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Process design of a hydrogen production plant from natural gas with CO_2 capture based on a novel Ca/Cu chemical loop

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HIGHLIGHTS

- Process design of a H_2 production plant based on a novel Ca/Cu looping process is presented.
- CuO reduction with syngas provides energy for $CaCO_3$ calcination.
- The effect of operating conditions on plant performance indexes is analysed.
- Carbon capture efficiencies of around 94% are obtained.
- Around 6% points of equivalent H_2 efficiency improvement on conventional reforming.

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ABSTRACT

A detailed and comprehensive design of a H_2 production plant based on a novel Ca/Cu chemical looping process is presented in this work. This H_2 production process is based on the sorption-enhanced reforming concept using natural gas together with a $CaO/CaCO_3$ chemical loop. A second Cu/CuO loop is incorporated to supply energy for the calcination of the $CaCO_3$ via the reduction of CuO with a fuel gas. A comprehensive energy integration description of the different gas streams available in the plant is provided to allow a thermodynamic assessment of the process and to highlight its advantages and drawbacks. Hydrogen equivalent efficiencies of up to 77% are feasible with this novel Ca/Cu looping process, using an active reforming catalyst based on Pt, high oxidation temperatures and moderate gas velocities in the fixed bed system, which are around 6% points above the efficiency of a reference H_2 production plant based on conventional steam reforming including CO_2 capture with MDEA. Non-converted carbon compounds in the reforming stage are removed as CO_2 in the calcination stage of the Ca/Cu looping process, which will be compressed and sent for storage. Carbon capture efficiencies of around 94% can be obtained with this Ca/Cu looping process, which are significantly higher than those obtained in the reference plant that uses MDEA absorption (around 85%). Additional advantages, such as its compact design and the use of cheaper materials compared to other commercial processes for H_2 production with CO_2 capture, confirm the potential of the Ca/Cu looping process as a pre-combustion CO_2 capture technology for H_2 production.

1. Background and scope

Hydrogen is mainly used today in ammonia, oil refining and methanol production plants. The share of hydrogen production in the global emissions of CO_2 is relatively small (the emissions from steam methane reformers are estimated to account for about 3% of the global emissions [1]), but the demand for hydrogen is expected to grow in the future due to the growth of ammonia production and to the increase in the use of H_2 for the production of light and low-sulphur oil distillates in hydrotreating and hydrocracking processes [2]. In addition, in a carbon-constrained world, the use of hydrogen as an energy carrier is expected to rise, in refineries as a fuel for power generation, in boilers and process heaters [3,4] or even as a fuel for transport assuming that the hydrogen economy continues to develop [5].

Synthesis gas (and therefore hydrogen) can be produced from almost any carbon source ranging from oil or natural gas to coal and biomass. Natural gas is the most widely used feedstock because of its low overall H_2 production costs at the most common

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Nomenclature

$e_{CO_2,NG}$	natural gas emission factor (2.65 kg CO_2/kg NG)
E_{eq}	equivalent CO_2 specific emission (g CO_2/MJ H_2 output)
$E_{eq\text{-}ref}$	equivalent CO_2 specific emission in the reference plant without capture (g CO_2/MJ H_2 output)
$\dot{m}_{CO_2,capt}$	mass flow rate of CO_2 captured
$\dot{m}_{H_2}$	mass flow rate of the H_2 output (kg/s)
$\dot{m}_{NG}$	mass flow rate of the natural gas input (kg/s)
$\dot{m}_{NG,eq}$	mass flow rate of the equivalent natural gas input (kg/s)
Q_{th}	thermal power output of the steam export (MW)
$T_{gin,i}$	gas temperature at the inlet of stage i of the Ca/Cu looping process (K)
$T_{max,i}$	maximum temperature achieved in stage i of the Ca/Cu looping process (K)
W_{el}	electricity power output of the plant (MW)

Acronyms

CCR	carbon capture ratio
CCR_{eq}	equivalent carbon capture ratio
CLC	chemical looping combustion
ECO	economiser
EVA	evaporator
FTR	fired tubular reformer
HP	high pressure
HT	high temperature
LHV	lower heating value
LT	low temperature
NG	natural gas
PSA	pressure swing adsorption
SER	sorption enhanced reforming
SH	superheater
SMR	steam methane reforming
SPECCA	specific primary energy consumption for CO_2 avoided
VLP	very low pressure
WGS	water gas shift

Greek letters

$\eta_{el,ref}$	electric efficiency of a conventional natural gas combined cycle
η_{eq,H_2}	equivalent H_2 production efficiency
η_{eq,H_2-ref}	equivalent H_2 production efficiency of the reference plant without capture
η_{H_2}	hydrogen production efficiency
$\eta_{th,ref}$	reference thermal efficiency of a conventional industrial boiler

plant scales. There is also widespread interest in mitigating climate change mainly by reducing the amount of CO_2 emitted to the atmosphere from large stationary sources. In the medium-to-long term, large fossil-fuel H_2 production plants fitted with CO_2 capture and storage systems (CCS) will form part of a privileged branch of technology, and therefore, R&D should be devoted to make CCS technically and commercially efficient by improving plant efficiency, reducing capital costs, and increasing the operational flexibility and reliability of hydrogen production systems.

The dominant H_2 production technology on a large scale is the steam methane reforming (SMR), which is responsible for around 50% of the hydrogen produced worldwide [6,7]. SMR comprises two reaction steps: a first reforming step operating at high temperature between 1073 and 1173 K and at high pressure using a nickel-based catalyst (reaction 1), and a second shift reaction which can be carried out either in a single stage or in two stages at different temperatures to enhance the conversion of CO to CO_2 (reaction 2). In the second case, the first shift stage is usually performed at high temperatures of 623–783 K over a chromium–iron oxide catalyst promoted by the addition of a small amount of copper (1–2 wt.%), whereas the second shift reactor operates at a lower temperature of 453–603 K over a copper–zinc catalyst so that the CO fraction is reduced to around 3 vol.% of the gas leaving the second shift reactor [6,8]. H_2 production by SMR is performed at a high pressure of around 1500–3000 kPa for the sake of economy despite its negative effect on methane conversion [8]. However, further purification steps are needed after the shift reactors to attain the high degree of H_2 purity necessary for its final use.

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H_{298\,K} = +206.2\ \text{kJ/mol} \tag{1}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H_{298\,K} = -41.5\ \text{kJ/mol} \tag{2}$$

Although SMR is the most efficient and economic process for H_2 production on a large scale compared to the rest of the technologies in common use today such as partial oxidation, coal gasification or autothermal reforming, it has serious drawbacks [8]. The stringent conditions of high pressure and high temperature that are required in the reforming reactor as well as the high endothermicity of the reforming reaction, entail large additional fuel requirements in the reactor to guarantee the supply of the energy needed for the reforming reaction. Although the thermal efficiency of a tubular reformer and waste heat recovery section is close to 95%, the overall efficiency has been estimated to be in the range of 70–80%, when defined as the energy (on a LHV basis) of the H_2 product obtained in relation to the total LHV thermal input (natural gas and additional fuel) [6,9–11]. Efficiency can be increased if the amount of heat transferred in the tubular reformer is reduced by using a pre-reformer to decompose the large hydrocarbons before the SMR. Another option for improving efficiency is to increase the energy transferred to the reformer via a convective heat-exchange reformer (also known as gas heated reformer), where the hot product gas is cooled with the transfer of heat to the gas inside the reformer [8,12]. However, this option also entails the risk of metal dusting corrosion. Proper construction materials and the coating of exposed surfaces are required for the efficient recovery of heat from a high CO content process gas with a carbon activity higher than 1 in the 673–1073 K temperature range [13,14].

Thermodynamic constraints require the SMR to be operated at high temperatures and low pressures to facilitate high methane conversion [15,16]. However, the production of low pressure H_2 would require a subsequent compression stage before it could be used in synthesis processes or as fuel for gas turbines, which would probably make the process economically unfeasible [8]. The possibility of combining reaction and separation in order to simplify the process, enhance efficiency and improve the hydrogen yield has gained in importance. By equipping the reforming reactor with a H_2 selective membrane, equilibrium limitations can be overcome since the H_2 produced can be continuously withdrawn from the reacting gas by allowing it to permeate through the membrane. Lower operating temperatures than those required in SMR would then be possible [6,17,18]. A large number of experimental and modelling studies have been undertaken not only to demonstrate the viability of this concept but also to reduce costs and improve the design features, performance and efficiency of this technology [18–22]. One of the disadvantages of this process is that the driving force for H_2 separation is the partial pressure difference between each side of the membrane, which results in low pressure hydro-