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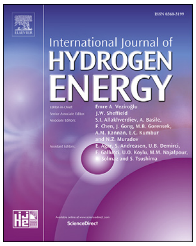

Hydrogen production with integrated CO_2 capture in a novel gas switching reforming reactor: Proof-of-concept

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ABSTRACT

This paper reports an experimental investigation on a novel reactor concept for steam-methane reforming with integrated CO_2 capture: the gas switching reforming (GSR). This concept uses a cluster of fluidized bed reactors which are dynamically operated between an oxidation stage (feeding air) and a reduction/reforming stage (feeding a fuel). Both oxygen carrier reduction and methane reforming take place during the reduction stage. This novel reactor configuration offers a simpler design compared with interconnected reactors and facilitates operation under pressurized conditions for improved process efficiency.

The performance of the bubbling fluidized bed reforming reactor (GSR) is evaluated and compared with thermodynamic equilibrium. Results showed that thermodynamic equilibrium is achieved under steam-methane reforming conditions. First, a two-stage GSR configuration was tested, where CH_4 and steam were fed during the entire reduction stage after the oxygen carrier was fully oxidized during the oxidation stage. In this configuration a large amount of CH_4 slippage was observed during the reduction stage. Therefore, a three-stage GSR configuration was proposed to maximize fuel conversion, where the reduction stage is completed with another fuel gas with better reactivity with the oxygen carrier, e.g. PSA-off gases, after a separate reforming stage with CH_4 and steam feeds. A high GSR performance was achieved when H_2 was used in the reduction stage. A sensitivity analysis of the GSR process performance on the oxygen carrier utilization and target working temperature was carried out and discussed.

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Introduction

In the last few decades there is a growing consensus that increasing levels of greenhouse gas emissions (primarily CO_2) associated to the use of fossil fuels for power generation, transport and industry are causing global warming. According to the fifth Intergovernmental Panel on Climate Change (IPCC) assessment report [1], warming of the climate system is unequivocal, and since the 1950s, many of the observed changes are unprecedented over decades to millennia. It is therefore very important that CO_2 emissions are reduced or if possible eliminated through conservation, efficiency improvement, low carbon energy systems (renewables, nuclear and CCS) and low carbon energy carriers (biofuels and hydrogen).

In this scenario, hydrogen is being progressively seen as an alternative clean energy carrier [2], which can be used as fuel in the transport sector (this will reduce the distributed CO_2 emissions, and increase the conversion efficiency). It is also a very important raw material in the production of several industrial products (ammonia, methanol, food processing, etc.). In addition, there is a steadily increasing hydrogen demand for refining, metallurgy and manufacturing of electronic components [3].

Hydrogen is mostly produced from natural gas through steam methane reforming (SMR), where a highly endothermic reforming reaction takes place in reformer tubes filled with nickel-based catalyst pellets [4,5]. This process involves large CO_2 emissions due to the burning of natural gas or an off-gas fuel inside a furnace in order to supply the energy required for the endothermic reforming reaction. Some additional drawbacks of this process are high intra-particle mass transfer resistance and high temperature gradients (drawbacks related to packed beds) [6,7].

Autothermal reforming is regarded as a possible alternative to the conventional SMR process, where the partial oxidation of methane is used as an energy source for the endothermic reforming reaction [8]. In this process, the reforming reactants (CH_4 and H_2O) and an oxidizing agent (pure O_2 or air) are fed together to an adiabatic reactor where both the partial oxidation and reforming reactions occur. However, production of a high quality syngas requires pure oxygen delivered by an air separation unit, which increases capital costs and energy consumption of the process.

The need for cost effective and environmentally friendly processes for hydrogen production has prompted research into novel reactor concepts [9,10]. Autothermal chemical looping reforming (CLR) technology was proposed as a new and promising process, in terms of process efficiency, for hydrogen production with integrated CO_2 capture without the need for an external heat supply [8,11,12]. CLR uses the same basic principle as chemical looping combustion (CLC), but with a different desired end product: syngas in CLR and heat for power production in CLC.

Similar to CLC, CLR can be carried out in two interconnected fluidized bed reactors, designated as air and fuel reactors (Fig. 1), where an oxygen carrier material (metal or metal oxide) transfers oxygen from the air reactor to the fuel. Additionally, in the case of CLR, the oxygen carrier material acts as a catalyst for the endothermic steam-methane reforming reaction. Similar to CLC, CLR achieves inherent separation of CO_2 and N_2 (from air) with a much lower energy penalty than conventional CO_2 capture processes [11,13,14]. In the CLR process, the oxygen-to-fuel ratio is usually kept low to prevent complete oxidation of the fuel to CO_2 and H_2O. Natural gas is converted into syngas via the SMR reaction, after which the products undergo additional steps, like water-gas-shift (WGS) and pressure swing adsorption (PSA) units if the desired end product is pure hydrogen [8,15].

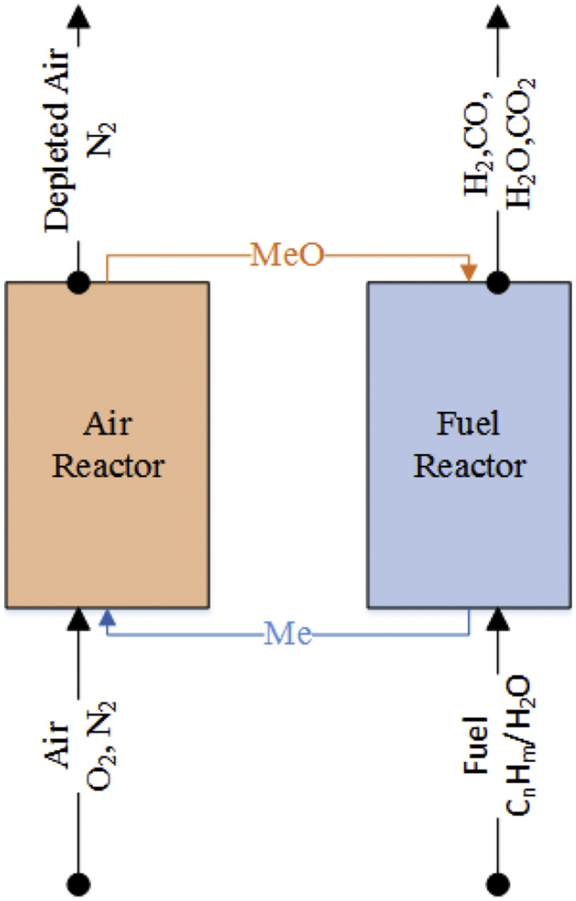

Fig. 1 – Schematic illustration of the chemical looping reforming reactor.

High-pressure operation is, however, a prerequisite to demonstrate the real potential of chemical looping technologies in achieving competitive overall energy efficiencies [16,17]. High pressure operation allows more homogeneous fluidization with better mass transfer rates [18], reduces the energy penalty and capital costs associated with compressing the final hydrogen product, and delivers a high pressure CO_2 stream for efficient compression, transport and storage. However, scale-up of pressurized fluidized bed-based chemical looping technologies, including CLR, has been slow, primarily due to technical challenges related to the circulation of solids between the reactors (especially in the operation of the loop seals) and separation of solids from the gas streams at high temperatures and pressures. To the authors' knowledge, only one study on pressurized CLC in interconnected fluidized beds has been completed to date [19]. This study was carried