Process modelling of ca-looping systems integrated in energy conversions systems

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Objectives and novelty

According to the recently published IPCC report, human contribution to detected changes in climate components is clear. CO_2 is the greenhouse gas that makes the largest contribution from human activities, mainly associated to fossil fuel combustion in power plants, refineries or large industrial facilities. Among the technological options proposed to reduce anthropogenic CO_2 emissions, Carbon Capture and Storage (CCS) is the only technology available to mitigate CO_2 emissions from large scale processes using fossil fuels. The implementation of a CO_2 capture system carries a reduction of the process efficiency led by an increased fuel requirements. Consequently, minimising energy requirements associated to CO_2 capture together with improving energy efficiency of conversion processes represent high priorities for future technology development.

Ca-looping processes involve the separation of CO_2 using the reversible carbonation reaction of CaO and CO_2 and the calcination of the $CaCO_3$ formed to regenerate the sorbent. This CO_2 capture concept represent a potential alternative to the commercially available capture processes since most of the energy introduced for sorbent regeneration is recovered from the process at sufficient high temperature as to power a new steam cycle, generating additional power and drastically reducing the efficiency penalty and the CO_2 capture cost. To evaluate this potential, the main objective of this work has been to analyse different energy conversion systems (where the end product is electricity, heat and/or hydrogen) including a Ca-looping process for CO_2 capture, and to find out those operating conditions that optimise plant performance from an efficiency and CO_2 emissions standpoints. Results from this work will contribute to the scaling up of this Ca-looping technology in post-combustion applications to coal-fired power plants and to the development of new pre-combustion CO_2 capture schemes focused on hydrogen or electricity production with reduced CO_2 emissions.

Results

The integration of a Ca-looping system into an existing coal-based power plant (Fig. 1) represents one of the most promising process configurations for this CO_2 capture technology, experiencing the fastest developing pace, because it relies on the use of commercially proven combustion technology in circulating fluidized beds and it is easy to be coupled into an existing power plant by exclusively feeding the flue gas into the carbonator. CO_2 capture efficiencies ranging from 70 to 90 % of the flue gas coming from the existing plant are feasible under different design and operation strategies. Low sorbent make-up flows are preferable from an efficiency penalty reduction point of view, since the high solid circulation rate in these cases maximise steam production in the carbonator. Efficiency penalties as low as 7.5 percentage points are obtained under these low make-up flow conditions (corresponding to solid purge ~ 2 % of the solid flow circulating from the calciner).

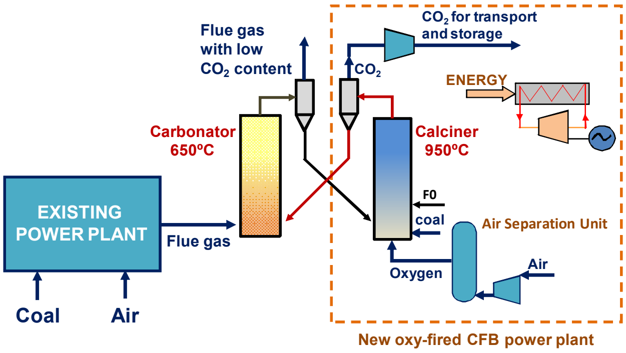

Fig. 1. Scheme of an existing power plant including a Ca-looping system for CO_2 capture

Despite the effective energy recovery associated to Ca-looping process configurations, there is a great potential for efficiency improvement in Ca-looping systems by reducing heat demand in the calciner or by looking for less-energy demanding alternatives to oxy-combustion in the calciner. In the first case, reducing operation temperature in the calciner implies a significant reduction of the energy needed for heating the solids flowing from the carbonator up to the calciner temperature, which is the main contribution to the heat demand in the calciner. Calciner temperature reductions of around 30-50ºC (with regard to the generally accepted value of 950ºC) are possible while getting calciner efficiencies as high as 95 %, which implies marked reduction in capital costs associated to calciner and air separation unit sizes. As for avoiding coal oxy-combustion in the calciner, an alternative Ca-looping process configuration where the energy required in the calciner is supplied by a solid heat carrier (mainly CaO) circulating from the combustor operating at high temperature (1030ºC), allows for a reduction of 2-2.5 percentage points in the aforementioned efficiency penalty.

The integration of a Ca-looping system as a pre-combustion CO_2 capture route in natural gas reforming processes for hydrogen and/or electricity production (Sorption Enhanced Reforming (SER) process) implies the addition of a Ca-based sorbent to the commercial reforming catalyst so that reforming, water gas shift and carbonation reactions occur in one reaction step (Fig.2). Noticeable high hydrogen yields are feasible in this SER process (2.78 moles of H_2 output/moles of equivalent CH_4) since the coupling of the carbonation reaction helps in overcoming the thermodynamic limitations of the widely used Steam Methane Reforming (SMR) technology for hydrogen production, where 2.29 moles of H_2 output/moles of equivalent CH_4 are produced. Moreover, energy consumption is around 20 % less than the energy needed in the SMR based plant featuring CO_2 capture with amines, despite the fact that energy consumption in the calciner is supplied by natural gas combustion using an O_2 pure gas stream coming from an air separation unit.

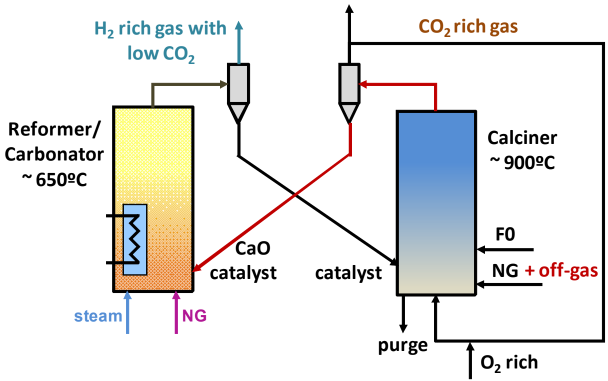

Fig. 2. Conceptual scheme of a H_2 production plant based on SER concept

Alternatively, SER process can be modified to incorporate a copper-based material that supplies the energy for $CaCO_3$ calcination via the reduction of CuO with a fuel gas. This process is performed in a series of fixed bed reactors where pressure and temperature are modified to favour the process stages of H_2 production, Cu oxidation and $CaCO_3$ calcination/CuO reduction. When focused on hydrogen production, this novel process allows for hydrogen yields as high as 2.63 moles of H_2 output/ moles of equivalent CH_4, higher than the SMR based process but slightly below that obtained for the previous SER configuration operating at atmospheric pressure. When focused on electricity production, integrated with a combined cycle (CC) using the H_2 gas obtained as fuel in the gas turbine, an efficiency penalty of around 8 percentage points with respect to a reference CC-based power plant without CO_2 capture is possible with emissions as low as 40 g_{CO2}/ kWh produced. Compared to other pre-combustion CO_2 capture routes applied to CC-based power plants, the potential of this novel concept in this electricity production configuration is demonstrated.

Conclusions

Ca-looping systems integrated in either post-combustion or pre-combustion routes allow for an efficient recovery of the energy introduced in the regeneration of the Ca-based sorbent as high-temperature energy streams. The **efficiency penalty resulting from the use of the Ca-looping process for CO_2 capture is noticeably lower than the efficiency penalty associated to commercially available CO_2 separation technologies when focused on electricity or hydrogen production from coal or natural gas**. Therefore, the potential of the Ca-looping process as a CO_2 capture technology both for power or hydrogen production processes is confirmed.

Related publications

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[3] Martínez, I., Grasa, G., Murillo, R., Arias, B., Abanades, J.C. Kinetics of calcination of partially carbonated particles in a Ca-looping system for CO_2 capture. Energy Fuels. 2012, 26, 1432-1440.

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[5] Martínez, I., Romano, M.C., Chiesa, P., Grasa, G., Murillo, R. Hydrogen production through Sorption Enhanced Steam Reforming of Natural Gas: Thermodynamic plant assessment. Int J Hydrogen Energ. 2013, 38 (35): 15180-15199

[6] Martínez, I., Romano, M.C., Fernández, J.R., Chiesa, P., Murillo, R., Abanades, J.C. Process design of a hydrogen production plant from natural gas with CO_2 capture based on a novel Ca/Cu chemical loop. Appl Energ. 2014, 114, 192-208.

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[8] García-Lario, A.L., Martínez, I., Murillo, R., Grasa, G., Fernández, J.R., Abanades, J.C. Reduction kinetics of a high load Cu-based pellet suitable for Ca/Cu chemical loops. Ind Eng Chem Res. 2013, 52 (4): 1481-1490.

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