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Parameter optimization and thermodynamic analysis of COG direct chemical looping hydrogen processes

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ABSTRACT

Coke-oven gas (COG) is largely by-produced in coking plants, being most burnt and resulting in serious energy waste and air pollutant emissions. Producing high-value hydrogen from COG is therefore promising, however, the traditional processes via steam methane reforming still suffer from high energy consumption and CO_2 emissions. In this work, we propose efficient COG-to-hydrogen processes by chemical looping hydrogen technology. Parameter optimization of the proposed systems without and with support has also been conducted for the optimum COG utilization and maximum hydrogen production. The optimum molar ratios for the oxygen carrier/COG, steam/oxygen carrier, and air/oxygen carrier were found to be 2.0, 1.2, and 0.81, respectively, for the process without support. In the supported system, due to the presence of the high-temperature support, the optimum molar ratio of the oxygen carrier/COG is decreased to 1.1, while the steam/oxygen carrier ratio is increased to 3.9. The exergy efficiency, and CO_2 capture efficiency, and hydrogen purity of the system with support are 63.8%, 73.3%, and 99.4 mol.%, respectively. It was found that the process including an intercooling between fuel reactor and steam reactor, and oxygen-enriched combustion in the heating air reactor provides a further improved exergy efficiency of 66.2% and CO_2 capture efficiency of about 100%.

1. Introduction

Hydrogen is regarded as one of the most important clean fuels in terms of the depletion of fossil fuels and their serious environmental impact [1]. Currently, steam methane reforming (SMR), partial oxidation, auto-thermal oxidation, gasification, and water splitting are the main hydrogen production technologies [2,3]. Among them, SMR is the dominant hydrogen production process owing to its mature technology and economic competitiveness [4]. However, the SMR process suffers from high energy consumption and CO_2 emissions, which is caused by large amounts of fuel burnt to maintain its high reaction temperature.

Chemical looping hydrogen (CLH) processes have been suggested as an innovative and promising method for hydrogen production with inherent CO_2 separation, high product purity, and high efficiency [1]. The three typical reactors in the CLH are fuel reactor (FR), air reactor (AR), and steam reactor (SR), where the reduced oxygen carrier (OC) is oxidized by steam for producing high-purity hydrogen [5]. The primary gas products of the FR are CO_2 and H_2O, from which high-purity CO_2 can be easily captured and stored through simple condensation [6]. The OC exiting the SR is completely oxidized using air in the AR and then the oxidized OC is recycled into the FR.

A number of researchers have conducted parameter optimization and thermodynamic analysis of CLH processes based on solid fuels (coal and biomass) and their syngas, liquid fuels, and natural gas [7]. Zeng et al. [8] and Aziz et al. [9] proposed novel coal direct chemical looping processes for hydrogen and power production. Energy and exergy analyses of coal-based syngas CLH processes have been performed for the tri-generation of power, hydrogen, and heating [10]. Kuo et al. [11], Zaini et al. [12], and Aghaie et al. [5] have also proposed novel processes of biomass-based syngas CLH and power generation. Biogas sorption-enhanced chemical looping reforming process for high-purity H_2 and then for power generation has been modeled and analyzed, in which the exergy efficiency reached 60%, as reported by Kasemanand et al. [13]. A novel power, methanol, and DME polygeneration process from coal and natural gas integrating with chemical looping systems have also been further proposed [14]. Sorption enhanced-chemical looping reforming has been proposed for hydrogen production from glycerol and ethanol [15,16].

For natural gas, Zhang et al. [17] proposed a dual-loop CLH process from ventilation air methane with hydrogen efficiency as high as 40%. Khan and Shamim [1] and Kathe et al. [18] developed thermodynamic model and reaction model for natural gas CLH to assess the effect of various operating parameters on the fuel conversion, hydrogen production, and reactor temperature. Alam et al. [19] and Fan et al. [20]

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proposed novel and efficient process schemes for the production of high-purity hydrogen via integration of SMR with chemical looping combustion. Edrisi et al. [21] proposed a new methane chemical looping plant for N_2 and H_2 production, in which 2.53 mol of N_2 and 2.65 mol of H_2 were produced per mole of methane. A novel process of ammonia synthesis integrated with CLH was further investigated and 30% increase of ammonia capacity was achieved in Ref. [22]. New systems integrating methane CLH and hydrogen-oxygen combined cycle was proposed by Zhang et al. [23] and about 60% net efficiency with CO_2 separation was realized in this work. Phuluanglue et al. [24] investigated the performance of methane sorption-enhanced chemical looping reforming for hydrogen production by a Ni based OC, in which a CH_4 conversion of 98% and H_2 purity of 98.4% were achieved. A chemical looping SMR method for hydrogen and syngas production by a perovskite-based OC was also studied [25]. A novel chemical looping carbon reforming process for hydrogen and then methanol production was further developed by Zhou et al. [26].

Coke-oven gas (COG), containing as high as 58–60 vol% H_2, is the most important by-product of coking plants [27]. Because of its hydrogen-rich characteristics, COG may be implemented for large-scale and efficient hydrogen production. There are several researches focused on hydrogen generation process from COG. Xie et al. [28] conducted thermodynamic analysis of a novel process for hydrogen production from COG via CO_2 sorption-enhanced steam reforming. Yang et al. [29] proposed a CaO sorption-enhanced COG steam reforming process integrated with chemical looping combustion. Wang et al. [30] proposed a new hydrogen production process from COG using a CO_2 adsorption-enhanced hydrogen amplification reactor. Svoboda et al. [31,32] also evaluated the thermodynamic possibilities for pure hydrogen production from a mixture of CO, H_2, and CH_4 by iron, nickel, and cobalt-based CLH systems.

To the best of our knowledge, few studies have investigated the COG chemical looping hydrogen (CG-CLH) process. Therefore, this study was aimed at the thorough parameter optimization and thermodynamic analysis of CG-CLH without and with support (denoted as CG-CLHwoS and CG-CLHwS, respectively) by process modeling. The initial COG fed into the AR for heating is directly combusted with air in the inner of the AR, as adopted from the natural gas CLH process in Ref. [18]. However, this configuration undoubtedly leads to a certain degree of CO_2 emissions. Thus, another configuration for COG combustion with pure oxygen from an air separation unit (ASU) in the outer of the AR was also investigated to mitigate the carbon emissions of the new process, which has been labeled as CG-CLHwS-ASU. Finally, the CG-CLH processes are compared with the natural gas SMR to demonstrate the advantages and drawbacks of these new processes.

2. Modeling and simulation of the CG-CLH

The CG-CLHwoS and CG-CLHwS systems mainly include FR, SR, and AR, as shown in Fig. 1. In this study, iron oxide (Fe_2O_3) was selected as the OC. It is well known that the use of support is critical to the OC performance and reaction temperature of the CLH processes. Therefore, 50 w.% Al_2O_3 was employed as the support in this study following a previous report [18]. The reactions between COG and Fe_2O_3 in the FR are usually endothermic, as shown in Eqs. (1)–(6). In these reactions, the Fe_2O_3 is reduced to wustite (FeO) and Fe upon oxidizing COG into H_2O and CO_2. Fe and FeO are then fed to the SR, where they are oxidized into magnetite (Fe_3O_4) and hydrogen is simultaneous produced by Eqs. (7) and (8) [33]. The highly exothermic reaction in the AR is shown in Eq. (9), in which Fe_3O_4 is completely oxidized into Fe_2O_3 by air for recycle utilization. The CG-CLHwS-ASU process is shown in Fig. 2. The major difference in the CG-CLHwS-ASU lies in its oxygen-enriched combustion of COG in the outer of the AR to provide further heat energy.

$$4\ Fe_2O_3 + CH_4 \rightarrow 8\ FeO + 2\ H_2O + CO_2 \tag{1}$$

$$Fe_2O_3 + H_2 \rightarrow 2\ FeO + H_2O \tag{2}$$

$$Fe_2O_3 + CO \rightarrow 2FeO + CO_2 \tag{3}$$

$$4\ Fe_2O_3 + 3\ CH_4 \rightarrow 8\ Fe + 6\ H_2O + 3\ CO_2 \tag{4}$$

$$Fe_2O_3 + 3\ H_2 \rightarrow 2\ Fe + 3\ H_2O \tag{5}$$

$$Fe_2O_3 + 3\ CO \rightarrow 2\ Fe + 3\ CO_2 \tag{6}$$

$$3\ Fe + 4\ H_2O \rightarrow Fe_3O_4 + 4\ H_2 \tag{7}$$

$$3\ FeO + H_2O \rightarrow Fe_3O_4 + H_2 \tag{8}$$

$$4\ Fe_3O_4 + O_2 \rightarrow 6\ Fe_2O_3 \tag{9}$$

The high pressure and temperature of the CO_2 stream from the FR and depleted air stream from the AR are employed to generate electricity by gas turbines and the remaining heat is used to generate steam for SR utilization. The CO_2 separated from water is compressed at 15 MPa for transportation and storage, and the depleted air stream is discharged into the air. The heat of the H_2 stream from the SR is firstly recovered to generate steam for SR utilization, then condensed for hydrogen purification, and finally compressed at 2 MPa for transportation. The isentropic efficiencies of the compressor and gas turbine were here set to 80% and 90%, following a previous report [34].

In this study, the most important components of the FR, SR, and AR were modeled, simulated, validated, and optimized in detail. The FR was designed as a counter-current moving bed reactor and modeled by five-stage RGibbs model in Aspen Plus since it can accurately simulate the experimental results of the counter-current moving bed reactor [18]. The SR and AR were also modeled using RGibbs models according to Ref. [1]. Regarding the subsidiary ASU, its mass and energy consumption were obtained from Ref. [35].

3. Optimization of key operational parameters

Many researchers have focused on the modeling and parameter optimization of the natural gas CLH processes, while studies on CG-CLH by three reactors is rare. The key conditions for fuel conversion, steam conversion, heat duty, etc. were therefore validated with those of reference reports to optimize the key operating parameters, i.e., the OC/COG, steam/OC (S/OC), and air/OC (A/OC) ratios, which were set in the range of 0–3.0, 0–5.0, and 0–3.0 in the following sections, respectively.

3.1. Technical analysis of the CG-CLHwoS system

(1) OC/COG ratio in the FR

In order to analyze the effect of the OC/COG ratio in the FR, the temperature of the OC input was first set to 1473 K [18]. The effect of the OC/COG on gas composition of the FR output in the CG-CLHwoS is shown in Fig. 3. When the OC/COG ratio was increased from 0 to 0.3, the H_2 composition decreased from 0.48 to 0.36, while a further increase to 1.3 resulted in a small reduction of the H_2 production. When the OC/COG ratio was increased from 0 to 1.3, the CH_4 fraction was gradually decrease to near zero, while the CO content barely changed. This is because that methane not only reacts with the OC as per Eqs. (1) and (4) to produce CO_2 and H_2O, but also via SMR to generate CO and H_2 at high reaction temperature. In addition, the H_2 reactivity with the OC is much larger than that of CO. When the OC/COG was increased from 1.3 to 2.0, H_2 and CO were fully converted into H_2O and CO_2 via oxidation by the OC. By continuously increasing the OC input, the COG conversion remains about 1.0, and the H_2O and CO_2 fractions are kept constant at 0.73 and 0.25, respectively. The corresponding CO_2 capture is thus 1771 kmol/h at OC/COG ratios equal or larger than 2.0.

On the other hand, the effect of the OC/COG ratio on the OC