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Double-stage chemical looping combustion combined with sorption enhanced natural gas steam reforming process for hydrogen and power cogeneration: Thermodynamic investigation

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ABSTRACT

Chemical looping combustion (CLC) is a high efficiency and clean power generation system. With the principle of energy cascade utilization and methodology of system integration, a cogeneration system for hydrogen and power from natural gas was proposed by thermally coupling high-pressure (HP) and low-pressure (LP) double-stage CLC and sorption-enhanced steam reforming unit. The effects of operating parameters on the different performances indicators (including product gas concentration, H₂ yield, and CH₄ conversion) were investigated. The proposed novel process and a benchmark cogeneration process (i.e., natural gas CLC combustion unit along with sorption-enhanced steam reforming process) were both evaluated and compared from a thermodynamic point of view.

Results show that increasing the $Fuel_{HP}/C$ and $Fuel_{LP}/C$ ratio (i.e., natural gas as fuel for HP-/LP-CLC divided by the feed molar flow for reformer ratio) leads significantly in improving the H₂ yield and CH₄ conversion. The addition of Ca-based sorbent and steam in reformer also has positive impacts on system performances. Under the conditions of $Fuel_{HP}/C = 0.42$ and $Fuel_{LP}/C = 0.70$, the novel process has a H₂ concentration of 92%, H₂ yield of 3.64, and CH₄ conversion of 75%, while for the benchmark process, the H₂ concentration is 89%, H₂ yield is 3.55, and has a CH₄ conversion of 69%. In addition, the optimized process minimizes exergy destruction and increases exergy efficiency over 6% when compared to the base-case system.

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1. Introduction

The 2015 Paris climate conference helped achieve a legally binding agreement which would have a vital impact on policy and developments in the clean, efficient and sustainable utilization of energy (Yu and Zhu, 2015). Hydrogen offers tremendous potential as a green renewable energy currency (Naqvi and Bolland, 2007). Natural gas steam reforming (SR) process has been used for several years as the principal for the generation of hydrogen, accounting for approximately 47% hydrogen production worldwide(Wang et al., 2014; Olivieri and Vegliò, 2008). The SR process consists of a strongly endothermic reverse methanation reaction (R1), and a moderately exothermic water gas shift (WGS) reaction (R2):

$$CH_4 + H_2O \rightarrow CO + 3H_2 \Delta H_{298K} = 206.3 \text{ kJ/mol}$$
 (R1)

$$CO + H_2O \leftrightarrow CO_2 + H_2 \Delta H_{298K} = -41.1 \text{ kJ/mol}$$
(R2)

As shown above, WGS emits a significant amount of CO_2 , which will increase global warming. Moreover, the reformer gas has low hydrogen

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Nomenclature	
AR	Air reactor

AK	All leactor
AR_1	High-pressure air reactor
AR_2	Low-pressure air reactor
AT	Air turbine
AT_1	High-pressure air turbine
AT_2	Low-pressure air turbine
CCS	Carbon dioxide capture and storage
CLC	Chemical looping combustion
Ex	Exergy flow rate. MW
Exair	Air feed exergy, MW
Exch	Chemical exergy, MW
Ex _{dest}	Sum of destroyed exergy, MW
Ex _{exhaust}	Exhaust gas exergy, MW
Ex _{in}	Sum of exergy input, MW
Ex _{NG}	Natural gas feed exergy, MW
Ex _{out}	Sum of exergy output, MW
Ex _{ph}	Physical exergy, MW
Exprod	Hydrogen product exergy, MW
ExQ	Heat exergy, MW
Exwater	Water feed exergy, MW
FR	Fuel reactor
GT	Gas turbine
GT_1	High-pressure gas turbine
GT_2	Low-pressure gas turbine
Н	Enthalpy, MW
H ₀	Enthalpy in reference state (298.15 K, 1 bar), MW
HRSG	Heat recovery & steam generator
HP	High pressure
LP	Low pressure
$m_{\rm in}$	Sum of mass input, kg/h
mout	Sum of mass output, kg/h
Me_xO_{v-1}	The solid reduced metal oxide
Me _x O _v	The solid mental oxide
n	Molar flow rate, mol/h
Q	Heat, MW
R	Ideal gas constant, 8.314×10^{-3} (kJ/mol K)
S	Entropy, MW/K
So	Entropy in reference state (298.15K, 1bar)
- 0	MW/K
To	Reference temperature, 298,15 K
TIT	Turbine inlet temperature
TET	Turbine exhaust temperature
W	Work. MW
Wnowor	Generated power. MW
X;	Mole fraction
£:	Standard chemical exergy kI/mol
ΔH	Molar enthalpy, kJ/mol
- ·	
Greek syr	nbols
Φ	Exergy efficiency
Subscripts	
298	The reference temperature, K
in	Inlet stream
out	Outlet stream

purity (about 29%, wet basis) because (R1) is endothermic while (R2) is exothermic and both reactions are equilibrium limited for typical reactor conditions (Rahimpour et al., 2013).

In order to tackle this problem, researchers efforts are being focused on creating an alternative which would combine steam reforming with in-situ CO₂ separation, also known as sorption enhanced steam reforming (SE-SR) (Antzara et al., 2015). The presence of CO₂ sorbent in the reforming reactor boosts the CO conversion, leading to high H_2 purity. Calcium oxide (CaO) is the most common sorbent which is suitable for the SE-SR process (Wang and Cao, 2013). The carbonation reaction is as follows:

 $CaO_{(s)} + CO_2 \leftrightarrow CaCO_{3(s)} \Delta H_{298K} = -178 \text{ kJ/mol}$ (R3)

Ca-based sorbent in the reformer helps shift the equilibrium of (R2) towards the right direction (according to Le Chatelier's principle), resulting in higher hydrogen yield beyond their conventional thermodynamic limitations. Moreover, regeneration of the sorbent (reverse of (R4) reaction) releases relatively pure CO₂, which is exactly suitable for geological or industrial usage with simple separation of CO₂ and solid calcium. It is important to note that sorbents regeneration is typically endothermic and takes place at above 850 °C and as such, additional energy is necessary in both calcinator and reformer (Tzanetis et al., 2012). Although Udomsirichakorn et al. (2014) designed a SE-SR process in which the required heat is provided by combustion of additional fuel with air, and Gopaul et al. (2014) also investigated a possibility of employing high-temperature streams of combustion gas as a heat resources for the calcinator, it would lead to huge energy penalty to separate CO₂, for CO₂ is produced from the calcinator, which was diluted by the combustion flue gas. Besides, the process is highly endothermic and remains energy intensive (Fan and Zhu, 2015; Anderson et al., 2014). Therefore, there is an urgent need to explore cost-effectively and eco-friendly innovative power supply systems for hydrogen generation.

For a long time, power systems and the chemical industry have been mutually independent. Consequently, developments in energy utilization efficiency and environmental performance of the two systems have been restricted, due to the great losses of chemical energy in power plants and the high energy consumption in the chemical industry. Therefore, a cogeneration of energy conversion and utilization system has been paid more attention.

Chemical looping combustion (CLC) is an emerging technology for energy generation that has several advantages, such as high net power efficiency, no extra energy usage for CO₂ separation and indirect mixing of fuel and air (Hamers et al., 2015; Raman et al., 2014; Fan et al., 2016). Based on this method, a feasible approach to produce highpurity hydrogen is provided by coupling CLC with Ca-based sorption enhanced steam reforming (CLC-SE-SR) system was proposed (Fan and Zhu, 2015; Lin and Fan, 2015). Although the CLC coupled reforming process can produce electricity and hydrogen without CO₂ emissions and expensive CO₂ storage/sequestration process, the overall efficiency of $\ensuremath{\mathsf{CLC}}\xspace$ so that of the CLC power plant (Fan and Zhu, 2015). This is because the strongly exothermic reaction happens in the air reactor (AR) which results in high reactor operation temperature (up to 1200 °C) (Zhu et al., 2015, 2016). If the heat released from AR is totally transferred into the reformer, the huge temperature difference of the two streams from the AR and the reformer would result in a large loss of thermal energy, which consequently results in a drop in total efficiency (Lyngfelt et al., 2001).

In order to achieve the ideal efficiency that closes to the Carnot efficiency, Naqvi and Bolland (2007) designed a series of multi-stage CLC method in natural gas-fired combined cycles in which the air flue–gas mixture from air turbine was reheated in next air reactor for improving turbine inlet temperature. Rezvani et al. (2009) also presented a multi-stage CLC co-generation system of coal using reheat air turbines to increase power efficiency. This system was not only practically utilized as a heating resource to provide the necessary heat for endothermic process, but also simultaneously achieved high efficiency with inherent separation of CO₂. Motivated by these ideas, and to obtain high-purity H₂ with high net power efficiency, we proposed a novel hydrogen-power cogeneration system with cascade utilization of energy: double-stage chemical looping combustion coupled with sorption-enhanced steam reforming of natural gas (double-stage CLC-SE-SR).

Using this mechanism, we hope that the process for energy production becomes much cleaner while maintaining low cost both financially Download English Version:

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