

Modeling of the calcium looping process with emphasis on bed hydrodynamics and sorbent characteristics

Fardin Sattari, Maryam Tahmasebpour¹, Mousa Mohammadpourfard

Faculty of Chemical & Petroleum Engineering, University of Tabriz, Tabriz, Iran

ABSTRACT

The calcium looping process is considered a promising technology to CO₂ capture emissions from combustion plants in recent decades. In order to model this process, the bed hydrodynamics as well as the sorbent characteristics will affect the calcium looping efficiency. In this study, CaO/Al₂O₃ sorbent is first synthesized by sol-gel method and then its performance is compared with pure CaO sorbent through 20 carbonation/calcination cycles. In addition, a general model based on bed hydrodynamics as well as sorbent properties for this process is presented and then the influence of parameters such as superficial gas velocity, carbonator height and sorbent inventory on process efficiency is investigated. TGA experiments reveal that CaO/Al₂O₃ sorbent preserves 73% of its activity at the end of 20 cycles, whereas it is obtained as 21 for pure CaO sorbent. The results obtained from modeling show that the adsorption efficiency is decreased from 78.69 to 22.68% for pure CaO, whereas, it is decreased from 86.5 to 74.1% for modified CaO/Al₂O₃ sorbent. Finally, by studying the affective parameters it is obtained that the solid inventory has a significant impact on the process efficiency while the gas velocity and the height of the carbonator are far less effective.

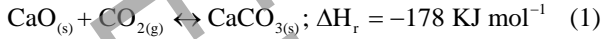
KEYWORDS

Calcium looping, Modeling CO₂ adsorption, Calcium oxide sorbent, Bed hydrodynamics, Carbonator

¹ Corresponding Author Email: tahmasebpour@tabrizu.ac.ir

1. Introduction

Carbon capture and storage (CCS) technology is recognized as a promising technology to reduce CO₂ emissions from fossil fuel power plants and classified into three categories including post-combustion, pre-combustion and oxy-fuel. The Ca-Looping (CaL) process which is an efficient post-combustion CO₂ capture technology using limestone based sorbents is based on a reversible chemical reaction (so called carbonation–calcination reaction of CaO/CaCO₃) as described in Eq. (1) [1]:



The CaL process firstly proposed by Shimizu et al. [2], is a system consisting of two interconnected fluidized bed reactors acting as carbonator and calciner. In the carbonator reactor, particles of CaO adsorb CO₂ and the partially carbonated solids are driven into the calciner, where the endothermic calcination reaction occurs at high temperatures, typically above 900°C.

Since the CaL process is still a technology at an early stage of development, modelling works are of great importance for studying the effect of the diverse parameters governing the CaL process. This work is aimed to present a model of the carbonator reactor taking into account the fluidized bed hydrodynamics as well as the sorbent characteristics. Furthermore, the effects of important parameters such as gas velocity, height of the carbonator and solid inventory on the CO₂ capture efficiency achieved by CaO and synthesized CaO/Al₂O₃ sorbents as a function of the cycle number are assessed.

2. Methodology

In order to prepare CaO/Al₂O₃ sorbent, sol-gel auto-combustion synthesis method is used [3]. The CO₂ adsorption efficiency of the carbonator is calculated by a 1D CFB model for fast fluidization as presented by Kunii and Levenspiel [4]. In this model, the reactor is divided into two regions: the dense region and the lean region.

To obtain the values for H_l and ε_{se} , Eqs. (2) and (3) are combined and subsequently solved using the Newton–Raphson method.

$$\varepsilon_{se} = \varepsilon_s^* + (\varepsilon_{sd} - \varepsilon_s^*)e^{-aH_l} \quad (2)$$

$$\frac{W_t}{A_t \rho_s} = \frac{\varepsilon_{sd} - \varepsilon_{se}}{a} + H_l \varepsilon_{sd} - H_l (\varepsilon_{sd} - \varepsilon_s^*) \quad (3)$$

In the last years, Ortiz et.al [5] proposed a modified equation for describing the sorbent CO₂ carrying capacity with the number of cycles as the Eq. (4):

$$\frac{X_N}{X_1} = \frac{X_r}{X_1} + \left(\frac{1}{\kappa(N-1) + \left(1 - \frac{X_r}{X_1}\right)^{-1}} \right) \quad (4)$$

The CO₂ concentration at the top of the dense region, $C_{CO_2,d}$, is derived from the Eqs. (5) – (8):

$$X_{\max,ave} = \sum_{N=1}^{N=\infty} r_N X_N \quad (5)$$

$$K_{ri} = k_s \frac{X_{\max,ave} S_0 \rho_{CaO}}{M_{CaO}} (1-X)^{2/3} \quad (6)$$

$$K_{ff} = \gamma_{core} K_r + \frac{1}{\left(\frac{1}{K_{be}}\right) + \left(\frac{1}{\gamma_{wall} K_r}\right)} \quad (7)$$

$$\ln \frac{C_{CO_2,in}}{C_{CO_2,d}} = \frac{K_{ff} \delta H_d}{u_0} \quad (8)$$

The CO₂ concentration at the carbonator exit, $C_{CO_2,ex}$, is calculated according to Eqs. (9) and (10):

$$\ln \frac{C_{CO_2,d}}{C_{CO_2,ex}} = \frac{(1-\varepsilon_f)_{bed} K_r}{u_0 a} \left[(1-e^{-aH_l}) - \frac{1-\eta_{bed}}{1+(a/a')} (1-e^{-(a+a')H_l}) \right] \quad (9)$$

$$\eta_{bed} = \left(\gamma_{core} + \frac{1}{\left(\frac{K_r}{K_{be}}\right) + \left(\frac{1}{\gamma_{wall}}\right)} \right) \frac{\delta}{1-\varepsilon_f} \quad (10)$$

After obtaining the $C_{CO_2,d}$ and $C_{CO_2,ex}$ by Eqs. (8) and (9) respectively, the CO₂ capture efficiency is calculated by:

$$E_{CO_2} = 1 - \frac{C_{CO_2,ex}}{C_{CO_2,in}} \quad (11)$$

3. Discussion and Results

The CO₂ capture efficiency achieved by CaO and CaO/Al₂O₃ sorbents during 100 carbonation/calcination cycles is calculated. Capture efficiency achieved by CaO sorbent is decreased from 78.69% to 22.68% at the end of the cycle, indicating a very severe deactivation of CaO under CaL conditions, while it is decreased from 86.5% to 74.1% in the case of modified CaO/Al₂O₃ sorbents.

In order to evaluate different parameters affecting the CO₂ capture efficiency achieved by CaO and CaO/Al₂O₃ sorbents, solid inventory, gas velocity and height of the carbonator are investigated. The effect of each parameter is discussed as below:

An increase of the incoming solids flow results in a larger fraction of CaO in the bed and also increases the height of the dense phase, which is definitely the main

factor affecting the CO₂ adsorption efficiency of the carbonator. As seen in Figure 1, increasing the solid inventory of the CaO sorbent has a greater effect on CO₂ capture efficiency, but this effect is less at the case of the modified CaO/Al₂O₃ sorbent.

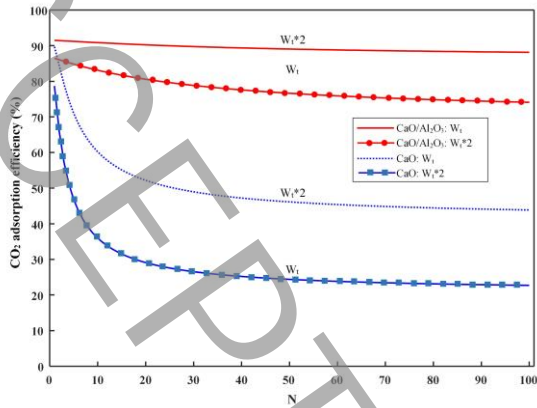


Figure 1. Effect of the solids inventory on CO₂ adsorption efficiency achieved by CaO and CaO/Al₂O₃ sorbents

The gas velocity affects the particle distribution in the fast fluidized bed, so that an increase of the superficial velocity of the gas results in decrease the height of the dense phase. As seen in Figure. 2, a smaller overall CO₂ capture efficiency is achieved at higher superficial gas velocities.

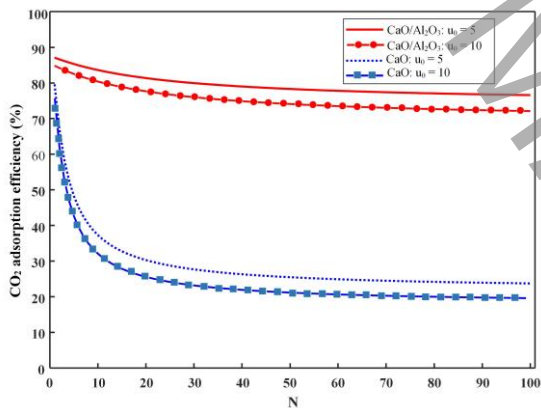


Figure 2. Effect of the superficial gas velocity on CO₂ adsorption efficiency achieved by CaO and CaO/Al₂O₃ sorbents

Keeping the solids inventory constant, the height of the dense region, H_d , decreases with increasing the height of the carbonator, according to the combination of Eqs. (2) and (3). As seen in Figure. 3, the overall CO₂ capture efficiency slightly decreases because the CO₂ adsorption occurs mainly in the dense region. It seems that the importance of the effect of height of the carbonator and gas velocity on both types of sorbents is the same.

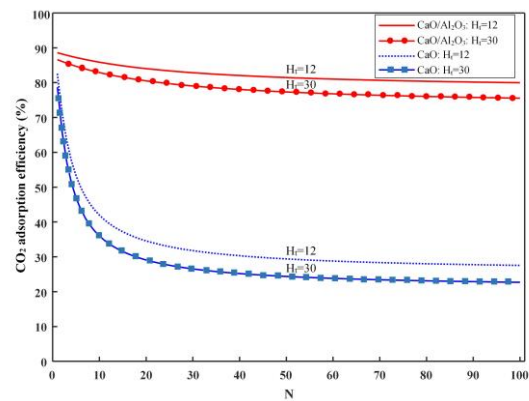


Figure 3. Effect of total height of the carbonator on CO₂ adsorption efficiency achieved by CaO and CaO/Al₂O₃ sorbents

4. Conclusions

In this work a model was presented for calculating CO₂ capture efficiency of the carbonator, taking into account the fluidized bed hydrodynamics in the fast fluidity regime as well as the sorbent characteristics. As a main conclusion from the simulation results, the capture efficiency was significantly improved by applying CaO/Al₂O₃ as the CO₂ sorbent. During 100 multi-cycles, the capture efficiency by CaO/Al₂O₃ sorbent decreased from 86.5% to 74.1% and it decreased from 78.69% to 22.68% using CaO. Furthermore, the effects of three parameters including solid inventory, gas velocity and height of the carbonator on the CO₂ capture efficiency were investigated. It was obtained that the solid inventory has a significant impact on the process efficiency while the other two are far less effective.

5. References

- [1] J. Valverde, P. Sanchez-Jimenez, L.A. Perez-Maqueda, Ca-looping for postcombustion CO₂ capture: a comparative analysis on the performances of dolomite and limestone, *Applied Energy*, 138 (2015) 202-215.
- [2] T. Shimizu, T. Hirama, H. Hosoda, K. Kitano, M. Inagaki, K. Tejima, A twin fluid-bed reactor for removal of CO₂ from combustion processes, *Chemical Engineering Research and Design*, 77(1) (1999) 62-68.
- [3] B. Azimi, M. Tahmasebpour, P.E. Sanchez-Jimenez, A. Perejon, J.M. Valverde, Multicycle CO₂ capture activity and fluidizability of Al-based synthesized CaO sorbents, *Chemical Engineering Journal*, 358 (2019) 679-690.
- [4] A. Lasheras, J. Ströhle, A. Galloy, B. Epple, Carbonate looping process simulation using a 1D fluidized bed model for the carbonator, *International Journal of Greenhouse Gas Control*, 5(4) (2011) 686-693.
- [5] C. Ortiz, R. Chacartegui, J. Valverde, J. Becerra, L.A. Perez-Maqueda, A new model of the carbonator reactor in the calcium looping technology for post-combustion CO₂ capture, *Fuel*, 160 (2015) 328-338.