

Optimized design and operation strategy of a Ca–Cu chemical looping process for hydrogen production



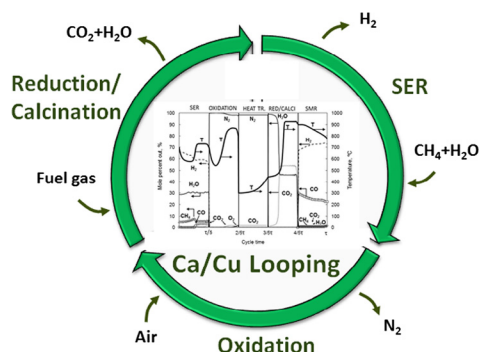
J.R. Fernández*, J.C. Abanades

Spanish Research Council, INCAR-CSIC, C/Francisco Pintado Fe, 26, 33011 Oviedo, Spain

HIGHLIGHTS

- New Ca–Cu looping process design leads to a more compact configuration.
- The use of PSA off-gas and syngas generated in SMR stage allows a reduction of Cu/Ca molar ratio.
- SER operation at a relatively low steam-to-carbon molar ratio and pressure to avoid CaO hydration.
- A complete cycle of the novel Ca–Cu looping process is simulated by means of a dynamic model.
- The H₂ production efficiency and the CO₂ capture efficiency show the feasibility of the process.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 30 November 2016
 Received in revised form 13 March 2017
 Accepted 15 March 2017
 Available online 18 March 2017

Keywords:

Hydrogen production
 CO₂ capture
 Sorption enhanced reforming
 Calcium looping
 Chemical looping
 Fixed bed

ABSTRACT

This work describes the performance of an improved Ca–Cu looping process designed to produce H₂ and/or power from natural gas while generating CO₂ suitable for reuse and/or permanent storage. The core of the process relies on an arrangement whereby fixed-bed reactors perform adiabatically. A sequence of five stages: sorption enhanced reforming (SER), Cu oxidation, solid/gas heat exchange, CuO reduction/CaCO₃ calcination and steam methane reforming (SMR) is used. A continuous flow rate of O₂-depleted gas is produced at a sufficiently high pressure and high temperature to drive a gas turbine for the generation of power. The new process design allows the number of reactors to be reduced from the 15 originally proposed in the original scheme to only five. The energy requirements for the reduction/calcination step can be reduced by using the PSA off-gas from the H₂ purification step and the syngas generated in a SMR stage. This also allows a reduction of the Cu/Ca molar ratio in the bed to a value of around 2. A dynamic reactor model partially validated in a previous work was used to simulate in detail a complete cycle of the Ca–Cu looping process under large-scale conditions. The simulations show that the progression of the reaction and heat exchange fronts can be regulated by the partial recirculation of the product gases. A process design for a base case with a reference output of 30,000 N m³/h of pure H₂ (88.5 MW_{th}), which is the typical production of fired tubular reformers installed in refineries, shows that reactors 6 m long with an inner diameter of 3 m would be sufficient to carry out the entire process, assuming a cycle duration of 15 min and a maximum drop in inlet pressure of 10% per stage. A hydrogen production efficiency of 77% is achievable, which is 6 net points above the efficiency of benchmarks based on fired tubular reformers that use amines (MDEA) to remove the CO₂. A CO₂ capture efficiency of about 95% is obtained, which is 10 net points higher than the values typically estimated for reference H₂ plants that use MDEA absorption.

© 2017 Elsevier Ltd. All rights reserved.

* Corresponding author.

E-mail address: jramon@incar.csic.es (J.R. Fernández).

1. Introduction

Carbon capture and storage (CCS) remains a promising alternative for drastically reducing CO₂ emissions from industries powered by fossil fuels or biomass (IPCC, 2014). Precombustion capture systems offer great theoretical advantages for new CCS systems in power and industry, as H₂ provides the flexibility and energy density of fossil fuels but has a potentially low carbon footprint (Boot-Handford et al., 2014). Nowadays, hydrogen is almost entirely used as feedstock in refining and chemical industries, but the demand for H₂ is expected to rise in the future because of its increasing use in hydrocracking and hydroprocessing processes, metallurgy, glass production and also in more recent applications, such as fuel for gas turbines, fuel cells and combustion engines (IEA, 2015). Steam methane reforming (SMR) is the dominant H₂ production technology at commercial scale (IEA, 2015). SMR involves the endothermic conversion of methane and steam to H₂ and CO, and is typically performed inside fired tubular reformers (FTR), where natural gas is fired in external burners to supply the necessary thermal power. The process requires high pressures (between 20–35 bar) and high temperatures (between 800 and 900 °C) to overcome the thermodynamic constraints of the reforming reaction and provide a high H₂ yield (Rostrup-Nielsen, 2009). Steam reforming is a highly efficient process (compared to other alternatives such as partial oxidation, autothermal reforming or coal gasification), but it requires a complex arrangement composed of several stages carried out in different conditions using different catalysts to facilitate the fuel conversion to H₂ (IEA, 2015).

The combination of reforming reaction with CO₂ separation to produce hydrogen in a single stage has gained importance in recent years because higher hydrogen yields are achieved with this simplified process (Aloisi et al., 2016; Wu et al., 2016). In the Sorption Enhanced Reforming (SER), the use of a calcium-based material in combination with a reforming catalyst allows the CO₂ to be removed from the gas phase as soon as it is produced, forming CaCO₃ (Harrison, 2008). The CO₂ sorption reaction (i.e. CaO carbonation) is exothermic and supplies “in situ” the heat required to carry out the endothermic reforming reaction. Moreover, the steam reforming and the WGS reactions are both shifted towards H₂ formation, with the result that very high conversions of methane to H₂ can be achieved in one single stage under moderate temperatures (600–700 °C) (Balasubramanian et al., 1999). The SER allows a product gas with almost pure H₂ (higher than 90 vol.% on a dry basis) to be obtained directly from the reformer, thereby simplifying the downstream purification procedure. Shift catalysts are not required and the operation at a lower temperature favours the use of cheaper materials (Johnsen et al., 2006). However, the CO₂-sorbent needs to be continuously regenerated to permit a multicycle operation. The calcination of CaCO₃ is an endothermic reaction that demands temperatures of around 900 °C in pure CO₂ at 1 atm. Therefore, the main challenge for the development of the SER technology on a large scale is to find a process scheme that allows the transfer of heat necessary for the calcination of CaCO₃ in CO₂-rich atmospheres. Various alternatives have been proposed in the literature. These include the oxy-combustion of additional fuel in a regenerator (Weimer et al., 2008; Chen et al., 2011; Martínez et al., 2013a), external heating through high temperature heat transfer surfaces (Abanades et al., 2005; Grasa and Abanades, 2007; Junk et al., 2013) or heating by direct contact with hot solids from an air-blown combustion chamber (Rodríguez et al., 2008; Martínez et al., 2011a). Another recent alternative for the indirect calcination of CaCO₃ is to use chemical looping combustion (CLC) systems. In the CLC, oxygen is transferred from the air to the fuel by means of an oxygen carrier (typically a metal oxide) (Lyngfelt

et al., 2001; Ishida et al., 2002). This avoids the dilution of the combustion products with nitrogen and generates a product gas that is highly concentrated in CO₂ (Adanez et al., 2012). General Electric initially proposed the “unmixed reforming” concept to calcine CaCO₃ in a reactor where the oxidation of nickel with air takes place simultaneously (Kumar et al., 2002). The coupling of both endothermic and exothermic reactions in one single stage favours a better integration as the heat is directly transferred from the oxygen carrier to the calcium carbonate without the need for intermediate heat exchange devices. However, this system generates CO₂ that is highly diluted by N₂, making the capture of CO₂ unfeasible without additional steps. More recent CLC configurations have envisaged carrying out the calcination of CaCO₃ with inherent CO₂ capture, taking advantage of the large heat-transfer capacity of NiO (Wolf and Yan, 2005) or of iron oxides (Fernández and Abanades, 2016) resulting from oxidation stages at temperatures above 1000 °C.

We recently described a novel Ca–Cu chemical looping process (Fernández et al., 2012a) for producing H₂ on the basis of the SER concept, in which a Cu/CuO chemical loop is incorporated to generate the heat needed for the CaCO₃ calcination. The main difference to previous looping concepts with similar objectives is that in this case the heat supply for calcination does not come from the oxidation step of the oxygen carrier, but from the exothermic reduction of CuO with gaseous fuels, generating a highly concentrated stream of CO₂ and H₂O(v). The basic Ca–Cu looping process consists of a sequence of three reaction steps (see Fig. 1), adiabatically carried out in fixed-bed reactors operating in parallel. In the first stage, an enriched stream of H₂ is produced by the sorption enhanced reforming (SER) of methane in the presence of a reforming catalyst, a CaO-based sorbent and a copper-based solid (that acts as inert in this stage). This takes place at 600–750 °C, at steam-to-carbon (S/C) molar ratios of between 2.5 and 5, and at pressures of between 10 and 35 bar in order to achieve high H₂ production yields with high CO₂ capture efficiencies (Fernández et al., 2012b). In the next step, the copper-based particles are oxidized with diluted air at high pressure. A low oxygen content in the feed moderates the increase in temperature during the oxidation of Cu to CuO, thereby avoiding the decomposition of CaCO₃ through partial calcination (Fernández et al., 2013). 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 the reduction of CuO is sufficient to com-

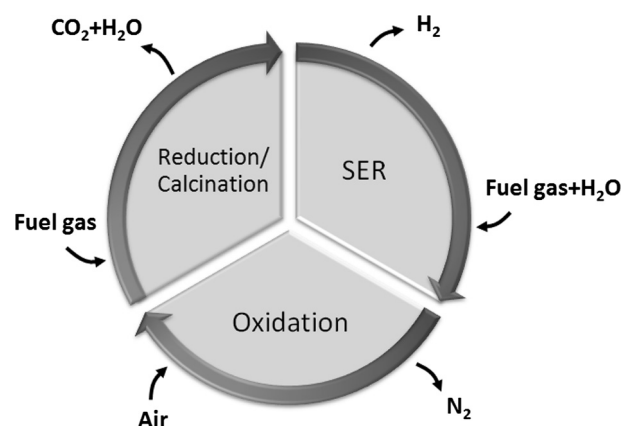


Fig. 1. Illustration of a process for hydrogen production using the Ca–Cu chemical looping reaction concept.

Download English Version:

<https://daneshyari.com/en/article/6467643>

Download Persian Version:

<https://daneshyari.com/article/6467643>

[Daneshyari.com](https://daneshyari.com)