STUDIA UBB CHEMIA, LVIII, 3, 2013 (p. 7 – 18)
(RECOMMENDED CITATION)

DYNAMIC MODELING OF CARBONATOR FROM CALCIUM-LOOPING PROCESS USED FOR CARBON CAPTURE

ANA-MARIA CORMOS[a], ABEL SIMON[a]

ABSTRACT. Carbon capture and storage (CCS) technologies are mitigation measures aimed to reduce CO_2 emissions from energy and other energy-intensive sectors. Among various CCS technologies, chemical looping systems (e.g. the calcium-looping process) are considered as potential solutions to reduce CO_2 capture energy penalty. The paper presents a dynamic mathematical model of carbonation reactor of calcium-looping process to be used for carbon capture in fossil fuel-based power plants. The mathematical model described the particle distribution in carbonator according a 1D model for fast fluidization presented by Kunii and Levenspiel. The CO_2 adsorption efficiency in the carbonator is divided in two terms taking into account the dense and lean regions of the bed.

Keywords: *carbon capture, Ca-looping process, dynamic mathematical modeling*

INTRODUCTION

Power generation sector which use fossil fuels (coal, lignite, natural gas etc.) is a major contributor to the increase of carbon dioxide concentration in the atmosphere and it consequently leads to global warming [1]. In order to limit the climate change modifications, it is now widely recognized that large-scale reductions in carbon dioxide (CO_2) emissions are required. However, the first generation CCS technology, i.e. scrubbing with amines, is energy intensive [2] and, thus, results in a substantial decrease in the overall plant efficiency (in the range of 10 net electrical percentage points [1]). To reduce the costs associated with the capture of CO_2, 2nd and 3rd generation CCS technologies, such as carbonate looping or chemical looping combustion (CLC) have been proposed [3]. The basic idea of the calcium looping process is to use calcium oxide as sorbent of CO_2, through the theoretically reversible, reaction: $CaO + CO_2 \leftrightarrow CaCO_3$.

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[a] *Babeş-Bolyai University, Faculty of Chemistry and Chemical Engineering, Arany Janos 11, RO-400028 Cluj-Napoca, Romania, cani@chem.ubbcluj.ro*

The use of a Ca-based sorbent as a CO_2 acceptor was first patented in 1933 and assessed by other scientists for sorption–enhanced hydrogen production [4], the application of a Ca-based sorbent in a post-combustion configuration was first proposed by Shimizu et al. (1999) [5]. The experimental validation of the Ca- looping concept has progressed rapidly. The experimental investigating of the cyclic CO_2 capture process occurring limestones have been performed in different reactor set-ups, e.g. thermogravimetric analysers [6,7], packed bed reactors [8, 9] or fluidized bed reactors [10-13] a rapid decrease in CO_2 uptake with number of repeated cycles of carbonation and calcination was reported.

In fluidized bed reactors configuration, carbon dioxide in the flue gas of a coal-fired power plant is captured by its reaction with calcium oxide in a fluidized bed reactor (carbonator) and removed at high temperature from the gaseous phase by producing $CaCO_3$. After heat recovery, decarbonized flue gas is vented in to the atmosphere, while calcium carbonate converted back into CaO and gaseous CO_2 in a calciner. The regenerated sorbent produced in the calciner is then returned to the carbonator for a new sorption cycle, while the CO_2-rich gas is cooled and compressed for permanent storage after final purification (figure 1).

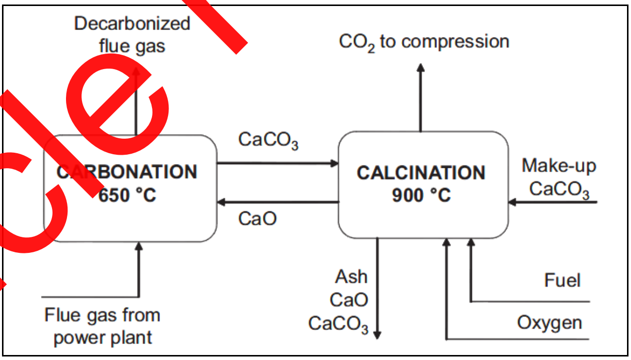

Figure 1. Scheme of the carbonate looping process [14]

Some studies on plant modeling and simulation have also been published to estimate the performance of complete power plants, which confirm the inherent thermodynamic advantages of the Ca-looping concept [5, 14, 15]. Abanades et al. [11] adapted the model proposed by Kunii and Levenspiel [16] for two-region reactor: bubble and emulsion to the conditions of the experiments carried out in a fluidised bed carbonator and included a full kinetic model for the carbonation reaction in two stages proposed by Bhatia and Perlmutter [17]. According to this kinetic model, carbonation reaction takes places in two stages at different reaction rate: a first regime of chemical reaction control where reaction occurs at the highest velocity and a second period of product layer diffusion control due to the fact that the $CaCO_3$ layer thickness increases. The models proposed by Hawthorne et al. [18]; Lasheras et al. [14] and Romano [19] have been based on the core-annulus model of Kunii and Levenspiel [20] and considered the reactor as a circulating fluidized bed where two zones were distinguished: a bottom dense zone and a lean one located above. The most detailed reactor model has been considered which was developed by Romano (2012) [19] that evaluated the CO_2 concentration profiles in the core and wall zone of the dense part, and the CO_2 profile in the lean zone. But a detailed dynamic model to describe the dynamic behaviour have not presented. Using modelling and simulation methods, the potential applications of calcium based chemical looping system to generate simultaneously hydrogen and power with almost total decarbonisation of the coal was investigated too [21]. The goal of this paper is to develop and validated against experimental data published in literature a dynamic model of the carbonator of a Ca-looping process and to investigate the effects of different operating conditions on its performance.

MATHEMATICAL MODELING

The mathematical model of carbonator is expressed by referring to an ideal plug-flow reactor and includes partial differential equations (PDE) to describe the time and space dependent parameters [19].

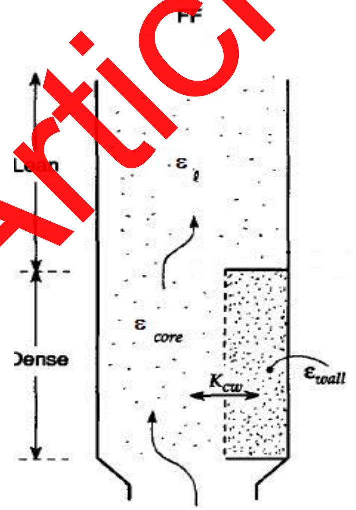

Figure 2. Particle distribution in the carbonator

The particles distribution in the carbonator is determined by a 1D model for fast fluidization as presented by Kunii and Levenspiel [16]. In this model, the reactor is divided into two regions: the dense region, in the lower part of the riser, where the volume fraction of the solids, ε_{sd} is constant, and the lean region where the volume fraction of solids decreases exponentially with height. In the dense zone, ε_{sd} value depends on the superficial velocity u_0 and the mean particle diameter d_p. In case of fast fluidization for ε_{sd} value a ranges 0.06–0.2 has been suggested by Kunii and Levenspiel [20]. The radial distribution consists of dense bottom zone is divided in two: a leaner core zone and a denser wall zone with solid volumetric fractions of ε_{sc} and ε_{sw}, respectively, figure 2 [16,20].

The hydrodynamics of circulating fluidized beds

Given the total reactor height H_t, the lean and dense zone height H_l, H_d and mass of solids in each zone W_l, W_d could be determinate using the following equations [20].

$$H_l = \frac{1}{a} \ln \frac{(\varepsilon_{sd} - \varepsilon_s^*)}{(\varepsilon_{se} - \varepsilon_s^*)} \tag{1}$$

$$H_d = H_t - H_l \tag{2}$$

$$W_d = A_t \rho_s H_d \varepsilon_{sd} \qquad W_l = A_t \rho_s H_l f_l \tag{3}$$

where

$$f_l = \varepsilon_s^* + \frac{\varepsilon_{sd} - \varepsilon_{se}}{H_l a} \tag{4}$$

The decay constant (a) used in equation 4 is determined from the values ranging from 2 to 7 s^{-1} proposed for the constant au_0 [20].

The volume fraction of solids at the reactor exit ε_s* could be determinate by following equation:

$$\varepsilon_{se} = \frac{G_s^*}{(u_0 - u_T) \cdot \rho_s} \tag{5}$$

$$\varepsilon_s^* = \frac{G_s^*}{u_0 \cdot \rho_s} \tag{6}$$

The mass velocity of solids at the exit of the riser G_s^* can be calculated as a function of terminal velocity u_T and superficial gas velocity u_0, assuming spherical particles [22].

$$G_s^* = 23.7 \rho_g u_0 \exp\left(-5.5 \frac{u_T}{u_0}\right) \tag{7}$$

The terminal free-fall velocity u_T, depends on the particle diameter d_p, solid and gas density ρ_s, ρ_g and the viscosity μ of the gas under the given conditions [20].

$$d_p^* = d_p \left[\frac{\rho_g (\rho_s - \rho_g) g}{\mu^2} \right]^{1/3} \tag{8}$$

$$u_T^* = \left[\frac{18}{\left(d_p^*\right)^2} + \frac{0{,}591}{\left(d_p^*\right)^{1/2}} \right]^{-1} \tag{9}$$

$$u_T = u_T^* \left[\frac{\mu\left(\rho_s - \rho_g\right)g}{\rho_g^2} \right]^{1/3} \tag{10}$$

Mass balance

The particle conversion model proposed by Grasa et al. [23] similar to that proposed by Bhatia and Perlmutter [17] is used in this work. According to this model, the correlation which defines the carbonation degree *X* can be expressed according to a first order kinetic law where the kinetic constant k_r is a function of the carbonation degree itself [19].

$$\frac{\mathrm{d}X}{\mathrm{d}t} = k_r\left(C_{CO_2} - C_{CO_2,eq}\right) = k_s S_N (1-X)^{2/3}\left(C_{CO_2} - C_{CO_2,eq}\right) \tag{11}$$

On base of particle conversion model the material balance for the lean region is:

$$\frac{\mathrm{d}\left(C_{CO_2} - C_{CO_2,eq}\right)}{\mathrm{d}t} = -u_0 \frac{\mathrm{d}\left(C_{CO_2} - C_{CO_2,eq}\right)}{\mathrm{d}z} - \xi\varepsilon_{sl}\eta_l k_{ri}\left(C_{CO_2} - C_{CO_2,eq}\right) \tag{12}$$

The dense region is divided into a wall and core region, where the material balances are described bellow.
For core zone:

$$\begin{aligned} \frac{\mathrm{d}\left(C_{CO_2,c} - C_{CO_2,eq}\right)}{\mathrm{d}t} = &- \\ &- u_c \frac{\mathrm{d}\left(C_{CO_2,c} - C_{CO_2,eq}\right)}{\mathrm{d}z} - \frac{\xi V_{s,c}}{V_{g,c}} k_{ri}\left(C_{CO_2,c} - C_{CO_2,eq}\right) - \\ &- k_{cw}\left(C_{CO_2,c} - C_{CO_2,w}\right) \end{aligned} \tag{13}$$

For wall zone:

$$\begin{aligned} A_{g,w}\frac{\mathrm{d}\left(C_{CO_2,w} - C_{CO_2,eq}\right)}{\mathrm{d}t} = &- \\ &- A_{g,w}u_w \frac{\mathrm{d}\left(C_{CO_2,w} - C_{CO_2,eq}\right)}{\mathrm{d}z} - A_{g,w}\frac{\xi V_{s,w}}{V_{g,w}} k_{ri}\left(C_{CO_2,w} - C_{CO_2,eq}\right) + \\ &+ A_{g,c}k_{cw}\left(C_{CO_2,c} - C_{CO_2,w}\right) \end{aligned} \tag{14}$$

where,

$$k_{ri} = \frac{k_r \rho_s}{M_s} \tag{15}$$

and ξk_{ri} - is the kinetic and volume ratio between the potentially active solids (CaO and $CaCO_3$) and the total solids [19]. By combining the developed model of process with an optimization algorithm and the experimental data published by Charitos et al. in 2011 [24], the ξk_{ri} values was been estimated.

The equilibrium CO_2 concentration ($C_{CO2,eq}$) is express by equilibrium pressure the equation proposed by Garcıa-Labiano [25] (equation 16).

$$p_{CO_2,eq} = 4.137 \cdot 10^{12} \exp\left(-\frac{20474}{T}\right) \tag{16}$$

RESULTS AND DISCUSSION

The mathematical model developed has been implemented in the equation oriented numerical computing environment Matlab/Simulink 2008. The dynamic model of carbon dioxide capture by Ca-looping has been validated with data collected from pilot plant, published by Charitos et al. [24] and Rodriguez et al. [12].

A summary of the fluidization column characteristics and operating data, used in this work is presented in Table 1 [19, 20, 24].

Table 1. Model parameters

Parameter	Carbonator
Mean particle size, d_p [μm]	170/350
Height, H_t [m]	12.4
Diameter, D [m]	0.07
Gas velocity, u_0 [m/s]	4 - 6
Inlet CO_2 concentration, C_{CO2in} [mol/m^3]	1.48
Temperature, T [°C]	650
Pressure, p [bar]	1
Fluidization regime	Fast

In Table 2, decay of the CO_2 carrying capacity, X_N, vs. the carbonation/ calcination cycle number N, for the German limestone used by IFK pilot plant [12] and value calculated by process simulator is presented.

Table 2. Pilot plant data and simulated results

	N = 1		*N* = 5		*N* = 10		*N* = 20	
	exp	sim	exp	Sim	exp	Sim	exp	sim
$C_{CO2,in}$ [mol/m^3]	1.4856	1.4856	1.4856	1.4856	1.4856	1.4856	1.4856	1.4856
$C_{CO2,out}$ [mol/m^3]	0.624	0.6934	1.07	1.1036	1.203	1.221	1.307	1.3058
X [-]	0.58	0.53	0.28	0.26	0.19	0.18	0.12	0.12

The superficial velocity of the gas has a major effect on the particle distribution in the fast fluidized bed [20]. The height of the dense region decreases with the increasing of the superficial velocity of the gas. The most of the carbonation reaction takes place in the dense region, therefore at smaller superficial gas velocities much higher carbonation degree can be achieved (Figure 3).

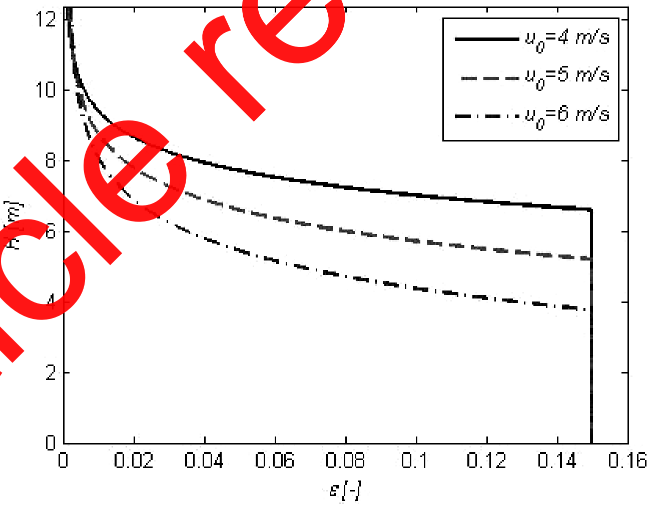

Figure 3. Vertical distribution of solid with variable superficial gas velocity

The particle diameters of the solid have effect on the particle distribution in the fast fluidized bed [21]. The height of the dense region decreases with changing of the superficial velocity of the gas and solid particle diameter (figure 4).

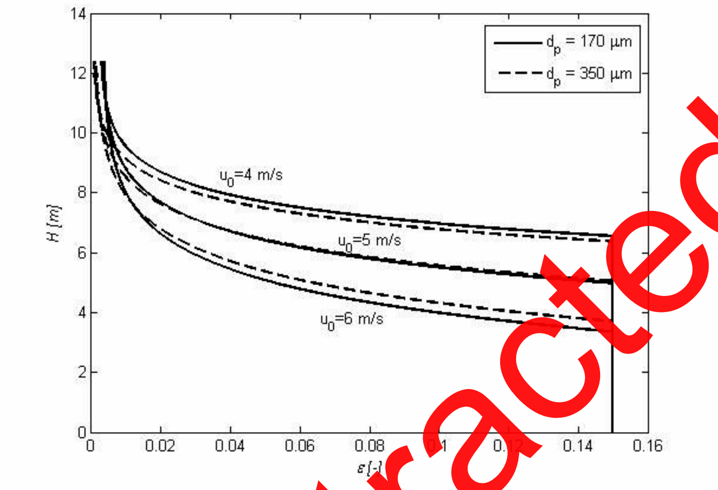

Figure 4. Solid distribution in fast fluidization with variable superficial gas velocity (u_0) and particle diameter (d_p),

The most part of the carbonation reaction takes place in the dense region and more precisely within the wall zone as can be seen from figure 5. Increasing the superficial velocity of the gas the difference between the concentration of the carbon dioxide in the wall and core zone becomes more significant. In the wall zone the volume fraction of solids is higher than in the core zone, the concentration drop there is more noticeable.

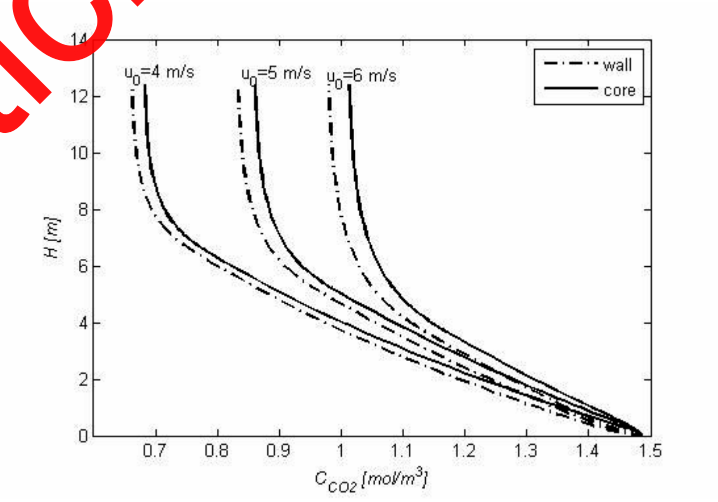

Figure 5. CO_2 concentration profile for carbonator for variable superficial gas velocity

In accord with experimental data, the model predicts that in every carbonation-calcination cycle the sorbent capacity decreases significant with the number of cycles. Figure 6 presents the variation of carbon dioxide concentration with carbonation/calcination number.

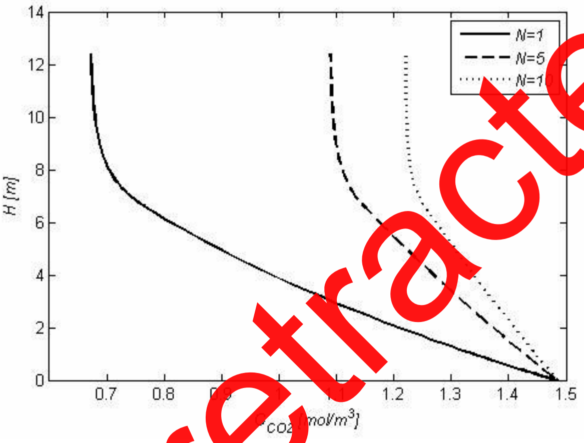

Figure 6. Mean CO_2 concentration profile for carbonator for variable carbonation/calcination cycle number

CONCLUSIONS

The dynamic carbon capture evaluation has a highly important role in establishing optimal operation procedure for power plants equipped with CCS. It is widely known that fossil power plants are required to be operated in dynamic scenario due to the timely variation of the grid demand.

In this paper, a dynamic mathematical model of carbonation reactor from calcium-looping process for carbon capture in fossil fuel-based power plants, was developed.

In the developed model has been taken into consideration the particle distribution in the reactor and the deactivation of the sorbent with the number of cycles (*N*). The particle distribution in the carbonator is described according to the 1D model for fast fluidization presented by Kunii and Levenspiel. The CO_2 adsorption efficiency in the carbonator is divided in two terms taking into account the dense and lean regions of the fluidized bed.

All mathematical equations used in this model have been implemented in Matlab /Simulink 2008. The dynamic model of CO_2 capture process has been validated with data collected from pilot plant, published in literature.

The simulation results showed more than 90 % of the total CO_2 capture has occurred in the dense region of the carbonator. The height of the dense region decreases significantly from 6.5 m to 4 m with the increasing of the superficial gas velocity from 4 m/s to 6 m/s, for carbonator. Moreover, within the dense zone a small difference can be noticed in capture efficiency in the wall and core zone which becomes significant at higher gas velocities.

Nomenclature

u_0	superficial gas velocity in the reactor (m/s)
d_p	particle diameter (m)
H_t	total height of the reactor (m)
H_l	height of the lean region (m)
H_d	height of the dense region (m)
W_l	mass of solids in the lean region (kg)
W_d	mass of solids in the dense region (kg)
W_t	mass of solids in the reactor (kg)
a	decay constant for solid fraction in the lean region (m^{-1})
A_t	cross-sectional area of the reactor (m^2)
f_l	average value of the volume of solids in the lean region (-)
G_s^*	saturated mass flux of solids (kg/m^2s)
u_T	terminal velocity of particle falling through the gas (m/s)
g	acceleration of gravity (m/s^2)
k_r	first order kinetic constant of the carbonation reaction (m^4/mol/ s)
k_s	intrinsic kinetic constant of the carbonation reaction (m^4/mol/ s)
S_N	the specific surface area available for reaction in particle having experienced N calcination-carbonation cycles (m^{-1})
A_w	cross-sectional area in the wall zone (m^2)
A_c	cross-sectional area in the core zone (m^2)
C_{CO2}	average concentration of carbon dioxide in a generic CFB riser cross-section (mol/m^3)
$C_{CO2,c}$	concentration of carbon dioxide in the core zone (mol/m^3)
$C_{CO2,w}$	concentration of carbon dioxide in the wall zone (mol/m^3)
k_{cw}	core-wall mass transfer coefficient (s^{-1})
k_{ri}	first order kinetic constant of the carbonation reaction (s^{-1})
$p_{CO2,eq}$	equilibrium carbon dioxide partial pressure
t	time (s)
V_M	molar volume (m^3/mol)
M_i	molecular weight of specie i (kg/kmol)

Greek letters

ε_{sd}	volume fraction of solids in the dense region (-)
ε_{sc}	volume fraction of solids in the core zone (-)
ε_{sw}	volume fraction of solids in the wall zone (-)
ε_s^*	saturated carrying capacity of a gas (-)
ε_{se}	volume fraction of solids at the reactor exit (-)

ε_{sl}	volume fraction of solids in the lean region (-)
ρ	density (kg/m^3)
μ	viscosity (Pa·s)
η	contacting efficiency in the CFB riser with respect to an ideal plug flow

ACKNOWLEDGMENTS

This work was supported by a grant of the Romanian National Authority for Scientific Research, CNCS - UEFISCDI, project PNII-CT-ERC-2012-1/2ERC: “Innovative systems for carbon dioxide capture applied to energy conversion processes”.

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STUDIA UBB CHEMIA, LVIII, 4, 2013 (p. 285)
(RECOMMENDED CITATION)

==ERRATUM==

STUDIA UBB CHEMIA, Volume 58 (LVIII), 3, 2013 (pp. 7-18)

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