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# Design and optimization of stand-alone triple combined cycle systems using calcium looping technology

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## ABSTRACT

In our approach, the “stand-alone” process is an off-the-grid electricity system or a fuel processor without external energy supplies. A syngas producer is developed as a stand-alone SMR + CaL process using a combination of a steam methane reformer (SMR), a calcium looping (CaL) and a pre-burner to enhance CO<sub>2</sub> concentration of exhaust gas and produce syngas for power generation. A stand-alone triple combined cycle system (TCCS), which mainly consists of a solid oxide fuel cell (SOFC), Brayton-Rankine combined cycles, and a syngas producer, is developed as a high efficiency power generation system with CO<sub>2</sub> capture by adding a post-burner and using the specific water/heat exchanger networks. Based on optimal operating conditions by solving two optimization algorithms, the simulation shows that the total power efficiency of the stand-alone TCCS is up to 60.56% and its CO<sub>2</sub> emissions per kWh of electricity is down to 7.18 gCO<sub>2</sub>.

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## 1. Introduction

Hydrogen is recognized as a clean fuel, approximately 95% hydrogen is generated by steam/partial oxidation reforming of natural gas, but carbon emissions of these processes cannot be avoided. Recently, the growing concern regarding the concentration of greenhouse gases has encouraged the development of hydrogen production processes with zero, or near-zero, CO<sub>2</sub> emissions. The hydrogen selective water-gas-shift (WGS) membrane reactors enable simultaneous high-purity hydrogen production and CO<sub>2</sub> capture (Georgis et al., 2014). Mueller et al. (2009) showed that synthetic CaO based sorbents significantly enhanced the production of H<sub>2</sub> during the WGS reaction, but the catalytic activity of CaO was gradually decayed. Wu and Kuo (2015) used the oxy combustion technique to capture CO<sub>2</sub> of flue gas in a liquefied hydrogen production process. However, those CO<sub>2</sub> capture methods would reduce the system efficiency by 20%–40%. On the other hand, Wu et al. (2014) presented a combination of steam methane reforming (SMR) and dry reforming of methane (DRM) to enhance CO<sub>2</sub> utilization and it can be treated as the fuel source of the hybrid SOFC/GT power system (Wu et al., 2016), but this hybrid power system cannot reduce net CO<sub>2</sub> emissions since external energy

supplies are not avoided.

The calcium looping (CaL) process was a promising method for large-scale CO<sub>2</sub> capture (Blamey et al., 2010). Martínez et al. (2011) indicated that the coal-fired subcritical power plant with 36% net efficiency by using the CaL process. The efficiency penalty for CO<sub>2</sub> capture estimates between 8.3 and 10.3%. On the other hand, the CaL process was developed for the production of H<sub>2</sub> since CaO sorbent could enhance H<sub>2</sub> yield in the absence of a water-gas-shift (WGS) catalyst (Ramkumar and Fan, 2010). The CaL technology was integrated into the cement plant for CO<sub>2</sub> capture (Atsonios et al., 2015). Notably, the CaL is superior to the amine scrubbing in terms of economic efficiency. The CaL process has been also demonstrated at 10 kWth lab scale plant as well as at the 200 kWth pilot scale plant (Duelli et al., 2015). For the improvement of CO<sub>2</sub> capture technologies, a dual chemical looping process using a combination of WGS and CaL is validated as an efficient method for hydrogen production and CO<sub>2</sub> capture (Zhu et al., 2016), a Ca/Cu chemical loop is applied to improve a hydrogen production plant from natural gas with CO<sub>2</sub> capture (Martínez et al., 2014), the combined calcium and chemical looping cycles with CaO/CuO-based pellets can enhance sorbent performance in CO<sub>2</sub> capture processes (Ridha et al., 2015), and a double calcium loop combined with a number of cyclonic preheaters can reduce the overall energy demand in the calciner (Diego et al., 2016). From aspects of system engineering, a coal-to-methanol process takes CO<sub>2</sub> capture and organic rankine cycle to improve energy efficiency by virtue of heat

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integration (Liu et al., 2016), and an integrated technical and environmental assessment methodology for integrated gasification combined cycle (IGCC) with different carbon capture techniques (gas-liquid absorption and chemical looping) is evaluated (Petrescu and Cormos, 2015).

In general, the solid oxide fuel cell (SOFC) is a highly efficient power generator that operates at high temperature. The combinations of SOFC and various gas turbine (GT) and steam turbine (ST) cycles can lead to improve the overall power efficiency (Palsson et al., 2000; Kuchonthara et al., 2003; Haseli et al., 2008). For the development of the power system with zero or near-zero emissions, Chen et al. (2012) showed that the gas/steam turbine combined cycle integrated with coal gasification and chemical looping using  $\text{Fe}_2\text{O}_3$  and  $\text{CuO}$  oxygen carriers could ensure a net power efficiency of 43.53% with zero  $\text{CO}_2$  emissions. Chen et al. (2015) indicated that the coal gasification integration with SOFC and chemical looping using  $\text{NiO}$  oxygen carries can increase the net power efficiency by 49.8%. Choi et al. (2014) presented a triple power generation cycle combining gas/steam turbine combined cycle and SOFC where the efficiency penalty of the post-combustion MEA-based carbon capture process is around 5%. In addition, Campanari et al. (2010) showed that the molten carbonate fuel cell (MCFC) was integrated into the natural gas fired combined cycle power plant to produce  $\text{CO}_2$ -rich exhaust gas, and Kuo and Wu (2016a) indicated that the co-gasification of biomass and coal under  $\text{CO}_2$  addition could contribute to reduce life-cycle carbon emissions of the hybrid power system. Recently, Kuo and Wu (2016b) showed that the gas/steam turbine combined cycle integrated with co-gasification of biomass and coal and a CaL scheme may achieve the power system with negative life-cycle  $\text{CO}_2$  emissions. These power systems are not stand alone, so  $\text{CO}_2$  emissions from external energy supplies could change life-cycle carbon emissions.

In this paper, first we introduce the stand-alone SMR + CaL process by using a combination of a steam methane reformer (SMR), internal burners, a specific water network and a calcium looping (CaL) for the syngas production as well as  $\text{CO}_2$  capture. The “stand-alone” approach increases the amount of waste heat and  $\text{CO}_2$  by adding a pre-burner to capture the more amount of  $\text{CO}_2$ . Second, we introduce a triple combined cycle system (TCCS) using a combination of a solid oxide fuel cell (SOFC), Brayton-Rankine combined cycles and a stand-alone SMR + CaL process to become the stand-alone power generation system with  $\text{CO}_2$  capture. Two constrained optimization algorithms are employed to improve the power efficiency and suppress  $\text{CO}_2$  emissions. Finally, the power system performance are successfully validated by the power efficiency, thermal efficiency, specific  $\text{CO}_2$  emissions and  $\text{CO}_2$  capture index.

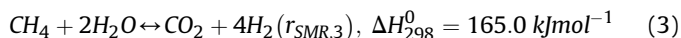
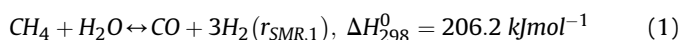
## 2. Syngas producer

Syngas, or synthesis gas, is a fuel gas mixture consisting primarily of  $\text{H}_2$  and  $\text{CO}$ . It is usually a product of gasification and the main application is electricity generation. In our approach, syngas is produced from natural gas, or methane; the methane-to-syngas process is developed as the syngas producer with carbon capture and low energy consumption. We introduce three types of syngas producers in the following subsections.

### 2.1. Steam methane reformer (SMR)

The SMR has been widely used in industry due to its high efficiency and low cost. Natural gas (methane) and water are fixed with a specific S/C ratio (inlet flowrate of  $\text{H}_2\text{O}$  divided by inlet flowrate of  $\text{CH}_4$ ) and accordingly fed into a tubular reactor at prescribed inlet

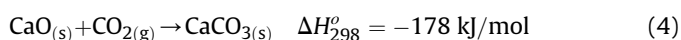
operating temperature, in which three major reactions are considered as follows.



where the corresponding rate equations by  $r_{\text{SMR},i}$  ( $i = 1, \dots, 3$ ) are shown in Appendix A. Fig. 1 shows that the syngas yield (total outlet flowrates of  $\text{H}_2$  and  $\text{CO}$  divided by inlet flowrate of  $\text{CH}_4$ ) of the SMR process is affected by S/C and inlet temperature of SMR ( $T_{\text{SMR},\text{in}}$ ). Apparently, the syngas yield is maximized while  $\text{S/C} > 2$  and  $T_{\text{SMR},\text{in}} > 670^\circ\text{C}$ . The specifications of the SMR process are shown in Table 1.

### 2.2. Modified calcium looping

The calcium looping (CaL) technology is a potentially low cost and highly efficient  $\text{CO}_2$  capture technology for post- and pre-combustion applications where energy integration and sorbent behavior play a relevant role on the process (Perejón et al., 2016). In Fig. 2, the CaL process is composed of carbonator and calcinator where two solids lime ( $\text{CaO}$ ) and limestone ( $\text{CaCO}_3$ ) are transported between reactors. The flue gas or fuel gas is fed into a fluidized bed carbonator at  $600\text{--}700^\circ\text{C}$  in which an exothermic carbonation reaction takes place



It shows that  $\text{CO}_2$  is captured by lime to become limestone. A  $\text{CO}_2$ -lean gas or product is exhausted. Notably, the water gas shift (WGS) reaction could appear in the carbonator if the fuel gas contains syngas,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (Muller et al., 2009). Under the equilibrium thermodynamic considerations, the compositions of  $\text{CO}_2$ -lean gas can be determined by a relation for the equilibrium constant ( $K_{\text{eq}}$ ) as a function of temperature is shown by (Callaghan (2006))

$$\log K_{\text{eq}} = -2.4198 + 0.0003855T_{\text{car}} + \frac{2180.6}{T_{\text{car}}} \quad (5)$$

Solid  $\text{CaCO}_3$  flows into a fluidized bed calciner at  $850\text{--}950^\circ\text{C}$  to carry out an endothermic calcination reaction

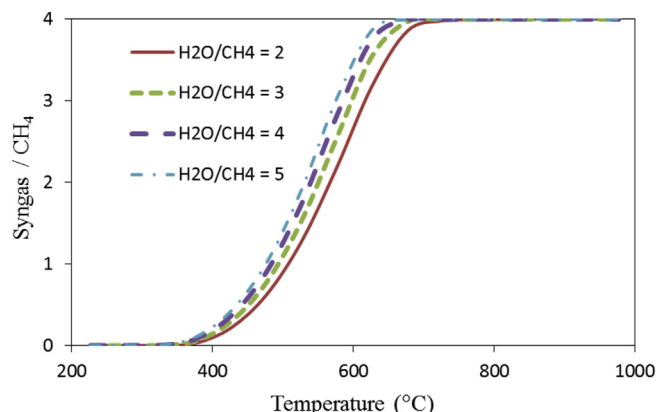


Fig. 1. SMR process with regard to effects of S/C ratio and  $T_{\text{SMR},\text{in}}$ .

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