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A hydrogen and oxygen combined cycle with chemical-looping combustion

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ABSTRACT

In the current paper, new systems integrating chemical-looping hydrogen (CLH) generation and the hydrogen (H_2) and oxygen (O_2) combined cycle have been proposed. The new methane-fueled cycle using CLH has been investigated with the aid of the exergy principle (energy utilization diagram methodology). First, H_2 is produced in the CLH, in which FeO and Fe_3O_4 are used as the looping material. The H_2 and O_2 combined cycle then uses H_2 as fuel. Two types of these combined cycles have been analyzed. Waste heat from the H_2–O_2 combined cycle is utilized in the CLH to produce H_2. The advantages of CLH and the H2 and O_2 combined cycle have resulted in a breakthrough in performance. The new system can achieve 59.8% net efficiency with CO_2 separation when the turbine inlet temperature is 1300 °C. Meanwhile, the cycle is environmentally superior because of the recovery of CO_2 without an energy penalty.

1. Introduction

At present, we face a potentially serious problem of rapid climate change attributed to anthropogenic emissions of greenhouse gases (e.g., CO_2). One option to control greenhouse gas emission is the use of CO_2 capture technologies from flue gases. In a fossil fuel-fired power plant, CO_2 capture can be carried out mainly through three available technologies: pre-combustion, post-combustion, and oxy-fuel combustion. The progress in this field has been addressed by Abu-Khader [1]. The main disadvantages of these techniques are the substantial addition to the power generation costs and the large amount of energy required for the CO_2 separation, which amounts to a relative reduction of 15–20% in the overall efficiency of a power plant [2,3]. A new method of separating CO_2 from flue gases in power plants with a negligible energy penalty is therefore urgently needed.

Chemical-looping combustion (CLC) with inherent separation of CO_2 is a promising technology proposed by Ishida and Jin in 1994 [4,5]. It is the most attractive, energy-efficient method of CO_2 capture from fuel conversion using the combustion process. CLC involves the use of a metal oxide as an oxygen (O_2) carrier, which transfers O_2 from the combustion air to the fuel, thereby avoiding direct contact between the fuel and the mixture of fuel and air. In this way, CO_2 and H_2O are inherently separated from the other components of flue gases, so that no energy is needed for CO_2 separation. This novel CO_2 capture technology simultaneously resolves both energy and environmental problems in combustion processes because the conversion of fuel-based chemical energy into thermal energy in traditional combustion not only results in the largest irreversibility in the power system, but also has serious environmental impact. In recent years, several researchers have investigated and contributed to the development of the CLC technology [6,7]. For example, Mattisson and Lyngfelt [8] designed and proposed a 10 kW fluidized-bed boiler using CLC [8]. Korea [9] developed a 50 kW CLC for future industrial application. A project for a novel CO_2 separation system using CLC has been initiated by the Department of Energy of the United States [10]. A recent 1 MWth chemical looping plant is reported by Ströhle et al. [11].

In addition, the use of the chemical-looping process was recently proposed for the production of hydrogen (H_2). There are two kinds of processes to product hydrogen with CLC, the chemical looping reforming (CLR) and chemical looping hydrogen generation (CLH). The CLR produces hydrogen using the CLC principle [12][13]. The main reactions in CLR are as follows, with nickel used as an example:

$$NiO + CH_4 \rightarrow Ni + 2H_2 + CO \quad \Delta H = 211\ \mathrm{kJ/mol}$$

$$2NiO + CH_4 \rightarrow 2Ni + 2H_2 + CO_2 \quad \Delta H = 148\ \mathrm{kJ/mol}$$

$$CH_4 + Ni \rightarrow C{-}Ni + 2H_2 \quad \Delta H = 191\ \mathrm{kJ/mol}$$

The first reaction is considered as the primary pathway, whereas the other two reactions are possible reactions. Natural gas is used as fuel in CLR research. To supply enough heat to drive the reforming reaction on the fuel reactor side, part of the natural

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Nomenclature

CC	combined cycle
CLC	chemical-looping combustion
CLH	chemical-looping hydrogen generation
HO-CLH	H_2 and O_2 combined cycle with CLH
RHO-CLH	reheat H_2 and O_2 combined cycle with CLH
TIT	turbine inlet temperature (°C)
π	pressure ratio
η	thermal efficiency (LHV)
ΔE	exergy change
ΔH	enthalpy change

Subscripts

Opt	optimal value
Ox	oxidation reaction
Re	reduction reaction
Comp	compressor
ST	steam turbine

gas is burned directly to support the reaction. Another method to produce hydrogen using CLC is water splitting applied to chemical looping (chemical looping hydrogen generation, CLH) [14]. The CLH process is based on two reactors. The CLH fuel reactor is similar to that used in CLC, but the CLC air reactor in is replaced with a steam reactor, in which steam reacts with the metal to produce hydrogen. In CLH, both sides of the reactions are endothermic. These reactions are as follows:

$$Ni + H_2O \rightarrow NiO + H_2 \quad \Delta H\ (900\,^{\circ}C) = 186\ kJ/mol$$

$$CH_4 + 4NiO \rightarrow Ni + CO_2 + 2H_2O \quad \Delta H\ (800\,^{\circ}C) = 58\ kJ/mol$$

Approximately 10–20% of natural gas is burned directly to supply the heat for the reactions in SMR and CLH systems. Sung et al. [15] reported that 3.7 L of H_2 per kilogram was generated through the reaction between the fully reduced copper-based oxide and steam. Kang et al. [16] investigated H_2 production using the chemical-looping of methane (CH_4) in a fluidized-bed reactor using an iron-based O_2 carrier.

The H_2 and O_2 combined cycle was first proposed by Cai and Fang [17]. A fairly high efficiency has been obtained based on the stoichiometric reaction of H_2 and O_2. The combination of CLH and the H_2 and O_2 combined cycle can capture CO_2 without an energy penalty and with high efficiency.

2. Description of the novel systems

Fig. 1 shows the plant scheme for the integration of the mixing H_2 and O_2 combined cycle with CLH (HO-CLH). The plant consists of three main parts, namely, the CLH subsystem, the H_2 and O_2 combined cycle subsystem, and the CO_2 separation subsystem.

2.1. CLH subsystem

In the CLH subsystem, two separate reactors, CH_4 with metal oxide (reduction) and the resulting metal with H_2O (oxidation), are used. In the current study, ferric oxide (Fe_3O_4) is used as a solid metal oxide (i.e., looping material) in the chemical-looping hydrogen generation. Oxygen is transferred between the two reactors through an O_2 carrier. CH_4 is first reacted with the solid Fe_3O_4 [reaction (1)] in a reduction reactor, producing solid ferrous oxide (FeO) and steam. When 95–98% of Fe_3O_4 is reduced, the equilibrium temperature of reaction (1) is approximately 600–800 °C. To achieve a higher Fe_3O_4 conversion ratio, the temperature of the reduction reaction should be higher than 600 °C. In the oxidation reactor, H_2O is reacted with solid FeO [reaction (2)] in the high temperature produced from the first reactor, yielding Fe_3O_4 and H_2 through strong exothermic oxidation.

Reduction:

$$CH_4 + 4Fe_3O_4 \rightarrow 12FeO + 2H_2O + CO_2 \quad \Delta H^0_{Red} = 406\ kJ/mol \qquad (1)$$

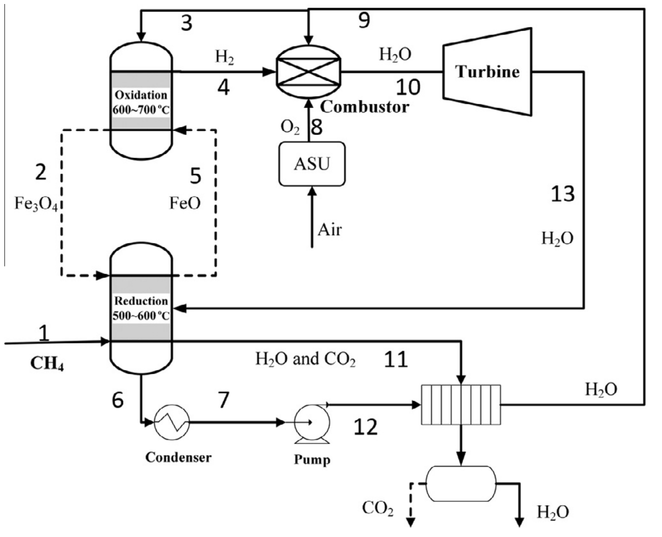

Fig. 1. Mixing H_2 and O_2 combined cycle with chemical-looping hydrogen (HO-CLH).

Oxidation:

$$H_2O + 3FeO \rightarrow Fe_3O_4 + H_2 \quad \Delta H^0_{Ox} = -60\ kJ/mol \qquad (2)$$

2.2. H_2 and O_2 combined cycle subsystem

H_2 produced by the CLH subsystem then enters the H_2 and O_2 combined cycle subsystem. The reaction per mole of H_2 and a half mole of O_2 produce one mole of H_2O, with a very large amount of energy released compared to any other conventional type of fuel. The oxygen comes from a low pressure air separate unit (ASU) outlet and is further compressed by a compressor. After the combustion with O_2 from the ASU, steam from the combustor can be used as the working fluid to generate power in the steam turbines. Finally, steam from the steam turbines releases heat in the reduction reaction, which is then used to supply the endothermic reaction.

2.3. CO_2 separation

The CO_2 separation subsystem is used to separate CO_2 from the CO_2/H_2O mixture. The mixture is cooled using liquid H_2O from the steam turbine, releasing heat in the reduction reactor. The mixture is then cooled to 70–90 °C in the condenser. At this temperature, H_2O turns into its liquid form and CO_2 is separated. After heating using the CO_2/H_2O mixture, the liquid H_2O is separated and flowed to the oxidation reactor and combustor.

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