Exergy analysis of the biogas sorption-enhanced chemical looping reforming process integrated with a high-temperature proton exchange membrane fuel cell

Sarunyou Kasemanand[a], Karittha Im-orb[a], Phanicha Tippawan[a], Wisitsree Wiyaratn[b], Amornchai Arpornwichanop[a],*

[a] Computational Process Engineering Research Unit, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand
[b] Faculty of Industrial Education and Technology, King Mongkut's University of Technology Thonburi, Bangkok 10140, Thailand

ABSTRACT

A biogas sorption-enhanced chemical looping reforming process integrated with a high-temperature proton exchange membrane fuel cell is analyzed. Modeling of such an integrated process is performed by using a flowsheet simulator (Aspen plus). The exergy analysis is performed to evaluate the energy utilization efficiency of each unit and that of the integrated process. The effect of steam and nickel oxide to biogas ratios on the exergetic performance of the stand-alone biogas sorption-enhanced chemical looping reforming process is investigated. The total exergy destruction increases as the steam or nickel oxide to biogas ratio increases. The main exergy destruction is found at the air reactor. For the high-temperature proton exchange membrane fuel cell, the main exergy destruction is found at the cathode. The total exergy destruction increases when cell temperature increases, whereas the inverse effect is found when the current density is considered as a key parameter. Regarding the exergy efficiency, the results show opposite trend to the exergy destruction. The heat integration analysis is performed to improve the exergetic performance. It is found that the integrated process including the heat integration system can improve the exergy destruction and exergy efficiency of 48% and 60%, respectively.

1. Introduction

At present, fossil fuels such as coal and natural gas are mainly used to generate electricity. The combustion of fossil fuels for electricity generation releases high amount of CO_2 that causes a global warming problem [1]. Furthermore, the energy demand continuously increases due to the increase in global population; however, an amount of fossil fuels is limited. The energy production of renewable fuels such as biomass, therefore, becomes an interesting topic [2].

Biogas is an interesting renewable energy which can be produced by anaerobic digestion of organic matters such as municipal wastes, food industry wastes and agricultural wastes [3]. Biogas consists of mainly CH_4 and CO_2 that can be used as a fuel for combustion or reforming processes [4]. Chungchaichana and Vivanpatarakij [5] reported that the 94.19 ton day^{-1} of waste from the Talad-Thai market in Thailand was converted to 17,807 m^3 day^{-1} of biogas that was used to produce 0.53–1.04 MW of electricity. Recently, various technologies have been developed to produce electricity from biogas and a combustion engine seems to be the most widely used one. Herringshaw [6] reported that

the electrical efficiency around 22–29% was obtained when biogas with 55% methane was used as a fuel for the internal combustion power generation units. In addition, Yingjian et al. [7] reported that the energy and exergy efficiencies of 27.36% and 28.45%, respectively, could be achieved from the internal combustion engines using the biogas fuel. As the energy and exergy efficiencies of the existing biogas power generation unit are quite low and the released flue gas contains a high amount of CO_2 greenhouse gas, designing of the biogas power generation process with high energy utilization and low greenhouse gas emissions has been received increased attention.

The energy production using fuel cells is regarded as a potential technology for electricity generation via electrochemical reactions due to its high efficiency and environmental friendliness [8]. There are several types of fuel cell such as a solid oxide fuel cell (SOFC) and a proton exchange membrane fuel cell (PEMFC). A PEMFC which consists of a polymeric membrane such as Nafion® and the catalyst layers (anode and cathode) is an attractive type of fuel cell suitable for several applications such as vehicles, residential power generators and auxiliary power units [9]. Although the PEMFC can be operated at a low

Table 1
Reactions involved in the SECLR process [20].

Fuel reactor (FR)		
(R1) Oxygen carrier reductions	$CH_4 + 4NiO \rightarrow 4Ni + CO_2 + 2H_2O$	$\Delta H^o_{298K} = 156 \text{ kJ mol}^{-1}$
(R2)	$H_2 + NiO \rightarrow Ni + H_2O$	$\Delta H^o_{298K} = -2.1 \text{ kJ mol}^{-1}$
(R3)	$CO + NiO \rightarrow Ni + CO_2$	$\Delta H^o_{298K} = -43.3 \text{ kJ mol}^{-1}$
(R4)	$C + NiO \rightarrow Ni + CO$	$\Delta H^o_{298K} = 129.2 \text{ kJ mol}^{-1}$
(R5)	$CH_4 + NiO \rightarrow Ni + CO + 2H_2$	$\Delta H^o_{298K} = 169.9 \text{ kJ mol}^{-1}$
(R6) Steam reforming	$CH_4 + H_2O \rightarrow CO + 3H_2$	$\Delta H^o_{298K} = 205.8 \text{ kJ mol}^{-1}$
(R7) Dry reforming	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	$\Delta H^o_{298K} = 247 \text{ kJ mol}^{-1}$
(R8) Methane decomposition	$CH_4 \rightarrow C + 2H_2$	$\Delta H^o_{298K} = 74.5 \text{ kJ mol}^{-1}$
(R9) Carbon gasification	$C + H_2O \rightarrow CO + H_2$	$\Delta H^o_{298K} = 131.3 \text{ kJ mol}^{-1}$
(R10) Boudouard	$2CO \rightarrow C + CO_2$	$\Delta H^o_{298K} = -172 \text{ kJ mol}^{-1}$
(R11) Combustion	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	$\Delta H^o_{298K} = -806 \text{ kJ mol}^{-1}$
(R12) Water-gas shift	$CO + H_2O \rightarrow CO_2 + H_2$	$\Delta H^o_{298K} = -41.2 \text{ kJ mol}^{-1}$
(R13) Carbonation	$CaO + CO_2 \rightarrow CaCO_3$	$\Delta H^o_{298K} = -178.8 \text{ kJ mol}^{-1}$
Calcinator (CAL)		
(R14) Calcination	$CaCO_3 \rightarrow CaO + CO_2$	$\Delta H^o_{298K} = 178 \text{ kJ mol}^{-1}$
Air reactor (AR)		
(R15) Oxygen carrier oxidation	$Ni + 0.5O_2 + 1.881N_2 \rightarrow NiO + 1.881N_2$	$\Delta H^o_{298K} = -239 \text{ kJ mol}^{-1}$

temperature (less than 90 °C) [10], it requires high purity H_2 feed gas with the CO concentration of less than 30 ppm as CO can poison the PEMFC catalyst [11]. To mitigate the CO poisoning problem, the operation of PEMFC at elevated temperatures ranging from 130 to 200 °C was proposed [12]. The high temperature PEMFC (HT-PEMFC) can tolerate CO at the concentration up to 3%. Therefore, its reactivity is improved. Moreover, the water management for HT-PEMFCs is simple and easy to be done [13].

Typically, a pure H_2 or H_2-rich gas is produced from a steam reforming process of pure methane or natural gas, which is a fossil-based fuel [14]. Alternatively, biogas can be used for hydrogen production; however, the primary problem associated with using biogas as a fuel is the CO_2 dilution which causes the decrease in calorific value of the product gas. Moreover, the use of H_2-rich gas containing high CO_2 as a fuel for fuel cell causes the cell efficiency decrease. To deal with these problems, the concept of combining the calcium looping process in which CaO is used to capture CO_2 via a carbonation reaction, with the chemical looping reforming (CLR) process in which a solid metal oxide is used as an oxygen carrier, was proposed (referred to as a sorption-enhanced chemical looping reforming (SECLR)) [15]. There were several works focused on the SECLR process. However, most studies were restricted by methane and natural gas feedstock. Rydén and Ramos [16] reported that the SECLR using methane was the attractive process for H_2 production with CO_2 capture. Yahom et al. [17] investigated the effects of steam and NiO to methane ratios on the H_2 purity and yield. They concluded that three moles of H_2 with the purity higher than 90% can be achieved when one mole of CH_4 was fed at the reforming temperature in a range of 500–600 °C and NiO, CaO and H_2O to methane ratios of 1, 1 and 2, respectively.

Due to the several advantages of HT-PEMFC, it is selected to be integrated with various reforming processes. Herdem et al. [18] studied the methanol reforming process and HT-PEMFC integrated process by performing the parametric analysis to investigate the effect of operating parameters on process performance. They found that the CO molar ratio in the reformate gas increased as the reforming temperature increased and decreased when steam to carbon (S/C) ratio increased. In addition, the CO concentration had less effect on the fuel cell performance at elevated temperatures. The integrated methane autothermal reforming process and HT-PEMFC process was studied by Authayanan et al. [19]. They reported that an increase in the S/C ratio and the reforming temperature could increase the hydrogen production while decreasing the CO formation. As the SECLR is an attractive H_2 production process offering high purity H_2 and consumes lower energy compared to the

conventional reforming process, the integration of SECLR and HT-PEMFC process is therefore expected to be a sustainable energy production process offering good energy utilization and low CO_2 emission when the biogas is a considered feedstock. Previous studies mostly performed the parametric analysis of the integrated conventional reforming process of fossil fuels and HT-PEMFC. However, the energy and exergy analysis of the integrated SECLR and HT-PEMFC process to produce the electricity has been less extensively studied.

The objective of the present study is to analyze the integrated SECLR and HT-PEFMC process using a thermodynamic model developed in Aspen plus. The biogas is a considered feedstock. The exergy analysis is performed to evaluate the energy utilization of each unit and that of the integrated process. The effect of operating parameters on the exergetic performance, i.e., exergy destruction and exergy efficiency of the stand-alone SECLR and HT-PEMFC, is investigated. Moreover, the exergetic performance of the integrated process is analyzed and improved by implementing the heat integration system.

2. Model development

The models of the sorption-enhanced chemical looping reforming (SECLR) and the high-temperature proton exchange membrane fuel cell (HT-PEMFC) are developed in Aspen plus based on the assumptions that all processes are operated under steady state, isothermal and isobaric conditions. The developed SECLR and HT-PEMFC models are used to simulate and analyze the SECLR and HT-PEMFC integrated process.

2.1. Sorption-enhanced chemical looping reforming process

The SECLR is the combined process of sorption-enhanced steam reforming (SESR) and chemical looping reforming (CLR). The SECLR process consists of three reactors, i.e. fuel reactor, air reactor and calcination reactor, and the NiO and CaO are used as an oxygen carrier and CO_2 adsorbent, respectively. There are several reactions taking place in the SECLR process as summarized in Table 1 [20]. For hydrogen production, the presence of metal oxide (NiO) causes the oxidization reactions (R1)–(R5). In order to shift the equilibrium of the reactions (R6)–(R12) forwardly to increase the hydrogen yield, CaO is used to capture CO_2 via exothermic carbonation reaction (R13). To regenerate the oxygen carrier, Ni is oxidized with air to form the NiO (R15). Regarding the CaO regeneration, $CaCO_3$ is converted to CaO by using an endothermic calcination reaction (R14).

In SECLR process, biogas is used as a feedstock and its composition