

# Performance of an Integrated Adsorption-Enhanced Glycerol Supercritical Water Reforming and Pressurized SOFC System

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**Abstract**—Glycerol supercritical water reforming is a promising process for hydrogen production. The hydrogen product has high pressure and temperature and thus, it can be used as fuel in pressurized solid oxide fuel cells (SOFC). However, the synthesis gas obtained from reforming process contains high amount of CO<sub>2</sub> and this leads to the deterioration of SOFC performance. Consequently, the adsorption process is used to remove CO<sub>2</sub> from the synthesis gas before feeding into SOFCs. This work aimed to develop models of an integrated system of adsorption-enhanced glycerol supercritical water reforming process and pressurized SOFC. The AspenPlus™ simulation software was used to calculate the equilibrium compositions of the products from reforming process by the minimization of Gibbs free energy method. The SOFC performance can be computed by electrochemical equations taking into account three voltage losses (activation, ohmic and concentration losses). Effect of operating conditions of SOFC (temperature, pressure and current density) was examined to identify the optimal operating condition. The simulation results indicated that the optimal conditions for SOFC are temperature of 900 °C, pressure of 4 atm and current density of 10,000 A/m<sup>2</sup>. The glycerol reformer which is operated at temperature of 800 °C, pressure of 240 atm and steam to glycerol molar ratio of 10 can provide the hydrogen product of 87% (dry basis). When the synthesis gas is fed into SOFC operated under the optimal condition, it was found that the integrated system can be achieved the SOFC efficiency of 71.56%.

**Keywords**—Glycerol, Performance analysis, Solid oxide fuel cell, supercritical water.

## I. INTRODUCTION

Hydrogen (H<sub>2</sub>) is a useful substance that can use in many industries; for example, 49 % of hydrogen is used in ammonia production and 37 % of hydrogen is used for refining and upgrading purpose in petroleum and petrochemical industry [1]. More significantly, hydrogen is sustainable energy source for fuel in recent year. It can be used as a fuel for combustion engines or fuel cells to produce power energy without carbon emissions [2].

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Glycerol is the main by-product of the biodiesel production by transesterification of vegetable oils [3]. Due to the increase in biodiesel production, crude glycerol, consisting of glycerol, methanol/ethanol, soap, catalyst, and organic matter, has led to increase simultaneously while its prices are low [4]. Although, glycerol can be used in many industries, e.g., cosmetics, pharmaceuticals food, and polymer, it needs to be in a high purity condition which causes high cost of production. One of attractive ways to add value of glycerol is the use of glycerol for hydrogen production. The usage of crude glycerol has been received much interest since both glycerol and methanol/ethanol can be converted into hydrogen via reforming process.

In general, there are three main reforming processes for hydrogen production, i.e., steam reforming, partial oxidation and autothermal reforming. Among these processes, steam reforming is well-known established process and provides the highest hydrogen yield [5]. However, due to its endothermic reaction, the external heat is highly required. Recently, there are many researchers focused on glycerol supercritical water reforming [4,6-10]. Since supercritical water has advantage properties such as a low dielectric constant that affects to the solubility of components in supercritical water. The solubilize capacity for organic compounds increase and inorganic compounds decrease and thus, reaction time and the requirement of energy in reactor are decrease [3,9]. Moreover, supercritical water is not only a processing medium but also a catalyst in reforming reaction [3]. Interestingly, the synthesis gas obtained from supercritical water reforming has high pressure and thus, it is easily and directly to store. Furthermore, it can be used as fuel for pressurized solid oxide fuel cell (SOFC) without the need of the external gas compression. The pressurize SOFC is referred to the SOFC operated under higher atmospheric pressure

However, the gas product from the glycerol reformer always contains highly content of CO<sub>2</sub>. This indicates that the hydrogen concentration is lower and this may cause the deterioration of SOFC performance. Therefore, the CO<sub>2</sub> removal process should be included in the reforming process to purify hydrogen. Among various CO<sub>2</sub> removal processes (e.g. pressure swing adsorption, temperature-swing adsorption, physical absorption and chemical absorption process), adsorption process by CO<sub>2</sub> adsorbent is an attractive process and commonly applied in reforming process. Calcium oxide (CaO) can be widely used as a CO<sub>2</sub> adsorbent because it is low

price, easy to find and considered as high adsorption ability [11]. The adsorption-enhanced reforming process in which adsorbents are added into the reformer to enhance the reactions and realize *in situ* CO<sub>2</sub> separation is focused in this work.

This work aims to investigate the performance of an integrated system of adsorption-enhanced glycerol supercritical water reforming process and pressurized SOFC in the thermodynamics aspects by using AspenPlus™. Effect of operating conditions of reformer (temperature, pressure and steam to glycerol molar ratio) and SOFC (temperature, pressure and current density) is examined to identify the optimal operating condition.

II. PROCESS DESCRIPTION

Fig. 1 presents the schematic of an integrated system of adsorption-enhanced glycerol supercritical water reforming and pressurized SOFC designed in the Aspen Plus flowsheet. First, crude glycerol and supercritical water is fed into mixer. The mixture stream is fed through heater to reach the operating temperature. Then, the mixture stream is fed to reformer. In this case, calcium carbonate (CaO) as a CO<sub>2</sub> adsorbent is added into reformer and thus, reforming reaction and CO<sub>2</sub> separation occur simultaneously. After that, CaCO<sub>3</sub> generated from CO<sub>2</sub> adsorption reaction is introduced into regenerator (REGEN) to revive by heat. Specification details of each unit model in the processes are shown in Table 1. The possible reactions in glycerol supercritical water reforming with *in situ* CO<sub>2</sub> removal processes are glycerol reforming (Eq. (1)), glycerol decomposition (Eq. (2)), water gas shift (Eq. (3)), methanol reforming (Eq. (4)), methanol decomposition (Eq. (5)), methane formation (Eq. (6)) and CO<sub>2</sub> adsorption (Eq. (7)).

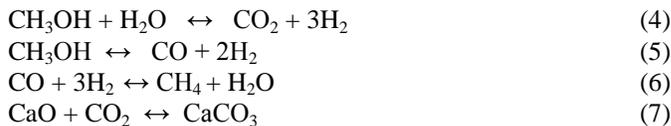


TABLE I:  
SPECIFICATION DETAILS OF EACH UNIT MODEL IN GLYCEROL SUPERCRITICAL WATER REFORMING PROCESS

Name	Unit Model	Standard Operating Conditions
MIXER	Mixer	-
HEATER	Heater	800 °C
REFORMER	RGibbs	800 °C, 240 atm
ADSORBER	RGibbs	600 °C, 5 atm
REGEN	RGibbs	850 °C, 1 atm
HEATER2	Heater	800 °C
ANODE	RGibbs	800 °C, 4 atm 5,000 A/m <sup>2</sup>
COMPR1	Compr	4 atm
HEATER3	Heater	800 °C
CATHODE	Sep	Mole fraction of oxygen = 0.21

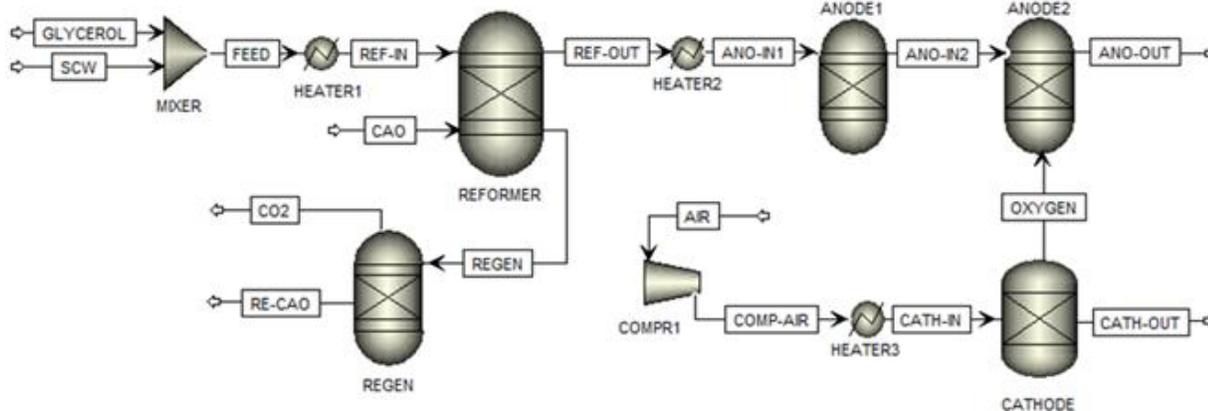
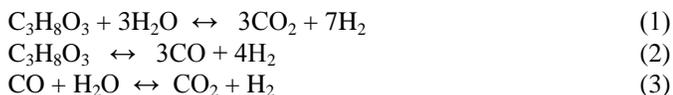


Fig. 1: A schematic of adsorption-enhanced glycerol supercritical water reforming integrated with pressurized SOFC

### III. SOFC MODEL

The compositions of hydrogen and oxygen are used to determine the performance of SOFC (e.g., cell voltage, power density and cell efficiency) through the detailed electrochemical model. The open-circuit voltage which is the maximum voltage of SOFC can be determined by the Nernst equation. However, the operating cell voltage is always lower than open-circuit voltage since there are three main voltage losses occurred in real operation: activation loss, ohmic loss and (3) concentration loss. The electrochemical equations of SOFC used in this study were reported in our previous work [12].

### IV. SOLUTION APPROACH

In this study, the thermodynamic calculation is performed by using AspenPlus™. The model is performed based on the following assumptions: (1) isothermal and steady state operation are considered; (2) pressure drops are neglected; (3) reforming and shift reactions reach chemical equilibrium; and (4) only H<sub>2</sub> is electrochemically oxidized. Firstly, for given operating conditions of reformer, the equilibrium compositions in the reforming process can be determined by using the total Gibbs free energy minimization method. The equation of state used in this calculation was based on the Soave-Redlich-Kwong (SRK). The molar flow rate of CH<sub>4</sub> ( $n_{CH_4}$ ), CO ( $n_{CO}$ ) and H<sub>2</sub> ( $n_{H_2}$ ) obtained from reforming process is further used as the input parameters for the SOFC calculation. It is noted that the electrochemical equations, as described in Section 3, is performed by a calculator block in the Aspen Plus flowsheet. When the operating conditions of SOFC (temperature, pressure and current density ( $i_{SOFC}$ )) and physical parameters of cell components are specified, the cell voltage ( $V$ ), power density ( $P_w$ ) and SOFC electrical efficiency ( $\epsilon_{SOFC}$ ) can be calculated as follows:

$$P_w = i_{SOFC} V \quad (8)$$

$$\epsilon_{SOFC} = \frac{P_w}{n_{CH_4} LHV_{CH_4} + n_{H_2} LHV_{H_2} + n_{CO} LHV_{CO}} \times 100\% \quad (9)$$

### V. RESULTS AND DISCUSSION

The standard operating conditions used in this study are shown in Table 1. The inlet flow rate of supercritical water and glycerol is 10 kmol/h and 1.25 kmol/h, respectively. Thus, supercritical water to glycerol (S/G) molar ratio is 10. For adsorption process, CaO feed rate of 2 kmol/h is introduced to the reformer. Under these operating conditions, the gas product obtained from glycerol supercritical water reforming process consists of 87 % H<sub>2</sub>, 0.7 % CO, 0.3 % CO<sub>2</sub> and 12 % CH<sub>4</sub> (dry basis). Then, the performance of an integrated adsorption-enhanced glycerol supercritical water reforming and pressurized SOFC system is investigated with respect to the impact of operating conditions, i.e., temperature, pressure and current density.

#### A. Effect of SOFC Temperature

Fig. 2 presents the SOFC efficiency as a function of SOFC temperature (800-1000°C). When the SOFC is operated at constant pressure of 4 atm and current density of 5,000 A/m<sup>2</sup>, it is found that increasing SOFC temperature can achieve higher cell voltage. Increase in operating temperature of SOFC increases the rate of electrochemical reaction; the consumption of hydrogen is higher and thus, the open-circuit voltage also increases. Considering cell voltage losses, it is also found that the increased operating temperature causes a decrease in voltage losses, particularly in ohmic and activation losses. Therefore, the efficiencies of SOFC system are increased with increasing temperature, as seen in Fig. 2.

#### B. Effect of SOFC Pressure

In order to study the pressure effect, SOFC temperature and current density are kept constant as 1,000 °C and 5,000 A/m<sup>2</sup>, respectively. In general, the SOFC operated at high pressure can provide higher cell voltage since higher partial pressure of H<sub>2</sub> can increase an open-circuit voltage. In addition, at high pressure operation, fuel and oxidant gases can easily diffuse to the reaction site and thus, the concentration loss is decreased. When cell voltage can be achieved, power density and SOFC efficiency are higher. However, in this simulation, it is found that increasing SOFC pressure in range of 4-8 atm has a slight influence to cell performance (Fig. 3).

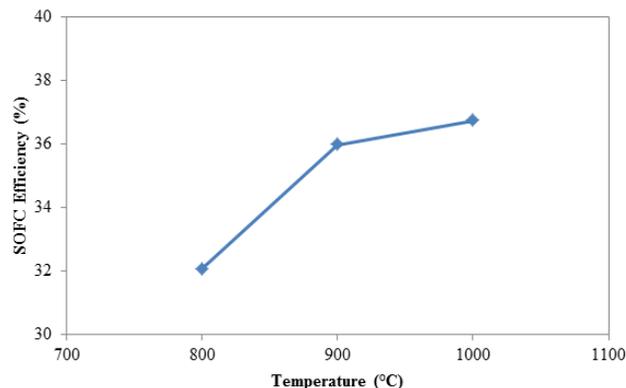


Fig. 2: Effect of temperature on SOFC electrical efficiency.

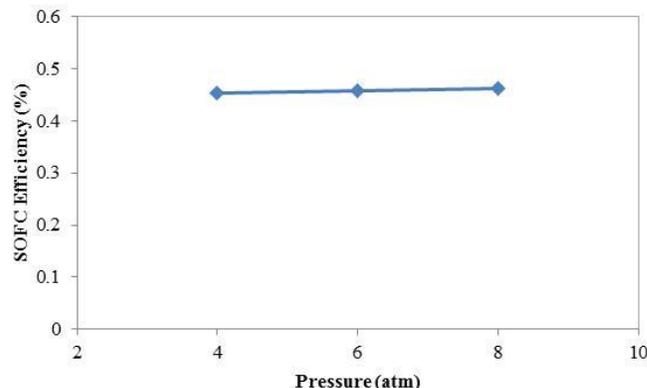


Fig. 2: Effect of pressure on SOFC electrical efficiency.

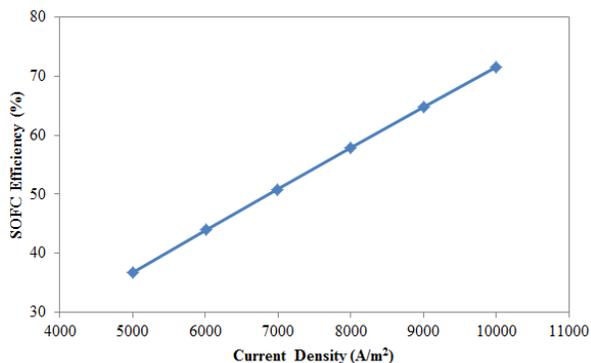


Fig.4: Effect of current density on SOFC electrical efficiency.

### C. Effect of Current Density

Finally, the effect of current density on SOFC efficiency is further investigated, as shown in Fig. 4. The current densities are varied in the range of 5,000 to 10,000 A/m<sup>2</sup> whereas SOFC temperature and pressure are kept constant as 1,000 °C and 4 atm, respectively. From the simulation result, it can be found that the cell voltage decreases strongly with increasing current density. This is because higher current density leads to increases in all voltage losses. Unlike cell voltage, the power density can be increased when the current density is higher and thus, the SOFC efficiency can be improved.

## VI. CONCLUSIONS

An integrated system of adsorption-enhanced glycerol supercritical water reforming and pressurized SOFC is proposed in this study. An integrated system is designed and developed via the Aspen Plus simulator. Among various parameters considered in the SOFC operation, it is found that the SOFC temperature and current density are significant parameters on system performance. Higher SOFC temperature and current density cause a considerable higher SOFC efficiency. The simulation results indicate that the optimal operating conditions of the SOFC are 900°C, 4 atm and current density of 10,000 A/m<sup>2</sup>, respectively. The integrated system can provide the SOFC electrical efficiency of 71.56%.

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