmol/s
F_R  CaO solids looping flow rate, kmol/s
H_b  height of the bed, m
H_d  heterogeneity index, -
k_{s,B}  surface carbonator rate constant, s^{-1}
k_c  calcination reaction rate constant
m_{Ca}  mass inventory, kg
n  exponential factor
n_{Ca,inv}  Ca particles in the inventory, kmol
Q_i  heat load, kW_{th}
p  pressure, Pa
r  grain radius, m
R  ideal gas constant, 8314 kJ/mol K
RR  reaction rate, kmol/ m^3 s^{-1}
S_e  surface constant
t^*  critical reaction time, s
t  time instant, s
T  temperature, K
u_g  real velocity of gas phase, m/s
u_s  real velocity of solid phase, m/s
X_{ave}  maximum average conversion of solids in the carbonator, -
X_{calc}  limestone content in the solids after the calciner, kmol CaCO_3/kmol Ca
X_{carb}  limestone content in the solids after the carbonator, kmol CaCO_3/kmol Ca
X_{CO2(in)}  mole fraction of CO_2 entering the calciner, kmol CO_2/kmol gas
X_{CO_2(out)} \text{ mole fraction of CO}_2 \text{ exiting the calciner, kmol CO}_2/\text{kmol gas}

X_{N_2} \text{ mole fraction of N}_2 \text{ in the gas phase, kmol N}_2/\text{kmol gas}

Y_{calc} \text{ limestone content in the solids after the calciner, kg CaCO}_3/kg Ca

Y_{carb} \text{ limestone content in the solids after the carbonator, kg CaCO}_3/kg Ca

Y_{CO_2(in)} \text{ mass fraction of CO}_2 \text{ entering the calciner, kg CO}_2/kg gas

Y_{CO_2(out)} \text{ mass fraction of CO}_2 \text{ exiting the calciner, kg CO}_2/kg gas

Y_{N_2} \text{ mass fraction of N}_2 \text{ in the gas phase, kg N}_2/kg gas

Greek letters

\beta \text{ momentum exchange coefficient, kg/(m}^3\text{s})

\varepsilon_g \text{ volume fraction of gas phase, m}^3\text{gas}/m^3\text{cell volume}

\varepsilon_s \text{ volume fraction of solid phase, m}^3\text{solid}/m^3\text{cell volume}

\theta \text{ Freundlich isotherm}

\mu_g \text{ viscosity, kg/m s}

\rho_s \text{ gas density, kg/m}^3

\rho_s \text{ solid density, kg/m}^3

\tau \text{ space time, s}

\phi \text{ gas-solid contacting factor, -}

References


