Sorption enhanced production of hydrogen in industrial processes using two chemical loops

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ABSTRACT

We analyze in this work a number of process concepts that involve the production of hydrogen (from natural gas reforming or shifting CO-rich gases) enhanced by the carbonation of CaO. This reaction removes CO$_2$ and shifts equilibria towards the formation of H$_2$. A second chemical loop is used to regenerate the sorbent back to CaO and produce a rich stream of CO$_2$. One of such generic systems is the Ca-Cu looping process (see Fig. 1, left), which has so far been developed for H$_2$ production and power generation [1-3]. The basic process scheme consists of a sequence of three reaction steps. In the first stage, an enriched stream of H$_2$ is produced by the sorption enhanced reforming (SER) of natural gas in the presence of a reforming catalyst, a CaO-based sorbent and a copper-based solid (that acts as inert in this stage). In the next stage, the Cu-based material is oxidized with air at a moderate temperature to avoid the decomposition of CaCO$_3$ through partial calcination. In the final stage, the calcination of the CaCO$_3$ is accomplished by means of the exothermic reduction of CuO with a gaseous fuel at atmospheric pressure. This critical reaction step has been recently demonstrated at TRL4 [4] under the FP7 ASCENT project, which aims at demonstrating under industrially relevant conditions the Ca-Cu looping process (and other two pre-combustion CO$_2$ capture technologies) that rely on the use of high temperature solids.

![Figure 1. Schemes of hydrogen production processes enhanced by CaO carbonation and combined with a second chemical loop to calcine CaCO$_3$ and produce a rich stream of CO$_2$.](image)

Martínez et al. [5] have recently assessed the integration of the Ca-Cu looping into a state-of-the-art ammonia production plant, exploiting the inherent advantage of providing almost pure streams of hydrogen and nitrogen as part of its products. As demonstrated, such integration
reduces the specific primary energy consumption per unit of NH₃ produced, even when accounting for the higher electric consumption associated to the Ca-Cu process. The Ca-Cu looping process has been also proposed for the production of a H₂-enriched fuel gas by means of the sorption enhanced water gas shift (SEWGS) of blast furnace (BFG) gas in steel mills [6]. The operation is carried out in an arrangement of interconnected fluidized-bed reactors at atmospheric pressure, which allows for a solids’ segregation step to be introduced that will reduce significantly the solid circulation between reactors. Around 27% of the BFG can be decarbonized in the SEWGS reactor with this process, decreasing in this way the CO₂ emissions associated to its use within the steel mill.

We compare recent advances in the Ca-Cu looping process with the performance of an alternative sorption enhanced reforming process that uses the Fe₂O₃/Fe₃O₄ chemical loop for the regeneration of the CO₂-sorbent (see Fig. 1, right). In this case, the enthalpy of reduction of Fe₂O₃ to Fe₃O₄ is slightly endothermic and the energy required for the simultaneous reduction/calcination reactions is transported as sensible heat by hot solids that circulate from the oxidation reactor [7]. The large heat-transfer capacity and the good performance at high temperatures (up to 1200°C) of the iron oxides allows the operation to be carried out with reasonable circulation of solids (within the typical ranges of CFB boilers). In this work, mass and energy balances of the hydrogen production processes shown in Fig.1 are compared when used in stand-alone hydrogen production plant from natural gas or in a steel mill for decarbonizing the exhaust gases in this process. Optimum operating conditions in each case are conveniently assessed, and process performance is discussed in terms of H₂ production efficiency, specific primary energy consumption per unit of CO₂ avoided and/or overall feasibility of the configuration proposed.

References