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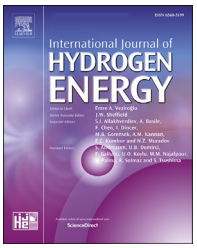

Techno-economic analysis of the Ca-Cu process integrated in hydrogen plants with CO_2 capture

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ABSTRACT

In this work, a techno-economic analysis of a hydrogen production plant based on the Ca-Cu process has been carried out. The simulation of the whole hydrogen production plant has been performed, including the calculation of the Ca-Cu fixed bed reactors system using a sharp front modelling approach. From the analyses carried out, it has been demonstrated that the optimal operation point from the energy performance point of view is reached when fuel needed for sorbent regeneration is entirely supplied by the off-gas from the PSA hydrogen purification unit, which corresponds to operating the plant with the minimum steam-to-carbon ratio in the reforming step. Moreover, lowering the operating pressure of the Ca-Cu system results beneficial from the hydrogen production efficiency, but the CO_2 emissions and the economics worsen.

The Ca-Cu based hydrogen production plant operating at a high pressure has been demonstrated to be cost efficient with respect to a benchmark hydrogen production plant based on conventional fired tubular reformer and CO_2 capture by MDEA absorption. A hydrogen production cost of 0.178 €/Nm^3 and a CO_2 avoided cost of 30.96 €/ton have been calculated for this Ca-Cu hydrogen production plant, which are respectively 8% and 52% lower than the corresponding costs of the benchmark.

Introduction

Currently, 90% of the hydrogen produced worldwide is used as a raw material in the synthesis of ammonia and methanol and in the oil refining industry for the hydrocracking of the heavy feedstocks as well as for the desulphurization of diesel fuel [1]. Hydrogen consumption is expected to keep on rising in the future due to the increase in the need of ammonia-based fertilizers and liquid hydrocarbons as a result of a growing global population and possibly due to the emerging economy based on the use of hydrogen as a clean fuel for transport and heating. Steam Methane Reforming (SMR) is the most widely used technology for hydrogen production at a commercial scale nowadays, being adopted in more than 50% of the hydrogen produced worldwide. This is a well-established technology with high hydrogen production efficiencies of 72–77% and the lowest hydrogen production costs with respect to the other hydrogen production processes based on coal gasification, water electrolysis or biomass gasification [2]. Regarding the carbon footprint of a large scale SMR-based plant, 8.1 tons of CO_2 per ton of H_2 are produced in the

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reformer furnace where the energy needed for the endothermic reforming process is supplied by air-fired combustion [3]. Modern SMR plants may achieve up to 10% of reduction in the CO_2 emissions to the atmosphere thanks to improved efficiency, but if significant CO_2 emissions reduction has to be fulfilled, CO_2 Capture and Storage (CCS) technologies need to be implemented, with CO_2 avoidance cost between 40 and 85 €/t, largely depending on natural gas and electricity price [1].

Among the different emerging technologies for hydrogen production with inherent CO_2 capture, there is a strong need of processes with reduced energy penalties and costs. The Ca-Cu looping process is one of such emerging technologies, having shown a noticeably improved performance when adopted for hydrogen production with respect to the commercial SMR systems [4]. This process performs SMR of methane in the presence of a CaO-based sorbent that reacts with the CO_2 produced by the water gas shift (WGS) reaction, forming solid $CaCO_3$. The subsequent calcination of the $CaCO_3$ is sustained by the exothermic reduction of a CuO-based material in the same solid bed. This process, which is carried out in a system of fixed bed reactors operating in parallel at different temperatures and pressures [5–7], consists of three main reacting stages, namely (i) sorption enhanced reforming (SER – Stage A), (ii) Cu oxidation with diluted air (Stage B), and (iii) CuO reduction and simultaneous $CaCO_3$ calcination (Stage C) using H_2, CO and CH_4 as fuel gas. Fig. 1 shows a schematic of the fixed bed reactor system proposed in this work, which consists of four groups of reactors (A, B, B', C) operating in parallel. The hydrogen production stage through the SER process corresponds to stage A in this figure, where pre-reformed natural gas is the feed gas. This stage operates at a high pressure of 10–30 bar. The H_2-rich gas produced in stage A is cooled and sent to a PSA unit for separating the high purity hydrogen product. The PSA off-gas, containing the unreacted CH_4, H_2, CO and CO_2, constitutes the fuel gas used in the reduction/calcination stage C, which may be integrated with an input of additional natural gas. The Cu oxidation corresponds to the stage B of the process shown in Fig. 1 and it is carried out at the same operating pressure of stage A. This reactor is fed with diluted air, which is obtained by mixing compressed air with a fraction of the N_2-rich gas recirculated from stage B outlet. Dilution with N_2 is needed to limit the maximum temperature reached within the solid bed during this oxidation stage. A heating stage B′ is then needed for heating up the solid bed before the reduction/calcination stage C begins. This heating process is performed by means of a stream of recirculated N_2-rich gas from stage B outlet.

This process has experienced a significant development in the recent years, especially in the framework of the FP7 EU project ASCENT [8]. Regarding the functional materials needed in the Ca-Cu process, CaO-based CO_2 sorbents and high load Cu-based materials with the appropriate proportions of Ca and Cu have been prepared, characterized and tested under conditions relevant for SER and reduction/calcination stages of the Ca-Cu process at large scale [8,9]. Dynamic 1-D pseudo homogeneous models have been also developed for simulating the operation of the fixed bed reactors of the Ca-Cu process and determine the operational window of each reacting stage of the process, as well as the effect of the kinetics and the Cu-to-Ca ratio needed in the solid bed [10–15]. Moreover, such reactor models have been used to evaluate the performance of alternative operation strategies that aim at increasing the CO_2 capture efficiency when the process is integrated in a power plant [16].

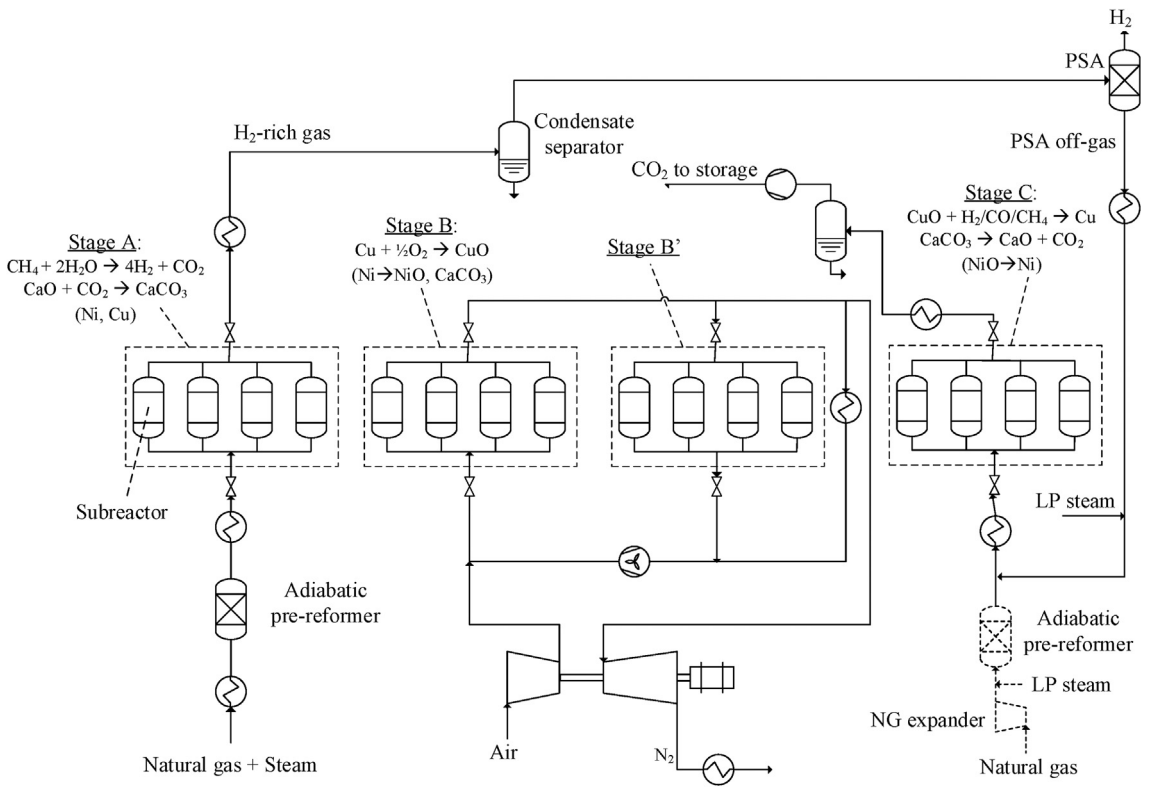

Fig. 1 – Simplified scheme of a H_2 production plant integrated with the Ca-Cu process.

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