Development of fluidized bed reactors to capture CO_2 with CaO

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Objectives and novelty

CO_2 emission levels have experienced a sharp increase in recent years mainly due to the use of fossil fuels to meet the increasing global energy demand. This phenomenon has led to changes in the behaviour of the climate system and has contributed to what is known as climate change, what makes clear that we need options that allow CO_2 emissions to be reduced to levels that are assumable and compatible with the climate system. However, all predictions clearly indicate that fossil fuel consumption will increase over the next few decades, entailing a substantial increase in CO_2 atmospheric concentration unless other measures are adopted. One of the alternatives proposed for the short and medium term consists in decoupling CO_2 emissions from fossil fuels usage by developing CO_2 capture processes. The objective of these processes is to separate the CO_2 present in the gas streams produced in large stationary emission sources for its permanent storage.

Among the different emerging technologies proposed, Calcium Looping (CaL) stands out as a promising option. It is based on the reversible reaction between CaO and CO_2 to form $CaCO_3$, which is then decomposed to initiate a new carbonation cycle, leading to a concentrated stream of CO_2 suitable for purification, compression and subsequent storage. An important advantage of the CaL technology is its reduced energy penalty, since heat can be efficiently recovered from high quality heat sources and then integrated into a steam cycle. In this context, two CaL processes have been studied in this Thesis: post-combustion CaL, where CO_2 is captured from the flue gases generated in a power plant, and *in situ* CaL, where biomass combustion and CO_2 capture take place simultaneously. The most accepted configuration for these processes involves the use of two circulating fluidized bed reactors, as outlined in Figure 1, namely a carbonator (or combustor-carbonator for *in situ* CO_2 capture) and a calciner. The work conducted for this Thesis has been focused on the development of the CO_2 capture technology at high temperature using CaO as sorbent in some of its main process routes with a view to its subsequent implementation at industrial scale. For this purpose, several pilot-scale experimental tests have been carried out, as well as studies related to the modeling of the reactors of the system and the incorporation of improvements to the process.

Results

Several experimental campaigns have been designed and executed to test the CaL process in two interconnected circulating fluidized bed facilities at pre-industrial scale: the 1.7 MW_{th} post-combustion CO_2 capture pilot plant in La Pereda (Asturias) and the 300 kW_{th} *in situ* CO_2 capture pilot plant in La Robla (León), both of which are shown in Figure 2. These studies have been mainly focused on the analysis of the carbonator (or combustor-carbonator in the *in situ* configuration), since this is the reactor where the CO_2 capture process occurs. During the experiments, the calciner was kept at conditions suitable for sorbent regeneration to ensure a continuous CaO flow that would be adequate for the carbonation process to take place. Tests conducted in these pilot plants were a success and have provided a wide experimental database of the high-temperature CO_2 capture calcium looping process at operating conditions close to those expected at industrial scale.

In the post-combustion CaL scheme, it has been demonstrated that high CO_2 capture efficiencies of over 90% can be attained under realistic operating conditions. It has also been proved that CO_2 capture can be performed effectively even with highly deactivated particles (CO_2 carrying capacity, X_{ave}, close to the

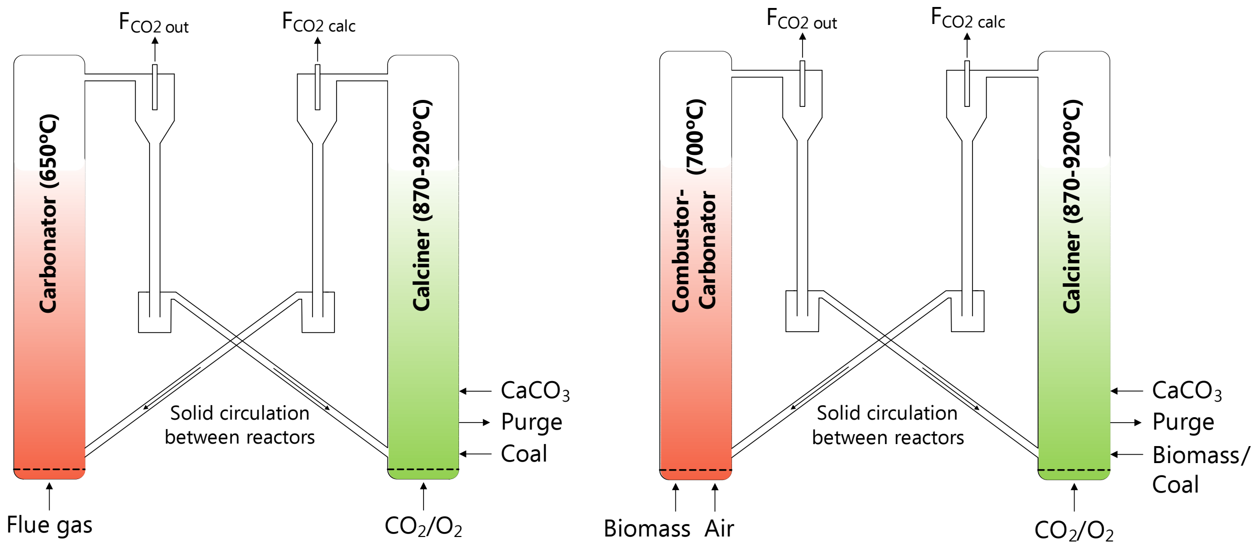

Figure 1. Left) Scheme of the post-combustion Calcium Looping process. Right) Scheme of the *in situ* Calcium Looping process.

Figure 2. Left) View of La Pereda 1.7 MW_{th} pilot plant. Right) View of La Robla 300 kW_{th} pilot plant.

residual activity) and moderate solid circulation rates (2-5 kg/m^2s) as long as there is a large inventory of solids inside the carbonator (500-1000 kg/m^2), which confirms that the active CaO carbonator inventory is a key variable for the process, together with the flow of Ca between the carbonator and calciner and the CO_2 carrying capacity of the particles. The tests also revealed that both the carbonator and calciner reactors are excellent desulfurization units, since the sulfur that enters the system with the flue gas and the coal fed to the calciner can be retained with a desulfurization efficiency higher than 95%. The *in situ* CaL tests showed that it is possible to capture the CO_2 generated during the simultaneous biomass combustion with an efficiency of between 70 and 95%. These experiments also demonstrated that the temperature inside the combustor-carbonator should be kept within a narrow window at around 700ºC in order to maximize both the combustion and the CO_2 capture efficiencies. It has also been confirmed that the solid inventory inside the combustor-carbonator, the solid circulation rate between the reactors and the CO_2 carrying capacity of the sorbent are key operating process parameters. Closure of the carbon and sulfur balances of the post-combustion experiments and the carbon balance during the *in situ* CaL tests has been successful and the experimental results have been adequately interpreted by means of a carbonator or combustor–carbonator model, respectively, that assumes plug flow for the gas phase and perfect mixing of the solids in the interior of the reactor. For the *in situ* configuration, simultaneous combustion and carbonation reactions have also been taken into account.

The second section of this Thesis comprises a series of in-depth studies into some of the key aspects of CO_2 capture processes by means of carbonation-calcination cycles. First, a hydrodynamic study of the interconnected circulating fluidized bed reactors used in the process was carried out. It was found that there is a mismatch between the flow of solids between the carbonator and calciner reactors resulting from the hydrodynamic conditions in the risers and the solid circulation required to attain a certain CO_2 capture efficiency. Therefore, the internal recirculation of excess solids to the same reactor may be an appropriate strategy of operation for most of the scenarios analyzed. Moreover, the effects of the presence of inerts (sulfur and ashes entering with the flue gas and the coal fed to the calciner) on the characteristics of the circulating solids and CO_2 capture efficiency have been evaluated. Several scenarios have been analyzed and the make-up flow of limestone and associated purge required in each case were calculated on the basis of mass balances and a carbonator model. Finally, a novel process for sorbent reactivation (recarbonation) has also been investigated. For this purpose, a kinetic study of the recarbonation reaction was carried out under different operating conditions, which showed that the optimum conditions for the process to proceed at high reaction rates are temperatures of around 800ºC, CO_2 concentrations of over 80%v and modest steam contents (10-20%v). Using all the kinetic information obtained during these tests, a reactor model capable of predicting the performance of the recarbonator has been developed based on the Kunii and Levenspiel model for gas-solid contact in bubbling bed reactors. This model has also been used to obtain a preliminary design of a recarbonator reactor. The results indicate that mean residence times of the particles inside the recarbonator of between 100 and 170 s are sufficient to almost double the residual activity of the particles by means of recarbonation.

Conclusions

Calcium looping post-combustion and *in situ* processes that employ circulating fluidized bed reactors are viable on a large pilot scale operating in conditions close to those that might be expected in future large-scale systems. It has been demonstrated that the trends previously observed in smaller facilities are also reproducible at the scale of 0.3-1.7 MW_{th} pilot plants. The experimental validation of carbonation-calcination technologies for CO_2 capture from flue gases derived from coal combustion (post-combustion) or during biomass combustion in fluidized beds (*in situ*) is a critical step for the scaling up of these technologies. Moreover, the studies carried out as part of this Thesis have contributed to improving the modeling approaches necessary for interpreting the experimental data and for identifying reasonable operating windows as well as improved configurations of the CO_2 capture system.

Related publications

[1] Diego, M. E., Arias, B. y Abanades, J. C. (2012), 'Modeling the solids circulation rates and solids inventories of an interconnected circulating fluidized bed reactor system for CO_2 capture by calcium looping', Chem. Eng. J., 198–199, 228-235.

[2] Diego, M. E., Arias, B., Alonso, M. y Abanades, J. C. (2013), 'The impact of calcium sulfate and inert solids accumulation in post-combustion calcium looping systems', Fuel, 109, 184-190.

[3] Arias, B., Diego, M. E., Abanades, J. C., Lorenzo, M., Diaz, L., Martínez, D., Alvarez, J. y Sánchez-Biezma, A. (2013), 'Demonstration of steady state CO_2 capture in a 1.7 MW_{th} calcium looping pilot', Int. J. Greenhouse Gas Control, 18, 237-245.

[4] Alonso, M., Diego, M. E., Pérez, C., Chamberlain, J. R. y Abanades, J. C. (2014), 'Biomass combustion with in situ CO_2 capture by CaO in a 300 kW_{th} circulating fluidized bed test facility', Int. J. Greenhouse Gas Control, 29, 142-152.

[5] Grasa, G., Martínez, I., Diego, M. E. y Abanades, J. C. (2014), 'Determination of CaO Carbonation Kinetics under Recarbonation Conditions', Energy Fuels, 28, 4033-4042.

[6] Diego, M. E., Arias, B., Grasa, G. y Abanades, J. C. (2014), 'Design of a Novel Fluidized Bed Reactor to Enhance Sorbent Performance in CO_2 Capture Systems Using CaO', Ind. Eng. Chem. Res., 53, 10059-10071.

Full text can be found in www.digital.csic.es