Analysis of the calcium looping system behavior by implementing simple reactor and attrition models at a 10 kW$_{th}$ dual fluidized bed facility under continuous operation

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HIGHLIGHTS

- A Ca looping pilot is analyzed by using simplified reactor and attrition models.
- Predicted and experimental data from the 10 kW$_{th}$ pilot are discussed.
- Model lines fit well to the experimental data.
- The main impact on the Ca-L performance is found to be the water vapor presence.
- The mean particle size of the limestone is observed to be unchanged.

ARTICLE INFO

ABSTRACT

In this work simplified kinetic and attrition models empirically oriented are implemented in the experimental results of the 10 kW$_{th}$ dual fluidized calcium looping facility at University of Stuttgart. The experimental data used are resulted from continuous operation of a calcium looping facility under conditions close to the industrial ones: wet atmosphere in the carbonator and oxyfired conditions in the regenerator (water vapor presence and high CO$_2$ volume concentration). The scope of work is to extend the knowledge on the calcium looping systems and to further validate tools which are useful for upscaling purposes as well as for interpretation of experimental results of pilot plants. By using simplified theoretical expressions, the efficiency of the carbonator and the regenerator in terms of CO$_2$ capture and sorbent calcination conversion respectively is related to the parameter of active space time. The evolution of the particle size of the lime in the course of the process is studied. Fitting constants are applied and a good agreement between the predicted and the actual values of the main process parameters is recorded. The effect of the water vapor presence in both calcination and carbonation reaction is discussed. Results showed CO$_2$ capture of more than 90% while the carbonator active space time was less than 30 s. Almost full sorbent calcination was recorded while the regenerator active space time was less than 0.11 h. During many hours of carbonator and regenerator operation, a constant particle size of around 400 μm was measured.

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1. Introduction

Calcium looping or carbonate looping is the process that makes use of the ability of calcium to capture and release CO$_2$. It is a techno-economically promising CO$_2$ capture technology that can contribute to the challenge of dealing with global warming and simultaneously providing affordable energy. The configuration as proposed by Shimizu et al. [1] is shown in Fig. 1 (left) and is based on the chemical reaction of Eq. (1):

$$CaO_{(s)} + CO_{2(g)} \Longleftrightarrow CaCO_{3(s)}, \ \Delta H_{25°C} = 178.2 \ kJ/mol \qquad (1)$$
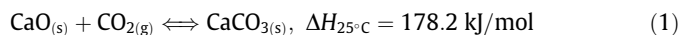
For the industrialization of the technology, pre-design and construction of pilot plants, modeling work is required to minimize the financial risk of the construction of such a unit. In this direction a lot of experimental work is performed achieving CO$_2$ capture efficiencies of more than 90% under continuous operation. This work is promoting the technological maturity of the process and is providing data for further upscaling purposes: (1) at several apparatus

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Nomenclature

$C_{CO_2,eq.}$	equilibrium concentration of CO_2 at the gas phase (mol/m^3)
C_{CO_2}	concentration of CO_2 at the gas phase mol/m^3
d_p	mean particle diameter mm
d_{p0}	initial mean particle size (mm)
d_{pmin}	minimum mean particle size (mm)
$\frac{dX_{carb}}{dt}$	carbonation reaction rate (1/s)
$\frac{dX_{calc}}{dt}$	calcination reaction rate (1/s)
E_{carb}	carbonator CO_2 capture efficiency (–)
E_{reg}	regenerator efficiency – CO_2 release (–)
$F_{CO_2,in}^{carb}$	carbonator CO_2 inlet flow (mol/s)
$F_{CO_2,r.}$	regenerator CO_2 recycle (mol/s)
F_{Ca}	Ca looping rate between the reactors (mol/s)
F_0	make up flow of $CaCO_3$ (mol/s)
$f_{active,carb}$	fraction of particles available for carbonation (–)
$f_{active,reg}$	fraction of particles available for calcination (–)
k_{calc}	calcination particle kinetic constant (1/s)
k_{carb}	carbonation kinetic constant (s^{-1})
$k_{carb} \cdot \phi_{carb}$	apparent rate carbonator constant (s^{-1})
k_{calc}	kinetic constant of $CaCO_3$ calcination $(m^3\,mol^{-1}\,s^{-1})$
$k_{calc} \cdot \phi_{reg}$	apparent rate regenerator constant $(m^3\,mol^{-1}\,s^{-1})$
K_a	attrition constant (m^2/s^{-3})
k	sorbent deactivation constant (–)
k_D	proportional constant in Eq. (14) (–)
$n_{ca,carb}$	amount of Ca in the regenerator (mol)
$n_{ca,reg}$	amount of Ca in the regenerator (mol)

N	number of calcination/carbonation cycles (–)
t_{carb}^*	time for sorbent carbonation conversion up to $X_{max,ave}$ (s)
t_{calc}^*	time for full lime calcination ($X_{calc} = 0$) (s)
$V_{CO_2,eq.}$	vol. fraction of CO_2 at the gas phase at equilibrium conditions (–)
V_{CO_2}	vol. fraction of CO_2 at the gas phase (–)
U	velocity of the solid phase (m/s)
U_{mf}	minimum fluidization velocity of the solid phase (m/s)
X_{carb}	sorbent carbonate content entering the regenerator (mol $CaCO_3$/mol Ca)
X_{calc}	sorbent carbonate content exiting the regenerator (mol $CaCO_3$/mol Ca)
$X_{max,ave}$	average maximum carbonation conversion (mol $CaCO_3$/mol Ca)
X_r	residual CaO conversion
X_{KN}	CaO molar conversion under the fast reaction regime
X_{DN}	CaO molar conversion under the diffusion controlled regime
τ_{carb}	carbonator space time (s)
τ_{reg}	regenerator space time (s)
$\tau_{active,reg}$	regenerator active space time (s)
$\tau_{Carb,KD}$	carbonator space time including both kinetic and diffusion regime (s)

[2–4] and facilities including the 10 kW$_{th}$ at University of Stuttgart [5–10], the 30 kW$_{th}$ at INCAR-CSIC [11–15] and the 75 kW$_{th}$ at CANMET [16] (2) at pilot scale including the 0.2 MW$_{th}$ at University of Stuttgart, the 1 MW$_{th}$ at Technical University of Darmstadt and the 1.7 MW$_{th}$ at La Pereda [17–22].

On the other hand several scientific groups have proposed various models from simple process ones up to computational fluid dynamics (CFD) simulations [23–36]. All these models are based on assumptions and simplifications nevertheless they increase the possibilities of a prototype technology to be realized industrially with a minimized financial risk.

In this frame, the first part of this paper deals with the study of the carbonator CO_2 capture efficiency and the regenerator efficiency – CO_2 release, of the 10 kW$_{th}$ dual fluidized bed calcium looping system at University of Stuttgart. For this purpose the models proposed by Alonso et al. [23] for the carbonator and Martínez et al. [24] for the regenerator are used. Both models are based on a simple fluid dynamic approach combined with a kinetic model for the carbonation and the calcination reaction respectively. Charitos et al. [7] and Duelli et al. [8] used the model of Alonso et al. [23] to characterize the carbonator under high and

low CO_2 volume concentration in the regenerator (representative of an air or oxyfuel combustion) in dry conditions. This work extends the work of [7] as it includes operation in wet conditions for both carbonator and regenerator and also high volume concentration of CO_2 (around 75 vol.%) characteristic of the oxy-fired regenerator. Moreover the experimental data used are referring to a different limestone as the one used in previous experiments [7,8]. Finally, the model of Martínez et al. [24] is implemented in the regenerator and is used to analyze the reactor performance in terms of limestone calcination conversion through the regenerator active space time. The regenerator active space time is a parameter that includes the particle residence time in the reactor, the carbonate content of the incoming solids and the carbonation conversion of solids in the reactor. In the second part of this work, the sorbent attrition is investigated through the study of the evolution of the particle size in the progress of time. Simple empirical correlations proposed by Cook et al. [36] and already used by [15] analyzing attrition at a 30 kW$_{th}$ calcium looping plant at INCAR-CSIC, are applied to experimental data. An experimental attrition constant for the limestone and the experimental set-up is presented and compared to the values reported by the literature.
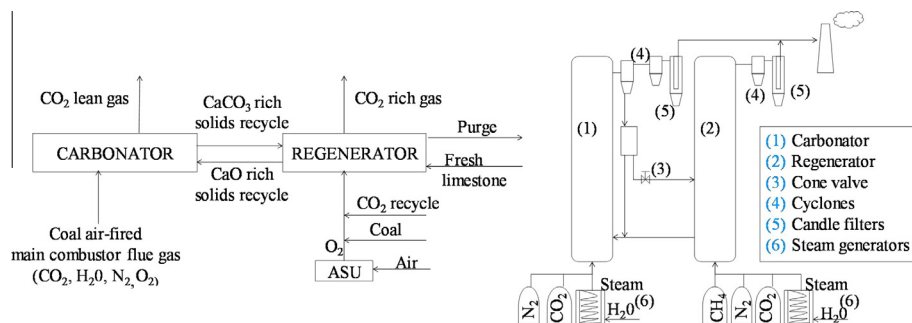

Fig. 1. The calcium looping simple process schematic (left) and the realization at the 10 kW$_{th}$ dual fluidized bed system at University of Stuttgart (right).