Experimental investigation of the Ca-Cu process for H₂ production: Evaluation of different reduction/calcination strategies.

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Abstract

New chemical processes for large scale H₂ production from fossil fuels joined with CO₂ capture systems have arisen in recent years with the objective of reducing the cost and the energy penalty associated to close to commercial capture processes. In this context, the Ca/Cu looping process has emerged as a novel intensified process as it is capable of producing a highly concentrated H₂ stream with inherent CO₂ capture via sorption enhanced steam methane reforming (SER) based on the CaO/CaCO₃ loop [1]. In this process, a second Cu/CuO chemical loop is coupled so that the exothermic reduction of CuO with H₂, CO or CH₄ provides the energy required for the calcination of CaCO₃. In this way, the coupling of both endothermic and exothermic reactions in one single stage allows for tighter integration as the heat is directly transferred within the solid bed without the need for intermediate heat exchange devices. The basic Ca/Cu looping process consists of a sequence of three main reaction steps, which are adiabatically carried out in fixed-bed reactors operating in parallel. In the first stage, an enriched stream of H₂ is produced by the SER of methane in the presence of a reforming catalyst, a CaO-based sorbent and a Cu-based solid. This process stage has been designed to take place at 873-1023 K, steam-to-carbon molar ratios (S/C) between 2.5 and 5, and pressures between 10 and 35 bar in order to achieve high H₂ production yields with high CO₂ capture efficiencies [2, 3]. In the next step, the Cu-based material is oxidized with diluted air at a high pressure. A low content of oxygen in the feed moderates the maximum bed temperature reached during the oxidation of Cu to CuO, thereby avoiding the prompt decomposition of CaCO₃ by partial calcination. In the following reaction stage, the calcination of the CaCO₃ formed during the SER is accomplished by means of the simultaneous reduction of CuO with a gaseous fuel at atmospheric pressure. A suitable CuO/CaCO₃ molar ratio in the bed composition has to be selected to ensure that the heat released during CuO reduction is sufficient to fully calcine the CaCO₃ without any external energy supply.

Different heat management strategies have been proposed to fulfil the fuel requirements in the calcination/reduction stage while achieving high CO₂ capture rates in the whole Ca/Cu process. One of them consists of incorporating an additional stage between the calcination/reduction and the SER stages where steam reforming of additional methane (or natural gas) occurs while cooling the solid bed [1]. A rich-H₂ gas with negligible amounts of CH₄ is produced in this case to be used as fuel gas for reducing the CuO in the calcination/reduction stage. Alternatively, it has been proposed the possibility of feeding to the calcination/reduction stage a pre-reformed natural gas stream (i.e. rich in CH₄) that cools down the solid bed while carrying out the calcination/reduction processes, reducing in this way the number of reactors required to run a complete cycle [4].
In this work, a complete Ca/Cu cycle that includes the three main reaction stages has been investigated in a lab scale fixed-bed reactor capable of operating under pressure. The objective of the work is to experimentally assess the good performance of the process in terms of H₂ production and CO₂ capture efficiencies. Three functional materials with the right amounts of active phase to run the process have been mixed in suitable proportions and introduced in the reactor: a CaO-based CO₂ sorbent, a Ni-based commercial reforming catalyst and a Cu-based material. The experimental rig allowed for the online analysis of product gas as well as for registering the evolution of temperature profiles along the reacting bed. Consecutive cycles of the three main stages SER, Cu oxidation and CuO reduction/CaCO₃ calcination have been performed. Moreover, the two heat management strategies aforementioned have been tested in the experimental rig to study their expected performance.

The system was able to fulfill the SER equilibrium at a CH₄ space velocity of 2.4 kg CH₄/h kg cat at an S/C of 3, at 10 bars with a bed material containing 2 % wt. Ni. The product gas stream contained 94 % vol. H₂ (dry basis). A concentrated CO₂ stream was generated in the reduction /calcination stage with calcination efficiencies around 95 % molar basis for a molar Cu/Ca ratio of 2. The presence of a steam methane reforming step at high temperature allowed cooling down the bed to adequate it to start the following reaction cycle.


References:

