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Hydrogen and power generation from supercritical water reforming of glycerol and pressurized SOFC integrated system: Use of different CO_2 adsorption process

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ABSTRACT

The performance analysis of an integrated system of glycerol supercritical water reforming and pressurized SOFC was presented. The use of different CO_2 adsorption processes that include *in situ* and *ex situ* processes was compared to determine the suitable process for hydrogen and power generations. The influence of operating condition, e.g., temperature and pressure of reformer, supercritical water to glycerol (S/G) molar ratio, and calcium oxide to glycerol (CaO/G) molar ratio was examined. Then, the electrical performance of each integrated process was considered with respect to the SOFC conditions comprising temperature, pressure, and current density. The simulation results revealed that both processes have same favourable conditions for temperature and pressure operated at 800 °C and 240 atm, respectively. The suitable S/G and CaO/G molar ratios for *in situ* process are 10 and 2 whereas those for *ex situ* process are 20 and 1. Under these conditions, maximum hydrogen can be achieved as 87% and 75% for *in situ* and *ex situ* processes, respectively. When both integrated processes are operated at the optimal SOFC conditions as 900 °C, 4 atm, and current density of 10,000 A/m^2, the SOFC efficiency of 71.56% and 62.12% can provide for *in situ* and *ex situ* processes, respectively.

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Introduction

Due to increasing energy demand and environmental concern, many researchers have explored alternative fuels with cleaner and more economical when compared to petroleum-based fuel. Hydrogen (H_2) is perceived as an ideal energy carrier with clean and sustainable energy in the near future. It can be considered as fuel for combustion engines or fuel cell for power generation without carbon emission [1] and thus, it is considered to be a pollutant-free energy carrier. In addition, it provides energy in transportation and energy storage system [2].

In general, there are several raw materials that can be converted to hydrogen such as biomass, methane, natural gas, methanol, or glycerol. Among these, glycerol is one of the attractive feedstock as a result of the growing of the biodiesel production leading to large amount of glycerol. The biodiesel production using transesterification process of vegetable oils or animal fats always produces glycerol as main by-product [3]. Crude glycerol as by product produced by biodiesel production process is expected to increase greatly in the future [4]. Commonly, glycerol is one of substances for production of cosmetics, pharmaceutics food, and polymer [5]. However, these industries require a purified glycerol, leading to high cost of production. Besides that, crude glycerol is regarded as an alternative and renewable fuel for hydrogen production because glycerol and methanol/ethanol that are presented on crude glycerol can be transformed into H_2 through reforming process without the requirement of purification process. Therefore, hydrogen production from glycerol is an attractive way to add value of low price glycerol.

Presently, steam reforming (SR), partial oxidation (PO), and autothermal reforming (ATR) are considered as reforming processes for hydrogen production. As mentioned above, the steam reforming process is the most commonly used process, outstanding established technique in the industry scales due to providing the highest hydrogen yield [6–8]. However, the external heating source is highly need to supply heat for the endothermic steam reforming reaction. In a recent year, many researchers have concentrated on the hydrogen production from glycerol using supercritical water [9,10]. Compared with steam, supercritical water (SCW), heated and compressed over its critical water (374 °C and 22.1 MPa), has lower dielectric constant and number of hydrogen bond which leads to high solubility of SCW with many organic solvent [11,12]. This is in turn the reduction of reaction time and required energy in reformer. In addition, the reforming process by using SCW can proceed without adding catalyst in the reformer due to the fact that SCW has high H^+ or OH^- concentrations and thus, it behaves like an acid or base catalyst.

However, the gas product or synthesis gas (syngas) obtained from the reforming process always provides considerably CO_2 content, leading to the difficulty of utilization for energy production. For example, in fuel cell application, the synthesis gas, contaminated with large CO_2 greatly drops the fuel cell efficiency. Consequently, the CO_2 removal process should be subsequently applied for glycerol reforming process to obtain clean H_2 [13]. Considering several techniques of CO_2 removal processes, the adsorption process by using calcium oxide (CaO) as adsorbent has been widely applied in the reforming process. CaO is suggested to use as adsorbent because it has low price, availability and high adsorption ability [14]. The CO_2 produced from steam reforming of ethanol was capably removed via using CaO based sorbent [15]. The energy efficiency of glycerol steam reforming with CO_2 adsorption was higher than that without adsorption [16]. Tippawan et al. [17] showed that the CO_2 removal by the addition of CaO sorbent in the reformer affects a higher hydrogen concentration. In general, there are two types of CO_2 adsorption process: *in situ* and *ex situ* processes. For the first approach, adsorbent is added in the reformer. The reforming reaction can be occurred simultaneously separation process. For the *ex situ* process, the CO_2 removal process occurs after the reforming reaction is accomplished. Dou et al. [18] reported that *in-situ* CO_2 removal integrated with steam reforming, water gas shift, and oxidation processes can accomplish the elevated purity hydrogen production. The removal of CO_2 can directly affect the increase of three reactions, leading to enhance the conversion of feeding and hydrogen production. Although most previous researchers have focused on hydrogen production with *in situ* CO_2 removal process, there are different significant features of each process depending on the purpose of use.

As an electrochemical device, a fuel cell can directly produce clean electrical energy from fuel by electrochemical reaction without the combustion reaction and has been considered as a good electricity generation strategy [19]. It is unlike internal combustion engines; therefore, this technology has high energy efficiency (direct energy conversion) and low environmental pollution due to by-products as only water and heat [20,21]. Solid oxide fuel cell (SOFC) is an interesting fuel cell technology owing to high operating temperature, flexibility in terms of fuel type and power production leading to focus on large-scale devices [22,23] and the possibility of its use in hybrid-power generation applications. Several researchers have focused on the performance of ambient SOFC [24–26] whereas the pressurized SOFC has received further attention [27–30]. Seidler et al. [31] studied the experimental and modeling of pressurized SOFC and revealed that the performance can be improved by pressurization. The power generation of anode-supported and electrolyte-supported SOFC under pressurized operation was studied by Hsieh et al. [32]. The results indicated that the pressurization increases the power density and cell performance because it can enhance the gas-phase diffusion in porous electrodes, leading to the further fuel and oxidant supply. Significantly, the hydrogen produced from supercritical water reforming has high pressure and temperature; therefore, it is suitable to use as fuel for pressurized SOFC without the requirement of external fuel compression.

In this study, glycerol supercritical water reforming (GSCWR) integrated with different CO_2 removal processes for hydrogen production is studied. The influences of operating condition at reformer are examined in terms of hydrogen production and heat duty to determine the optimal operating condition to produce hydrogen for pressurized SOFC. Furthermore, the performance of an integrated system of GSCWR process and pressurized SOFC is also investigated. The optimal operating condition of SOFC is identified with respect to the effects of SOFC operating conditions. The

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